



Inhomogeneous evolution of an ensemble of optically pumped excitons to a charge transfer state viewed as the excitonic insulator.

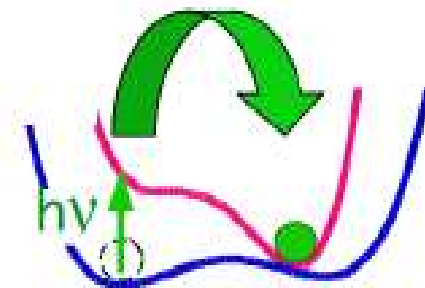
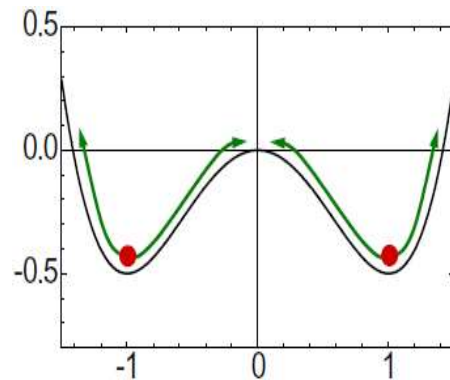
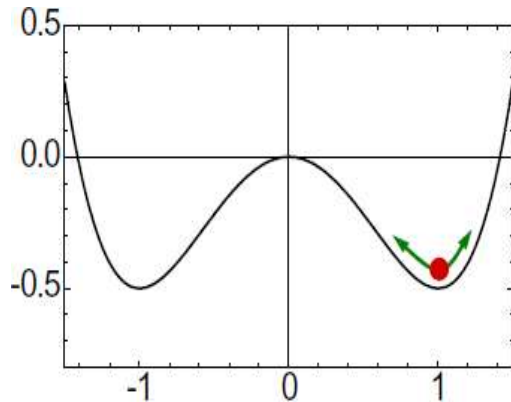
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After collaboration : with S. Brazovskii
Inspired : by visiting of H.Okamoto lab.

Typical routs in pump-induced evolution in electronic systems:

pumping the e-h plasma to affect the correlated electronic states:
CDWs; superconductors; Peierls, Mott or excitonic insulators.



The almost unexploited land of neutral excitations –

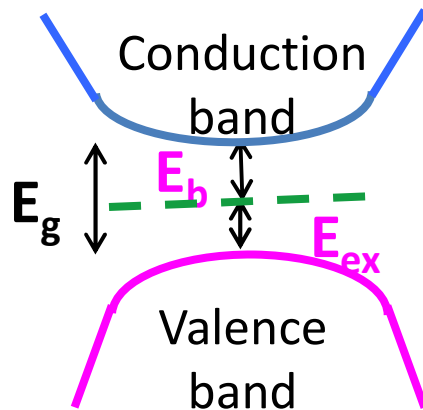
the pumped excitons in insulators prone to
electronic, magnetic, electric, or structural instabilities.

The particular region:

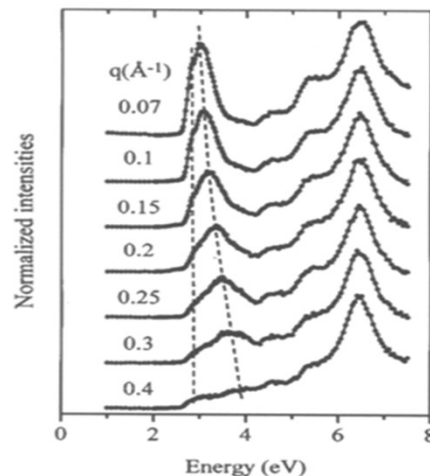
pumping to the Excitonic Insulator, e.g. a Charge Transfer State
- the subject of this presentation

The excitons in semiconductors or insulators

Excited pairs are either **free carriers – the fermions**,
 or their neutral bosonic **bound states – the excitons**.
Free pairs: minimal energy - the band gap E_g .

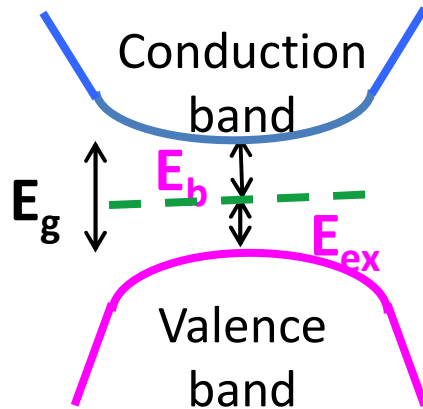


$$\text{Excitons: } E_{ex} = E_g - E_b < E_g, E_b = e^2/\epsilon R_{ex}$$



Exciton is a quasi-particle, a plane wave
 with a momentum k and the spectrum $E(k)$
 Only $k=0$ is measured in optics.
 Full $E(k)$ is available via the EELS

FIG. 3. Loss function, $\text{Im}(-1/\epsilon)$, of mLPPP as a function of the momentum transfer q .



Direct resonance pumping to excitons:

$$E_{\text{photon}} < E_g$$

- Excitons are initially delocalized plane waves: photons create them at $\mathbf{k}=\mathbf{0}$
- Excitons are initially ready to form macroscopic quantum state.

Deviation from the resonance $E_{\text{photon}} \approx E_{ex}$ (hot excitations)

- the phonon-assistant processes requiring for a stage of the energy relaxation.
- Intermediate stage of hot excitons as delocalized waves with momenta \mathbf{k} .
- Cooling below the bandwidth. Fast development of a quasi-condensate -the distribution peak at the lowest energy.

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

EXCITONS and PHOTO INDUCED PHASE TRANSITIONS

The interplay of pumping to excitons and incipient thermodynamic instabilities can be studied in numerous systems showing phase transitions from an insulating phase.

Three possibilities:

1. *Exciton density just interacts with the order parameter*, e.g. shifts the transition temperature. (intramolecular exciton)
2. a. *Exciton density contributes directly to thermodynamic order parameter*, this is the case of the charge transfer excitons with respect to the charge ordering transition.
2. b. *The growing concentration of excitons provokes an instability in another degree of freedom* – the case of the most intriguing experimental system : neutral-ionic transition in DA chains

experimental motivation for cases 2 a,b: studies of neutral-ionic phase transitions in organic-stack compounds

Neutral-Ionic Transition

TTF-CA: stacks of alternating donors D=TTF and acceptors A=CA.

$T > T_c = 81 \text{ K}$: molecules are weakly charged.

$T = T_c$: quasi-neutral to ionic transition.

Charge transfer ρ_n jumps from 0.3 to 0.7

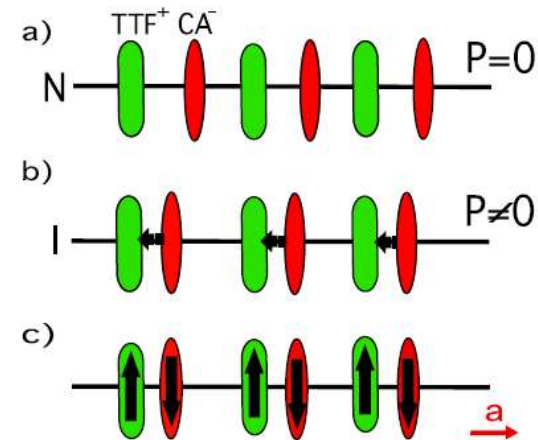
Charged molecules shift relative to each other – interpretations as either Coulomb or spin-Peierls instabilities, creating alternating long and short bonds.

