Founded: 1959

Gigantic magnetoresistence	Nobel prize 2007,	A. Fert
Liquid crystals	Nobel prize 1997,	P.-G. de Gennes
Organic superconductivity	1980,	D. Jerome

Dynamical phase transition to the excitonic insulator state induced by an optical pulse

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After collaboration with S. Brazovskii, pbl. Phys. Rev. B 2016

OUTLINE

- Optical pumping of excitons in insulators .
- Two types of relations among excitons and the order parameter: a common interaction and the special identity of densities.
- ***Motivation:*** charge transfer excitons merging with the order parameter of the charge disproportionation.
- ***Theory challenge:*** Joint description and evolution of the ensemble of excitons from the condensate of pumped excitons to their density in the new ground state.
- Self-focusing, sub-barrier dynamical phase transition, and persistent stratification.

Optical pumping: creation of electron-hole pairs under illumination

Excited pairs are either free, or bound.

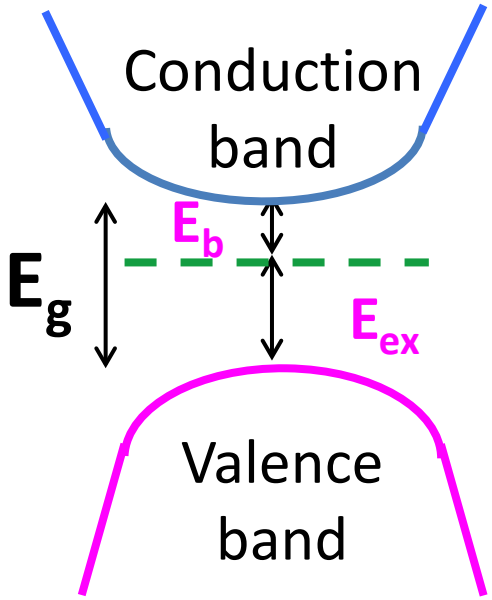
Differences: *irrelevant* in small systems,

ultimate in optics of semiconductors, light emitting polymers, etc.

Free pairs: minimal energy - the band gap Eg.

Excitons: $\mathbf{E_{ex} = E_g - E_b < E_g}$

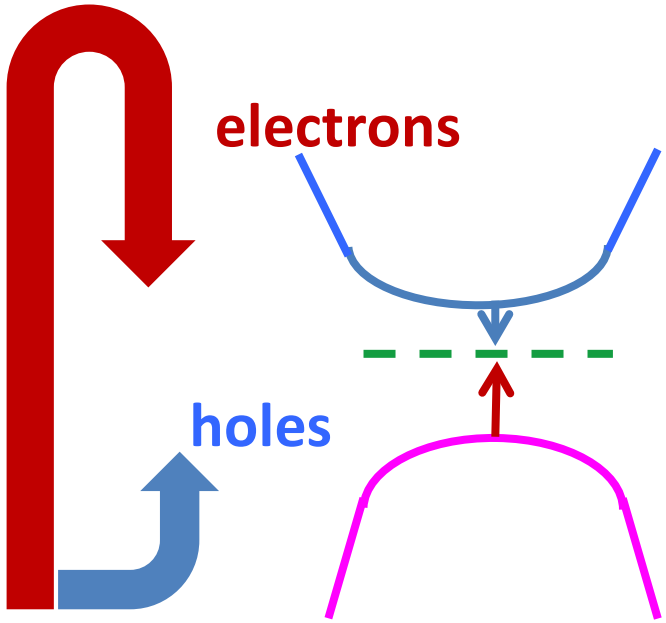
Wannier-Mott (charge-transfer) exciton: electron-hole pair bound by long range Coulomb forces. Binding energy: $\mathbf{E_b = e^2/\varepsilon R_{ex}}$



Intramolecular Frenkel exciton: $\mathbf{E_b}$ = molecular ionization energy

N.B. Exciton is a quantum state in both the internal and the center of mass coordinates

EXCITONS and PHOTO INDUCED PHASE TRANSITIONS



Two speps optical pumping to excitons:

- Relaxation and binding in e-h population.
- Intermediate stage of hot excitons.
- Cooling below the bandwidth. Fast development of the distribution peak at the lowest energy – a quasi-condensate.

