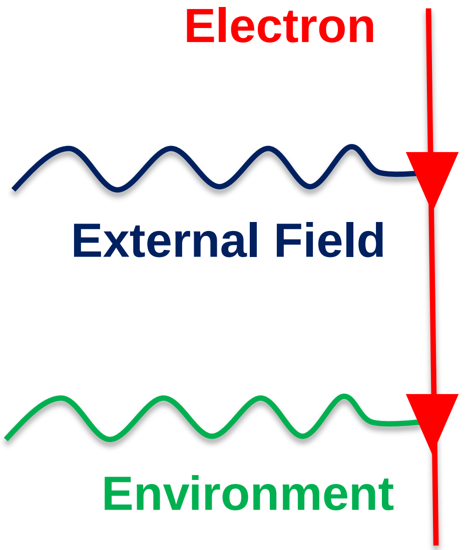
Combining Density Matrix and Density Functional Theory

Excitation, Propagation and Relaxation of Non-Equilibrium States

Andreas Knorr



Matthias Scheffler,
Norbert Bücking
Fritz-Haber Institut Berlin

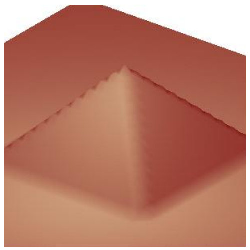
Peter Kratzer
Universität Essen

Marten Richter, Norbert Bücking,
Carsten Weber, Julia Kabuß
Technische Universität Berlin

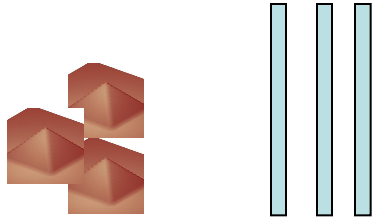
Nonlinear Optics and Quantum Electronics at TUB

Theoretical Physics

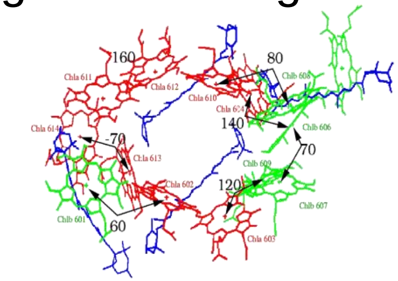
- semiconductor quantum dots



- coupled nano structures

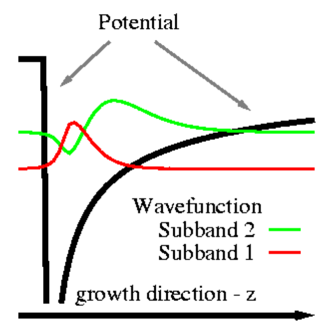


- light harvesting complex

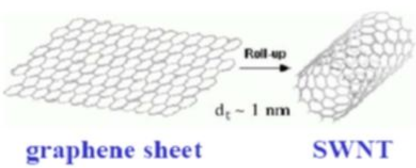


Density Matrix Theory, Radiation- and Electron-Transfer Processes

- intersubband transitions

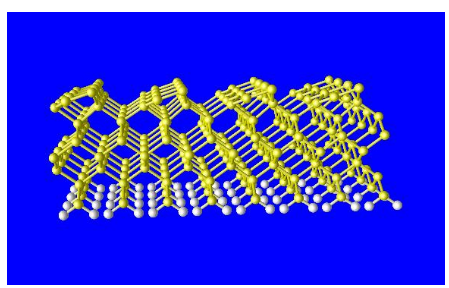


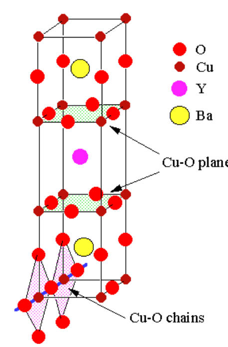
- carbon-nanostructures



- confined electron gases

- surface structures





- HTc

From Basics Concepts to Real Materials:

„Combination of density matrix dynamics with interaction matrix-elements beyond simple model wave functions is a way to describe ultrafast dynamics of (real) materials“

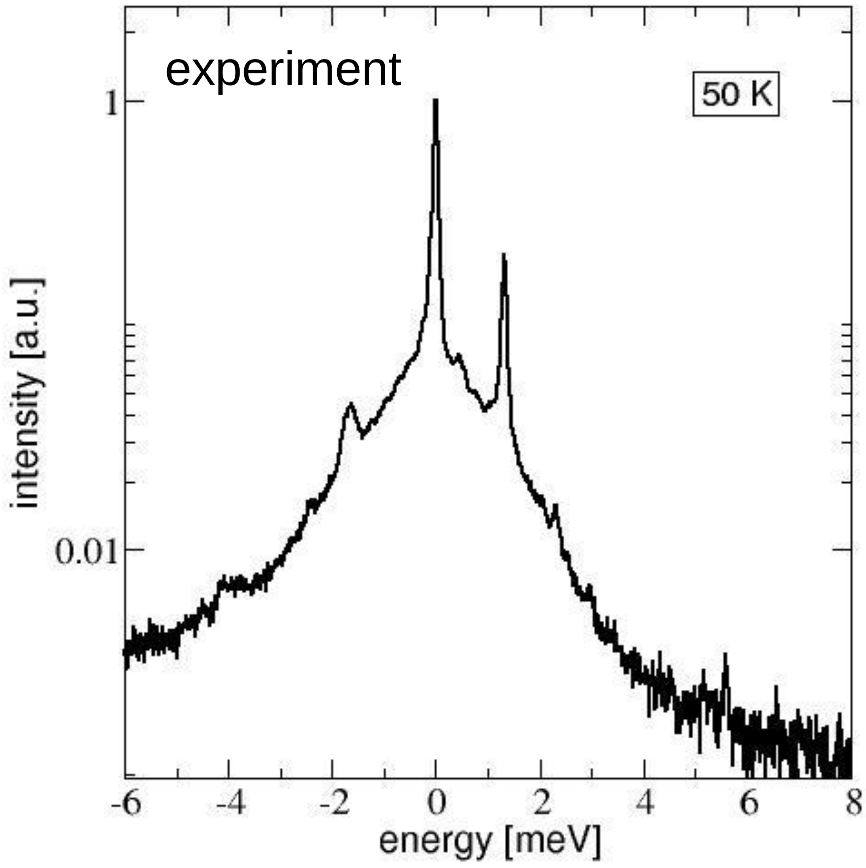
Outline:

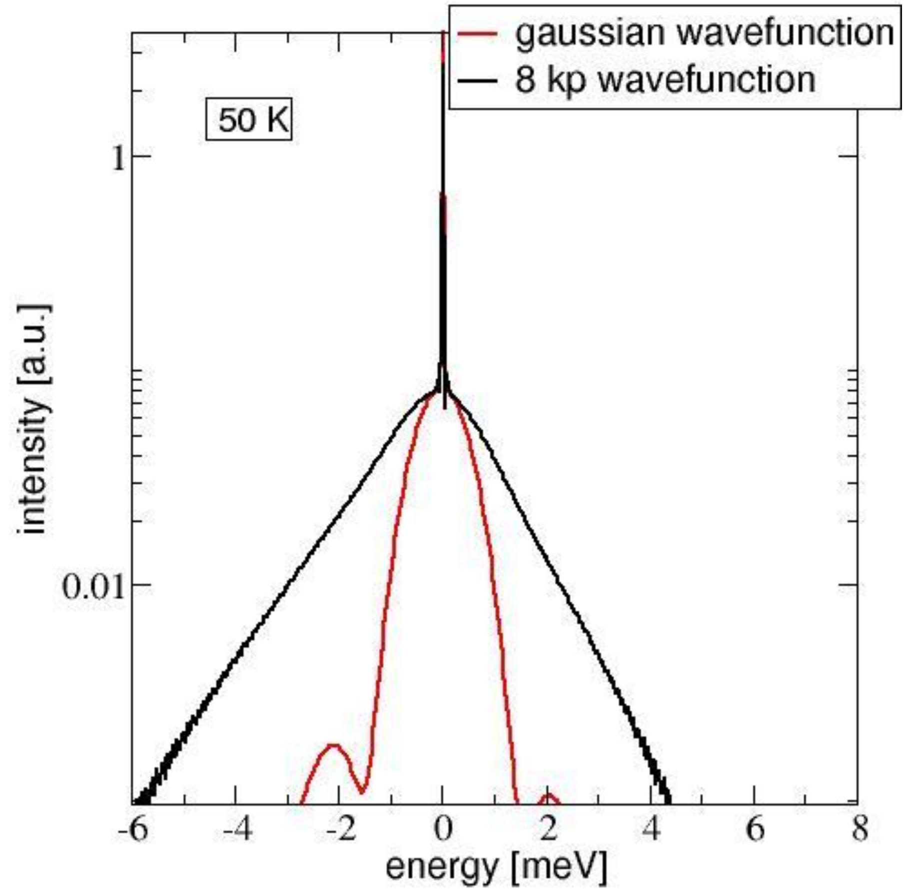
Theory of Quantum-Dynamics: Time Scales

Examples: Quantum Dots, Graphene, Surfaces

(increase of complexity in used wave functions)

Luminescence of a Quantum Dot – Spectral Lineshape





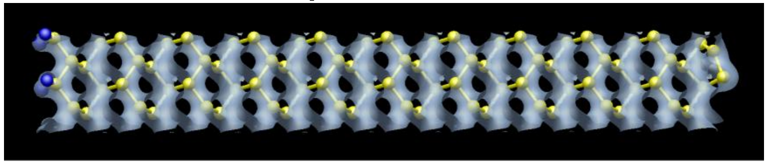
measurements of single InAs-QD luminescence by (E. Stock et al, TU Berlin)

calculations using density matrix dynamics (independent boson model)

Si surface: matrix elements using DFT

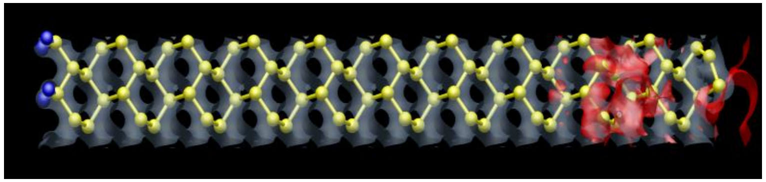
Light Pulse

before the pulse



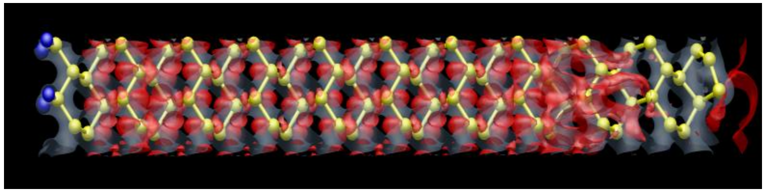
1. excitation process of electrons from equilibrium into non-equilibrium

t=0fs



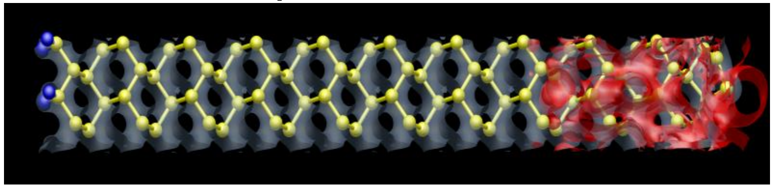
2. time propagation of non-equilibrium into new (quasi-) equilibrium via interaction with phonons

t=2ps



after the pulse

t>20ps



dipole- P and electron density n correspond to sum over **all transitions/occupations**

$$P(r,t) = \sum_{i,j} \varphi_i^*(r) q\mathbf{r} \varphi_j(r) \rho_{ij}(t), \quad n(r,t) = \sum_{i,j} \varphi_i^*(r) \varphi_j(r) \rho_{ij}(t)$$

single particle states $\{\varphi_i(r)\}$
and energies, matrix elements

expansion coefficients:
transitions / occupations

$$\rho_{ij}(t) = tr\left(a_i^\dagger a_j \rho(t)\right); \rho_{ii}(t) = tr\left(a_i^\dagger a_i \rho(t)\right)$$