With all inversion and mirror symmetries lifted, this might be the ferroelectric state.

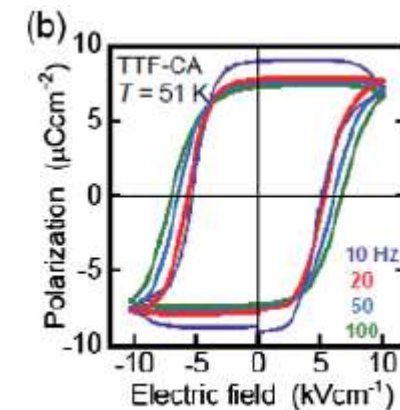
Thermodynamic charge transfer.

Primary effect: redistribution of the charge density ρ with no symmetry breaking, hence an isomorphic (liquid-gas class, 1st order) transition described by the single real field $q = \rho - \rho_n$.

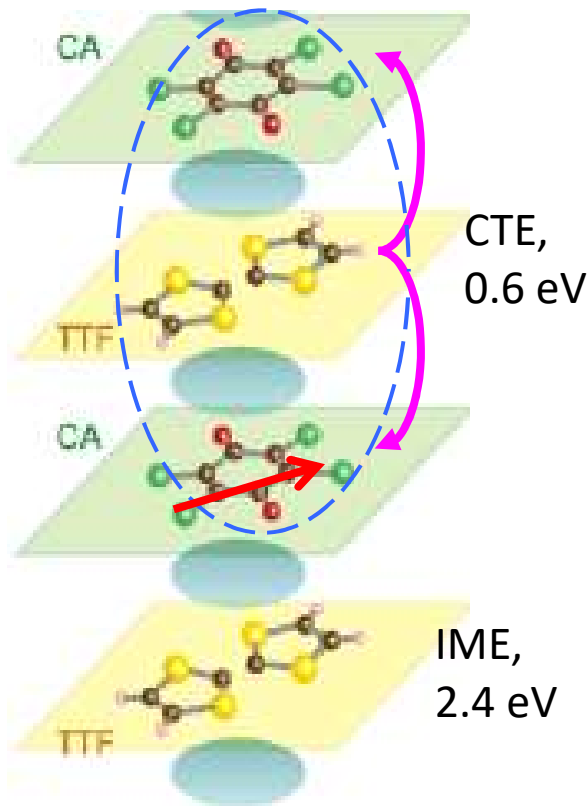
Actually – symmetry breaking because of complementary dimerization.



Electronic ferroelectricity



Excitons in organic donor-acceptor stack compounds.



Inter-molecular = charge-transfer excitons

CTE (H. Okamoto). (Wannier-Mott exciton)

Exciton density contributes directly to thermodynamic order parameter, this is the case of the charge transfer excitons with respect to the charge ordering transition.

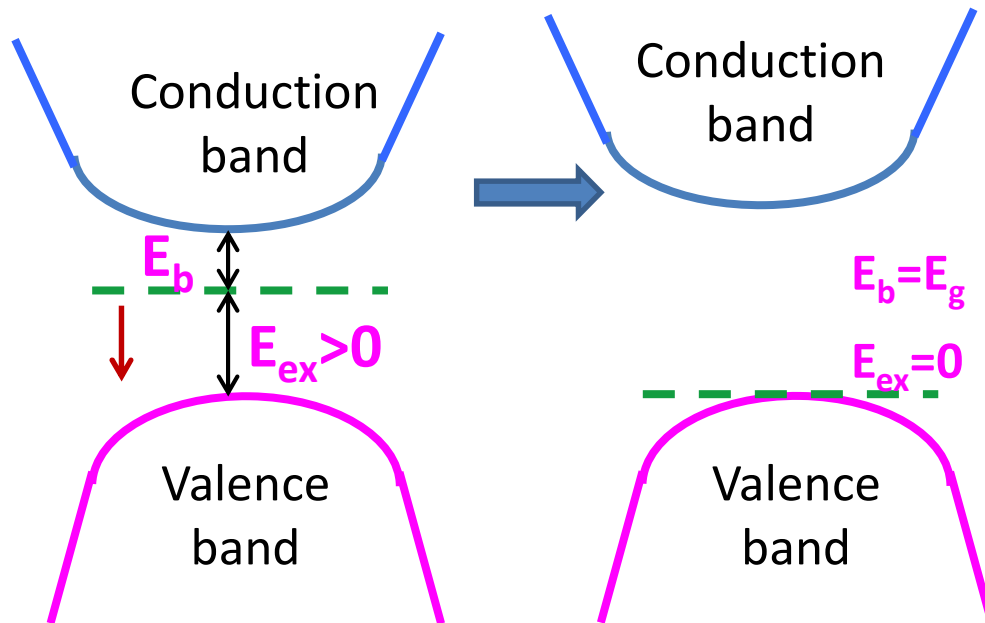
The growing concentration of excitons provokes an instability in another degree of freedom – the case of the most intriguing experimental system : neutral-ionic transition in DA chains

Thermodynamic order parameter and intensity $q = |\Psi|^2$ of pumped excitation are of the same origin.

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

Exciton density just interacts with the order parameter, e.g. shifts the transition temperature. (beyond today's scope)

EXCITONIC INSULATOR



Bose-Einstein condensation (BEC) of excitons L. Keldysh,
 Dielectrization of semi-metals
 Keldysh and Kopaev
 The excitonic insulator (EI) state
 J. des Cloizeaux, then
 W. Kohn, T.M. Rice, D. Jerome,
 summary by B.I. Halperin and T.M. Rice

Insulator – Insulator transition:

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

Below the transition: $E_{ex} < 0$:

finite density of excitons appears in the ground state,
 definitely described by the single wave function.

Evolution of the pump-induced condensate of excitons into the EI

- 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.
- **Plausibility:** 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
$$\Psi = |\Psi| \exp(i\varphi) \quad E_{ex}(t) = -\hbar \partial_t \varphi$$
- **Generic case:** the thermodynamic transition is governed by only one field: the charge transfer density \mathbf{q}
- **Field is not symmetry breaking,** a first order phase transition is expected as known experimentally.

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

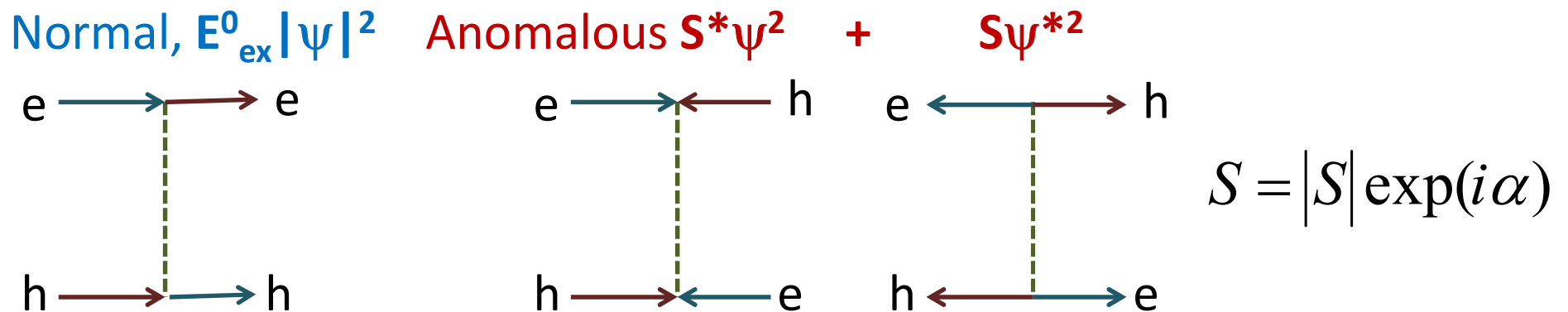
<i>Thermodynamic charge ordering</i>	<i>Pumping of charge transfer excitons</i>
order parameter $\mathbf{q} = \rho - \rho_n$.	Density of excitons $\mathbf{q} = \Psi ^2$
a single real non-conserved field.	Then \mathbf{q} is the <i>conserved</i> field
<p>The expected eq. allows for <i>unrestricted oscillations with a final evolution</i> towards the energy minimum in q</p> $\frac{d^2 q}{dt^2} + \gamma \frac{dq}{dt} \propto - \frac{\delta W}{\delta q}$	<p>$\Psi = \Psi \exp(i\phi)$ - the phase ϕ - appears as <i>hidden degree of freedom</i>.</p> $i\hbar \frac{\partial \Psi}{\partial t} = - \frac{\hbar^2}{2M} \frac{\partial^2 \Psi}{\partial x^2} + V(q)\Psi$ $\int \Psi \Psi^* dx = const$