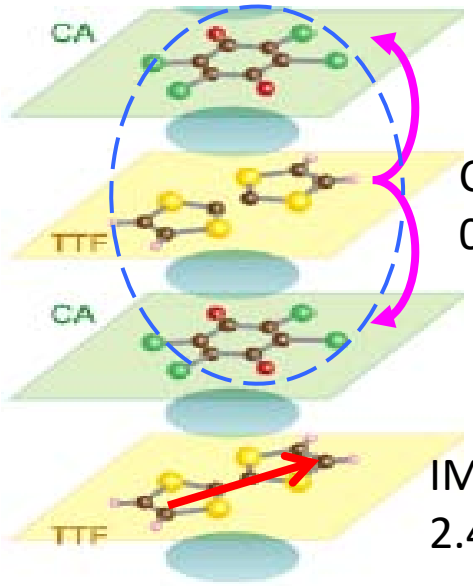
Less understood following steps:

- Establishing of the phase coherence.
- Wave function Ψ of the condensate evolves interacting with other degrees of freedom.

Direct pumping to excitons: $E_{photon}<E_g$

- Excitons are initially delocalized plane waves: photons create them at **k=0**
- Excitons are initially ready to form macroscopic quantum state.
- Deviation from the resonance $\mathbf{E_{photon}\approx E_{ex}}$ (***hot excitons***) invokes the phonon-assistant processes requiring for a stage of the energy relaxation.

Excitons in organic donor-acceptor stack compounds.

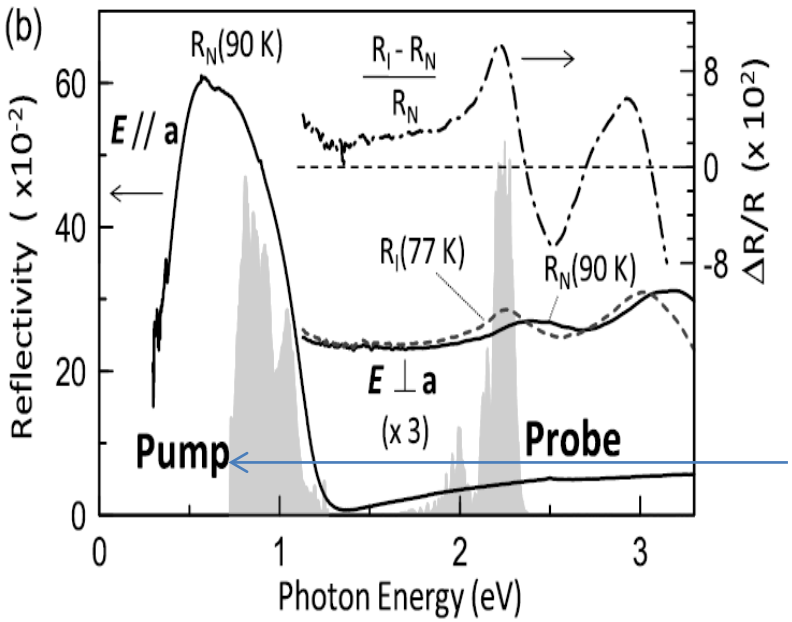


CTE,
0.6 eV

IME,
2.4 eV

Intra-molecular excitons IME (S. Koshihara)
Pumping into the IME : the excitons and the order parameter are different while interacting fields.

Inter-molecular = charge-transfer excitons CTE (H. Okamoto). Both the exciton and the charge ordering are built from processes of electronic transfer with a density $\rho = \rho_n + q$ between donor and acceptor molecules.
Thermodynamic order parameter and intensity $q = |\Psi|^2$ of pumped excitation are of the same origin.



Looks to be a nearly resonance pumping
H. Uemura, H. Okamoto, PRL, 2010.

Collective effects at high density of excitons.

1. Bose-Einstein condensation BEC.

Considered (Cu_2O) or achieved (heterostructures) in semiconductors.
Limited to low T_{BEC} because of low concentration n.
n is limited and needs continuous pumping because of "short"
$\propto$nanosec life time of excitons.
In conditions of femtosecond pumping and picosecond probes,
n grows to $\propto 10^{-2}$ yielding expectations T_{BEC} up to 100K.
The "short" time becomes "long" more than enough.

