Ab-initio wave packet dynamical simulation of defects in 2D materials

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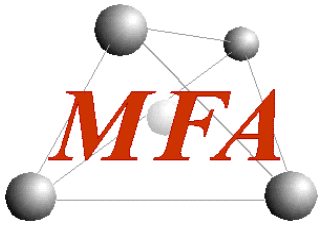

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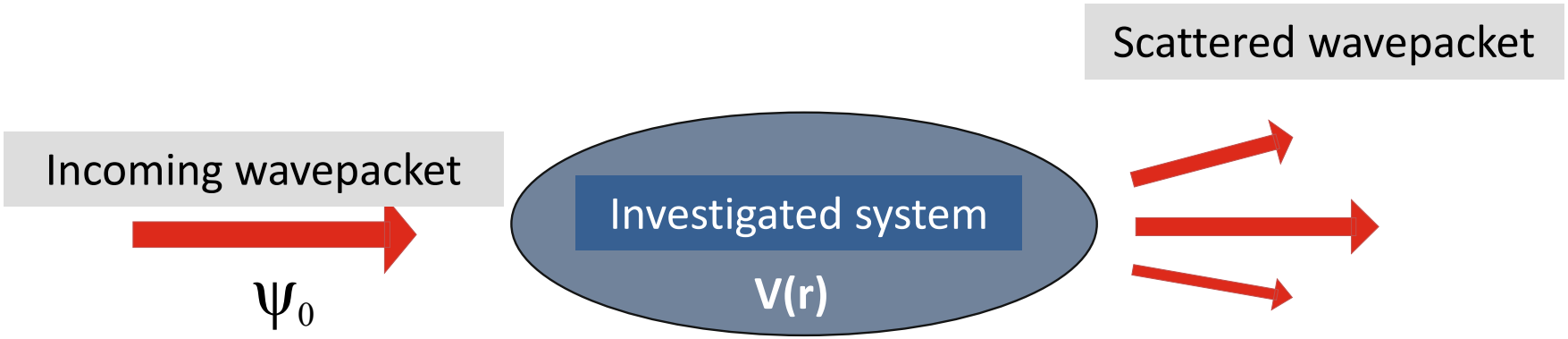
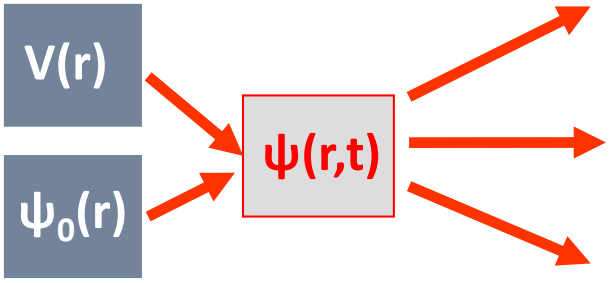
Outline

- The wave packet dynamical method
- How to prepare the initial state?
- Bloch function wave packet construction
- Bloch function wave packet scattering on defect
- Band structure in kinetic energy operator
- Describing
  - infinite 2D crystal with kinetic energy and
  - local defects by potential energy

General principles of the wave packet dynamical method (WPD)





probability density $\rho(\vec{r},t) = |\psi(\vec{r},t)|^2$

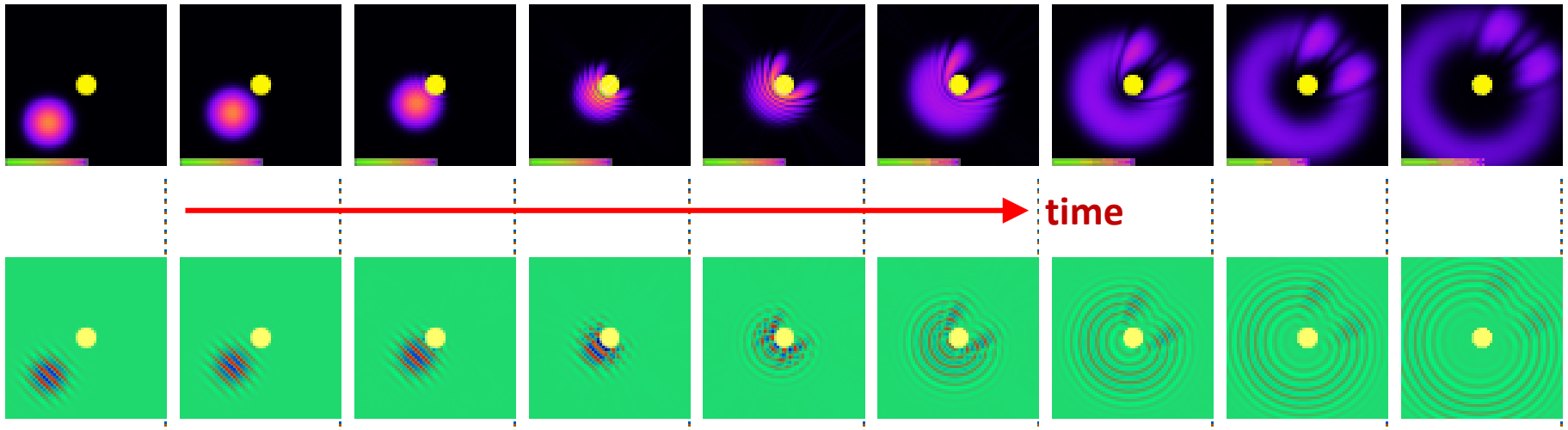
probability current $j(\vec{r},t) = -\frac{i\hbar}{2m}[\psi^*\nabla\psi - \psi\nabla\psi^*]$

eigenstates $\psi(\vec{r},E_n)$

Scattering of a hardcore potential

2D

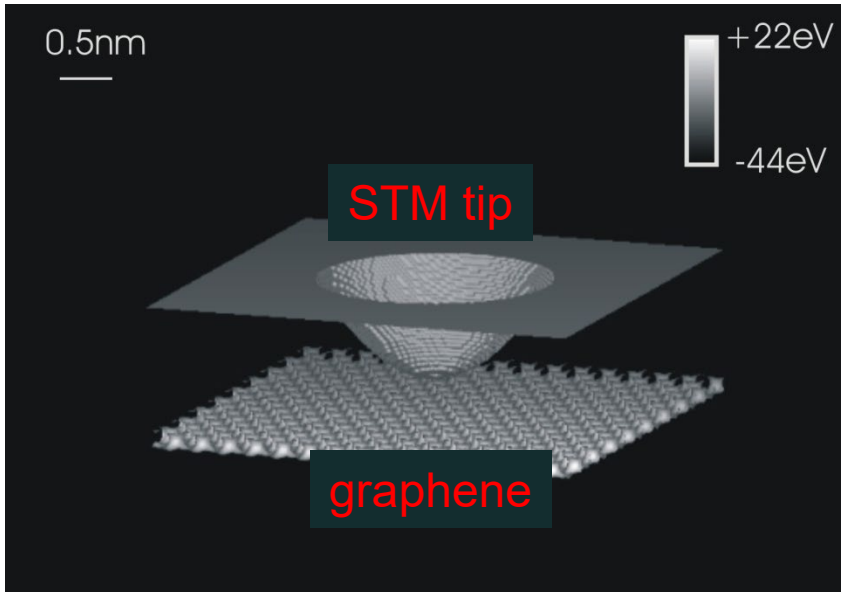
Probability density

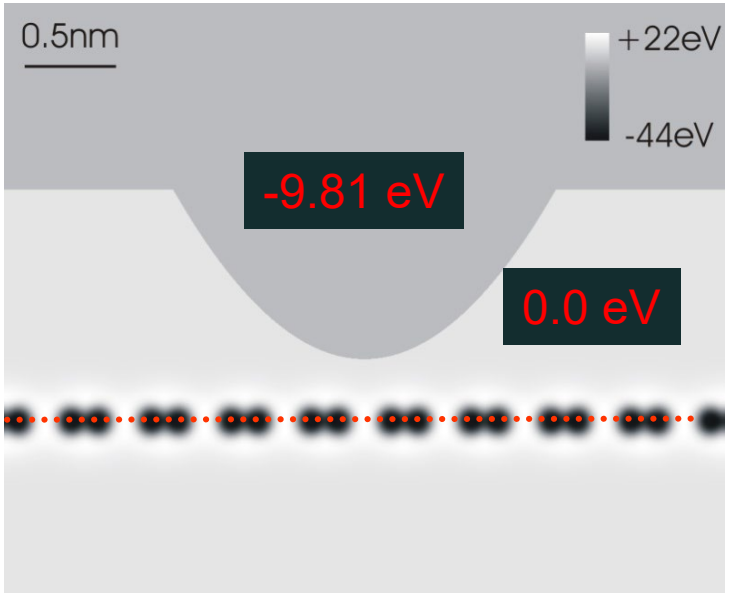


Real part of the wawe packet

Carbon pseudopotential

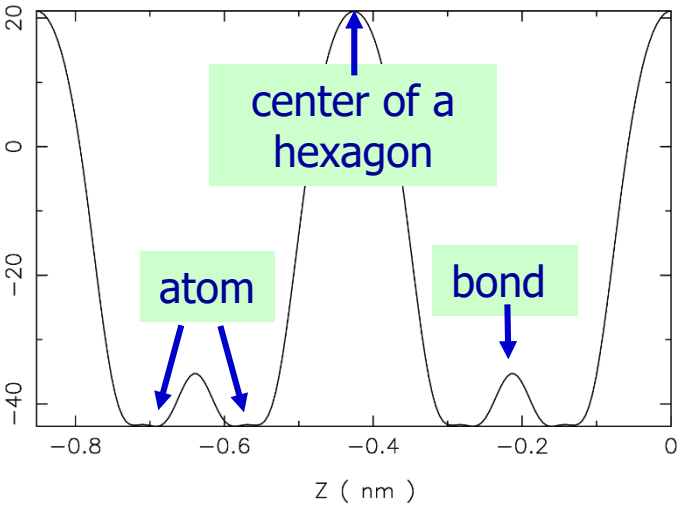
Metallic STM tip + graphene



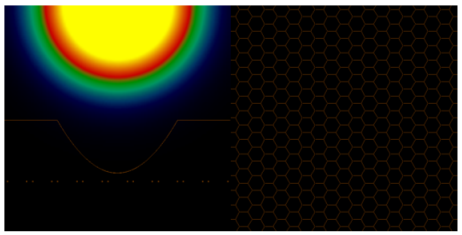


Potential–energy distribution (eV)

