Local phase transformations induced by optical pumping: application to neutral-ionic transition

Natasha Kirova

Laboratoire de Physique des Solides,
CNRS & Université Paris-Sud, Orsay, France

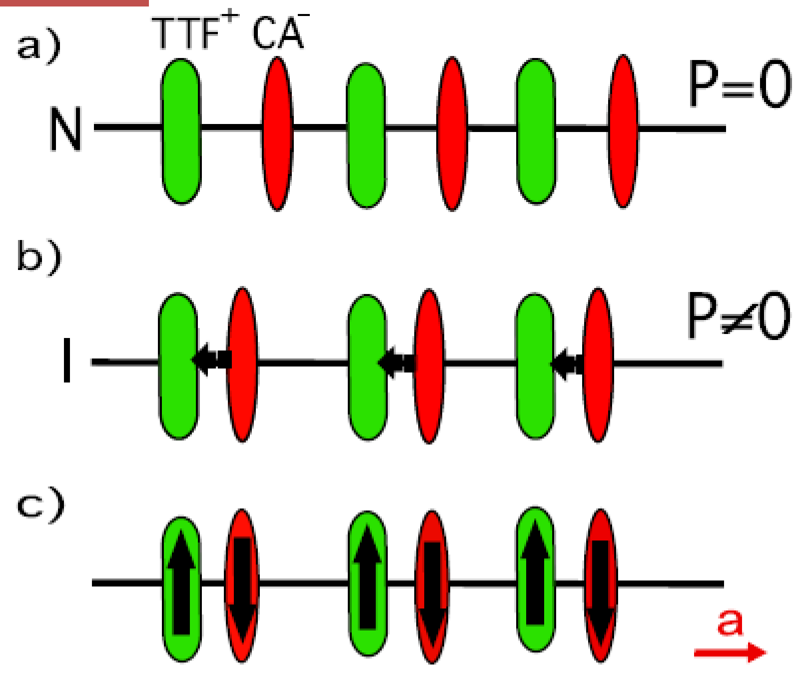
in collaboration with S. Brazovskii

OUTLINE

- Introduction
- External (intramolecular) excitons in a media prone to an instability:
  entangled dynamics of the excitonic condensate and the order parameter.
  Spacio-temporal evolution: space segregation from self-focusing.
  Local dynamic transitions at subcritical pumping.
- Internal (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 excitonic condensate.
- Conclusion

Neutral-Ionic Transition

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.
Charge transfer **ρ** jumps from $\boldsymbol{\rho}_n$ =0.3 to $\boldsymbol{\rho}_i$ = 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 is the ferroelectric.



Thermodynamic CT.
Primary effect: redistribution of the charge density **ρ** with no symmetry breaking, hence an isomorphic (liquid-gas class) transition described by the single real field $q=\boldsymbol{\rho}-\boldsymbol{\rho}_n$.
Actually – symmetry breaking because of the complementary dimerization.

EXCITONS and PHOTO INDUCED PHASE TRANSITIONS

Resonance pumping to excitons (Rec. H. Okamoto)
Intermediate stage after the electronic pumping.

Excitons:
initially delocalized (photon **k=0**)

High density, a quasi-condensate, a macroscopic quantum state.

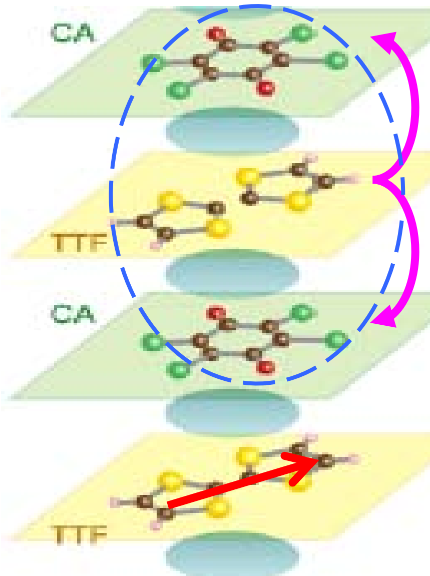
Wave function **Ψ** which evolves interacting with other degrees of freedom prone to instability.

Subject to self-trapping (akin to self-focusing of light).

Locally enhanced density can trigger the phase transformation, even if the mean density is below the global threshold.