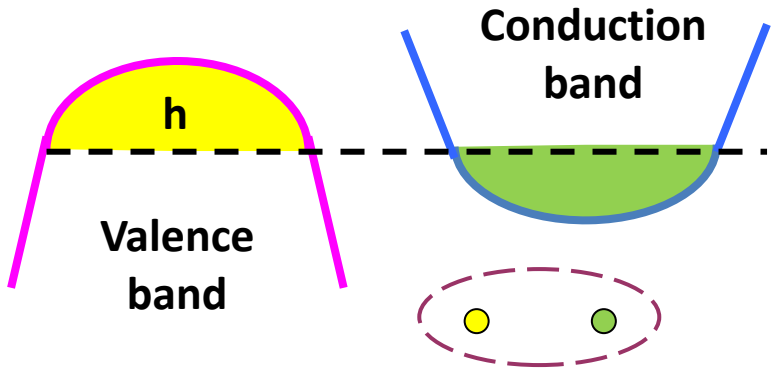
2. Excitonic insulator - EI. Excitons's density stays for ever as a component of the spontaneous interband hybridization.
Guessed for special conditions in low-gap semiconductors and in semimetals, the system can be thrown to the EI (meta)stabe state as the PIPT

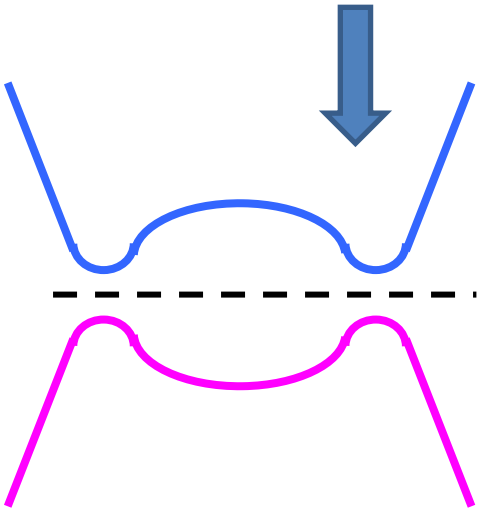
EXCITONIC INSULATOR

Metal – Insulator transition, CDW phase formation of almost pure electronic origin e.g. $TiSe_2$

Insulator – Insulator transition

Negative single particle gap, Eg<0

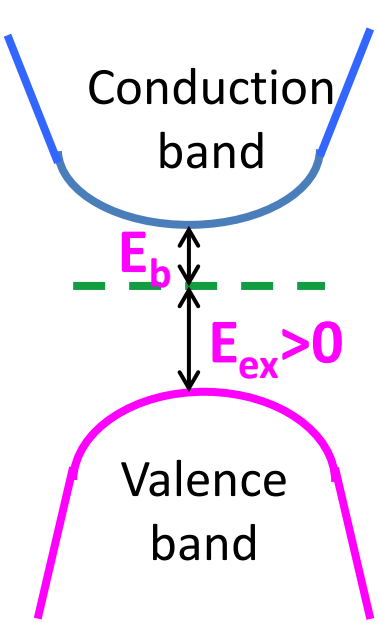


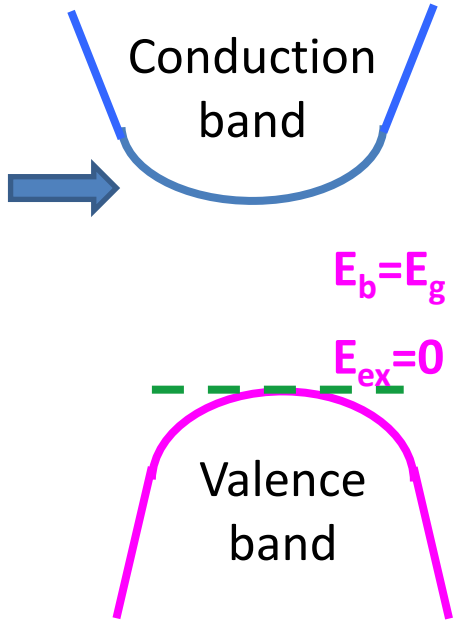


Positive single particle gap, Eg>0

$E_{ex}<0$

Energy of the exciton drops to zero: $E_{ex} = E_g - E_b \Longrightarrow 0$





Excitonic insulator (EI, nicknamed by W. Kohn et al): Tree of concepts

2nd order phase transition: Exciton energy $E_{ex} \longrightarrow 0$

Weakly 1st order insulator $\Longrightarrow$ insulator transition

We profit to view it as the EI

EI transition:

Insulator $\Longrightarrow$ Insulator

Neutral – Ionic transition with charge transfer excitons involved

Application to Donor-Acceptor System

EI transition as:

(semi)metal $\Longrightarrow$ insulator (Keldysh - Kopaev)

A contemporary version: CDW formation of almost pure electronic origin e.g. $TiSe_2$