$$V_{carbon}(\vec{r}) = \sum_{j=1}^{N}\sum_{i=1}^{3} A_i e^{-a_i|\vec{r}-\vec{r}_j|^2}$$

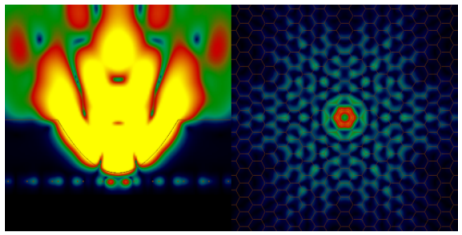


Time dev.– 2D sections



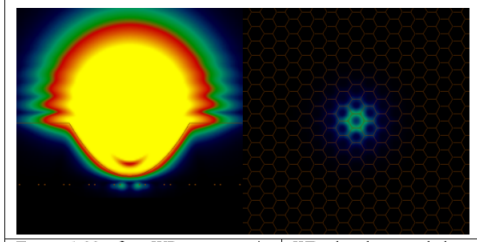
T = 0.00 fs. Initial WP in tip bulk

Empty graphene sheet



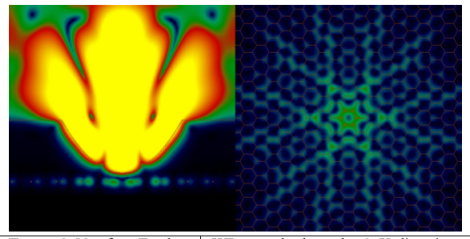
T = 3.14 fs. WP begins to retract from the tip apex into the tip bulk

Note the switching of the spreading direction from that corresponding to the C-C bonds to that determined by the band structure



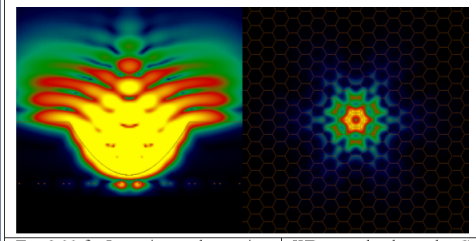
T = 1.22 fs. WP enters tip hyperboloid and is reflected from tip surface into tip bulk. Note the interference patterns inside tip bulk

WP already tunneled onto graphene sheet. WP appears on the central hexagon



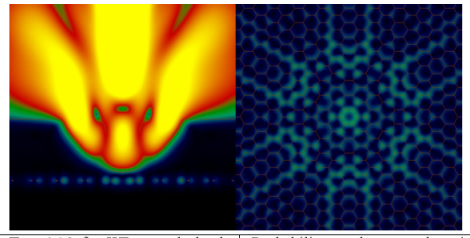
T = 3.52 fs. Further retraction into tip bulk. Interference patterns disappear

WP spreads along the 6 γK directions of the Brillouin zone



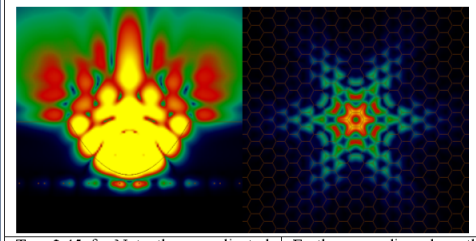
T = 2.00 fs. Incoming and outgoing waves cause interferences in tip bulk. WP begins to spread on the graphene sheet

WP spreads along the C-C bonds



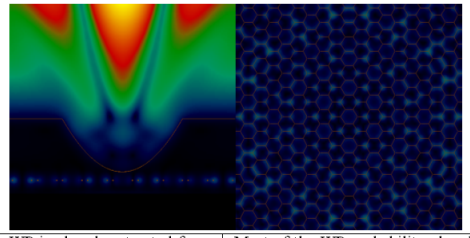
T = 4.19 fs. WP tunnels back from the central hexagon into the tip bulk with a small probability

Probability at the central region begins to decrease



T = 2.45 fs. Note the complicated interference pattern in tip bulk and apex regions due to the hyperbolic tip shape

Further spreading along the C-C bonds



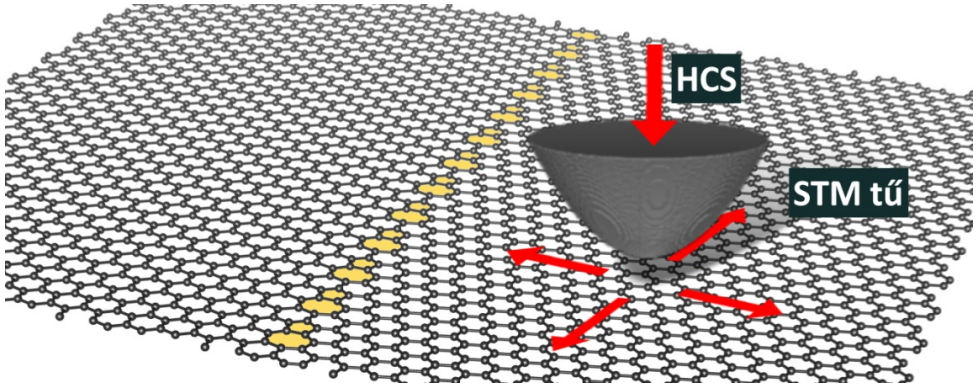
WP is already retracted from the tip apex region

Most of the WP probability already spreaded outside the central hexagon

G. T. Mark et at, Phys. Rev. B 85(2012)125443

Modelling the transport through a grain boundary

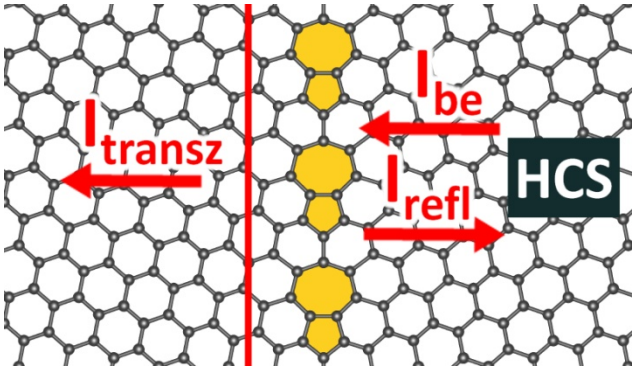
Model system – STM tip and two graphene grains



Calculating the transmission

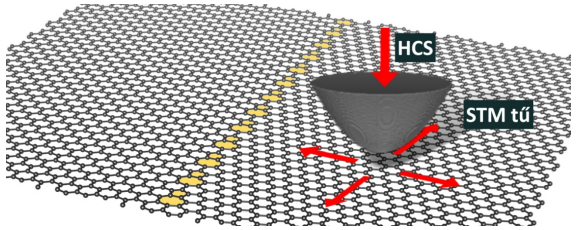
$$j(\vec{r},E) = -\frac{i\hbar}{2m}[\psi^*\nabla\psi - \psi\nabla\psi^*]$$