Theoretical Physics

dipole- P and electron density n correspond to sum over **all transitions/occupations**

$$P(r,t) = \sum_{i,j} \varphi_i^*(r) q\mathbf{r} \varphi_j(r) \rho_{ij}(t), \quad n(r,t) = \sum_{i,j} \varphi_i^*(r) \varphi_j(r) \rho_{ij}(t)$$

Effective Mass / Tight Binding

single particle states $\{\varphi_i\}$
and energies, matrix elements

Density Functional Theory For Complex Systems

expansion coefficients: transitions / occupations

$$\rho_{ij}(t) = tr\left(a_i^\dagger a_j \rho(t)\right); \rho_{ii}(t) = tr\left(a_i^\dagger a_i \rho(t)\right)$$

Observables: Combined Material- and Density Matrix Theory

dipole- P and electron density n correspond to sum over **all transitions/occupations**

$$P(r,t)=\sum_{i,j}\varphi_i^*(r)q\mathbf{r}\varphi_j(r)\rho_{ij}(t), \quad n(r,t)=\sum_{i,j}\varphi_i^*(r)\varphi_j(r)\rho_{ij}(t)$$

Effective Mass / Tight Binding

single particle states $\{\varphi_i\}$ **and energies, matrix elements**

Density Functional Theory For Complex Systems

$$i\hbar\dot{\rho}(t)=[H(t),\rho(t)]$$

Density Matrix Theory

expansion coefficients: transitions / occupations

$$\rho_{ij}(t)=tr\left(a_i^\dagger a_j\rho(t)\right);\rho_{ii}(t)=tr\left(a_i^\dagger a_i\rho(t)\right)$$

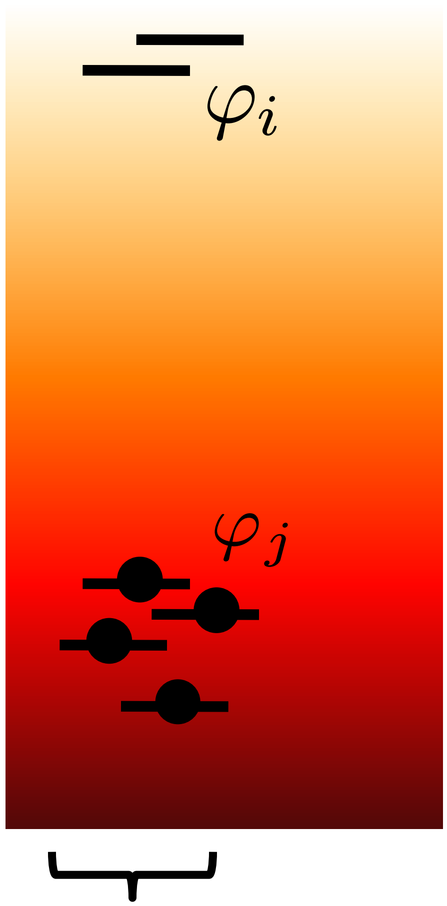
Model and Hamiltonian

$$\rho_{ij}(t) = tr\left(a_i^\dagger a_j \rho(t)\right); \rho_{ii}(t) = tr\left(a_i^\dagger a_i \rho(t)\right)$$

