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

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OUTLINE

- Introduction. Time resolved phase transformations induced by optical pumping of excitons in a media prone to an instability.
- The workshop of excitons in donor-acceptor chains with neutral-ionic transitions
- Intramolecular excitons interaction with the order parameter: Entangled dynamics of the excitonic condensate and the order parameter. Spacio-temporal evolution: space segregation from self-focusing. Local dynamic transitions at subcritical pumping.
- Charge transfer excitons merging with the order parameter: Joint Shroedinger eq. for the excitonic condensate and the ordering. Evolution of the exciton energy down to zero in the ordered state. Coherent oscillations from quantum interference in the exciton condensate.
- Conclusions, unsolved problems.

Femto-second pump&probe technique: goals and advantages.

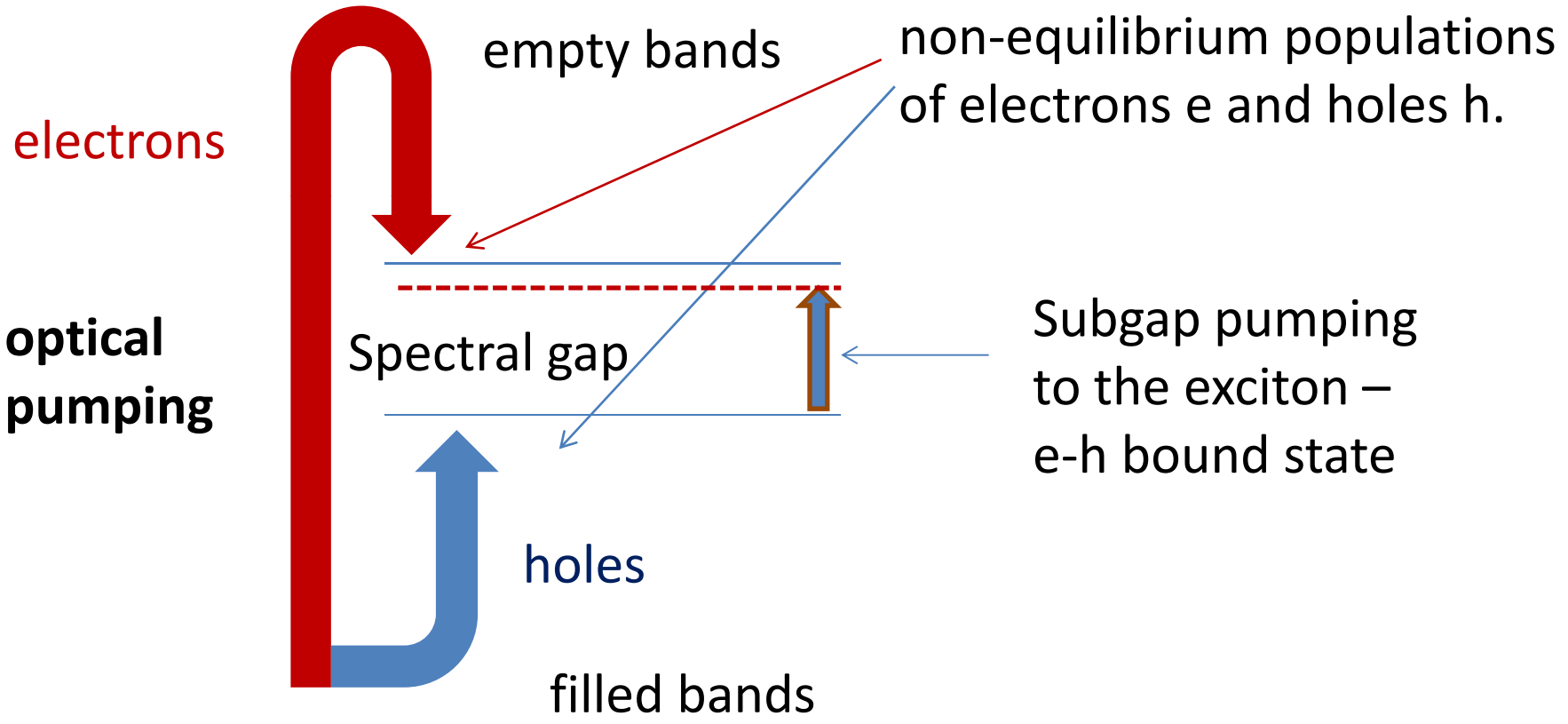
Technique: pump sharply to a very high (up to 10%)
concentrations of excitations (electron-hole pairs or bound excitons)
and follow the evolution – with a resolution down to 10fs –
by means of fast probes – optics, ARPES, diffraction.

Goals and advantages:

Disentangle fast (10^{1-2} fs) electronic and
"slow" (ps) lattice degrees of freedom,
Understand properties of the starting system,
Provoke the dynamic evolution over
a wide range of the known phase diagram,
Reach short leaving hidden H states
unavailable in thermodynamic approaches,
Obtain a truly stable H state with an unlimited life time.
The last super-goal has been just realized,
for the first time in an electronic system
– the content of this presentation.

Nonlinear "femto-second" optics - time resolution ~**10fs~10^{-14}** sec
Shorter than pico-second scale of phonon's periods