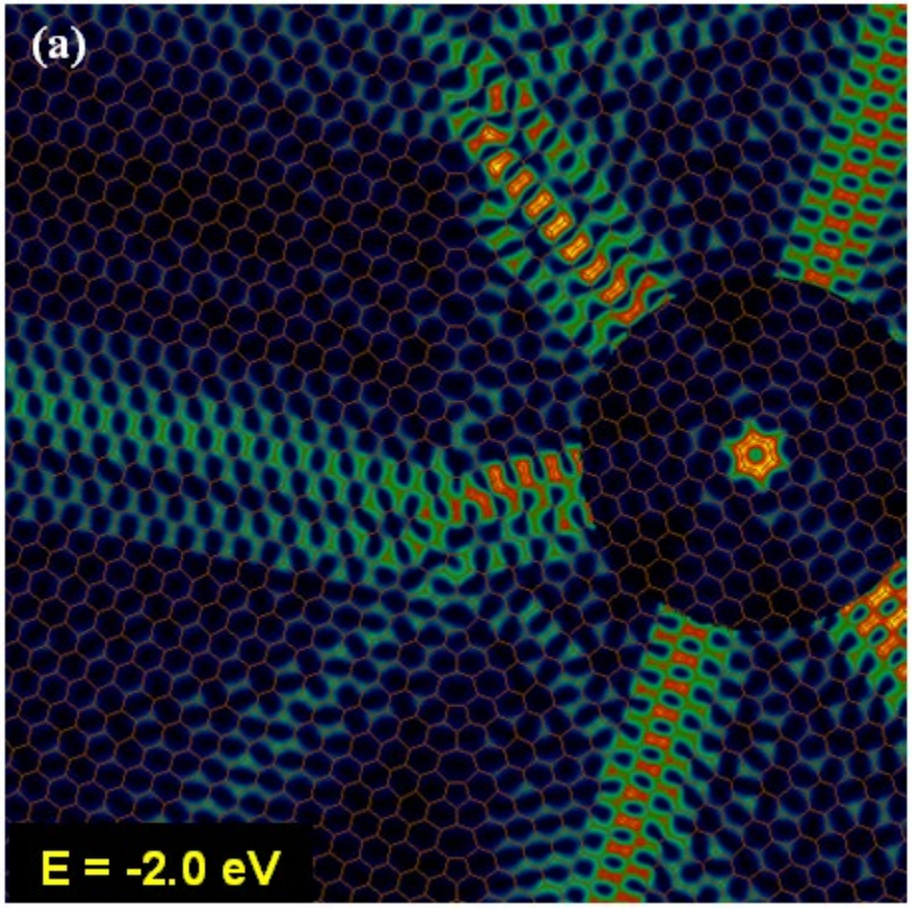
$$T(E) = I_{transz}(E)/I_{be}(E)$$

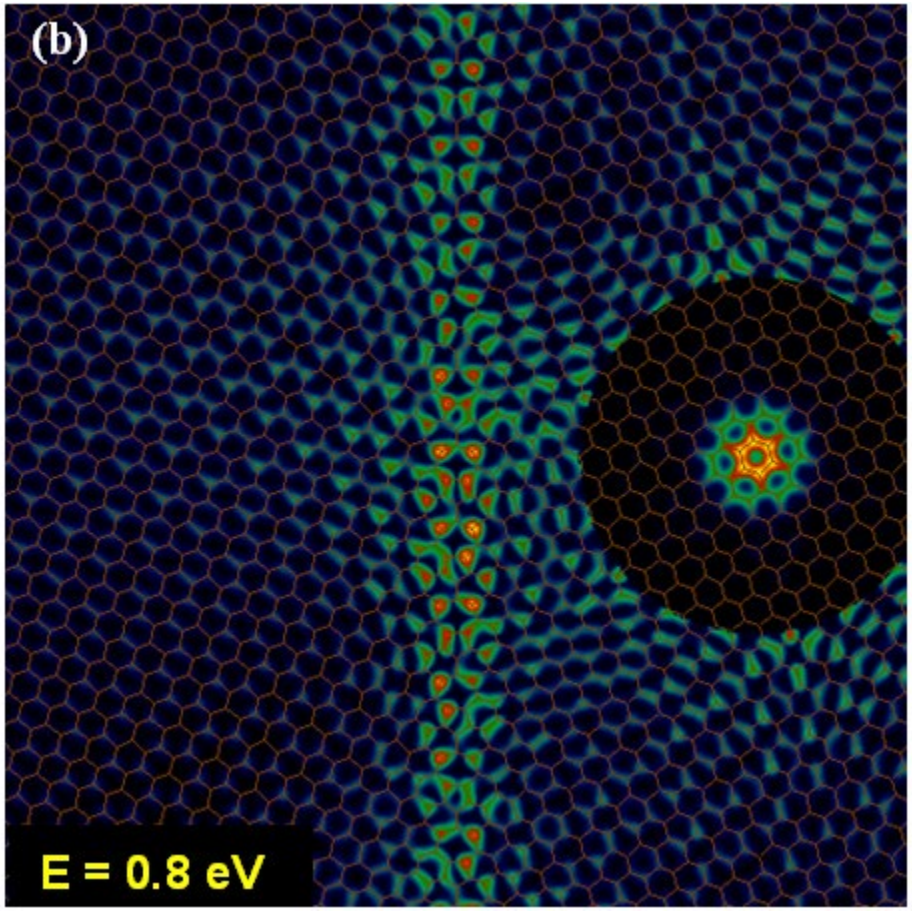


P. Vancsó et al, *Appl. Surf. Sci.*, vol. 291, pp. 58–63, 2014.

ρ(E) -- grain boundary in graphene







Beam splitting

Localized states on GB

How to create precisely controlled initial wave packets? Build them from Bloch waves!

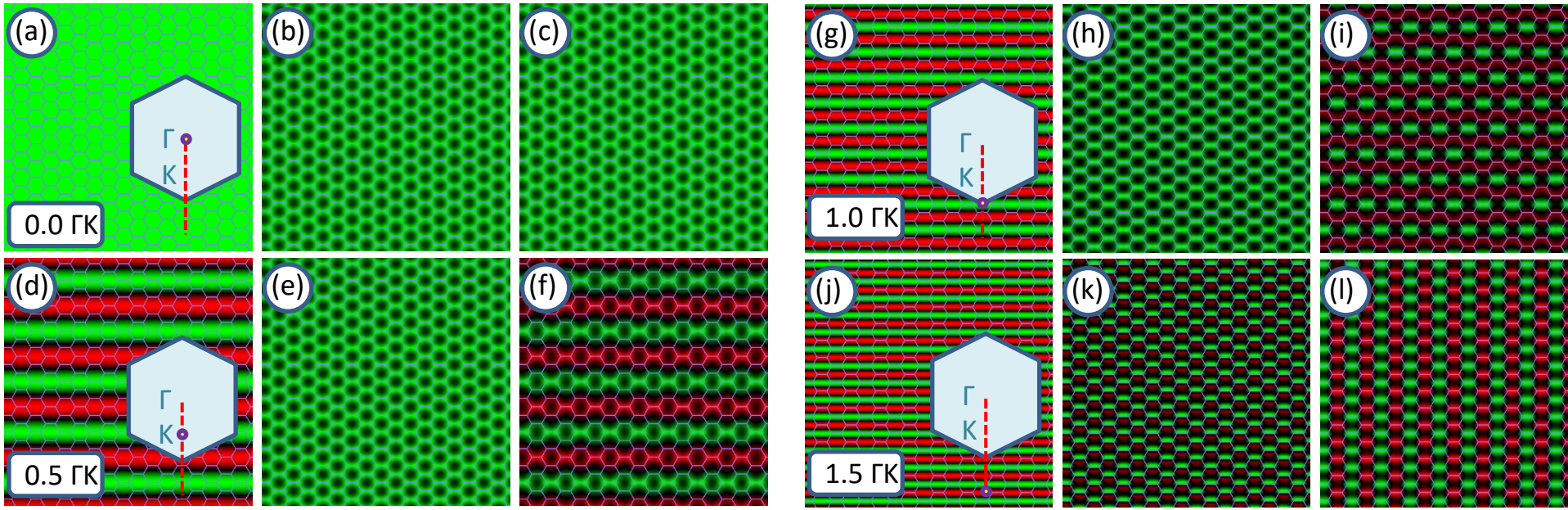
If $V(\vec{r})$ is periodic:

$\boldsymbol{\varphi(\vec{r}, \vec{k}_{Bloch}) = u(\vec{r}, \vec{k}_{Bloch}) e^{i\vec{k}_{Bloch}\vec{r}}}$, where

$u(\vec{r}, \vec{k}_{Bloch})$ is periodic and $\vec{k}_{Bloch}$ is the Bloch wave vector.

These $\varphi(\vec{r}, \vec{k}_{Bloch})$ functions are called Bloch functions.