Basic Approach in Second Quantization

electronic system, single particle states $\{\varphi_i\}$

excited states

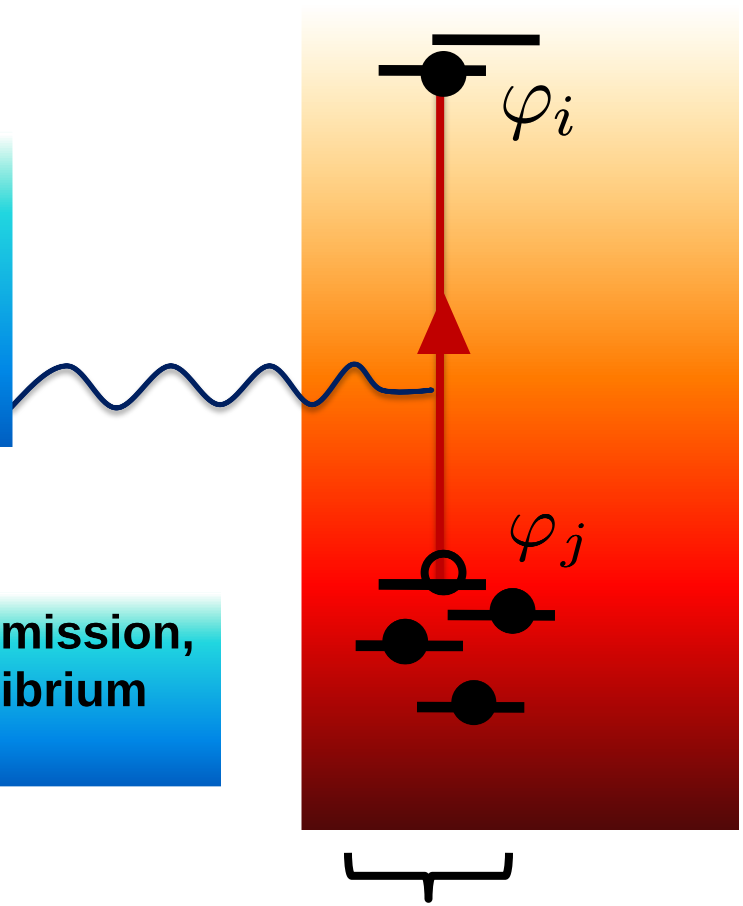


correlated or Hartree-Fock electronic groundstate

Basic Approach in Second Quantization

electronic system, single particle states $\{\varphi_i\}$

ext./int. fields:
normal modes n



optical excitation/emission, prepares non-equilibrium situation

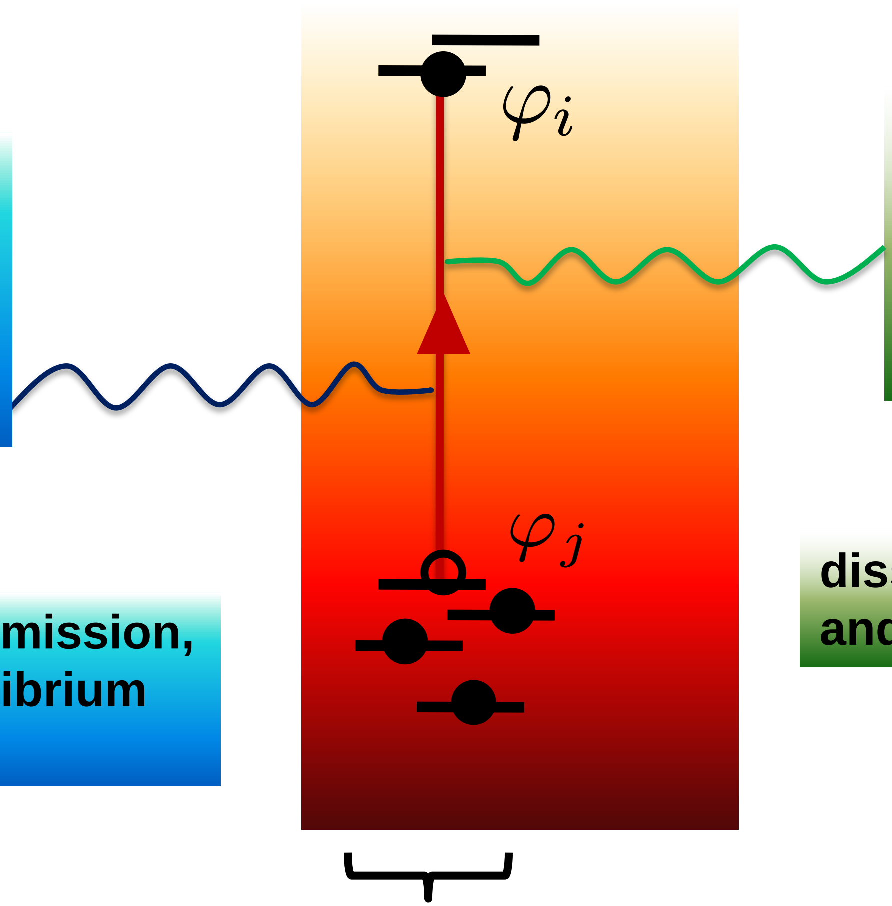
correlated or Hartree-Fock electronic groundstate

Basic Approach in Second Quantization

electronic system, single particle states $\{\varphi_i\}$

external - fields: normal modes n

reservoir phonon – modes:



optical excitation/emission, prepares non-equilibrium situation

dissipates system energy and heats reservoir

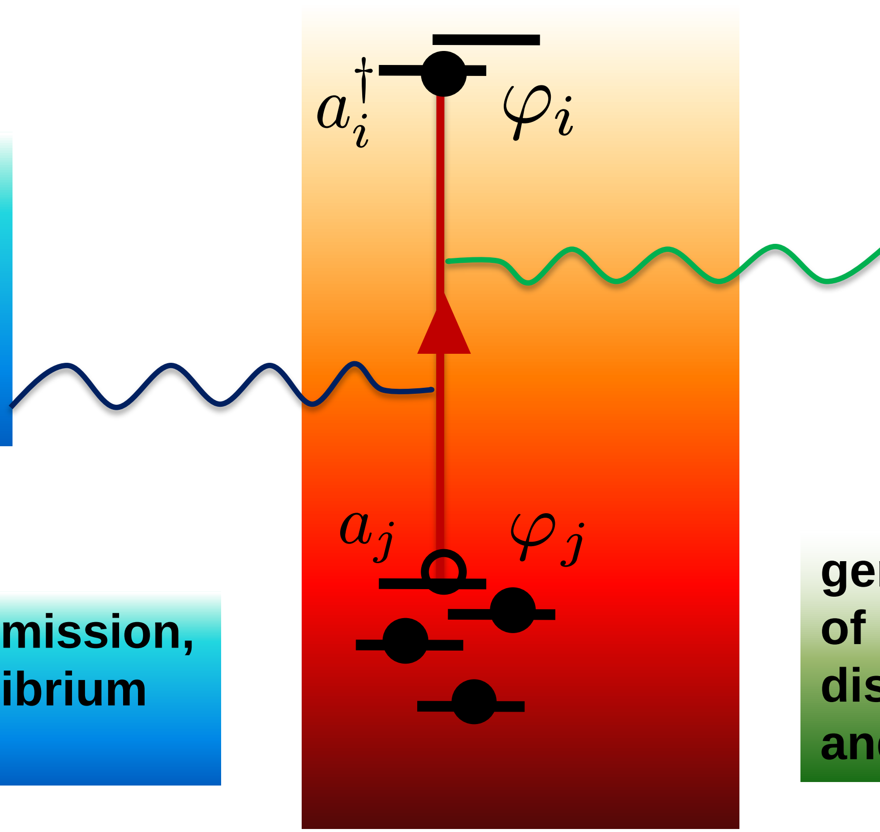
correlated or Hartree-Fock electronic groundstate

Basic Approach in Second Quantization

electronic system, single particle states $\{\varphi_i\}$

external - fields:
normal modes n

$c_n^\dagger, c_n$



reservoir
phonon – modes:

$b_\alpha^\dagger, b_\alpha$

optical excitation/emission, prepares non-equilibrium situation

generation/destruction of mode quanta: dissipates system energy and heats reservoir

distribution function:

$$\rho_{ij} = tr\left(a_i^\dagger a_j \rho(t)\right)$$

Hamiltonian, Elementary Excitations

$$\rho_{ij} = tr\left(a_i^\dagger a_j \rho(t)\right)$$

Theoretical Physics

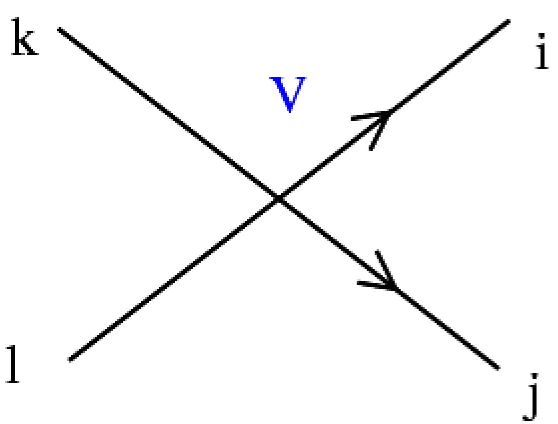
von Neumann Eq. for the statistical operator

$$\dot{\rho}(t) = \frac{-i}{\hbar}[H(t), \rho(t)] = -iL\rho(t)$$

Hamiltonian:

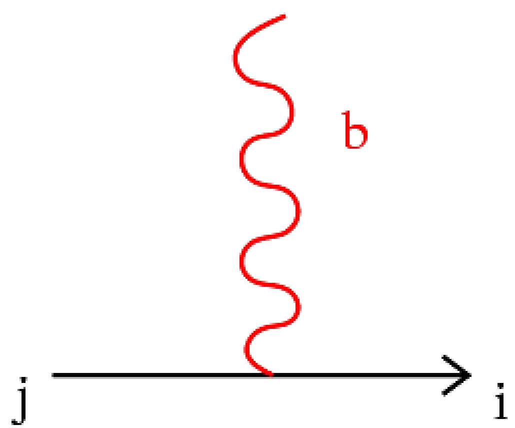
$$H = H_{\mathrm{nano}} + H_{\mathrm{field}} + H_{\mathrm{int}}$$

Coulomb–Interaction

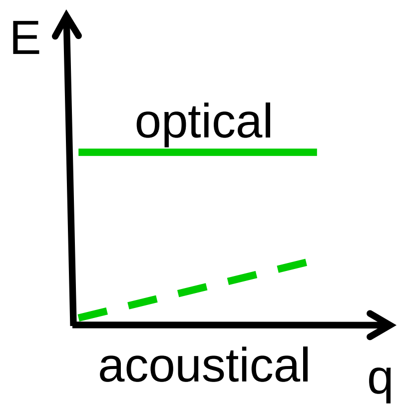


$$H_{int} \sim V a_i^\dagger a_j^\dagger a_k a_l$$

Electron–Photon / Phonon



$$H_{int} \sim D(b_\alpha^\dagger + b_\alpha) a_i^\dagger a_j$$



Density Matrix Theory (Focus on Electron-Phonon)

$$\rho_{ij} = tr\left(a_i^\dagger a_j \rho(t)\right) = ?$$

Projection of statistical operator: Electron-Phonon Interaction

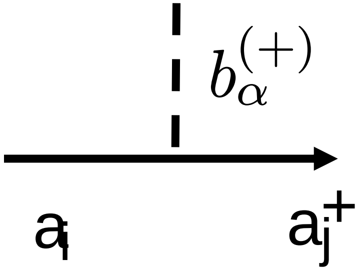
Theoretical Physics

$$\dot{\rho}(t) = \frac{-i}{\hbar}[H(t),\rho(t)] = -iL\rho(t)$$

$$H_{SB} = \sum_{\alpha,i,j} D_\alpha(i,j)(b_\alpha^\dagger + b_\alpha)a_i^\dagger a_j$$

density operator system S, reference B (phonons)

$$\boxed{\rho_S = tr_B\,(\rho) \quad P. = \rho_B tr_B. \quad Q = 1 - P}$$



L_{SB}

Nakajima –Zwanzig-Eq.

$$\dot{\rho}_S(t) = -iL_S\rho_S - \int^t dt' tr_B\left(L_{SB}e^{-i(L_0+QL_{SB})t'}L_{SB}\right)\rho_S(t-t')$$

electronic system only

multiple scatterings in propagators

memory: interaction takes time t‘ -> introduces time scales

Interaction Regimes

$$\rho_{ij}(t) = tr(\rho_S(t)a_i^\dagger a_j)$$

Perturbation Theory,
or Linked Cluster/Cumulants:

$$e_+^{-iQ\int^t dt' L_{SB}(t')} = exp\left(\sum_n \frac{(-i)^n}{n!} L_n^w(t)\right)$$

Quantum Kinetic Regime:

interference as waves

no energy conservation

in a collision

$$w_{i,j} \sim \int dt' e^{i(\epsilon_i - \epsilon_j \pm N\hbar\omega_{ph})t'}$$

Kinetic Regime:

energy conserving collisions

Master - Equations

$$w_{i,j} \sim \delta\left(\epsilon_i - \epsilon_j - N\hbar\omega_{ph}\right)$$

Local Equilibrium:

hydrodynamics, assume a temperature…

$$\rho_{ij} \rightarrow \rho_{ii}(T, \epsilon_i)$$

Quantum dot spectra and temporal dynamics

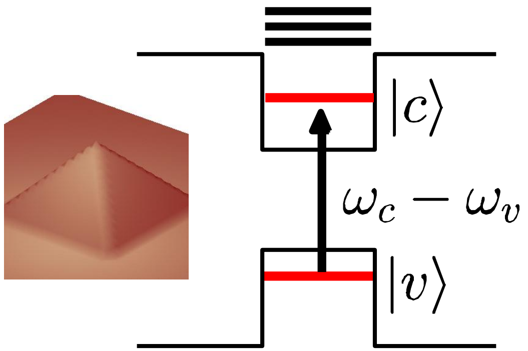
Beyond perturbation theory, quantum kinetics