$1/\nu_0 = 2\pi/\omega_0 \sim 1ps = 10^{-12}$ sec



Donor-acceptor chains - workshop for pumping of excitons

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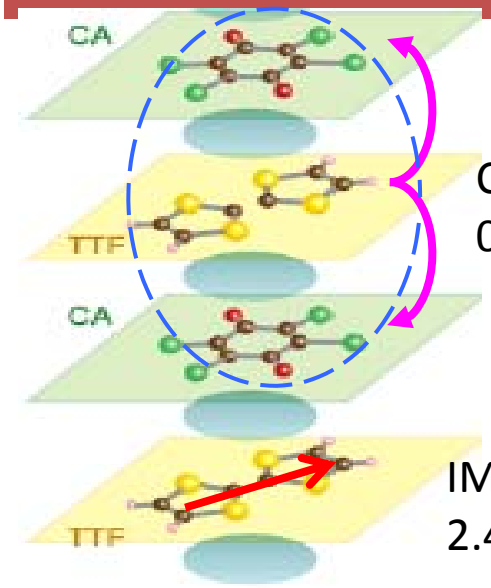
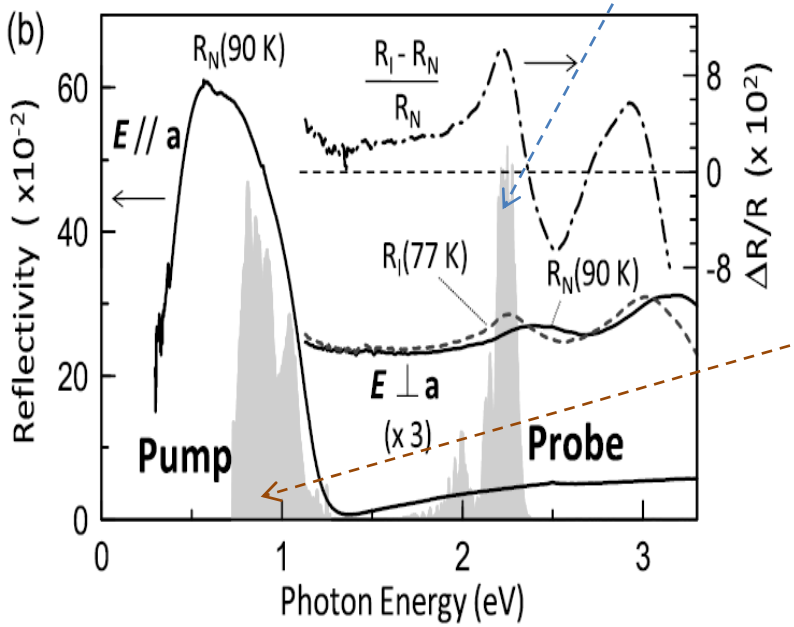


CTE,
0.6 eV

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.

H. Uemura, H. Okamoto,
PRL, 105, 2010.

Neutral-Ionic Transition in donor-acceptor chains.

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

T>Tc=81 K: molecules are weakly charged.

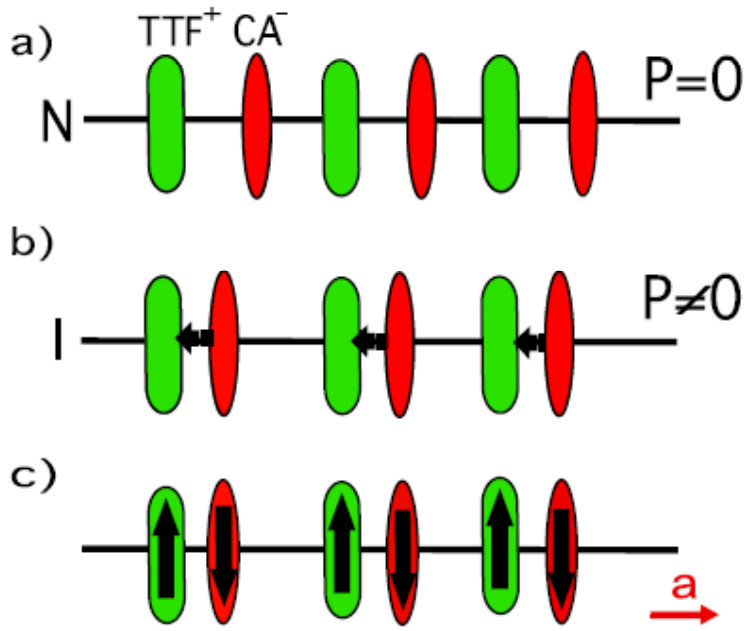
T=Tc: quasi-neutral to ionic transition – 1st order.

Charge transfer **ρ** jumps from ρ_n =0.32 to ρ_i = 0.52

Charged molecules shift relative to each other – Coulomb or spin-Peierls instabilities:

alternation of long and short bonds.

With all inversion and mirror symmetries lifted, this is the electronic ferroelectric.



Tokura teams, Nagaosa, Koshihara and Okamoto, Luty , Caileux

Thermodynamic charge transfer. *Primary effect:*
redistribution of the charge density **ρ** with no symmetry breaking -
an isomorphic transition described by the single real field q=**ρ- ρ_n**.
Actually – symmetry breaking because of the complementary dimerization;
Still of the 1st order by influence of **ρ**

Intramolecular exciton interacting with order parameter.

h – dimerizational displacement of molecules

$q=\rho-\rho_n$ - charge transfer, with respect to the neutral phase,

q_c – monitoring parameter $q_c(T)$

The energy density:

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

$q_c > q_n$– critical value of q for instability in h:

$$h=0 \Rightarrow h=\pm\sqrt{\frac{q-q_c}{q_c}\frac{c}{f}}$$

At presence of N pumped excitons in the state with a wave function ψ,

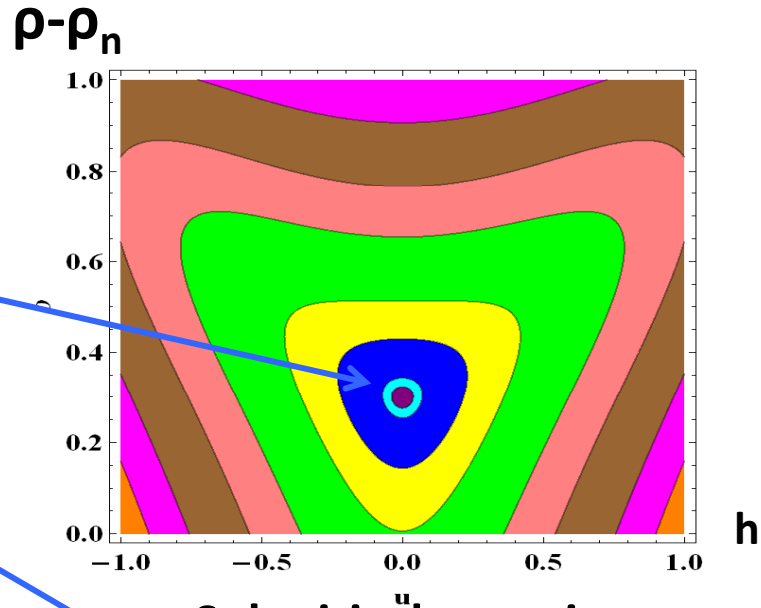
- add the coupling energy $-g\,\rho|\psi|^2$
- add the excitons' repulsion energy $k|\psi|^4/2$
- ψ should be normalized to the total number N of pumped excitons.