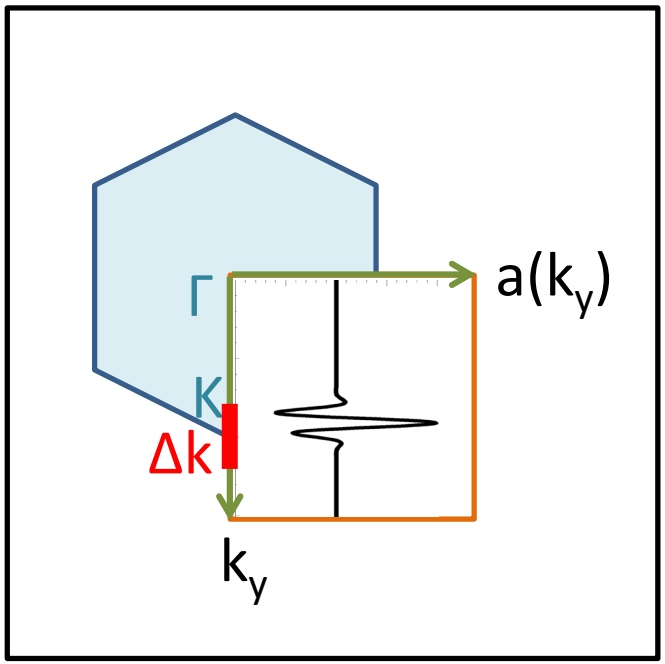
Graphene Bloch functions

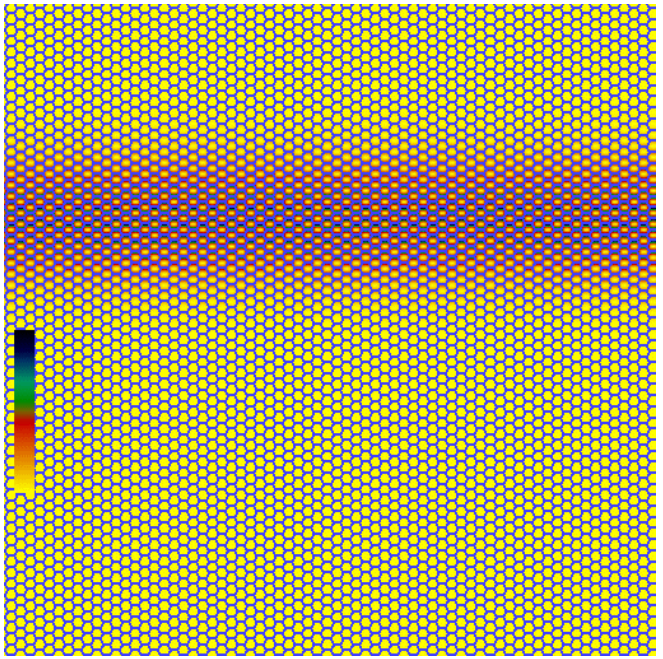


$e^{i\vec{k}_{Bloch}\vec{r}}$ $u(\vec{r},\vec{k}_{Bloch})$ $\varphi(\vec{r},\vec{k}_{Bloch})$ $e^{i\vec{k}_{Bloch}\vec{r}}$ $u(\vec{r},\vec{k}_{Bloch})$ $\varphi(\vec{r},\vec{k}_{Bloch})$

$$\varphi(\vec{r},\vec{k}_{Bloch}) = u(\vec{r},\vec{k}_{Bloch})e^{i\vec{k}_{Bloch}\vec{r}}$$

Construction of wave packets from graphene Bloch functions

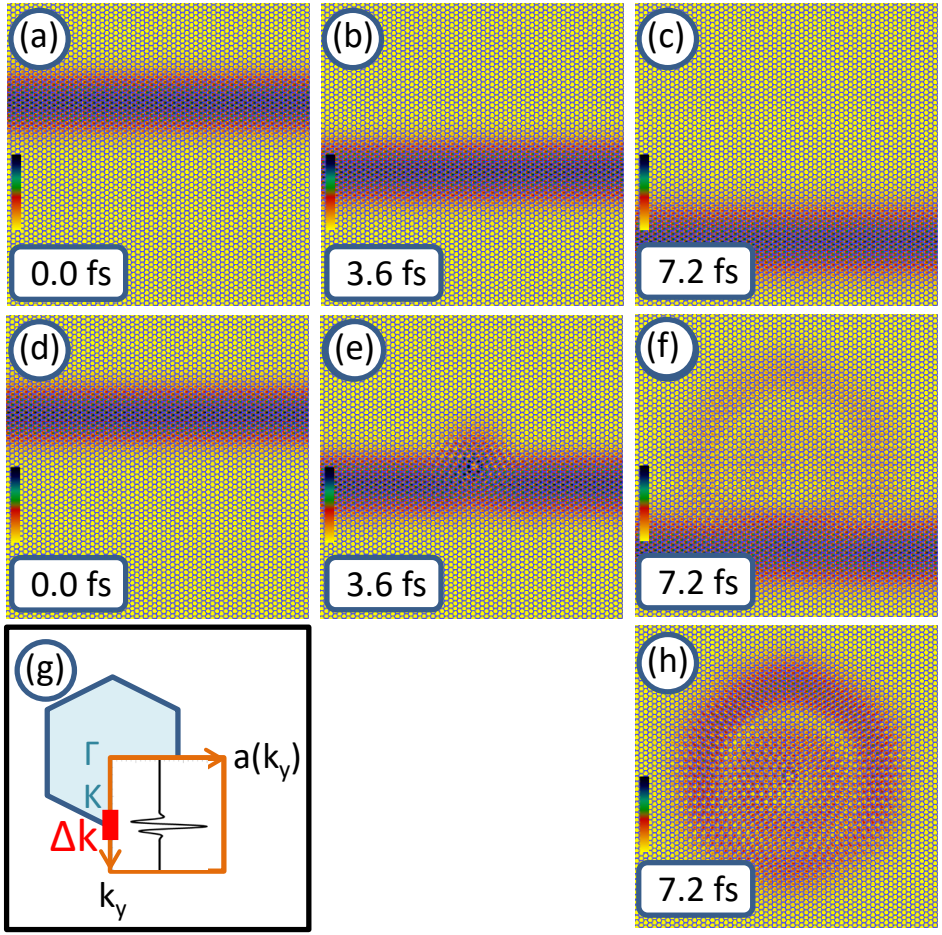




$\boldsymbol{\phi(\vec{r})}$

$$\underbrace{\boldsymbol{\phi(\vec{r})}}_{\text{Bloch wave packet}} = \int \underbrace{\boldsymbol{e^{-\frac{|\vec{k}-\vec{k}_0|^2}{4\Delta k^2}} e^{i\vec{r}_0\vec{k}}}}_{a(k_y)} \underbrace{\boldsymbol{\varphi(\vec{r},\vec{k})}}_{\text{Bloch function}} \boldsymbol{d^3\vec{k}}$$

Time development of a Bloch function Wave packet



Pristine graphene

Graphene with defect

Difference of (f) and (c)

How to make WPD for other materials?

- In the split operator method the kinetic energy is calculated in k space

$$e^{A+B} \cong e^{A/2} e^{B} e^{A/2}$$

$$Exp\left[-\frac{i}{\hbar}\hat{H}\delta t\right] \cong$$

$$\cong Exp\left[-\frac{i}{\hbar}\frac{\hat{K}}{2}\delta t\right] Exp\left[-\frac{i}{\hbar}\hat{V}\delta t\right] Exp\left[-\frac{i}{\hbar}\frac{\hat{K}}{2}\delta t\right]$$

$$\Delta\psi(\vec{r},t) = F^{(-1)}\left[e^{-\left|\vec{k}\right|^2/2} F\left[\psi(\vec{r},t)\right]\right]$$

This is nothing else but the E = $k^2/2$ free space dispersion relation … what happens, if we modify this?

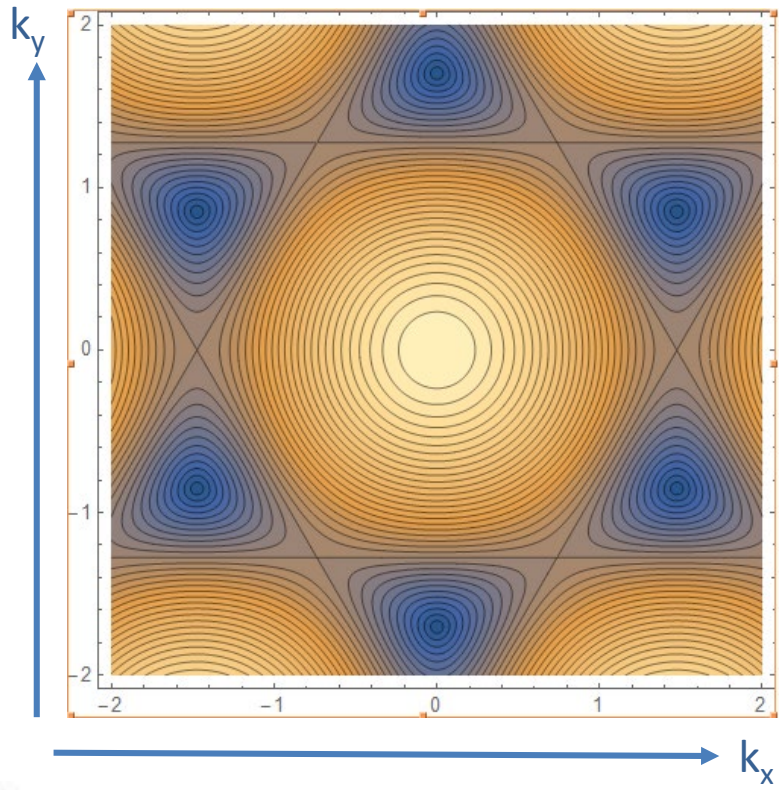
EUREKA!!!

Change the dispersion relation!!