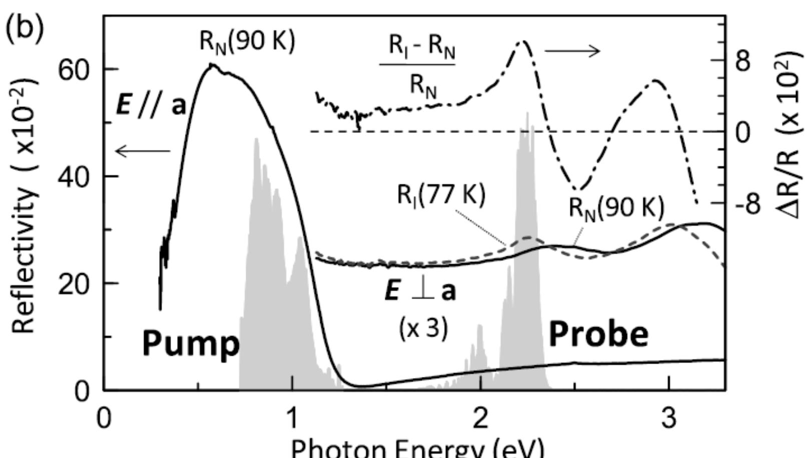
N.B. Exciton is a quantum state in both the internal and the center of mass coordinats

Excitons in organic stack compounds.



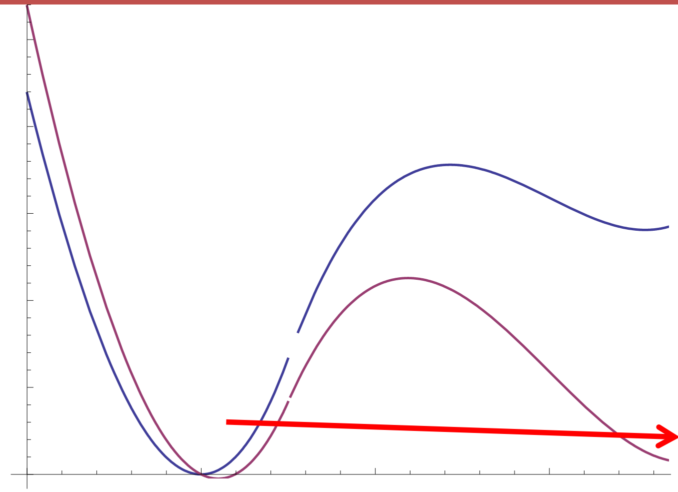
Intra-molecular excitons IME (S. Koshihara)
Pumping into the IME : the excitons and the order parameter are different while interacting fields.

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.

Complete model of light induced neutral-ionic transformation

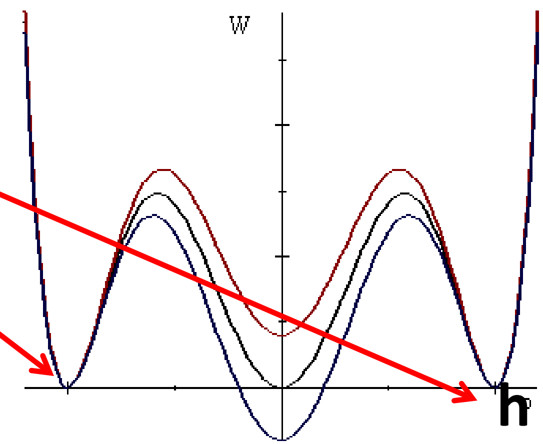


quasi-neutral

ionic

ρ

Deepening of the energy minima of the I state at low T, high P or under pumping



Metastable state at $\rho > \rho_c$ itself is unstable to symmetry breaking of dimerization, **h**

3 possible states - 2 are equivalent

ionic & dimerized & feroelectric

Game of principle variables.

h – dimerizational displacement of molecules
ρ - charge transfer, in neutral phase $\rho = \rho_n$,
ρ_c – monitoring parameter $\rho_c = \rho_c(T)$
The energy density:

$$W(\rho,h) = \frac{a}{2}(\rho-\rho_n)^2 + \frac{b}{3}(\rho-\rho_n)^3 + \frac{c}{4}(\rho-\rho_n)^4 + d(\rho_c-\rho)h^2 + fh^4$$