$$\int_{-L/2}^{L/2}\psi(x)\psi^*(x)dx = N = nL$$

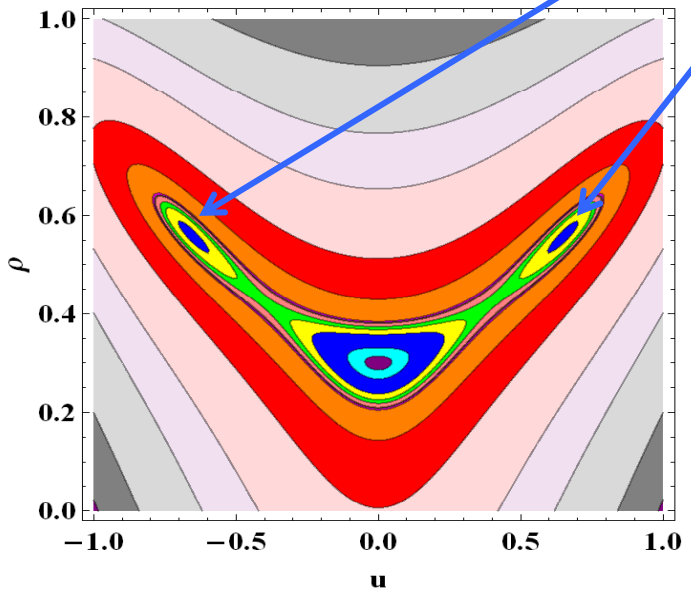
Changing the energy landscape by pumping excitations

Trivial minimum at $\rho=\rho_n$, $h=0$

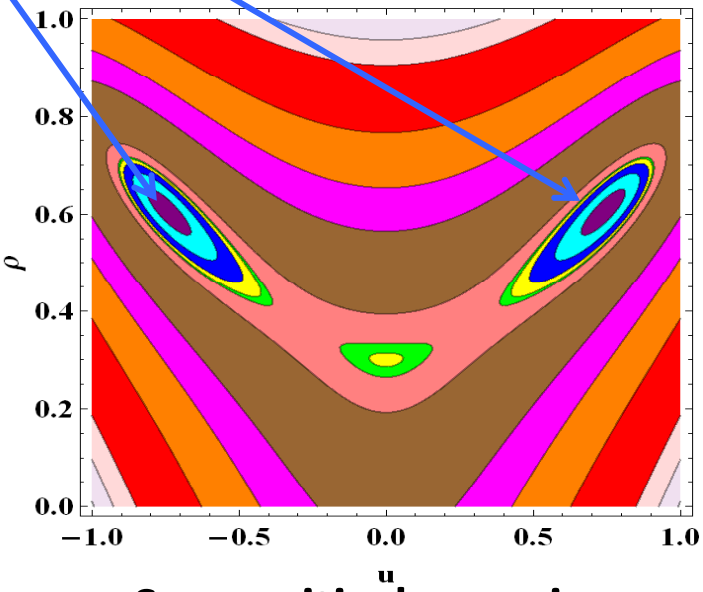
Double minima at $\rho>\rho_n$, $h=\pm h_0$ appear and evolve to the ionic state



Subcritical pumping



Critical pumping



Supercritical pumping

Modeling of self-trapping evolution

$$-g|\psi|^2 + aq + bq^2 - \frac{c}{q_c}h^2 = 0$$

Energy minimum over ***q***

Lattice dynamics affected by ***q***

$$\frac{1}{\omega^2}\frac{\partial^2 h}{\partial t^2} + \frac{\gamma}{\omega}\frac{\partial h}{\partial t} - \frac{s^2}{a^2\omega^2}\frac{\partial^2 h}{\partial x^2} + 2\frac{f}{c}h^3 + 2h(q_c - q) = 0$$

$$i\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} - gq\psi + k|\psi|^2\psi$$

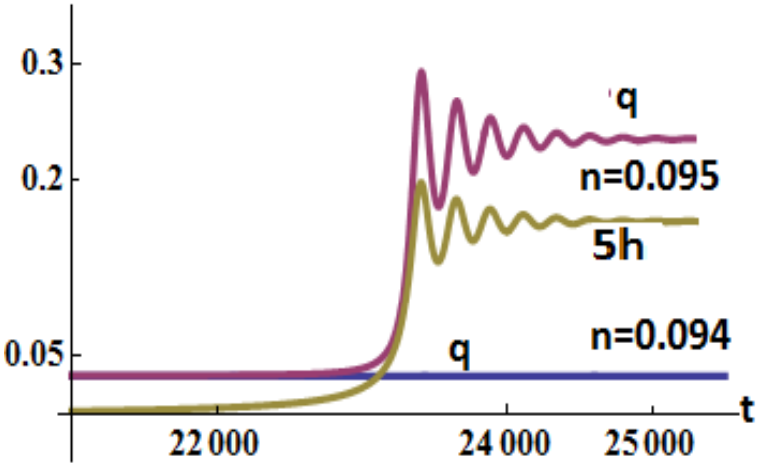
NLSE = generalized Gross-Pitaevskii eq.
with excitons repulsion **~k** and their energy shift ***-gq***