Easy to calculate from the band structure

Test case: graphene tight binding dispersion relation

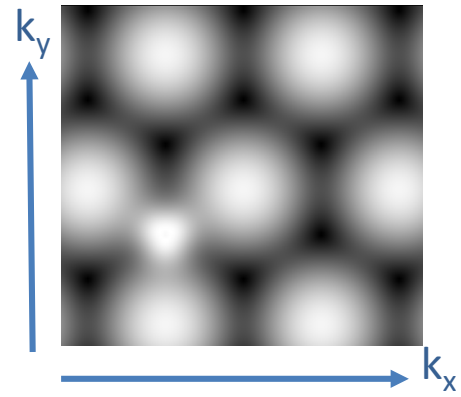
Graphene TB dispersion relation

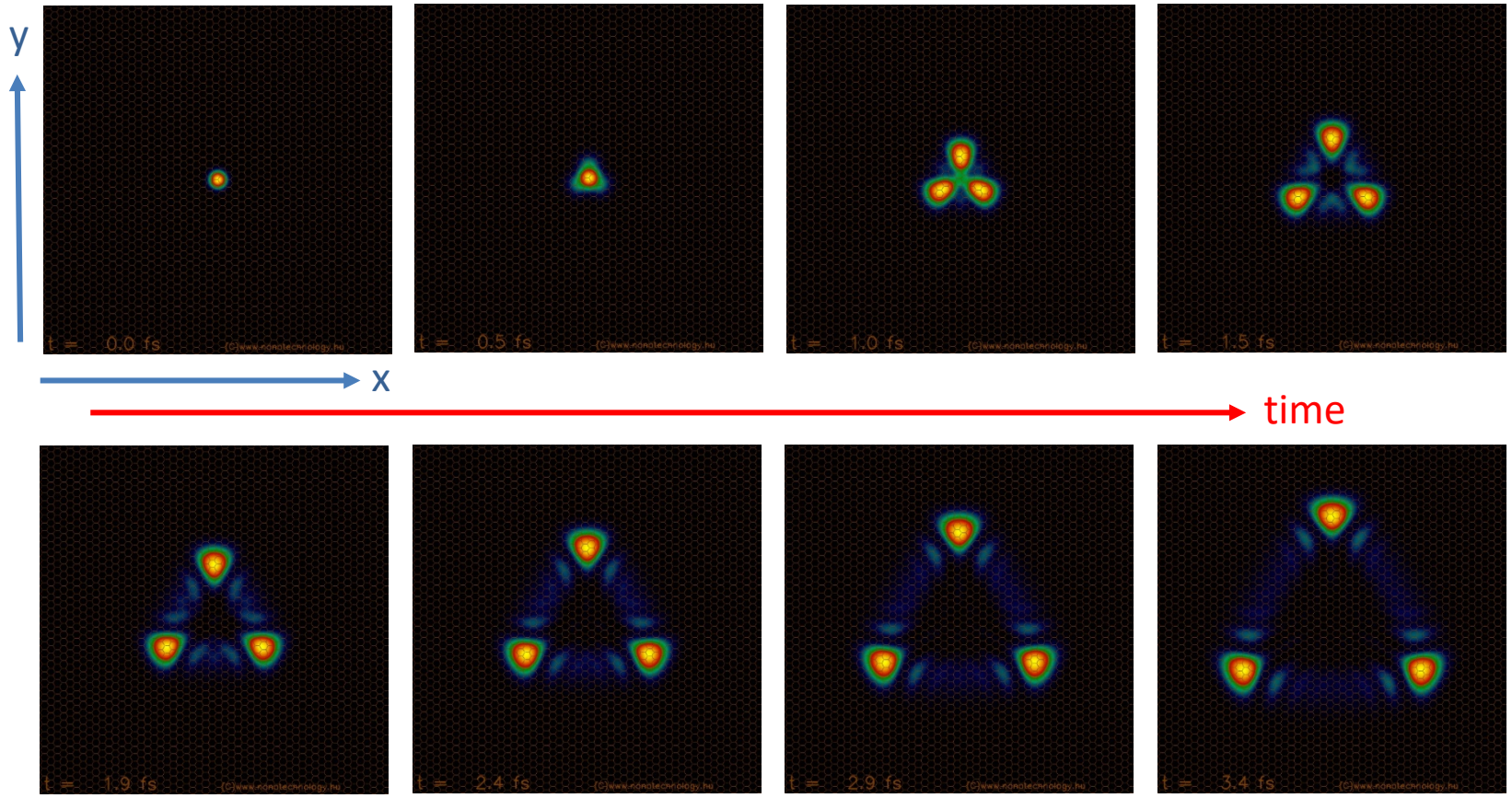


$$E_{1,2} = \alpha \pm A^{1/2}\beta$$

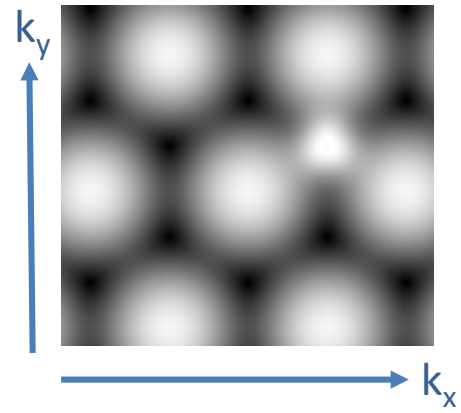
$$A = 3 + 2\cos[\mathbf{k}\cdot(\mathbf{a}_1 + \mathbf{a}_2)] + 2\cos(\mathbf{k}\cdot\mathbf{a}_2) + 2\cos(\mathbf{k}\cdot\mathbf{a}_1)$$