$\rho_c > \rho_n$ – critical value of ρ for instability in h:

$$h = 0 \Rightarrow h = \pm\sqrt{(\rho-\rho_c)d/2f}$$

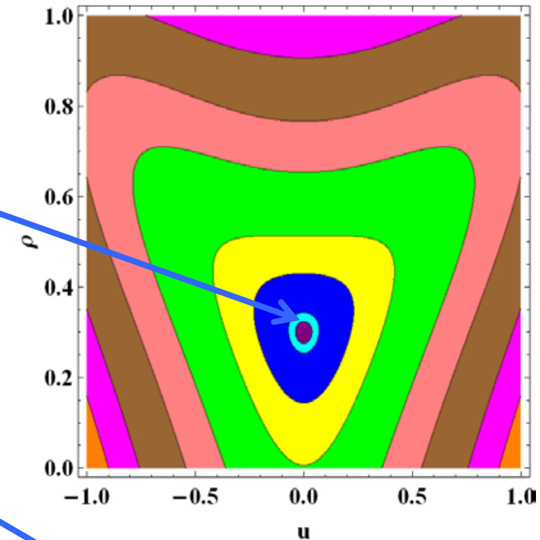
At presence of N external excitons in the state with a wave function ψ,
- add the coupling energy $-g\,\rho|\psi|^2$
- add the excitons' repulsion energy $k|\psi|^4/2$
- ψ should be normalized to the total number N of pumped excitons.

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

Changing the energy landscape by pumping excitations

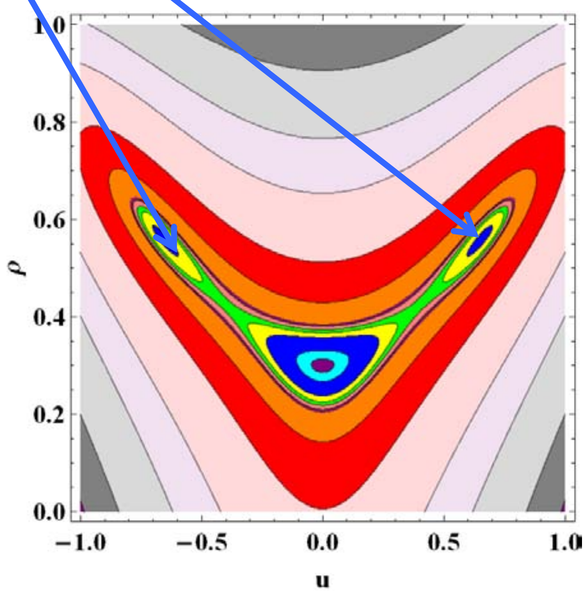
n=0.04

ρ-ρ_n



Trivial minimum at $\boldsymbol{\rho=\rho_n}$, **h=0**

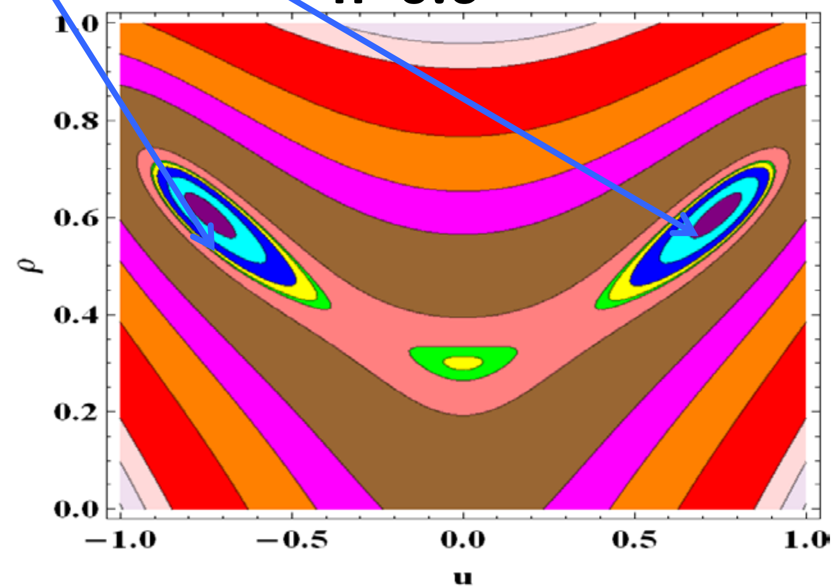
Double minima at $\boldsymbol{\rho>\rho_n}$, $\boldsymbol{h=\pm h_0}$ appear and evolve to the ionic state



n=0.4

u

n=0.6



Modeling of self-trapping evolution

$$-g|\psi|^2 + a(\rho-\rho_n) + b(\rho-\rho_n)^2 + c(\rho-\rho_n)^3 - \frac{d}{2}h^2 = 0$$