Initial conditions:

h(x,0)=0 , q(x,0)= 0 - *no deformations and charge transfer.*

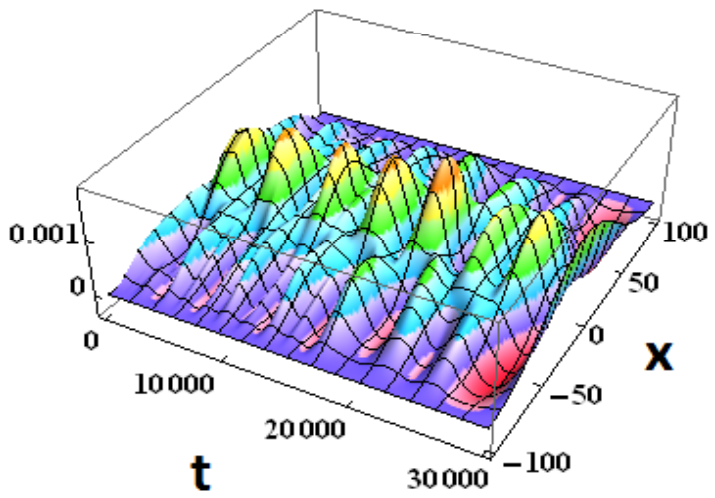
ψ(x,0)=cos(πx/2L)(πN/L)$^{1/2}$ – *wave state delocalized over the sample* ***(-L,L)***

No space dependence: a homogeneous regime or a quantum dot.

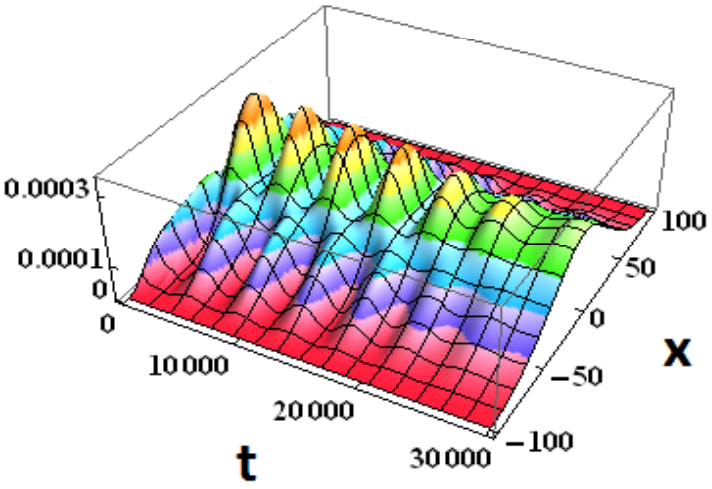


Very precise determination of the critical pumping between switching (left) and restoring (right) regimes.

Space dependence, subcritical pumping: n=0.0001, 0<t<30000 fs

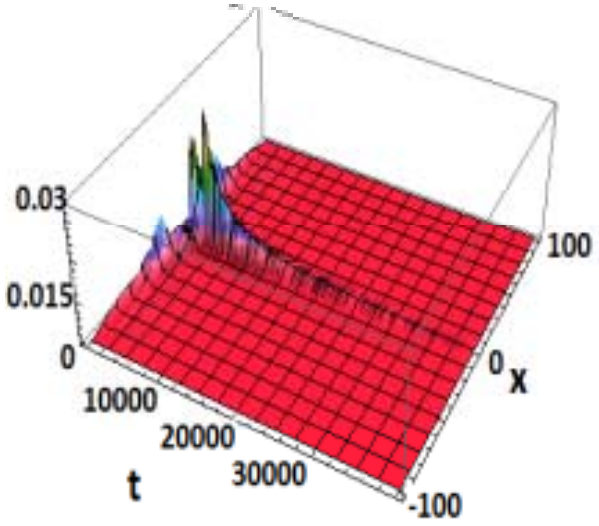


q(t,x)

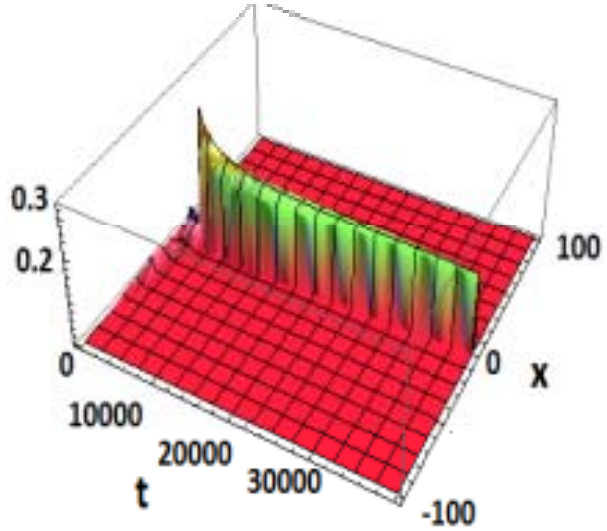


ψ(t,x)

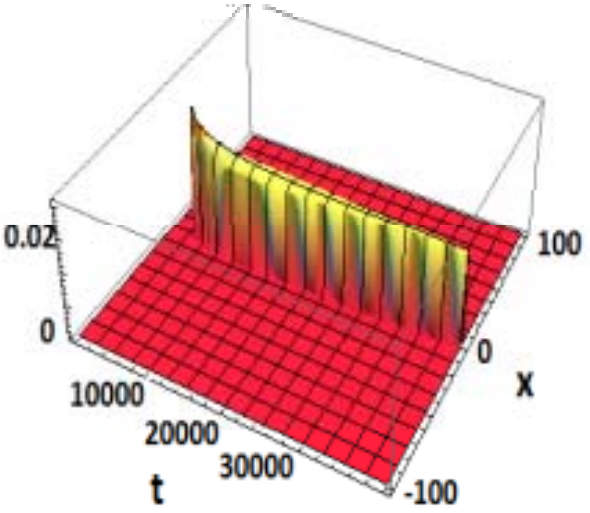
Supercritical pumping: n=0.0025, 0<t<40000 fs



ψ(t,x)