First order phase transition

Phenomenological energy density

$$W(q) = E_{ex}^{0} q + \frac{a}{2} q^2 + \frac{b}{3} q^3 \qquad q = |\Psi|^2$$

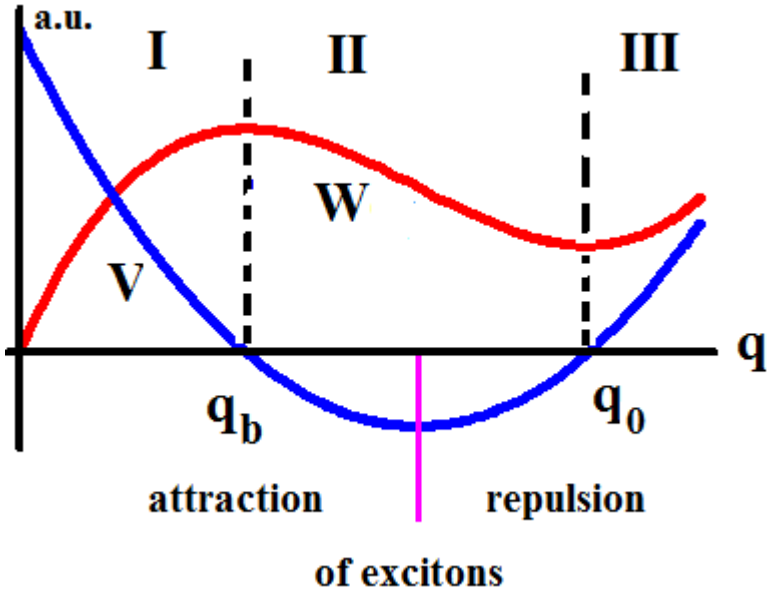
q – charge transfer

E_{ex}^{0} - bare exciton energy

$$E_{ex}(q) = V(q) = \frac{dW}{dq}$$

$$= E_{ex}^{0} + aq + bq^2$$

Thermodynamic definition of the exciton energy:



I : $E_{ex}(q)>0$ decreases with q, attraction of excitons

II : $E_{ex}(q)<0$, creation of excitons growing of $q \longrightarrow q_0$

III : $E_{ex}(q)>0$ increases with q, repulsion of excitons

Collective wave function of excitons $\Psi = |\Psi| \exp(i\varphi)$

Dynamical definition of the exciton energy: $E_{ex}(t) = -\hbar \frac{\partial \varphi}{\partial t}$

Enigma: Both *the exciton and the charge ordering* are built from processes of electronic transfer between D and A molecules.

Thermodynamic charge transfer :

- the order parameter and intensity of pumped excitation are of the **same origin**.
- Density of excitons $\mathbf{q=|\Psi|^2}$ is not distinguishable from the thermodynamic order parameter $\mathbf{q=\rho-\rho_n}$.
- Redistribution of the charge density **q**

  - a single real **non-conserved** field.

  The expected eq. allows for unrestricted evolution towards the energy minimum $d^2q/dt^2 \propto -dW/dq$

Charge transfer under pumping

First contradiction: **q** is the approximately **conserved** field $\mathbf{q=|\Psi|^2}$

Second contradiction: $\mathbf{\Psi = |\Psi| \exp(i\varphi)}$ -

the phase φ - appears as a hidden degree of freedom.

How can we make that compatible ?

Excitonic insulator EI instability when the exciton energy goes to zero.

Most general concept that some excitation energy $\mathbf{E_{ex}}$=0
covers all quantum phase transitions in insulators.

The focused concept of the EI is distinguished when the number of excitons, both in the ground state and out-of-equilibrium,
is approximately conserved.

(If it were conserved precisely, then there would be no dynamical path to the new equilibrium which is of particular importance for PIPT.)

Microscopic theories of the Bose condensate of pumped excitons and of the EI transition are closely related, differing mostly by monitoring parameters: the chemical potential $\boldsymbol{\mu_{ex}}$ and the density $\mathbf{n_{ex}}$.
(*L. Keldysh et al. P.B. Littlewood*)

That allows us to build a model describing jointly the dynamics of excitons and the evolution of the phase transition after the pumping.

Pump Induced Phase transition

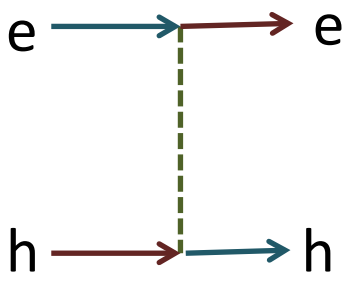
- The optical pumping gives rise to a high density of excitons
- Our main assumption: the quasi-condensate of optically pumped excitons appears sufficiently early as the macroscopic quantum state.
- Plausible: the very high initial pumping (up to 0.1 per site i.e. about 1 per exciton core length).
- Condensate part can be described by a macroscopic wave function $\Psi(x,t)$
- Generic case: the thermodynamic transition is governed by only one field: the charge transfer density q
- Field is not symmetry breaking, a first order phase transition is expected.