Energy minimum over $\boldsymbol{\rho}$

$$K\left(\partial_t^2 h + \gamma\partial_t h\right) = \xi^2 \frac{\partial^2 h}{\partial x^2} - fh^3 - dh(\rho_c - \rho)$$

Lattice dynamics affected by $\boldsymbol{\rho}$

$$i\partial_t \psi = -\frac{1}{2m}\partial_x{}^2\psi - g\rho\psi + k|\psi|^2\psi$$

Shroedinger eq. with excitons repulsion ~k and their energy shift -g $\boldsymbol{\rho}$

Initial conditions:

h(x,0)=0 , ρ(x,0)= ρ$_n$ - *no deformations and charge transfer.*

ψ(x,0)=cos(πx/2L)(N/L)$^{1/2}$ –

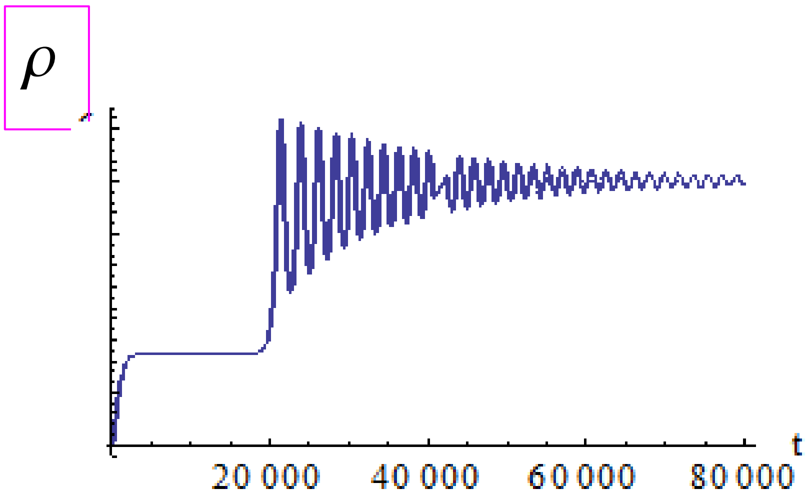
*lowest wave state delocalized over the sample box **(-L,L)***

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

Evolutions of **ρ** and **h** just above and below the power threshold for the dynamic phase transition