How can we make both compatible ?

Possibility to exchange pairs of real excitons with the ground state.

We have to 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 only virtual usually, the transition amplitudes acquire nonzero averages for macroscopic averages



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

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

S-term fixes the wave function phase in the EI ground state (Keldysh & Guseinov, 1973)

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

First order phase transition, generic model for the excitonic insulator, no deformations, only charge transfer is involved

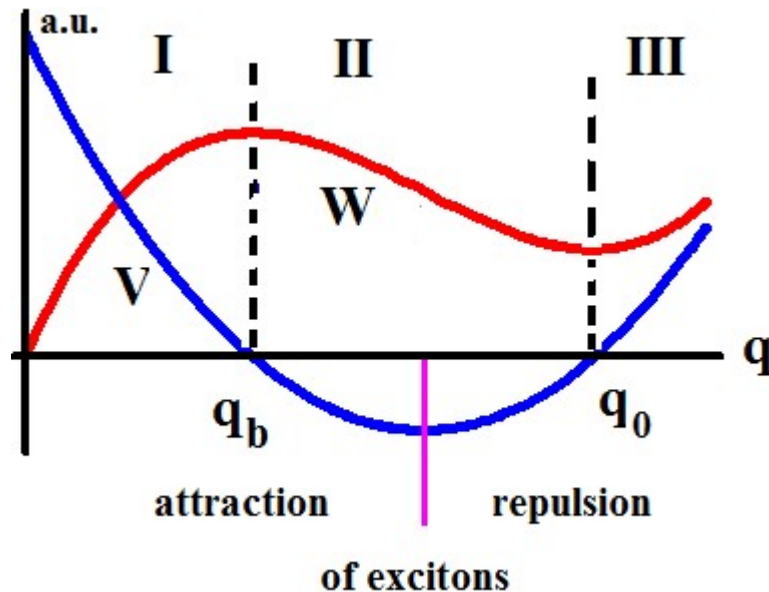
Phenomenological energy density:

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

E_{ex}^0 - bare exciton energy, $q = |\Psi|^2$ - charge transfer

Thermodynamic definition of the exciton energy:

$$E_{ex}(q) = V(q) = \frac{dW}{dq} = E_{ex}^0 + aq + bq^2$$



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

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

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

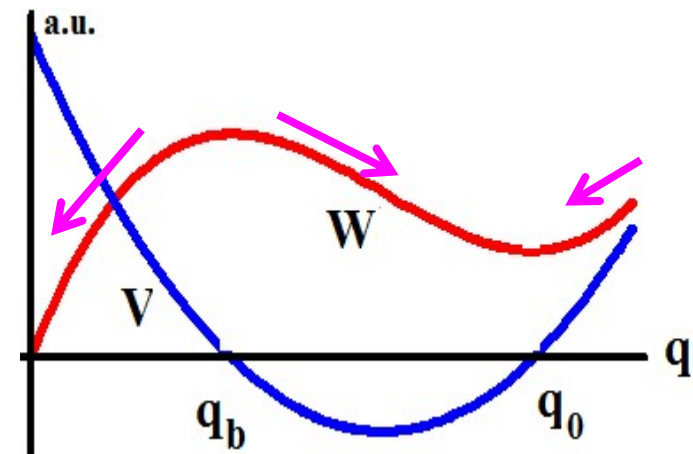
Schrödinger eq. for the time evolution of excitons' wave function.

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

Two channels to break conservation of number of excitons
nondissipative **S** & dissipative **Γ** :

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

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



$\Gamma(q)$ = decay rate of the excitons' density q :

constant at very small q (single-particle and recombination), not our case

$\propto q$ at moderate q (Auger processes, proved in semiconductor),

*vanishes in the minimum of **W** at $q \approx q_0$ as $\Gamma \sim V(q)$*

- no energy relaxation from the local minimum.

No space dependence – a homogeneous regime or a multi-stable quantum dot. Ground state switching by pumping the exciton

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

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

Dilute limit $q \rightarrow 0$ $E_{ex} = \sqrt{(E_{ex}^0)^2 - |S|^2}$

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

- 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

$\mathbf{q}_0 \rightarrow \mathbf{q}_1$ where $\mathbf{v}(\mathbf{q}_1) = |S|$

Modeling for an enforced homogenous regime:

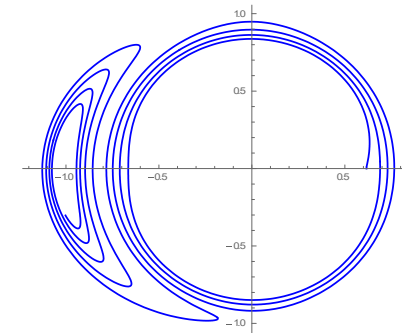
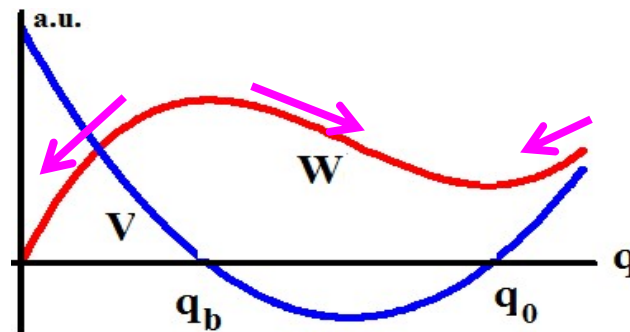
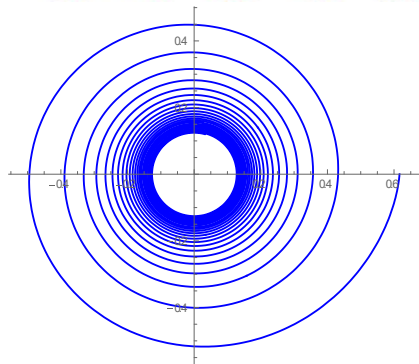
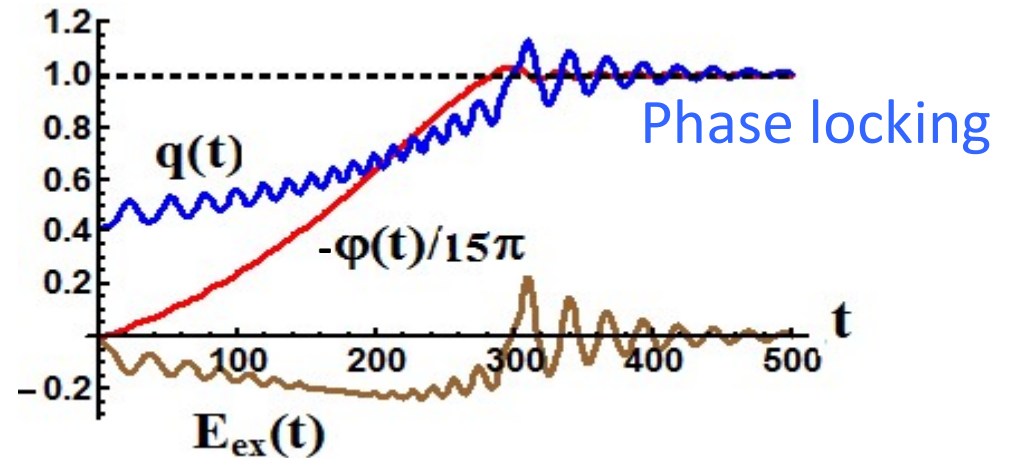
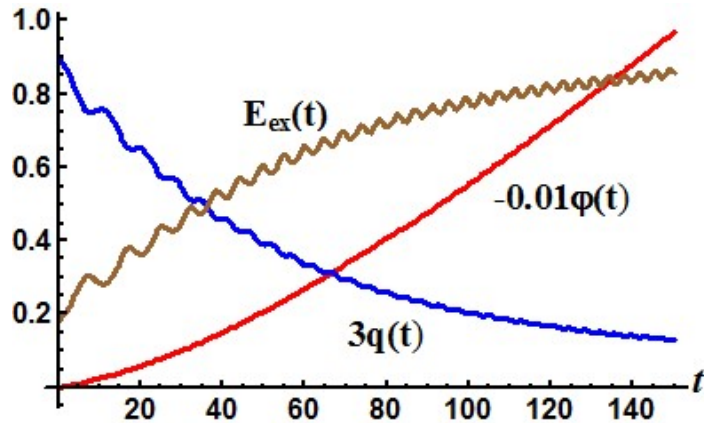
$S=0.01, q_b = 0.4$

Dynamical phase transition and quantum interference

$q_i =$ - initial concentration after the pumping pulse

Sub-barrier pumping, $q_i=0.39$

Super-barrier pumping, $q_i=0.41$



Polar trajectory $q(\phi)$

Polar trajectory $q(\phi)$

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

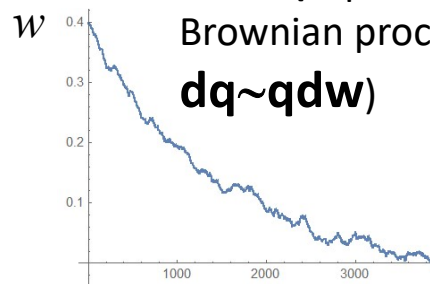
**Normal \rightarrow condensate conversion and decoherence.
Attempt of modelling for a small system.**

Schroedinger Eq. augmented by a stochastic processes

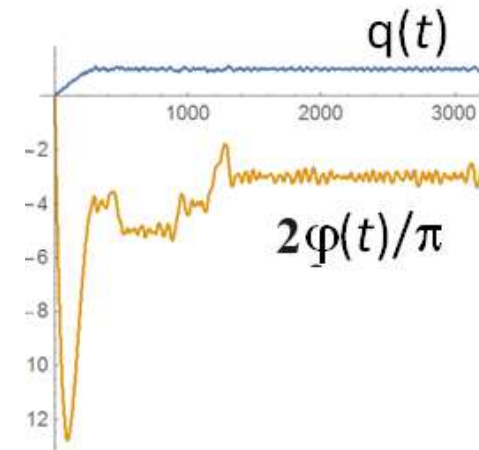
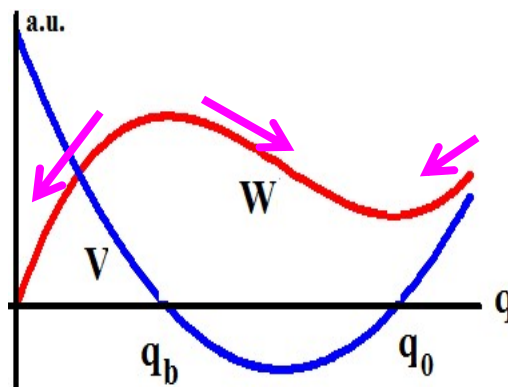
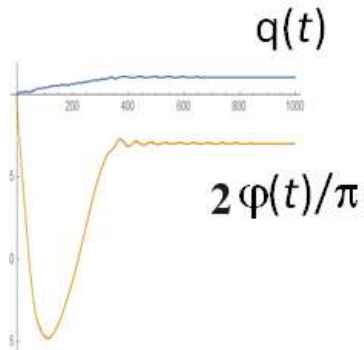
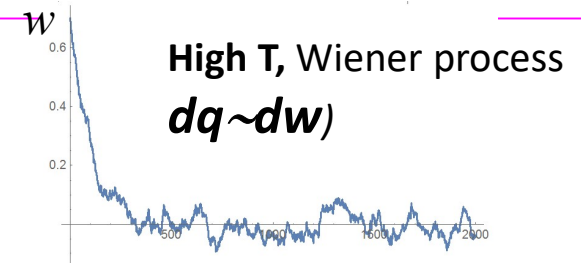
$$\partial_t \varphi = -V + S \cos(2\varphi) \quad \partial_t q = -\frac{G}{\hbar} q^2 (V - |S| \cos 2\varphi) + |S| q \sin 2\varphi - \frac{dw}{dt}$$

A random function w describes in average the exponential exhaustion of the reservoir of the normal particles by their diffusion in energy space down to the condensate

**Low T (exponential
Brownian process
 $dq \sim q dw$)**

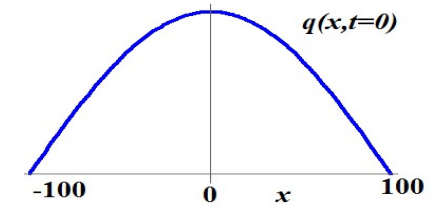


Random increments of q
are transferred to the
frequency kicks hence to
the **Phase decoherence**

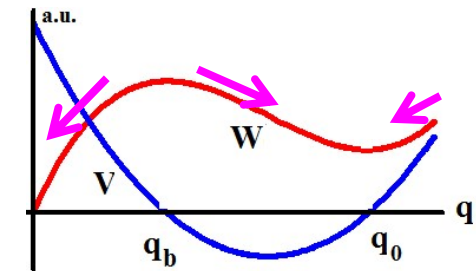
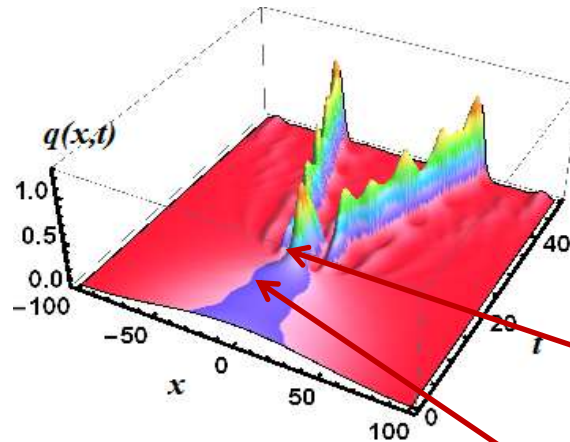