Excitonic insulator – instability when an exciton energy goes to zero.

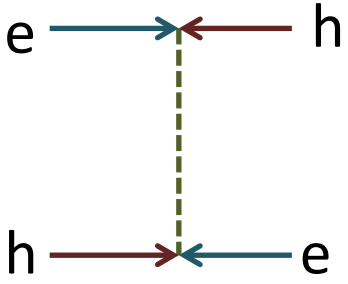
We take into account anomalous matrix element of Coulomb interactions transferring two electrons across the gap, from filled to empty band = simultaneous creation or annihilation of two e-h pairs = creation/destruction of two excitons from/to the vacuum.

Being virtual normally, the transition amplitudes acquire nonzero averages for macroscopic concentrations.

Normal, $E_{ex0}|\psi|^2$



Anomalous $S(\psi^2+\psi^{*2})$



$$S = |S| \exp(i\alpha)$$

S-term fixes the wave function phase in the EI ground state.

Dynamically it gives rise to oscillations of quantum interference among states which numbers of excitons differ by 2.

$$\Delta W = \frac{1}{2}(S^* \Psi^2 + S\Psi^{*2}) = |S| q \cos 2(\varphi - \alpha)$$

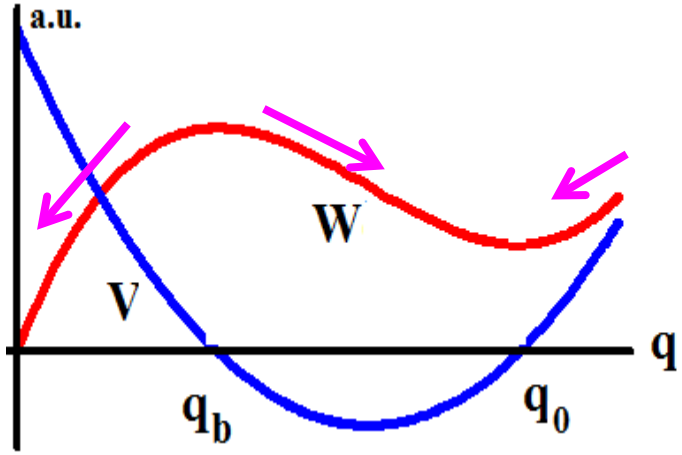
Shroedinger eq. for the time evolution of excitons' wave function.

$$i\hbar\frac{\partial\Psi}{\partial t}=-\frac{\hbar^2}{2M}\frac{\partial^2\Psi}{\partial x^2}+[V(q)-i\hbar\Gamma(q)]\Psi-S\Psi^*$$

Two channels to break the conservation of number of excitons:

$$\Gamma(q)\propto qV(q)\Rightarrow$$

$$qE_{ex}(t)\Rightarrow -q\frac{\partial\varphi}{\partial t}$$



Γ(*q*) = decay rate of the excitons' density ***q***:

- *constant at small q* (single-particle and recombination**)**
- ∝ ***q*** at moderate ***q*** (Auget processes, proved in semiconductor),
- vanishes in the minimum of **W** at **q≈q_0** as

Γ ~V(q) - no way to give up the energy from the local minimum.

No space dependence: a homogeneous regime or a multi-stable quantum dot - switching by absorbing the exciton

$$\partial_t q = -\frac{G}{\hbar} q^2 \left(V - |S| \cos 2\varphi\right) + |S| q \sin 2\varphi$$

$$\partial_t \varphi = -V + S\cos(2\varphi) = -E_{ex}(t)$$

Dilute limit q⟶0

$$E_{ex} = \sqrt{\left(E_{ex}^0\right)^2 - |S|^2}$$

$$\Psi(t) \propto \sqrt{E_{ex}^0 - |S|}\cos\frac{tE_{ex}}{\hbar} - i\sqrt{E_{ex}^0 + |S|}\sin\frac{tE_{ex}}{\hbar}$$

- Excitonic level is down-shifted
- Both positive and negative energies are present in the eigen mode
- Consequence of pair creation (annihilation) from (to) vacuum