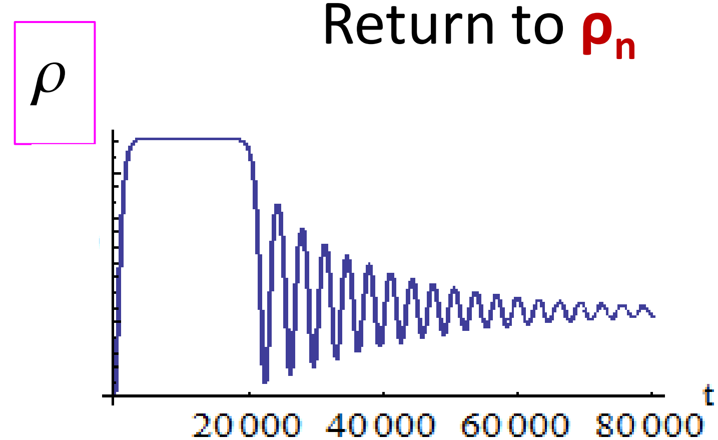
n=0.39061306500694

Stabilization at ρ_i



n=0.39061306500693

Return to ρ_n



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

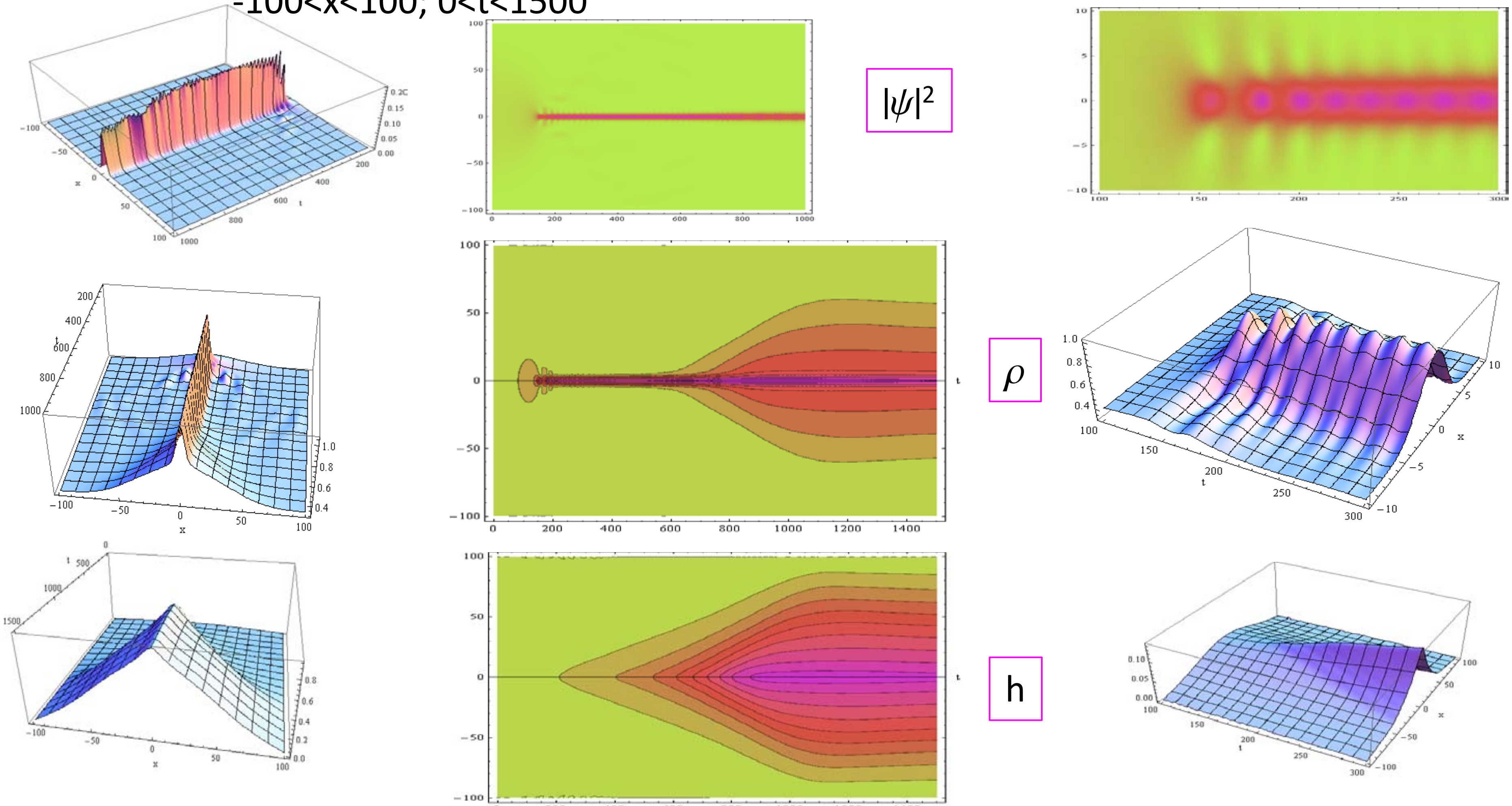
Small repulsion among the excitons

Critical time and the self-trapping length shorten

n=0.05, k=0.1, n_t=0.0795

-10<x<10; 100<t<300

-100<x<100; 0<t<1500



ρ becomes well localized similar to **Ψ**, within (-10,10),

h- emerges much later at t> $\mathbf{t_{cu}}$>> $\mathbf{t_c}$ and wider - within (-60,60).

time $\mathbf{t_{cu}}$ > $\mathbf{t_c}$ of the second dynamic phase transition. ($\mathbf{t_c}$=150, $\mathbf{t_{cu}}$≈1000)

It brings shoulders to ρ, but **Ψ** is almost not affected.

Charge transfer exciton:

$$\rho - \rho_n = q = |\Psi|^2$$

Basic energy functional :

$$W_1(q,h) = E^0_{ex} q + \frac{a}{2} q^2 + \frac{b}{3} q^3 + \frac{d}{2}(q_c - q)h^2 + \frac{f}{4} h^4$$

$\mathbf{q_c}$ - critical value of **q** for instability of the non-dimerized phase with **h=0**.

*Coupling between **q** and **h*** (from the inversion symmetry breaking at **h≠0**):

➢ $\mathbf{-qh^2}$ is a decrease of $\mathbf{E_{ex}}$ by the dimerization which comes from mixing of even and odd excitonic states . It is negative as the second order perturbation in **h**.