Space-time modeling : from self-focusing to stratification

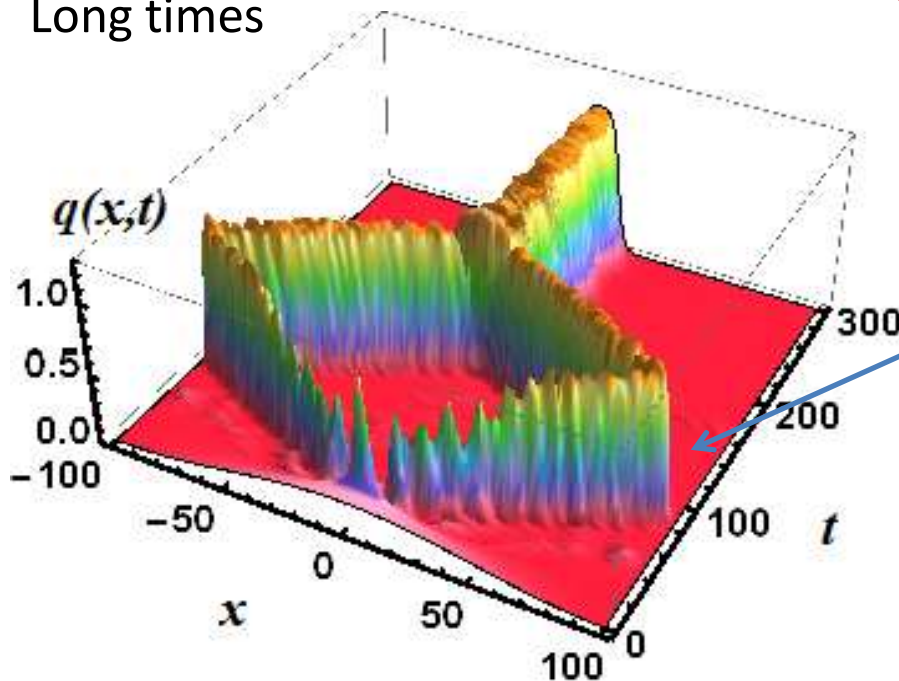
Well-shaped initial distribution - *everywhere subbarrier*



Short times



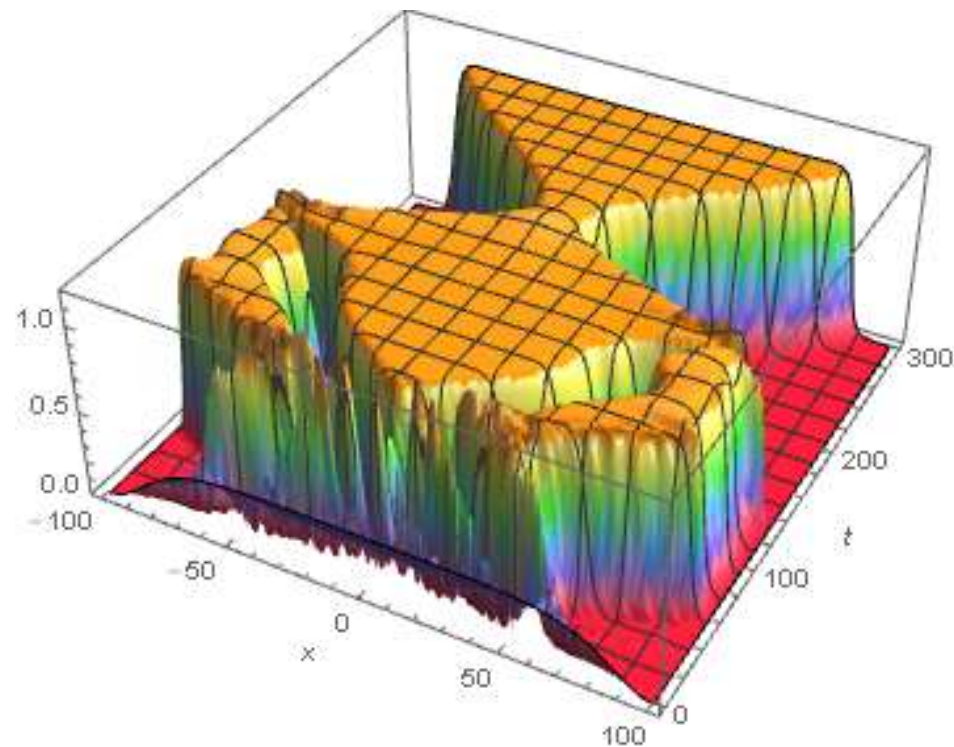
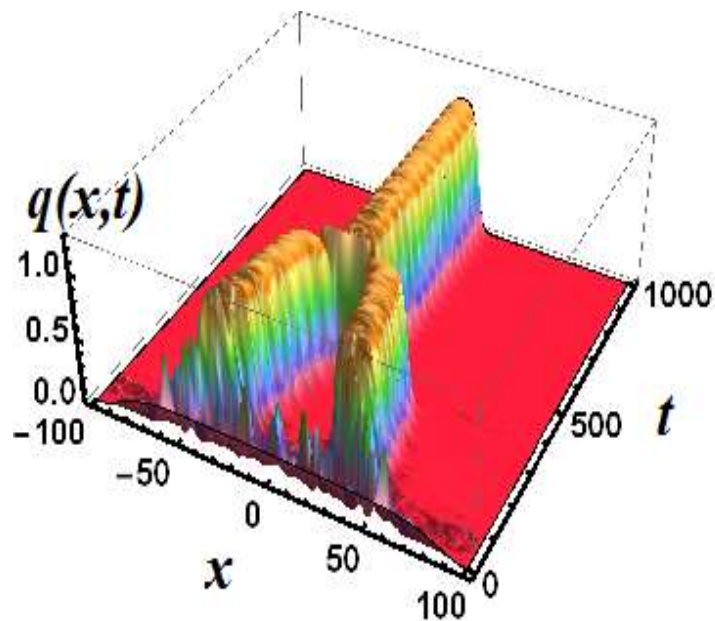
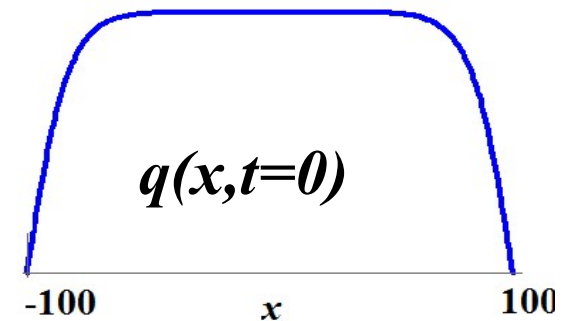
Long times