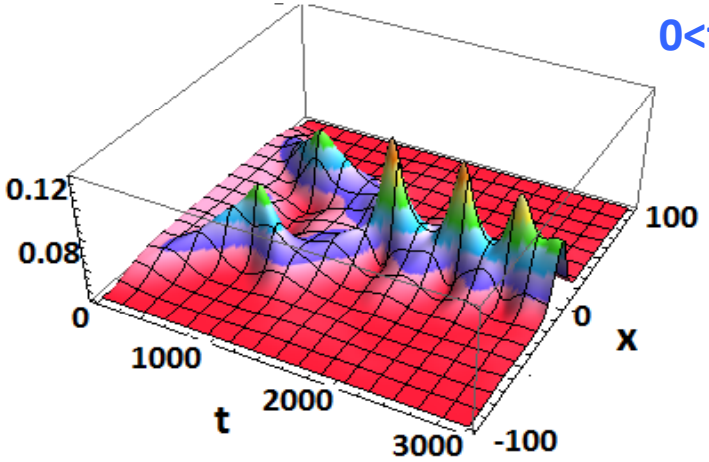
q(t,x)

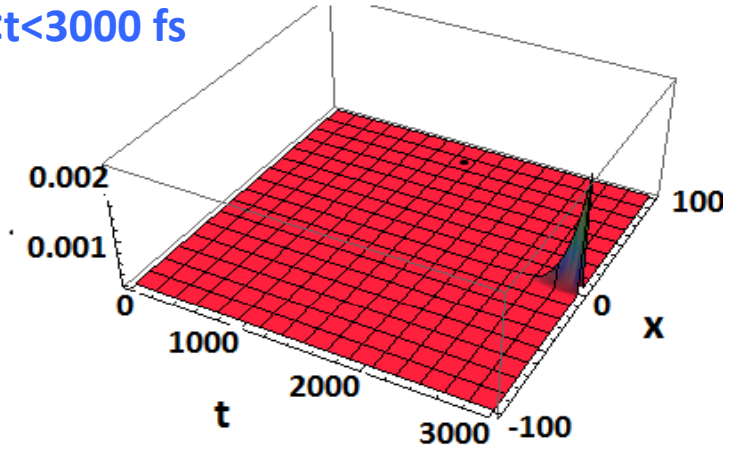


h(t,x)

0<t<3000 fs

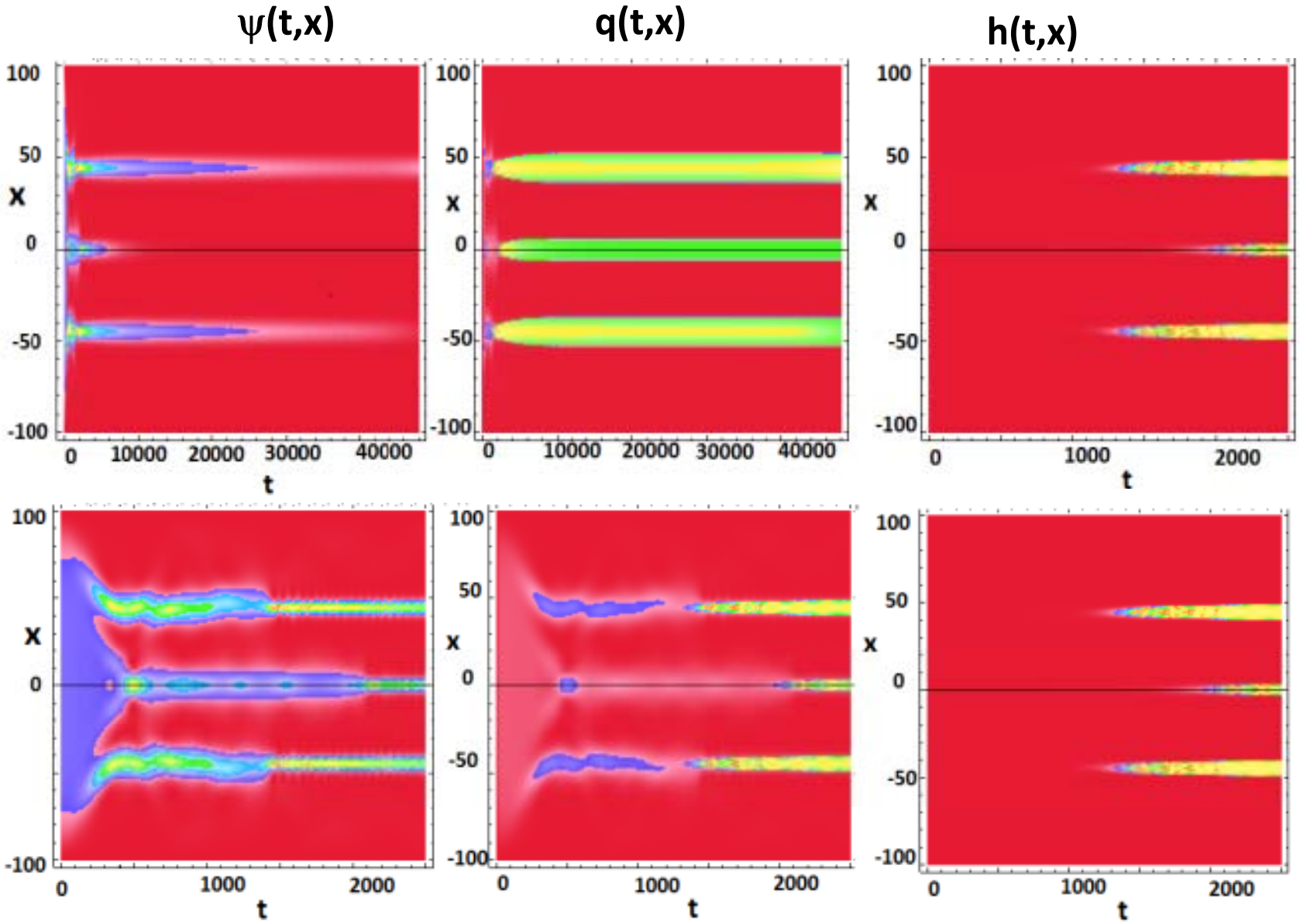
q(t,x)





h(t,x)

Strong pumping, formation of persistent space domains: n=0.007



Charge transfer exciton CTE:

$$q = |\Psi|^2$$

Thermodynamic CT and the excitons' density are the same entity !