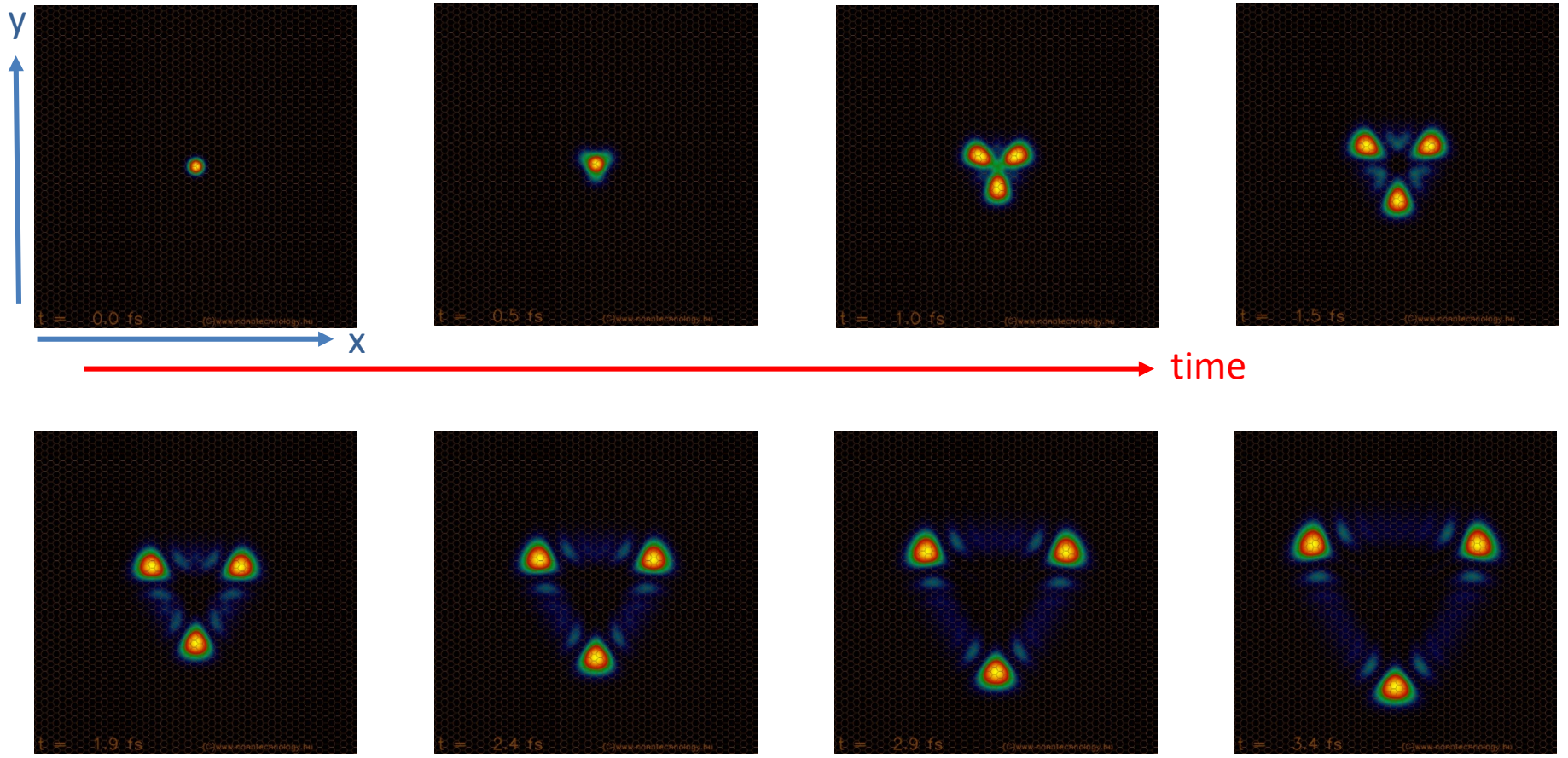
Time development – K point



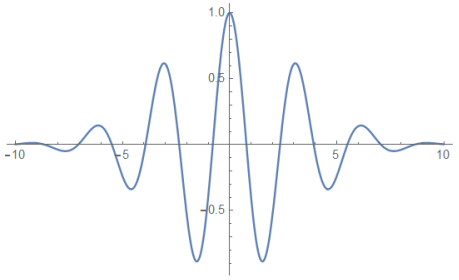


Time development – K’ point

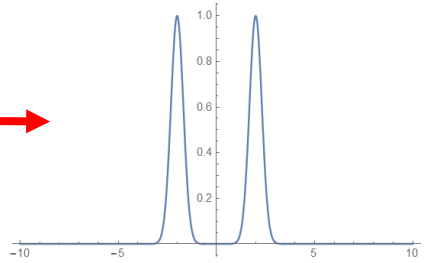


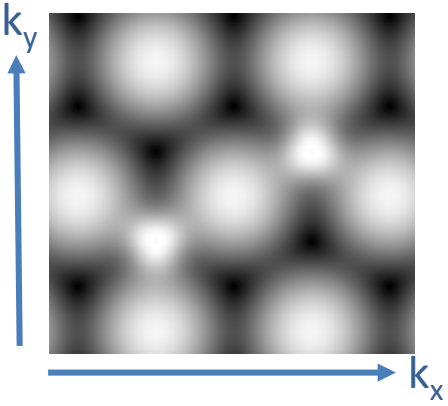


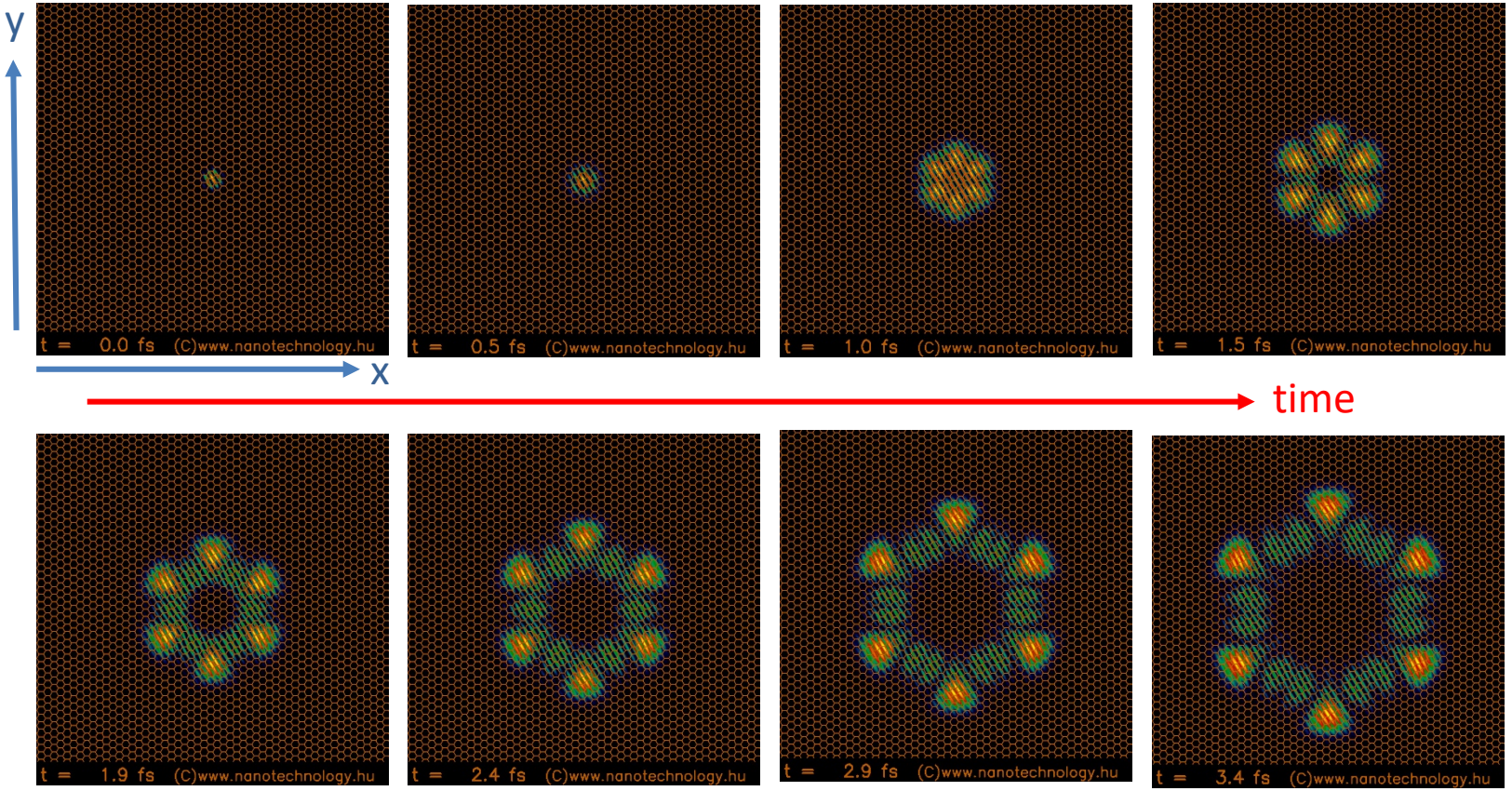
Time development – K and K’ point



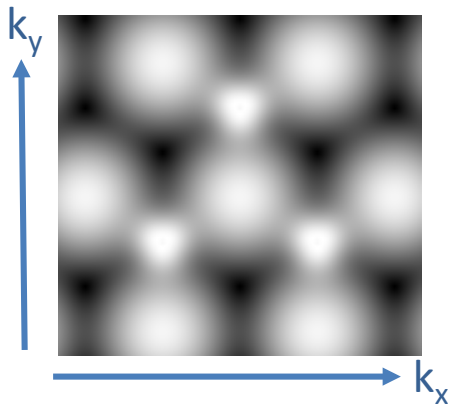
FFT

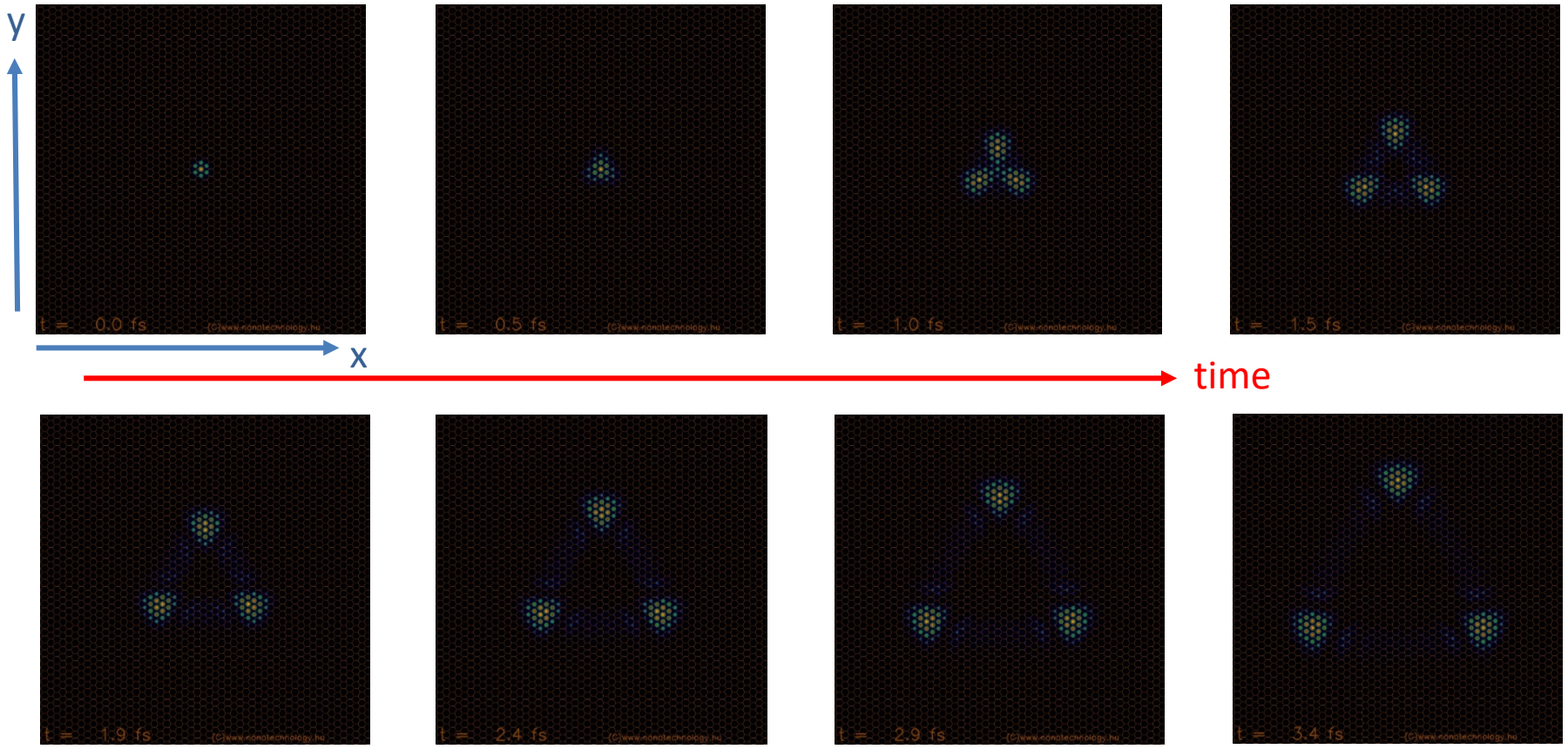




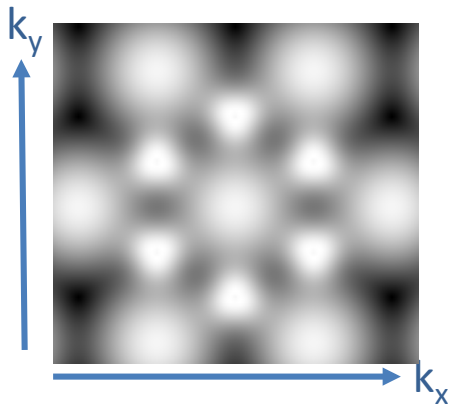


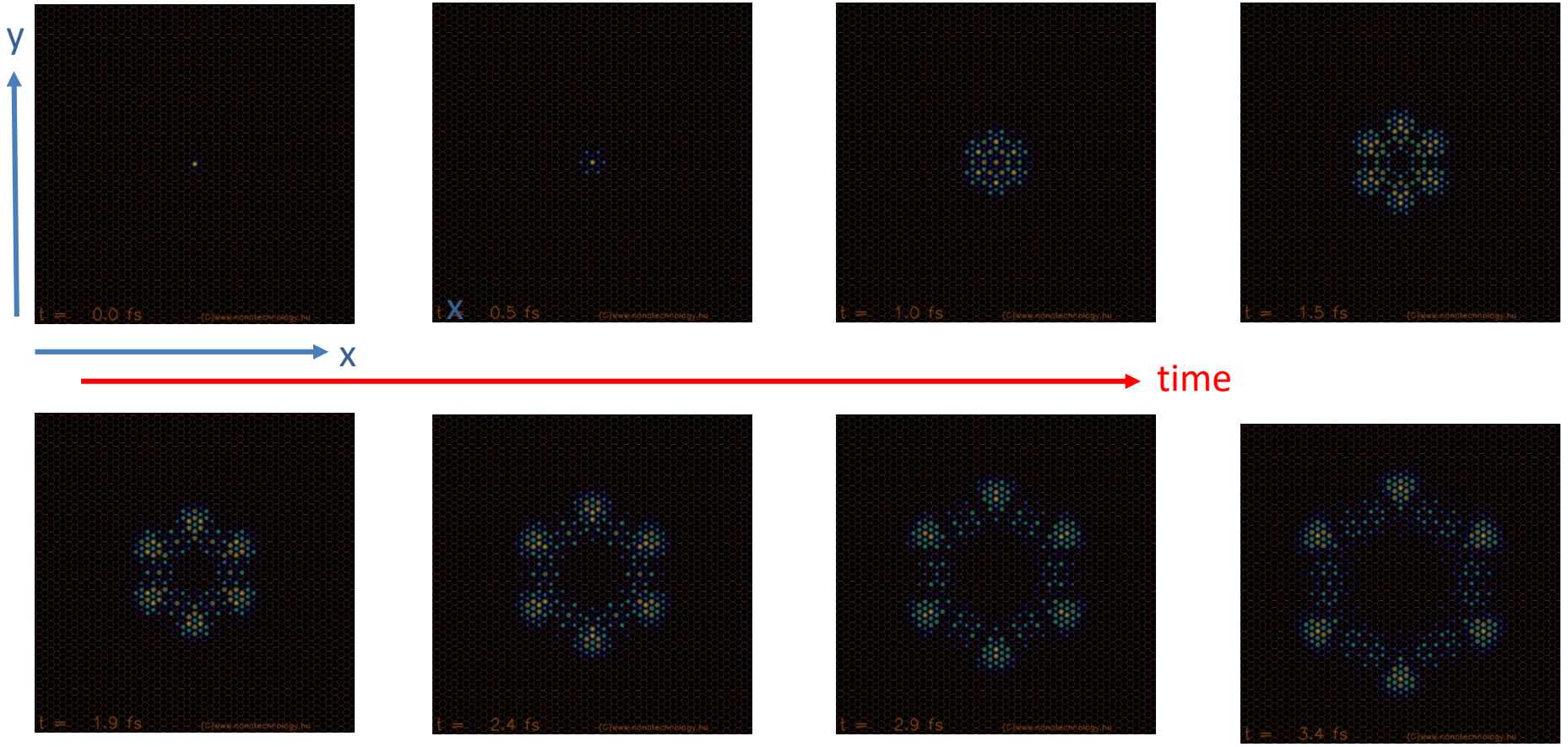
Time development – 3 K points





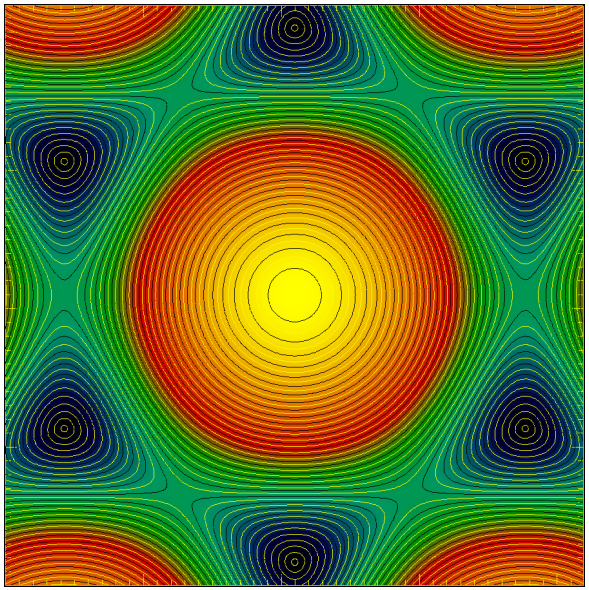
Time development – 3 K and 3 K’ points





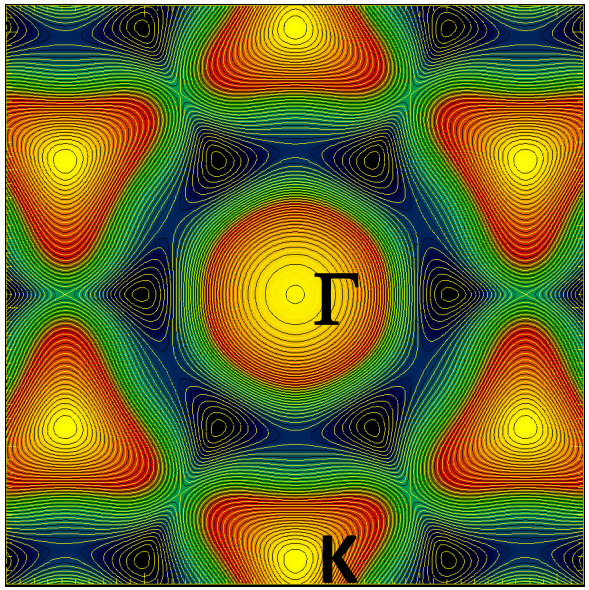
Graphene and MoS_2 dispersion relations

Graphene conduction band



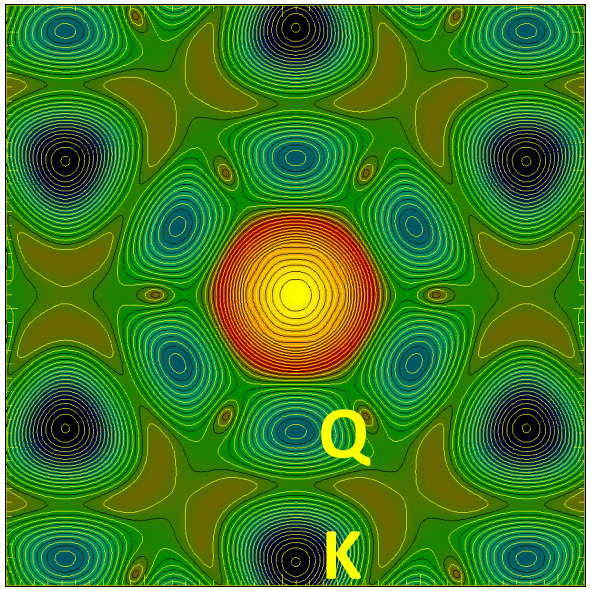
$E \in [0.00, 9.00] eV$