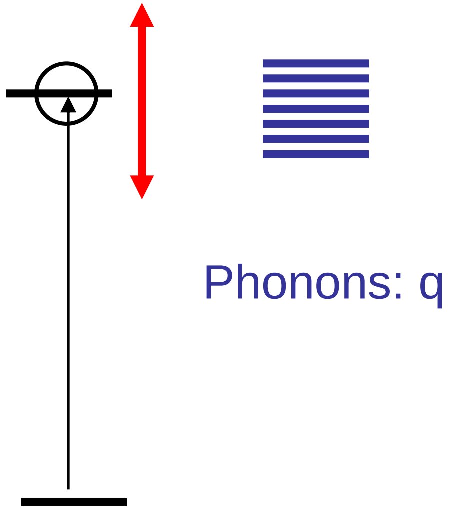
$$w_{i,j} \sim \int dt' e^{i(\epsilon_i - \epsilon_j \pm N\hbar\omega_{ph})t'}$$

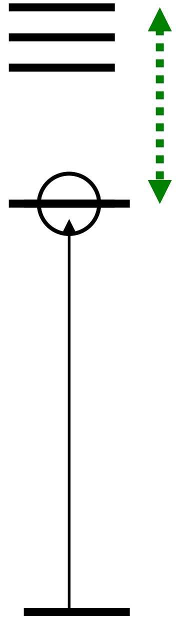
Electron-Phonon Coupling in a QD

Off-resonant levels
real transitions

virtual transitions



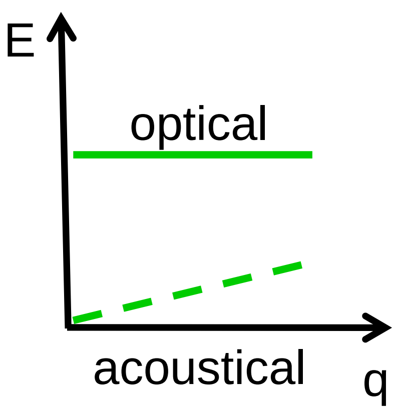




confined level system
plus wetting layer
coupled to phonons

-broad phonon band
-sharp zero phonon line

Zero-phonon-line broadening

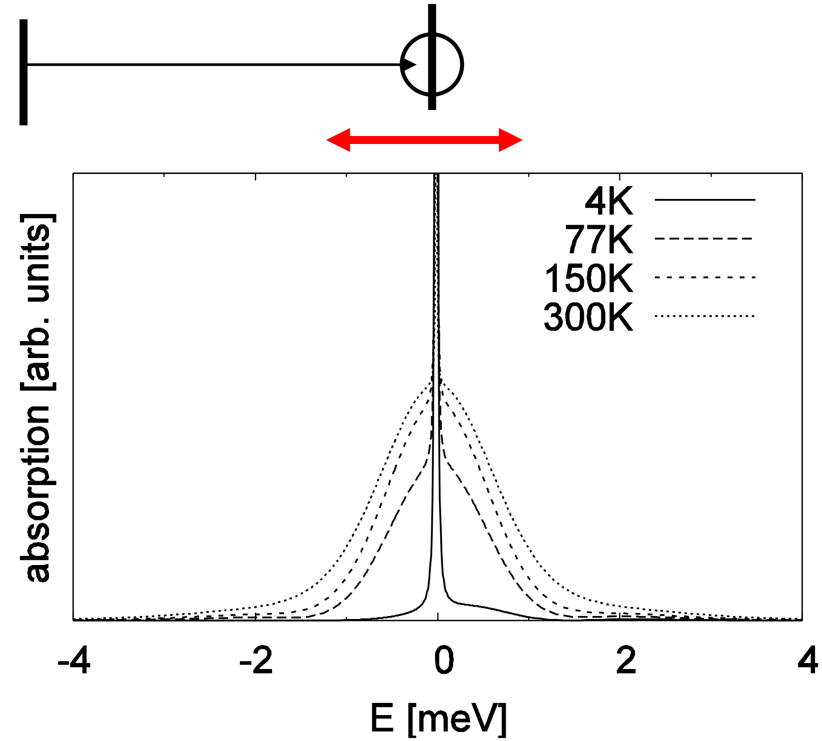


Quantum Dot -Spectra

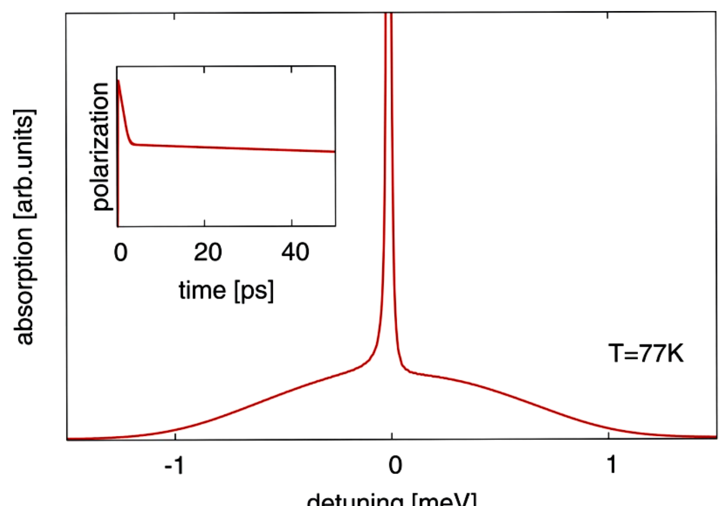
Theory:
two confined levels
acoustic phonon bath (T)

exact solution – all orders:
zero phonon line, phonon side bands

$$e_{+}^{-iQ\int^{t} dt' L_{SB}(t')} = exp\left(\sum_{n} \frac{(-i)^n}{n!} L_n^w(t)\right)$$