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

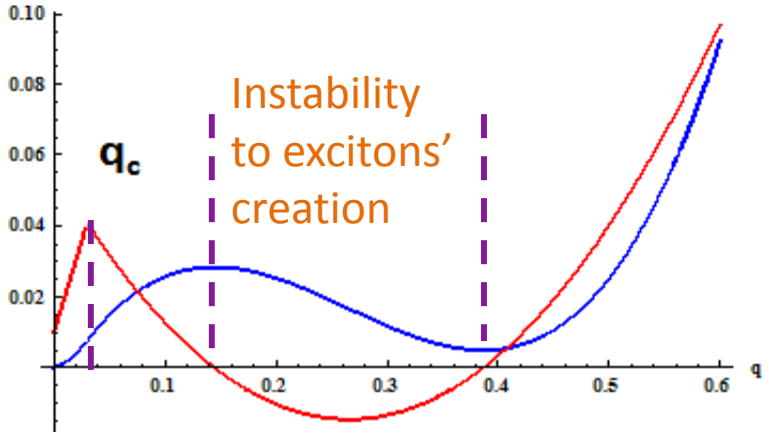
$$\frac{\partial^2 h}{\partial t^2} = \frac{\partial}{\partial h} W(q,h) = d(q_c - q)h + fh^3$$

$$i\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial q} W(q,h)\Psi = E_{ex}\Psi$$

$$V(q,h) = E_{ex}(q,h) = E_0 + aq + bq^2 + \frac{d}{2} h^2 (q_c - q)$$

E_{ex} (q,h) - instantaneous exciton energy

*Coupling between **q** and **h**:* ***-qh²*** is a decrease of $\mathbf{E_{ex}}$ by the dimerization



Energy **W(q,h)→W(q)** and the potential **V(q,h)→V(q)** after minimization over **h**.

At $\mathbf{q>q_c}$, the microscopic repulsion is taken by attraction via dimerization **h**.

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

To treat both thermodynamic and dynamic effects on the same root, we adopt for the phase transition a view of the Excitonic Insulator (EI). *1960's: Knox, Kohn et al, Halperin and Rice, Keldysh et al, Kozlov and Maksimov* - well revived nowadays . A hypothetical phase of a semiconductor which appears if the total energy of an exciton $\mathbf{E_{ex}=E_g-E_b}$ vanishes: $\mathbf{E_{ex}\rightarrow 0}$.
The too general concept $\mathbf{E_{ex}}=0$ covers all quantum phase transitions.
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 EI state which is of particular importance in the context of PIPT.)

Microscopic theories of the Bose condensate of pumped excitons (recall *experiments by Timofeev et al in ChG*) and of the EI transition are closely related, differing mostly by the monitoring parameters: the chemical potential $\boldsymbol{\mu_{ex}}$ and the density $\mathbf{n_{ex}}$ correspondingly.

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

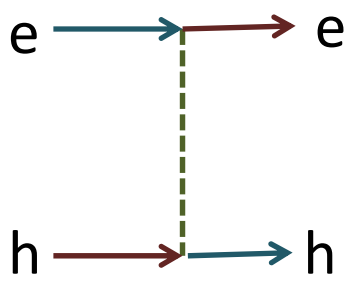
Enigma: thermodynamic charge transfer = redistribution of the charge density **q** is a single real field.

Charge transfer under pumping is $q=|\Psi|^2$, but $\Psi = |\Psi| \exp(i\varphi)$:
the phase φ - appears as a hidden degree of freedom.

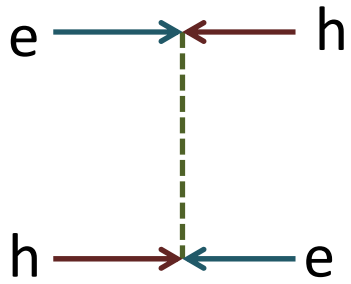
How can we hunt to see it?

We have to take into account additionally: 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.
Virtual normally, the transitions become real for macroscopic concentration.

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



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



S-term fixes the wave function phase in the ionic ground state.
Dynamically it gives rise to oscillations of quantum interference among states which numbers of excitons differ by 2.

$$W(q,h,\varphi) = E_{ex}^0 q + \frac{a}{2}q^2 + \frac{b}{3}q^3 + \frac{d}{2}(q_c - q)h^2 + \frac{f}{4}h^4 + Sq\cos 2\varphi$$

Generalized Gross-Pitaevskii eq. for evolution of excitons' wave function

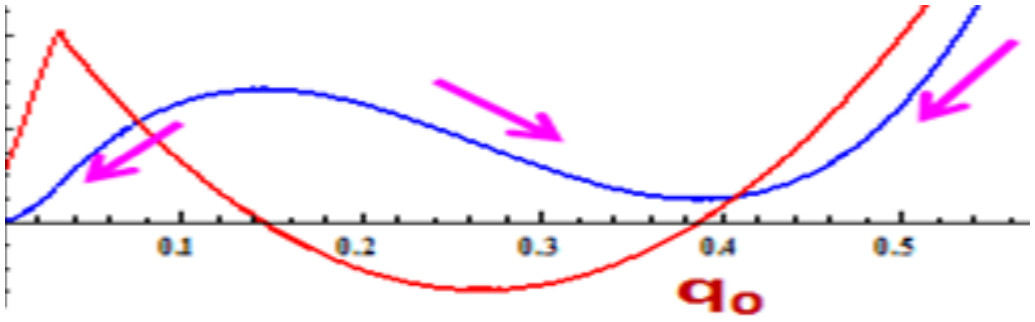
$$i\partial_t \Psi = H\Psi - i\Gamma\Psi - S\Psi^* \qquad H = \hat{p}^2/2M + V(q,h)$$

Γ(*q*,*h*) = decay rate for the excitons' density q:

1. constant at q→0 (single-particle recombination) – *neglect in modeling*
2. ∝ **q** at moderate **q** (BE statistics - stimulated emission),
3. vanishes in the minimum of **W** at **q≈q$_0$** - no way to release the energy from the local minimum, hence a guess as **Γ ~V(q)** if S=0.