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

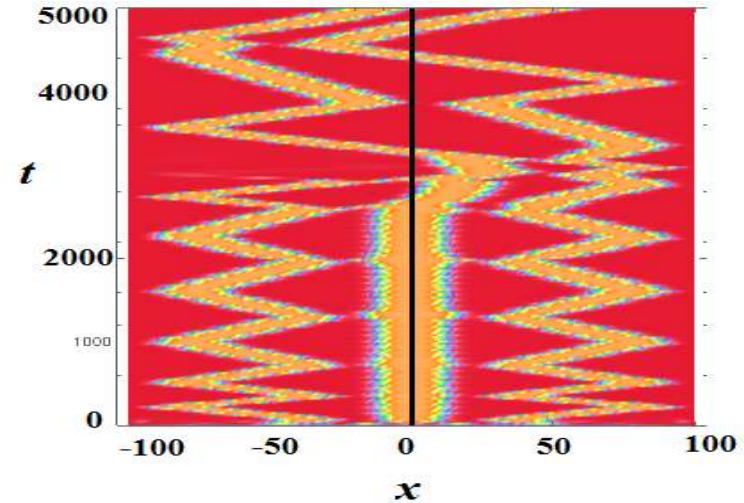
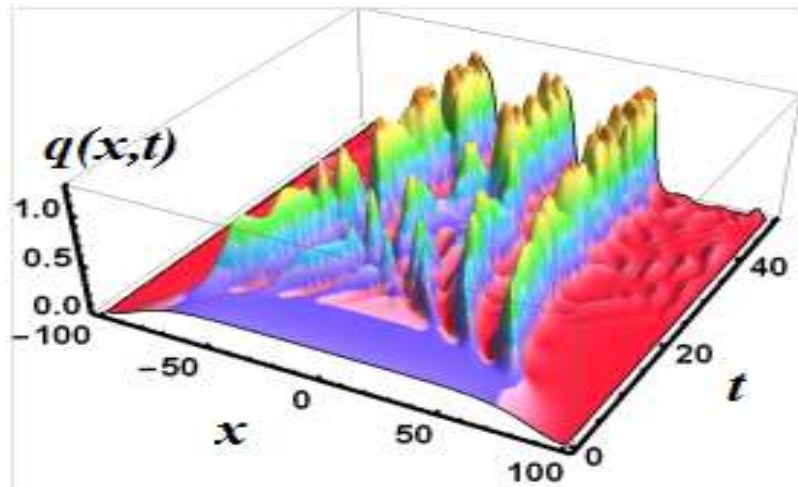
Flat initial conditions, except for near the boundary:

In all cases, new lower critical value $q_0 < q_b$ appears allowing for PIPT already at $q_i < q_b$

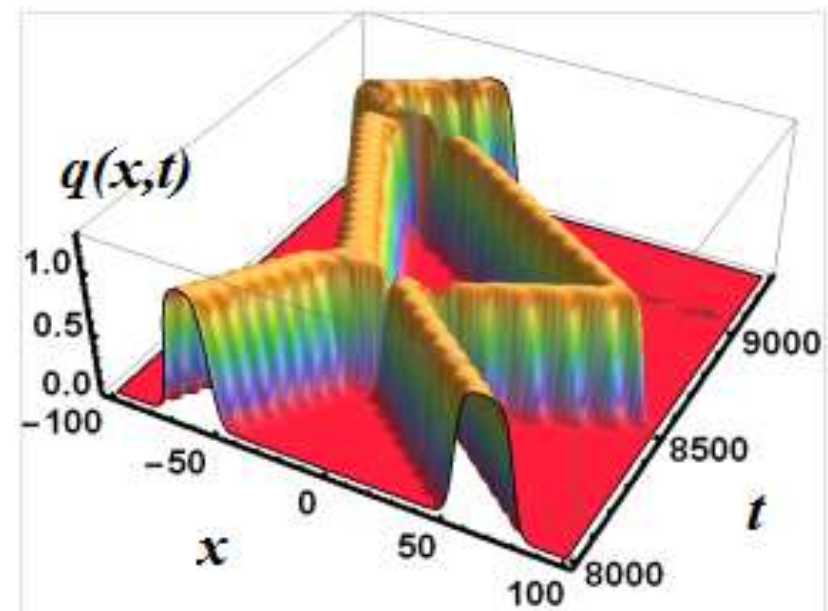
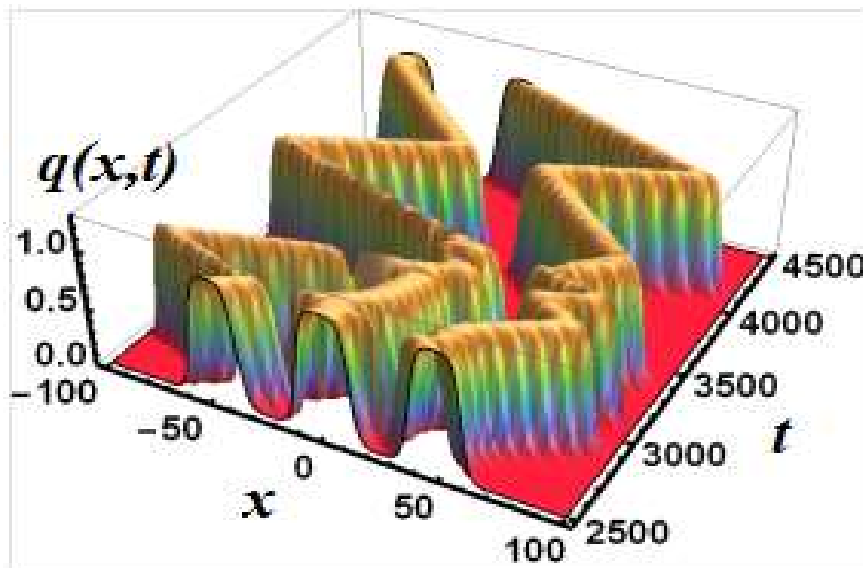


$q_i \sim q_0$ Two or three domains are nucleated, attracting and finally merging into the infinitely stable stripe

Stronger pumping, still sub-barrier



$q_i > q_c$ Three high density domains are nucleated. The side domains undulate, in a while they bump destroying the central stationary domain, then they merge together.



Conclusion

- The excitons can be pumped to a system prone to a first order transition to the excitonic insulator state.
- A quasi-condensate of pumped excitons evolves interacting with other degrees of freedom prone to instability, with self-trapping of excitons akin to self-focusing in optics.
- Both thermodynamic and dynamic effects can be described on the same root by viewing the ordered state as the Excitonic Insulator.
- The excitation and the long range ordering can be built from the same intermolecular electronic transfer.
- 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.

Hidden problems: from incoherently pumped excitons to their Bose condensate.

➤ *Initial hot excitons:*

Conventional ensemble of Bose particles, occupation numbers n_k of normal states $|k\rangle$ are ~ 1 with respect to the total large number N of particles. Ensemble of uncorrelated wave functions $\Psi_k \sim \exp(i\mathbf{k}\cdot\mathbf{x} - E_k t)$.

Description: Boltzmann kinetics.

➤ *Under cooling process* –

➤ an intermediate state of a quasi-condensate at lowest E_k , $n_k \gg 1$.

Description: quasi-classical Gross-Pitaevskii eq. in the turbulent regime for the condensate plus the kinetics for the down-flow of normal particles.

➤ *Low T equilibration:* $n_0 \sim N$ described by the single wave function

$$\Psi_0 \sim n_0^{1/2} \exp(i\varphi(\mathbf{x}, t)), \quad \partial \varphi / \partial t = -E_0$$

plus the equilibrium Bose-Einstein distribution (with the chemical potential locked at E_0) for normal particles. Our assumption.