➢ $\mathbf{-q^2h^2}$ is the attraction of excitonic dipoles which appear only at **h≠0**.

Enigma:

thermodynamic CT : redistribution of the charge density **ρ**, a single real field.

CT under pumping: q= ρ- ρ_n ∝ **|Ψ|²** , **Ψ=exp**(iφ**)** ,

the phase φ is a hidden degree of freedom. How can we hunt to see it?

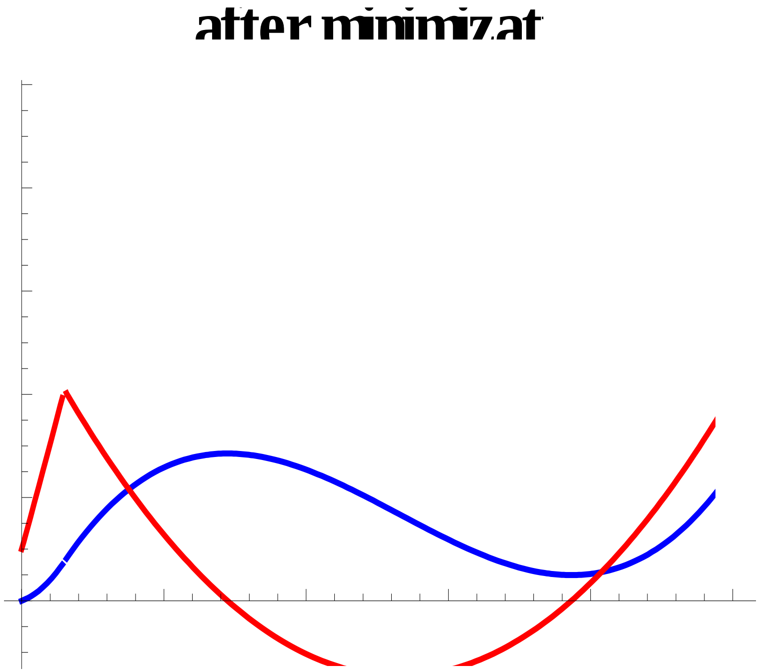
$$F(q,h) = \frac{\partial}{\partial h} W(q,h) = d(q_c - q)h + fh^3$$

Force upon lattice displacements **h**

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

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

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



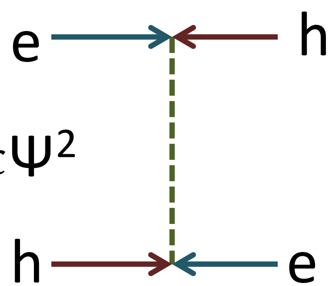
q_c=0.03

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

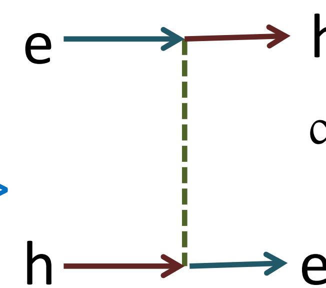
Excitonic insulator – instability when an exciton energy goes to zero.

We have to take into account: 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.

$\propto \Psi^2$



Coulomb interactions
<- anomalous ~S | normal ->



$\propto |\Psi|^2$

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

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.

Shroedinger eq. for the time evolution of excitons' wave function.
Peculiarities – two channels to break the conservation of number of excitons:

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

Peculiarities – two channels to break the conservation of number of excitons:

$\boldsymbol{\Gamma(q,h)}$ = decay rate for the excitons' density q . It is:

constant at small q (single-particle and non-radiational recombination,

$\propto \boldsymbol{q}$ at moderate $\boldsymbol{q}$

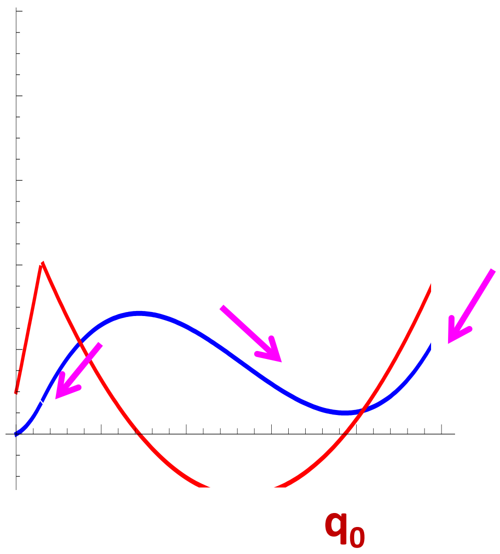
(BE statistics - stimulated emission),

vanishes in the minimum of **W** at

$q \approx q_0$ as **$\Gamma \sim V(q)$**

- no way to give up the energy from the local minimum.