The interpolation **Γ(q,h)** ∝ **(q+δ)V(q,h)**
ensures the relaxation towards the local energy minima at **q=0** and **q=q$_0$**.
At S≠0, with phase dependence: the generalization:

$$\Gamma(q,h) \propto (q+\delta)V(q,h) \Rightarrow (q+\delta)E_{ex}(t) \Rightarrow -(q+\delta)\frac{\partial\varphi}{\partial t}$$



W(q)

V(q)

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

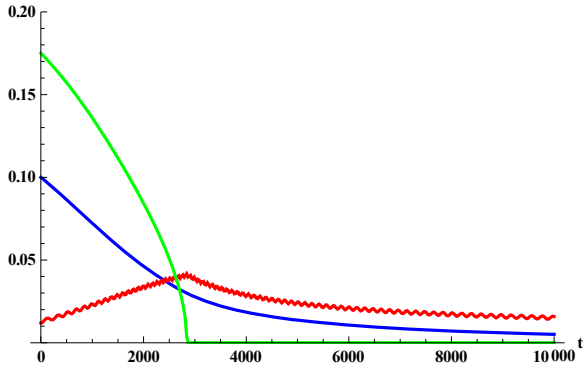
$$\frac{\partial q}{\partial t} = -\Gamma q + Sq\sin(2\varphi) \qquad \Gamma(q,h) \approx -Kq\frac{\partial \varphi}{\partial t}$$

$$\partial_t \varphi = -V + S\cos(2\varphi)$$

Γ describes relaxation of the amplitude. ***S-term*** gives rise to either locking of the phase approaching the EI phase, ***|V|<S***
or, in the phase of dilute gas of excitons q→0,
to oscillations of quantum interference among states
which numbers of excitons differ by 2.

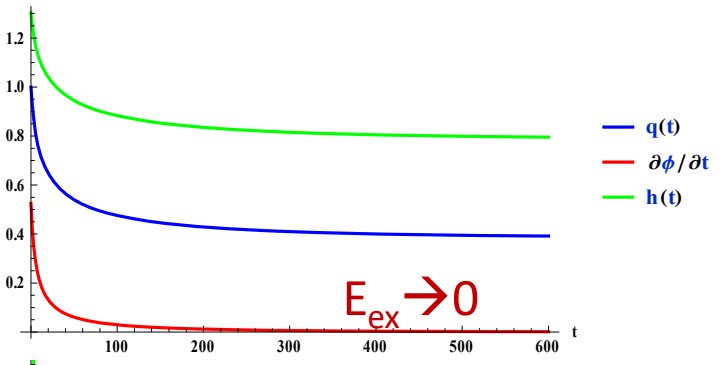
$$\frac{1}{\omega^2}\frac{\partial^2 h}{\partial t^2} + \frac{\gamma}{\omega}\frac{\partial h}{\partial t} - \frac{s^2}{a^2\omega^2}\frac{\partial^2 h}{\partial x^2} + 2\frac{f}{c}h^3 + 2h(q_c - q) = 0$$

Charge transfer exciton at no space dependence: Dynamic phase transitions and quantum interference