Dense excitons, high q

$$\partial_t \Psi = 0, \quad \varphi = \pi n$$

Phase locking

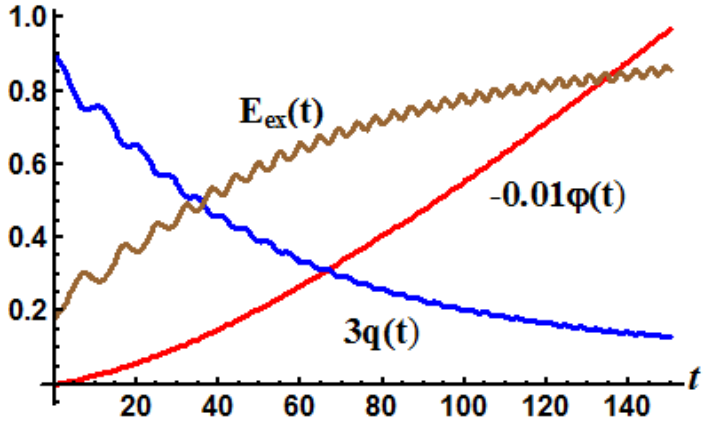
$\mathbf{q_0 \longrightarrow q_1}$ where $\mathbf{V(q_1) = |S|}$

Charge transfer exciton, modeling for quantum dot: Dynamical phase transition and quantum interference

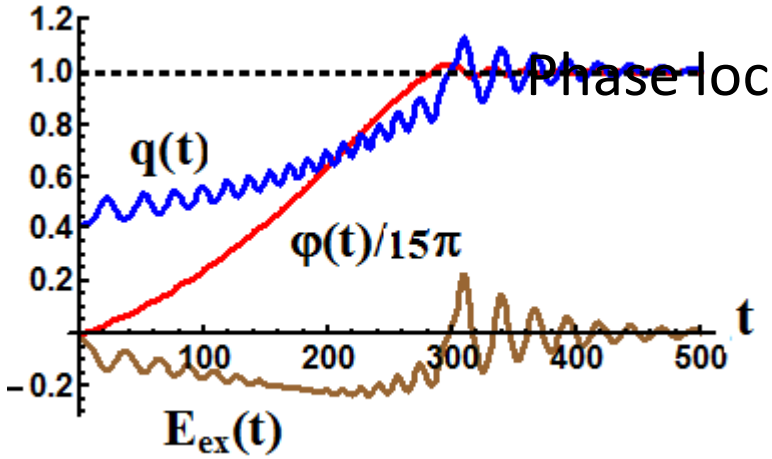
$S=0.01$, $q_b = 0.4$

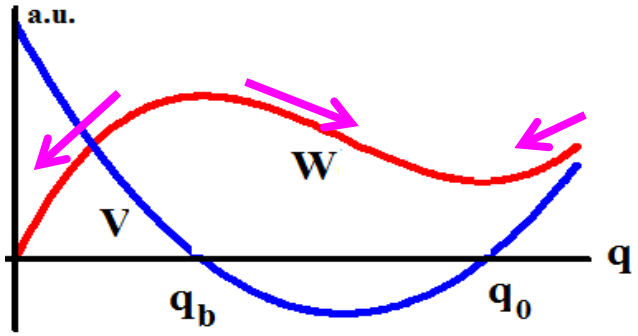
q_i= - initial concentration after pumping