Hence the interpolation: **$\Gamma(q,h) \propto (q+\delta)V(q,h)$** which ensures the relaxation towards the local energy minima at **$q=0$** and **$q=q_0$**.



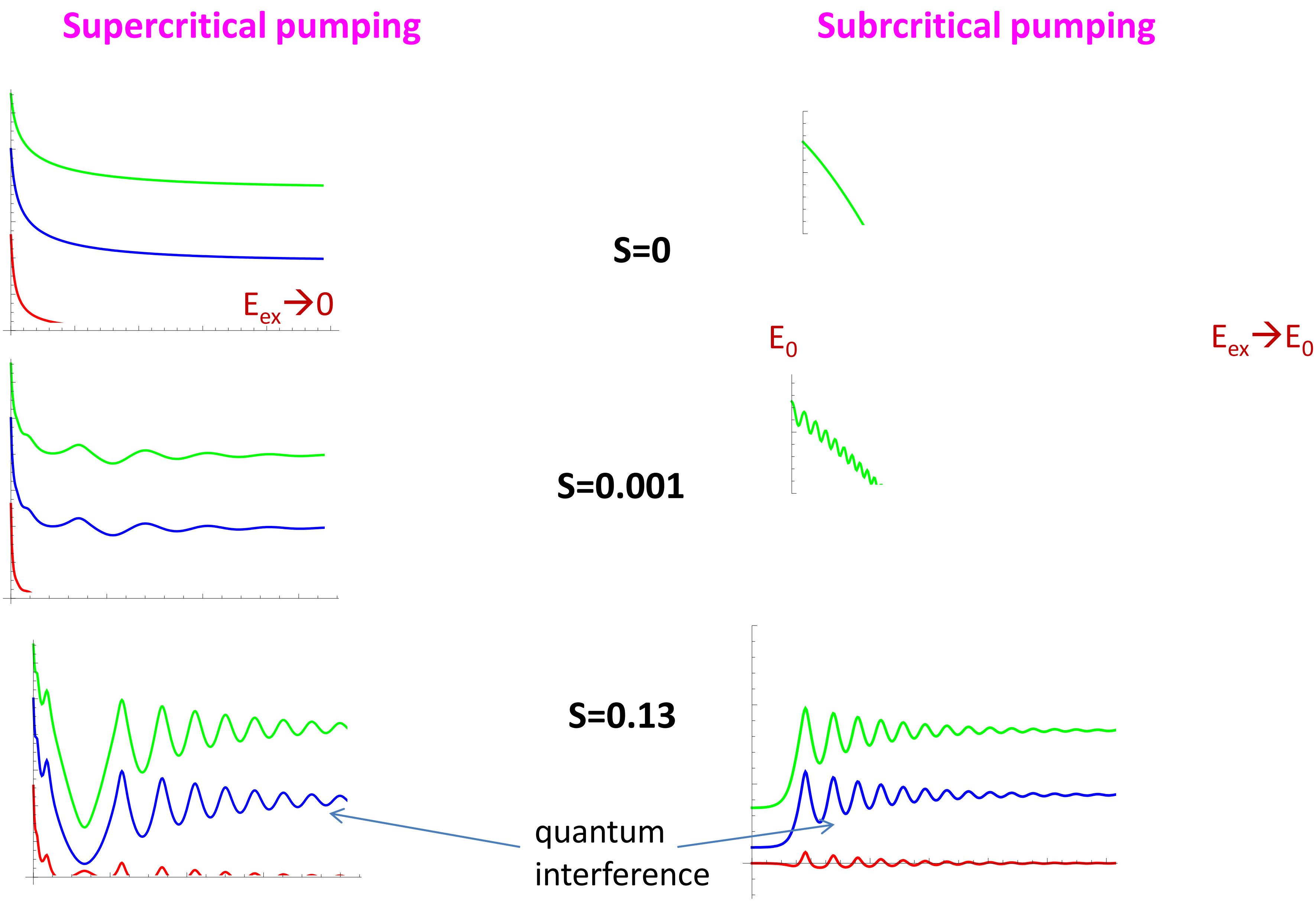
No space dependence:
a homogeneous regime or a multi-stable quantum dot
- switching by absorbing the exciton