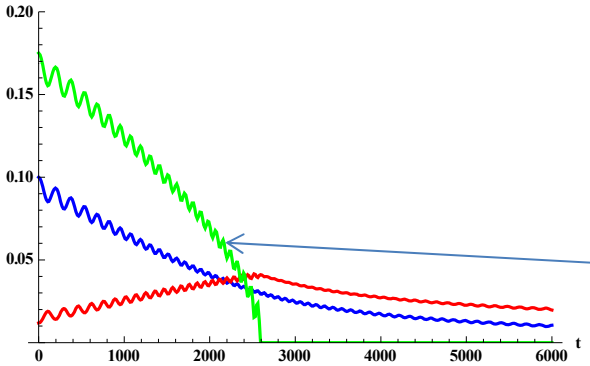


$E_{ex} \rightarrow E_0$

S=0



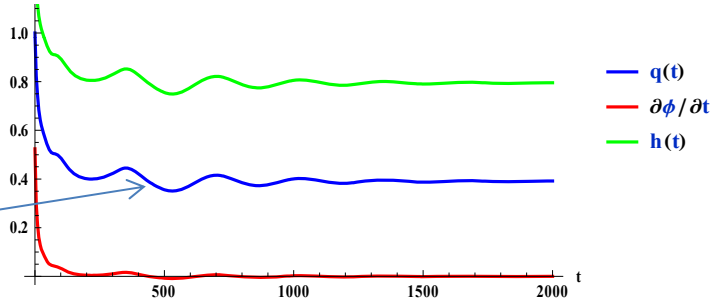
$E_{ex} \rightarrow 0$



S=0.001

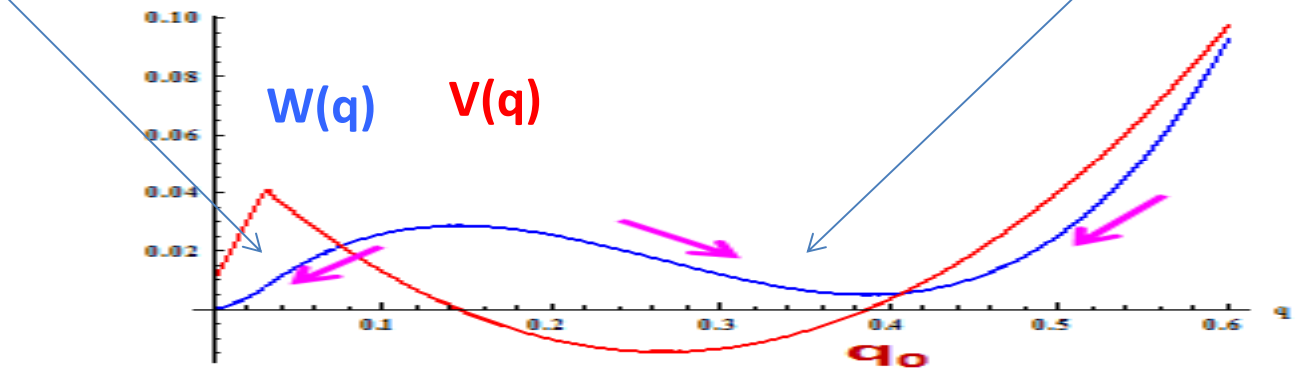
quantum interference

E_0

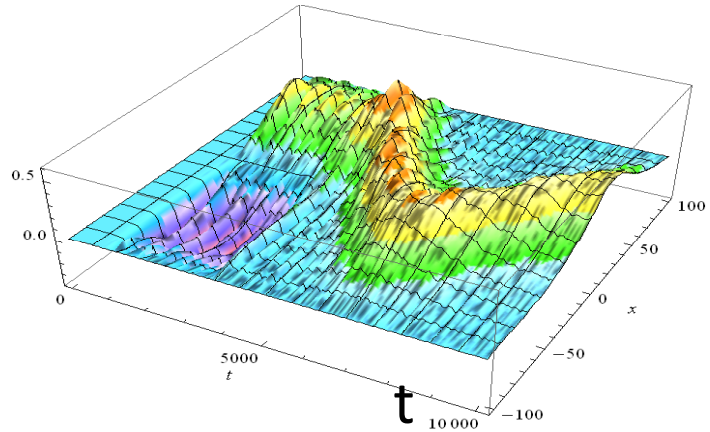


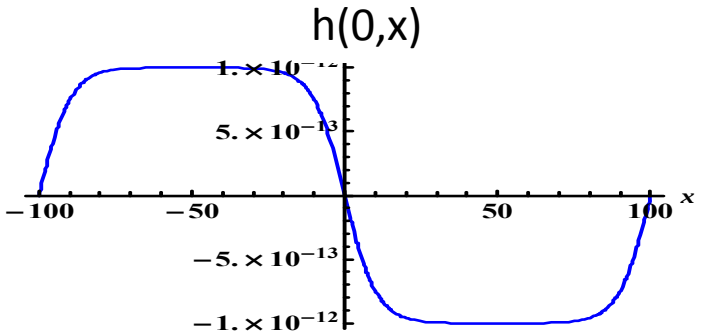
Subrcritical pumping

Supercritical pumping

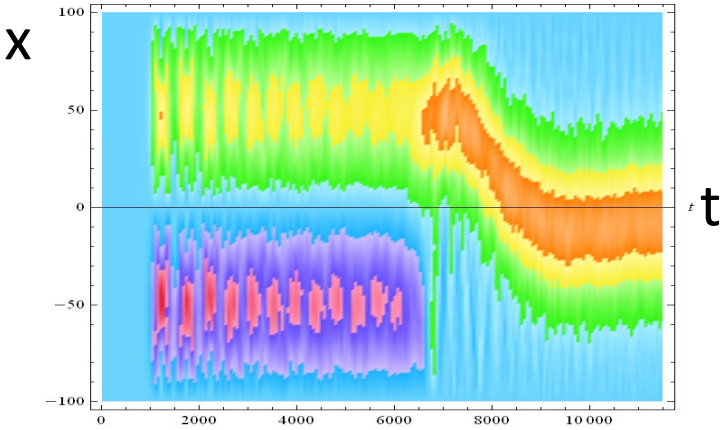


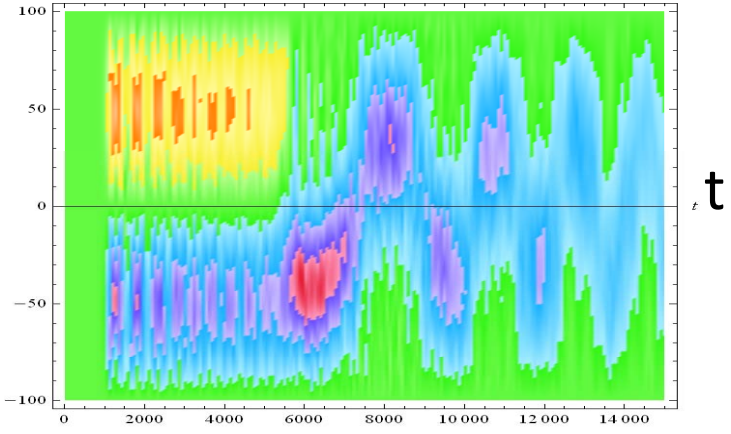
Space-time modeling, CTE, S=0: developing of domain structure





Undulating (only 10^{-12}) initial condition





High damping - plots of h(t,x):
one domain takes over,
with increased self-focusing

Low damping - plot of h(t,x):
one domain takes over,
with increased self-focusing;
wave packet oscillates around the middle

Conclusion

Intra-molecular and charge transfer excitons

- A quasi-condensate of optically pumped excitons appears as a macroscopic quantum state.
- It evolves interacting with other degrees of freedom prone to instability, with 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.

Charge transfer excitons

- The excitation and the long range ordering can be built from the same intermolecular electronic transfer.
- Both thermodynamic and dynamic effects can be described on the same root by viewing the ordered state as the Excitonic Insulator.

REGRETS and EXCUSES:
what has not, or could not, be done.

1. Take into account the normal, non-condensed density of excitons and its (re)conversion to/from the condensate.

1a. Starting temperatures T are comparable with the degeneracy T of the Bose-Einstain condensation T_{BEC}. The not-quite-resonance pumping will also contribute to the initial incoherent density.

1b. With diluting because of the relaxation,
the BEC transition will be passed back even at low T.

2. A microscopic theory of a dynamical BEC offers something to learn – provoked by problems in polaritons and cold atoms.
But the emergence of the Gross-Pitaevskii kind eq. has not been clearly derived yet.

3. Applications to neutral-ionic transitions face a fermionisation of excitons as initially Bose particles, because of the rather 1D structute of these materials.