MoS_2 valence band



$E \in [-1.06, -0.10] eV$

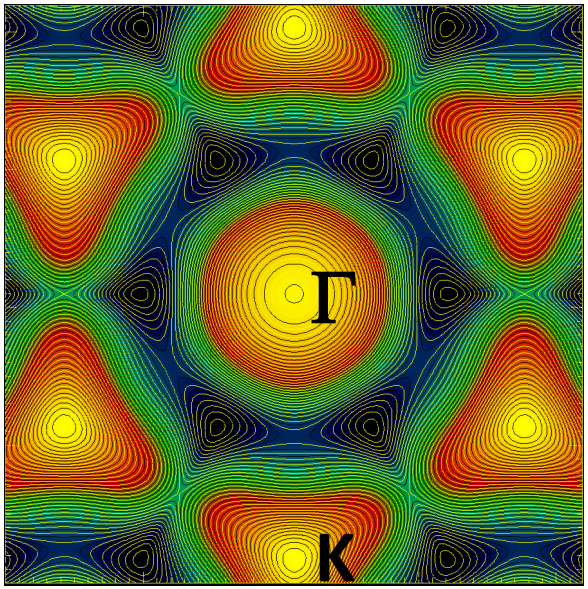
MoS_2 conduction band

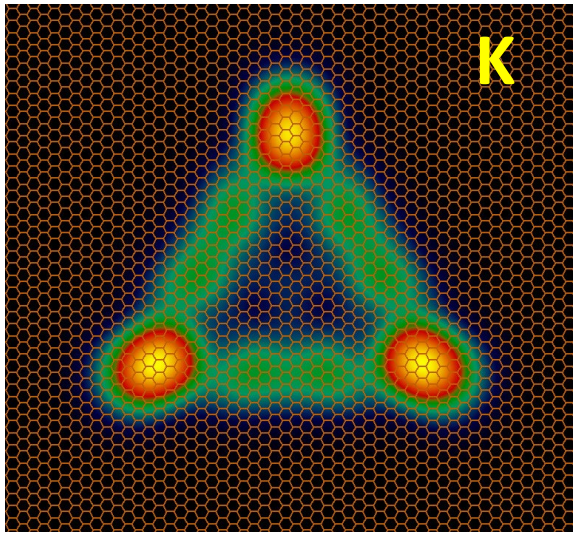


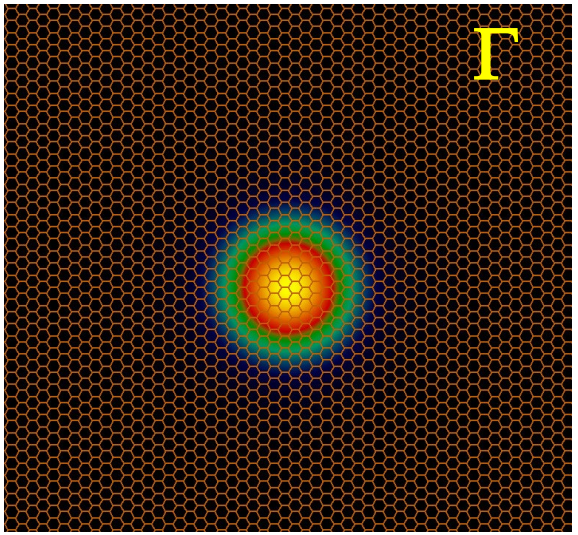
$E \in [1.58, 2.70] eV$

MoS_2 wave packet dynamics

MoS_2 valence band

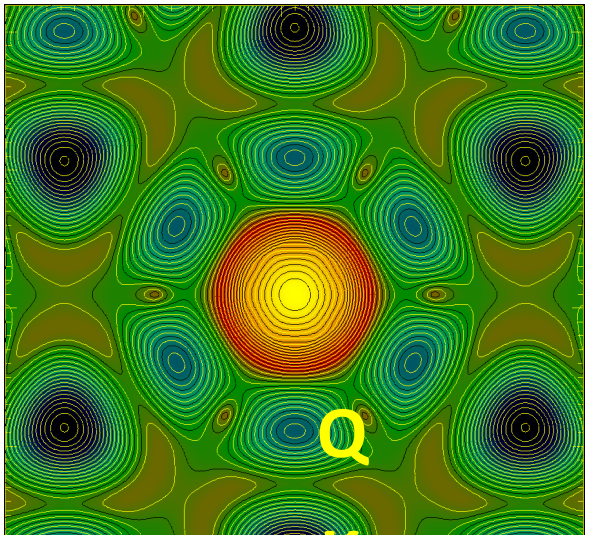


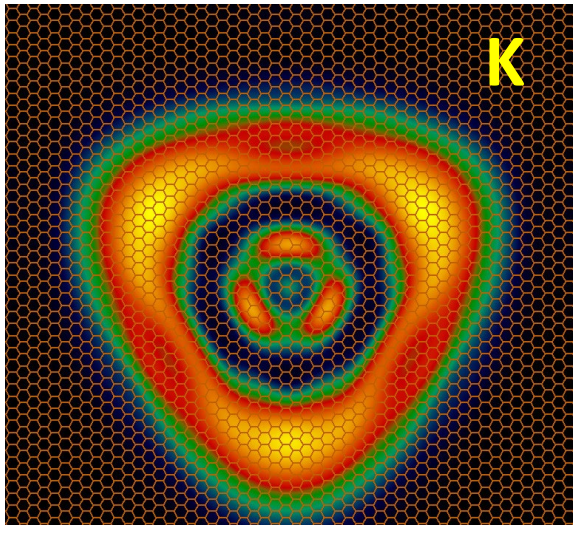


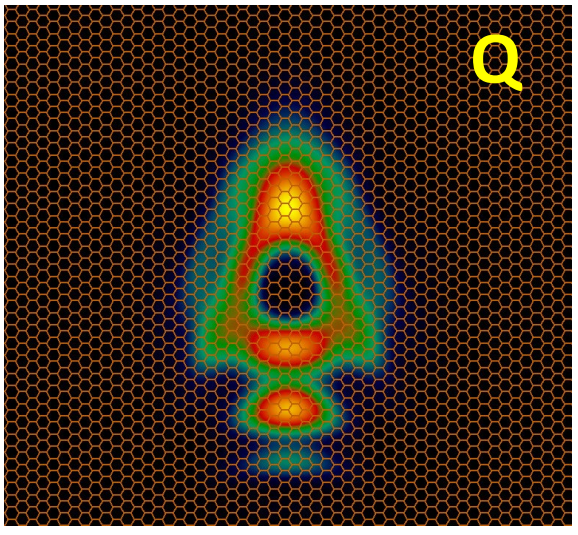


G. I. Márk et al, *Phys. Status Solidi Basic Res.*, vol. 254, no. 11, 2017.

MoS_2 conduction band



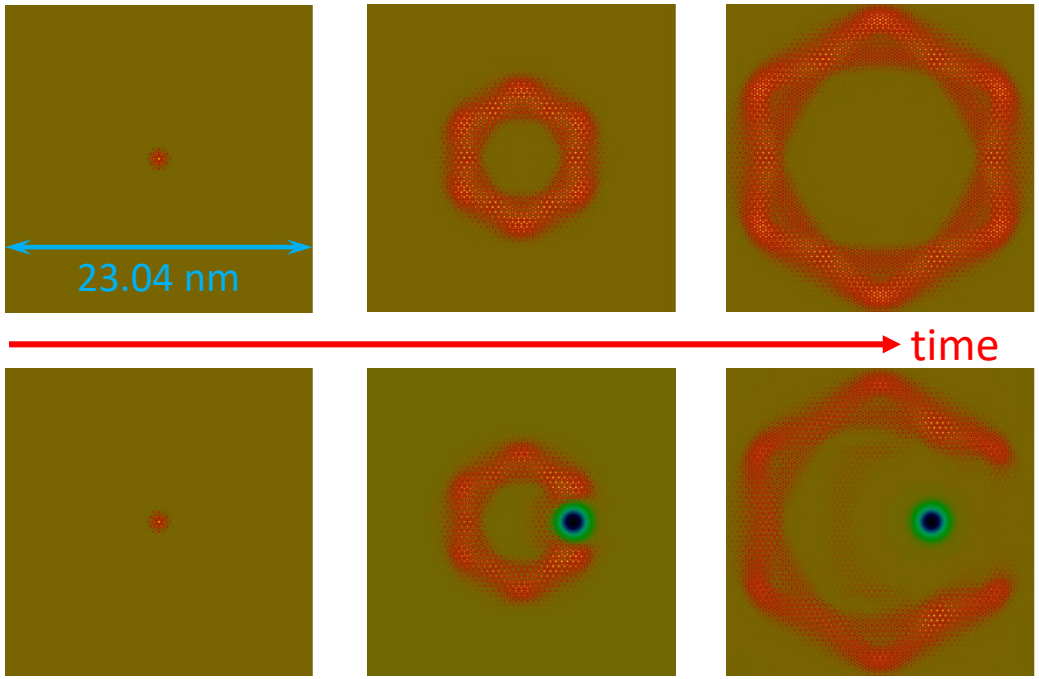




Inserting physics in both the kinetic and potential energy operator

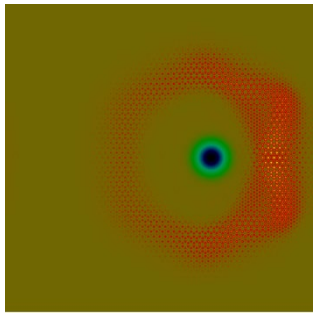
- $H = K + V$
- $K(k)$ kinetic energy operator, defined in k space, describes the infinite crystal lattice
- $V(r)$ potential energy operator, defined in r space, describes the local perturbations

Wave packet spreading on graphene without and with local defect



- K(k): graphene tight-binding dispersion relation
- V(r) = 0

- K(k): graphene tight-binding dispersion relation
- V(r): localized defect, V_0=-2 eV. ΔX = 0.48 nm



- Probability density of the difference wave function, Abs($Psi_{withpot} - Psi_{free}$)^2
- Scattering dictated by a “modified Huygens principle” – the local scattering has a hexagonal pattern, because of the anisotropic nature of the graphene dispersion relation

How to proceed?

- Calculate WPD for more 2D materials
- Multidomain method: different E(k) for different regions (e.g. grain boundaries)

THANK YOU FOR THE ATTENTION!

QUESTIONS?