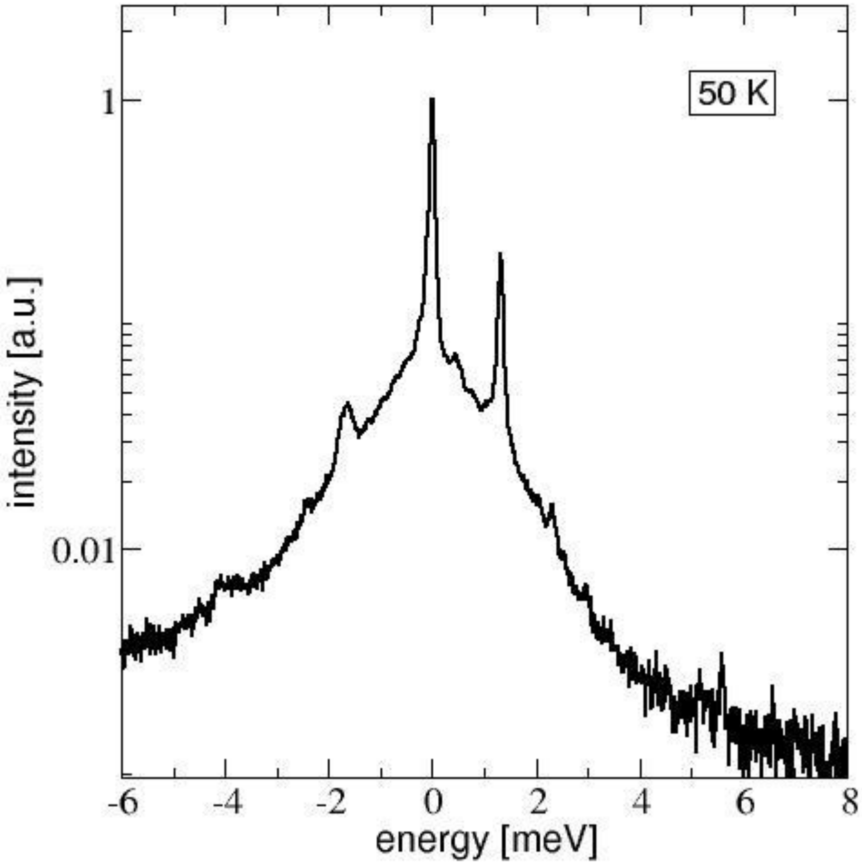
Carsten Weber



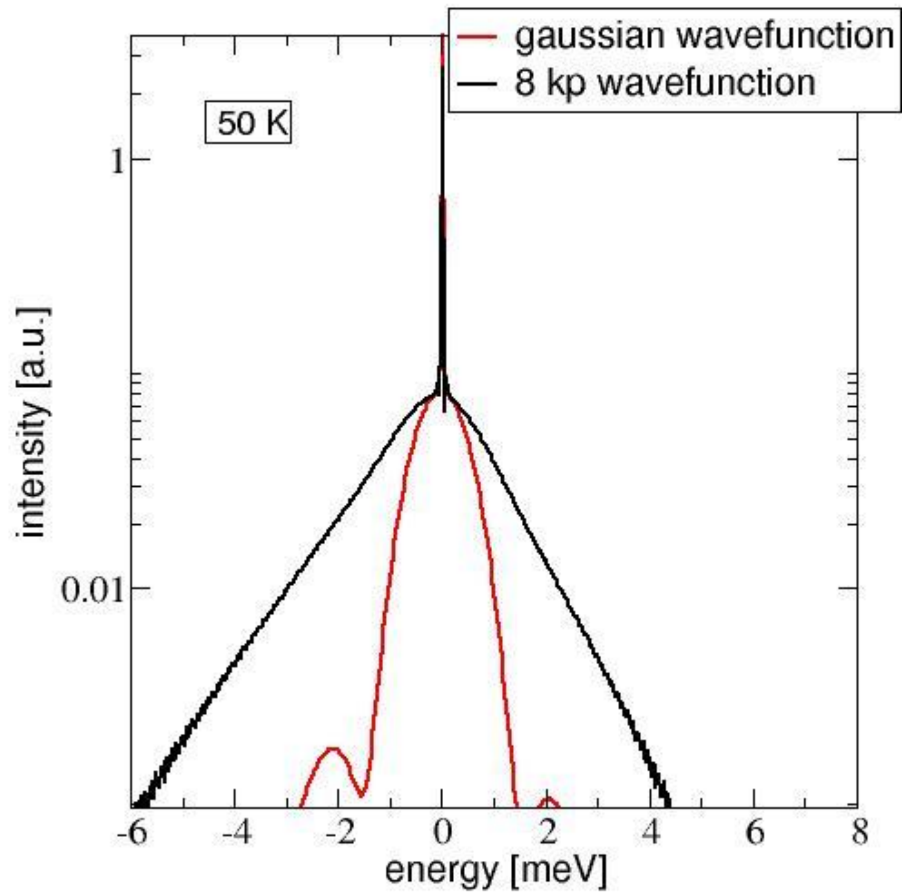
Line shape as interference effect of many virtual transitions!

Model Wave Function vs. 8 kp-Wave Function

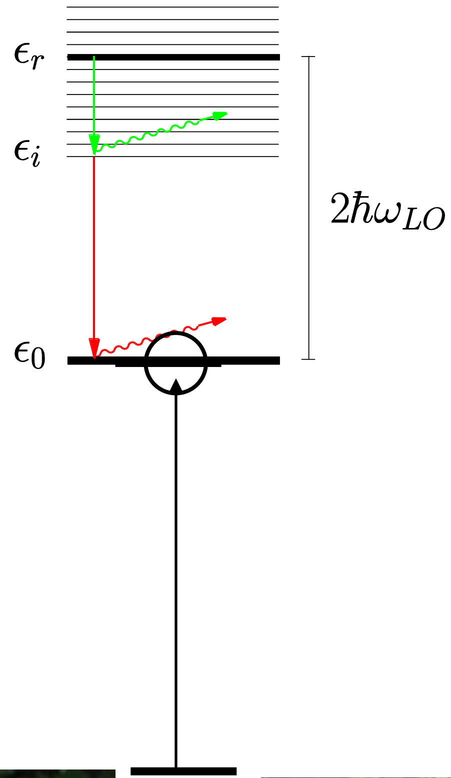
measurements of single QD luminescence by E. Stock et al