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 a low concentration n of excitons.

n is limited and needs continuous pumping because of “short”

\propto nanosec life time of exciton

In conditions of femtosecond pumping and picosecond probes,

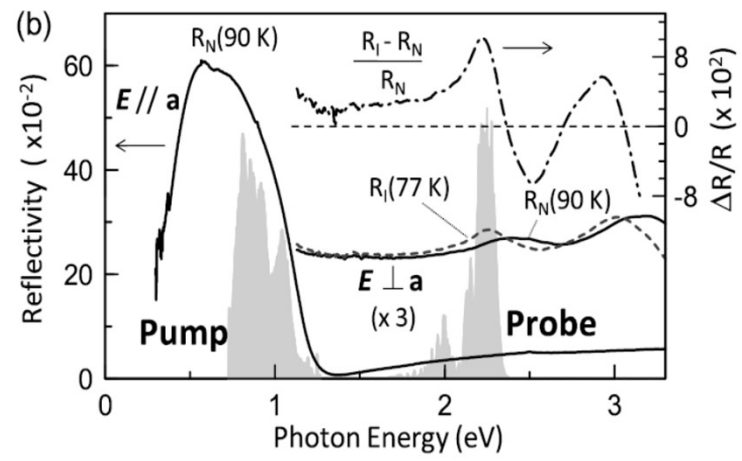
n grows to huge $\propto 10^{22}$ yielding expectations T_{BEC} up to **100K**.

The “short” life time becomes “long” more than enough.

2. *Excitonic insulator - EI.* Excitons’s density is built-in as a component of the spontaneous interband hybridization. (μ)

Guessed for special conditions in low-gap semiconductors and in semimetals.

The bare system can be thrown to the **EI** (meta)stable state as PIPT



Excitonic insulator under optical pumping (EI): the tree of concepts

Any case of quantum phase transition ==
2nd order phase transition:
The energy of some excitation $E_{\text{ex}} \rightarrow 0$

Weakly 1st order insulator
to insulator transition
We profit to view it as the EI

EI transition:
Insulator to Insulator

Neutral – Ionic transition
with charge transfer excitons
involved

Application to Donor-
Acceptor Crystals

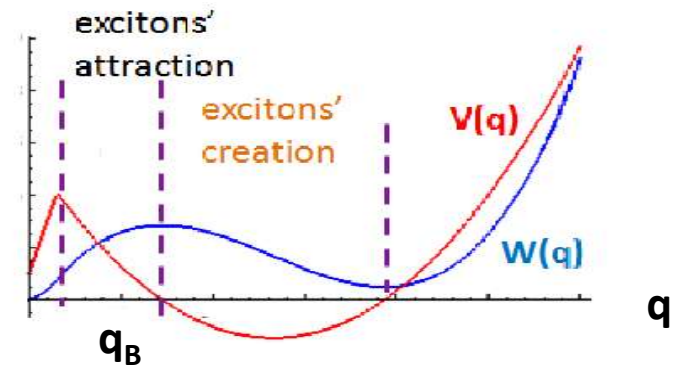
Including these secondary symmetry breaking order parameter.

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

h – dimerizational displacement

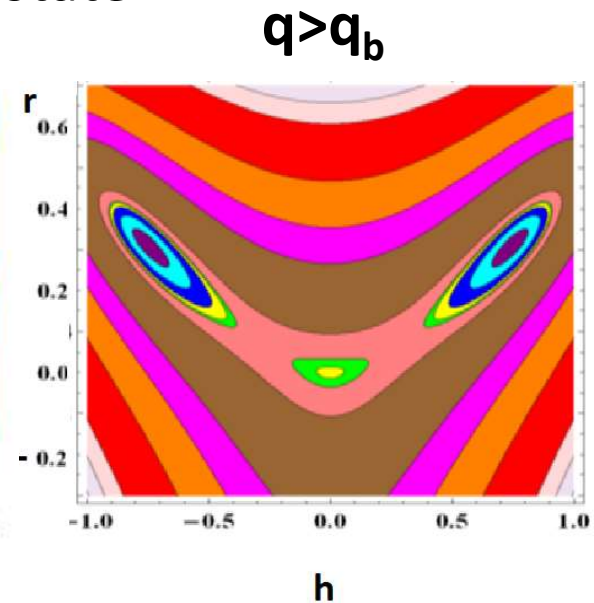
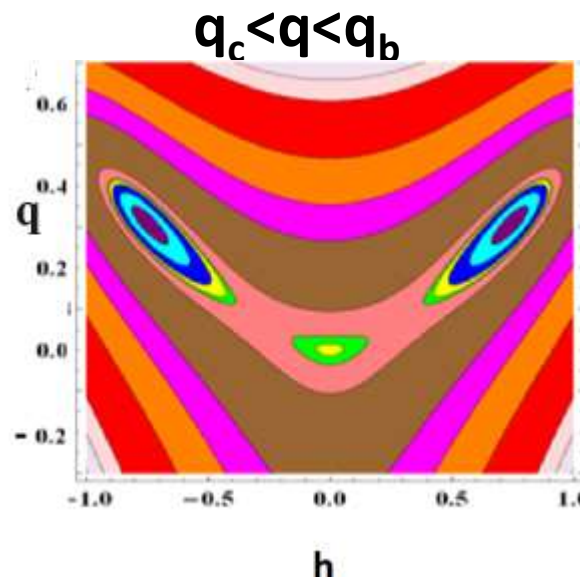
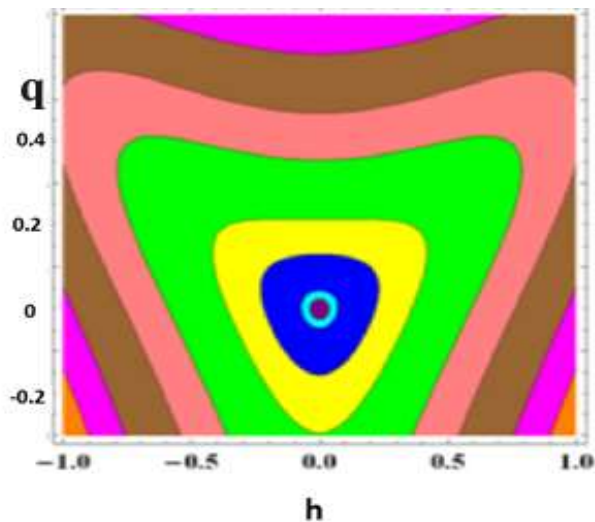
$q_c(T)$ - monitoring parameter:

critical value of q for instability in h



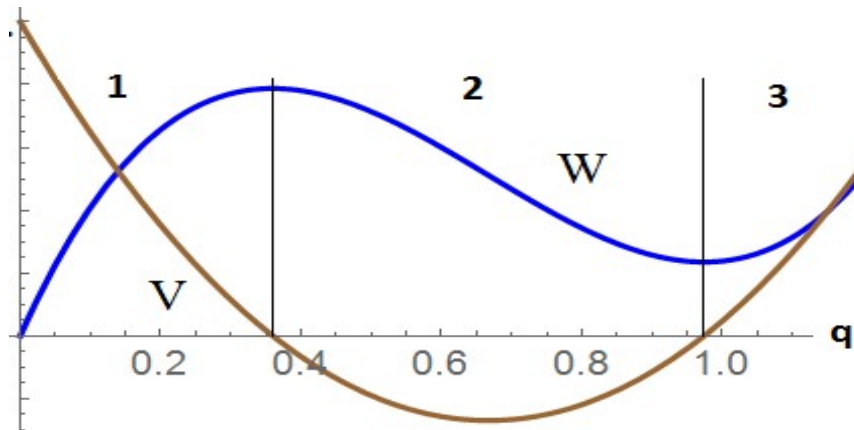
$q < q_c$: trivial minimum
at $q=0$, $h=0$