Sub-barrier pumping, q_i=0.39



Super-barrier pumping, q_i=0.41



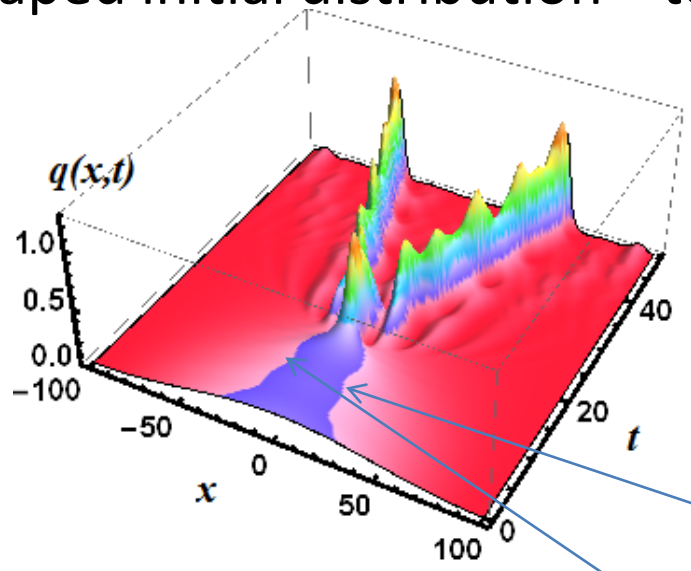


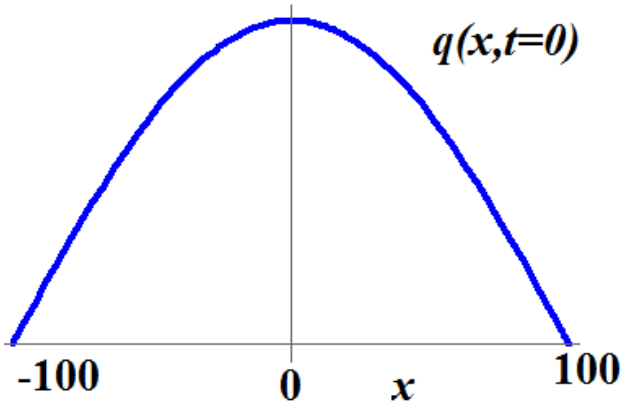
S-term gives rise to oscillations of quantum interference among states which numbers of excitons differ by 2.

Space-time modeling : from self-focusing to stratification

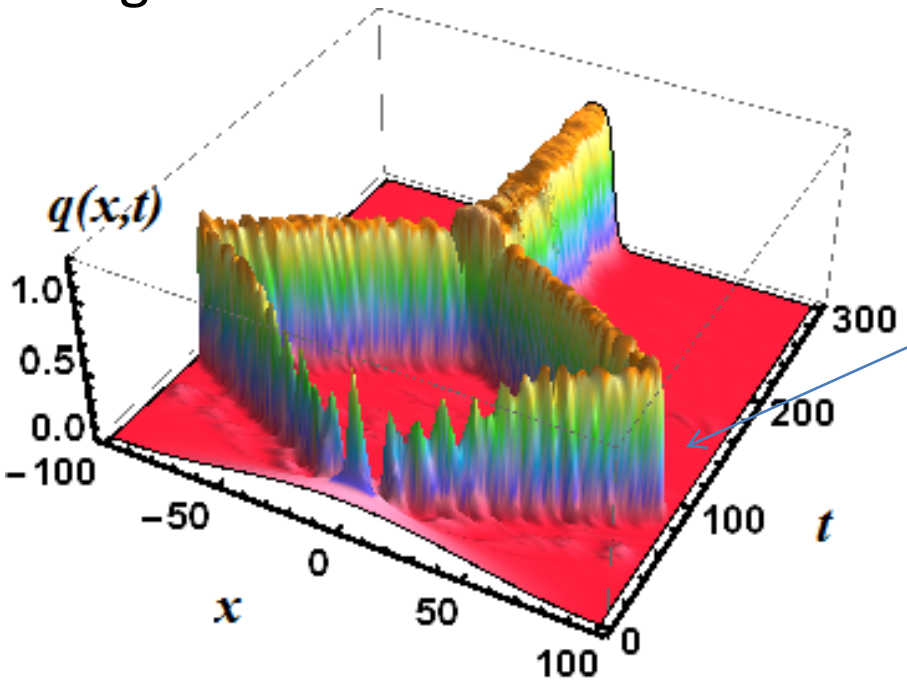
1. Well shaped initial distribution – to emulate inhomogeneuties

Short times



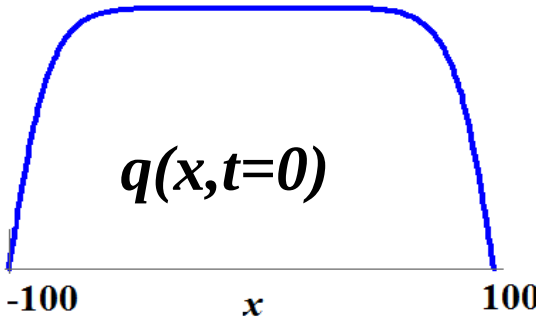


Long times

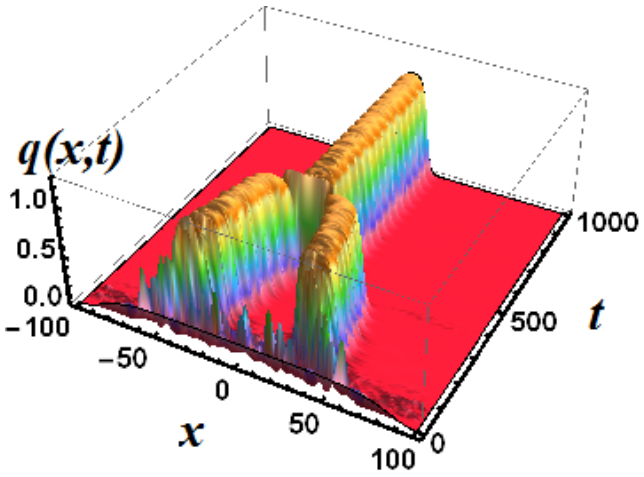


Pumping → self-focusing → single nucleation of two domains → their divergence → reflection from boundaries → collision → merging → persistent stratification to high- and low density domains