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

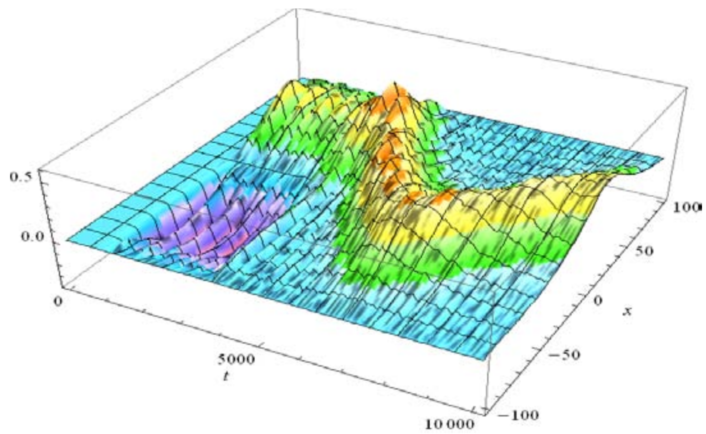
E_{ex}(t) - instantaneous value of the exciton energy.

Γ and S describe relaxation of the amplitude and locking of the phase .

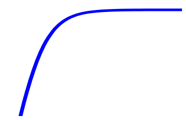
Charge transfer exciton at no space dependence: Dynamic phase transitions (DFT) and quantum interference



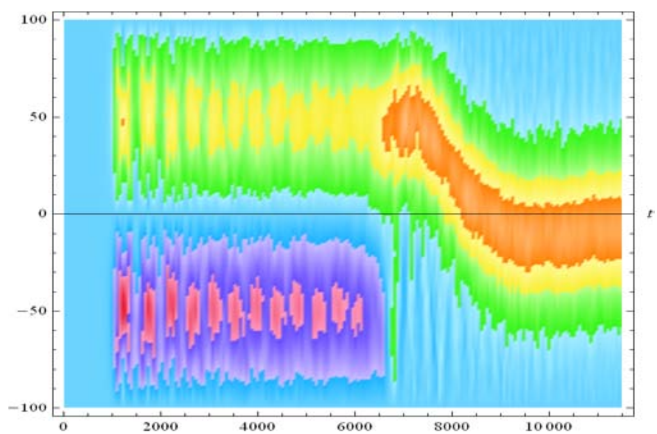
Space-time modeling: developing of domain structure

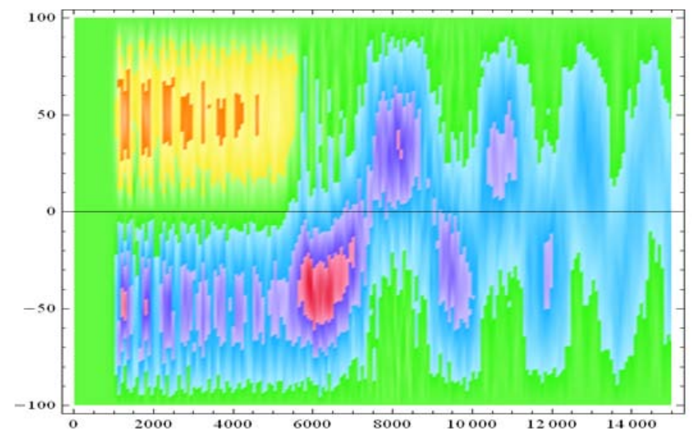


h(0,x)



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.

- Experiments on rapid processes and their modeling recover general quantum mechanisms behind phase transformations
and formation of inhomogeneous electronic states.
- Phenomenological approach takes successfully into account
collective degrees of freedom both at the classical level
(deformations, order parameter) and for quantum Bose field of excitons.
- Local instability, possibly with no barrier or thresholds, of the initial phase
with respect to self-trapping of optical excitations can bring to a threshold of
the second dynamic transition triggering the new phase with a symmetry breaking.
- The suggested scenario looks to be a minimally sufficient one to take into account
the quantum nature of excitons and their cooperative effects, to understand
stabilization of a long string and the efficiency of phase transformations.
- The results can be already applied to well studied neutral-ionic transitions.