Double minima at $q > q_c$, $h = \pm h_0$ appear and
evolve to the ionic state

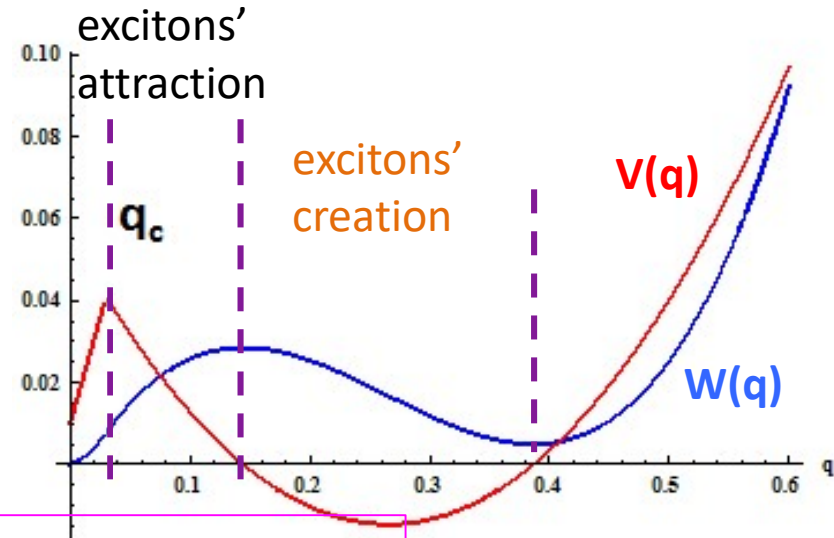


Pecularity of the system with two order parameters -
inflation point in $W(q)$ and the critical parameter q_c

Generic EI



$W(q,h) \rightarrow W^*(q)$ and $V(q,h) \rightarrow V^*(q)$
after minimization over h .



Inflation point **Concave** \rightarrow **Convex** .

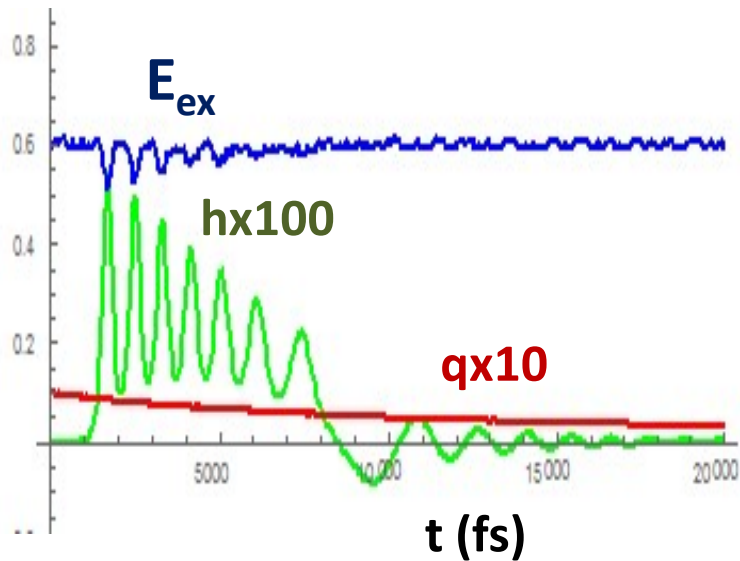
4 intervals of q : **repulsion**, attraction, creation, repulsion of excitons

$q_c > 0$ - critical value of q for instability in h :

$$h(q < q_c) = 0 \Rightarrow h(q \geq q_c) = \pm \sqrt{(q - q_c)d / 2f}$$

Homogeneous regime or multi-stable quantum dot $S=0.01$

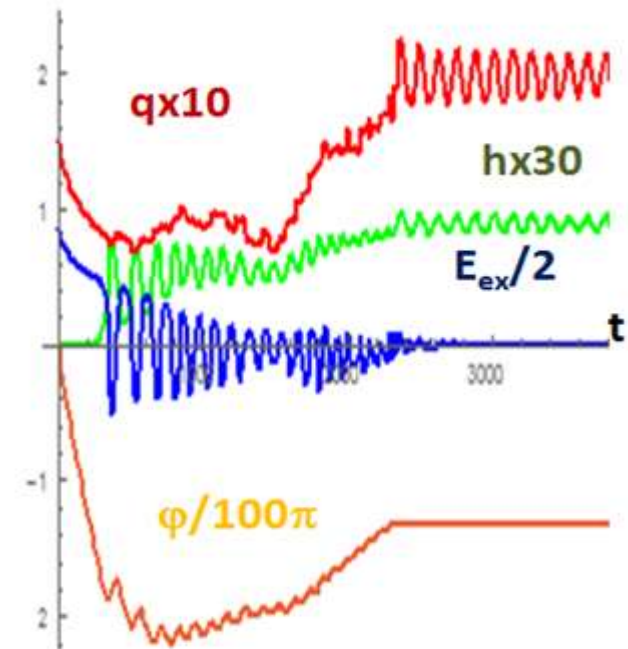
Subcritical pumping $q(0) < q_B$



Strong initial perturbation,
 q and h vain at large t .
Small oscillations of the exciton
energy from the macroscopic
quantum interference:
excitons' pair creation from the
vacuum

Supercritical pumping $q(0) > q_B$

q rises above the initial pumping level by
generation of excitons from the vacuum.



Strong unharmonic oscillations at
intermediate times.
Sharp lock-in transition of the phase
 \rightarrow the new set of strong oscillations.

The excitons in semiconductors or insulators

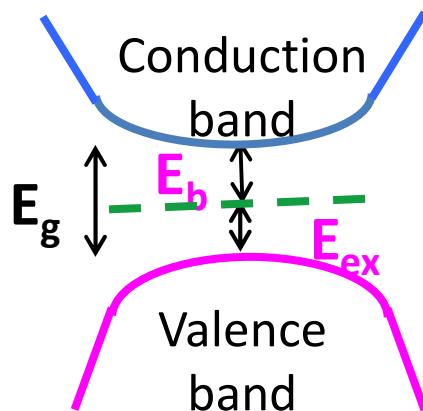
Excited pairs are either **free carriers** – the fermions,
or their neutral bosonic **bound states** – the excitons.

Free pairs: minimal energy - the band gap E_g .

Wannier-Mott exciton:

electron-hole pair bound by long range Coulomb forces.

Its energy $E_{ex} = E_g - E_b < E_g$, $E_b = e^2/\epsilon R_{ex}$ - the binding energy:



An exceptional fortune: direct resonance pumping to excitons:

$$E_{\text{photon}} \approx E_{\text{ex}}$$

Excitons are initially delocalized plane waves created by photons at $\mathbf{k}=\mathbf{0}$
These excitons are initially ready to form macroscopic quantum state.

Deviation from the resonance $E_{\text{photon}} > E_{\text{ex}}$ (hot excitons)

Phonon-assistant processes are required for a stage of the energy relaxation.

Intermediate stage of hot excitons as delocalized waves with a distribution of momenta \mathbf{k} .

After cooling below the bandwidth - fast development of a quasi-condensate -the distribution peak at the lowest energy.

Less understood : Establishing of the phase coherence.

Wave function Ψ of the condensate evolves interacting with other degrees of freedom.