2. Flat initial conditions except near the boundary:

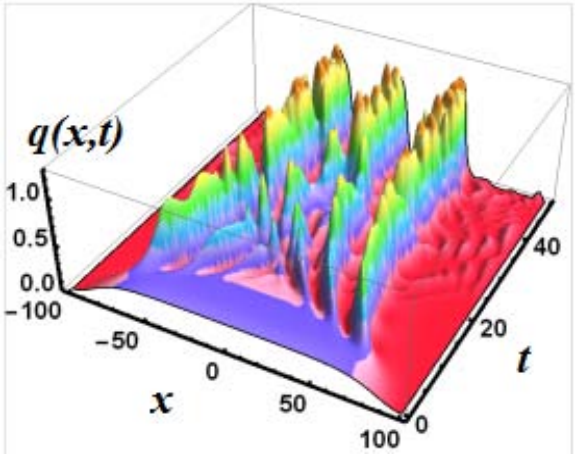


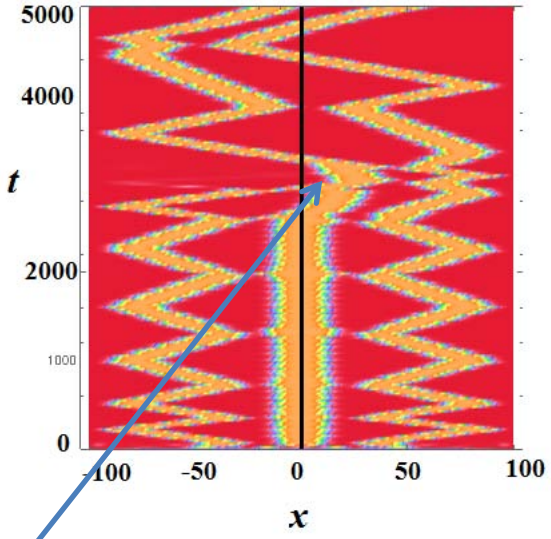
In both cases 1,2 new lower critical value $q_c<q_b$ appears allowing for PIPT already at $q_i<q_b$



$q_i \sim q_c$

Two domains are nucleated, attracting and finally merging into the infinitely stable stripe

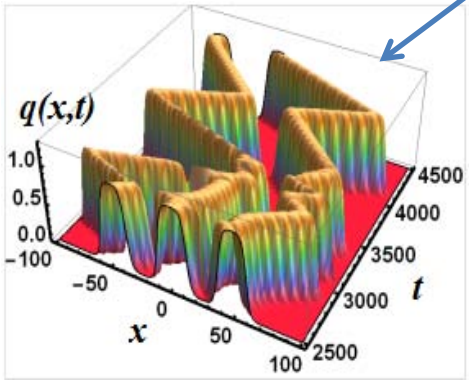


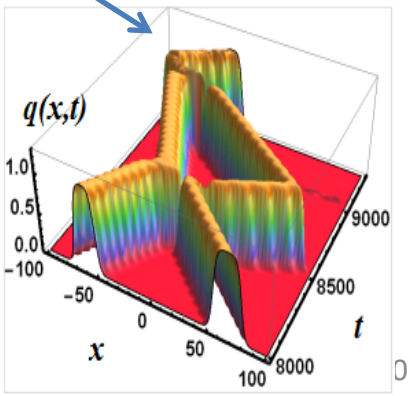


$q_i > q_c$

Three high density domains are nucleated.

The the side domains undulate, in a while they bumps destroy the central stationary domain, then they merge together.





Summary of the studied scenario

- A quasi-condensate of optically pumped excitons appears as a macroscopic quantum state.
- It evolves prone to instability, to self-trapping of excitons 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 which evolve through dynamical phase transitions and may persist even after the excitons recombine.
- Both thermodynamic and dynamic effects can be described on the same root by viewing the ordered state as the Excitonic Insulator.