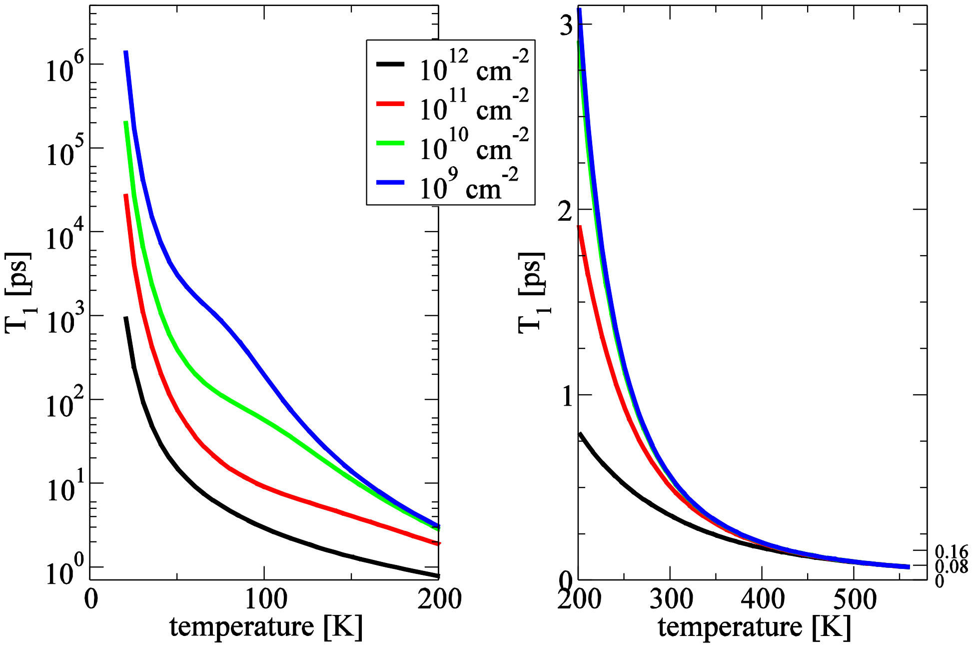
corresponding calculations using only virtual transitions



Zero Phonon Linewidth: Off-Resonant States



$$w_{i,j} \sim \delta\left(\epsilon_i - \epsilon_j - N\hbar\omega_{ph}\right)$$



- depend on WL-carrier density and temperature
- well below radiative damping

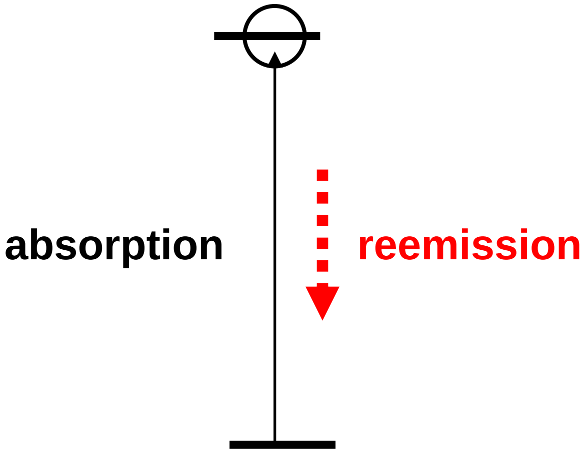
Matthias-Rene Dachner

Marten Richter

Rabi-Oscillations in InGaAs Quantum Dots

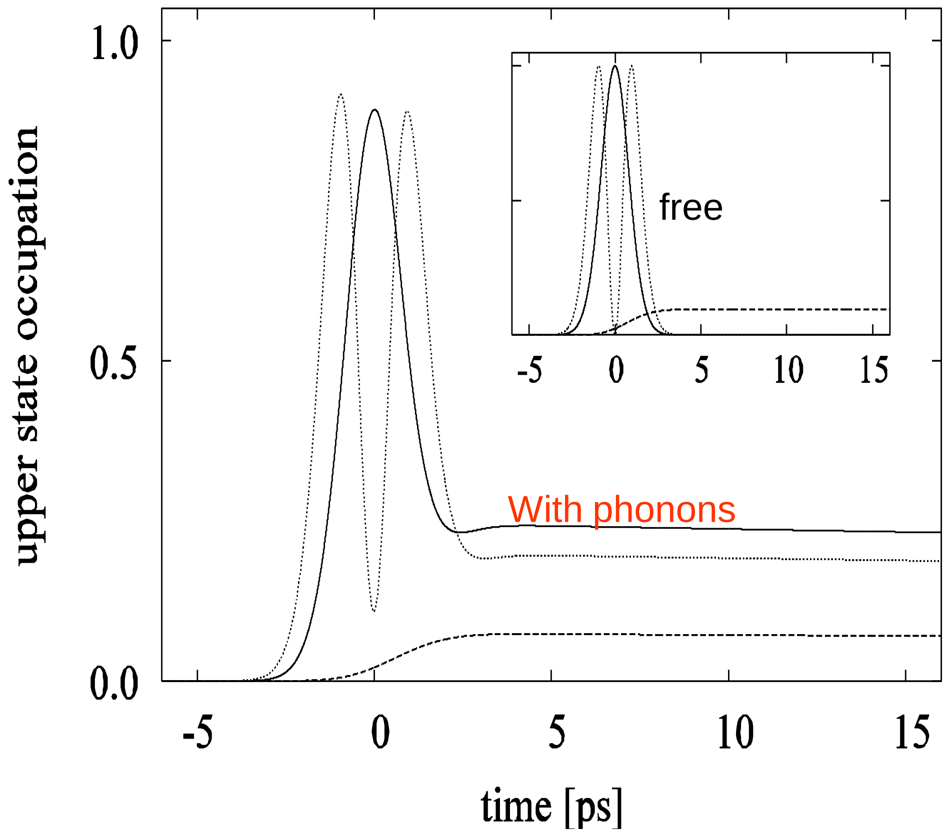
Theoretical Physics

Strong pulsed excitation

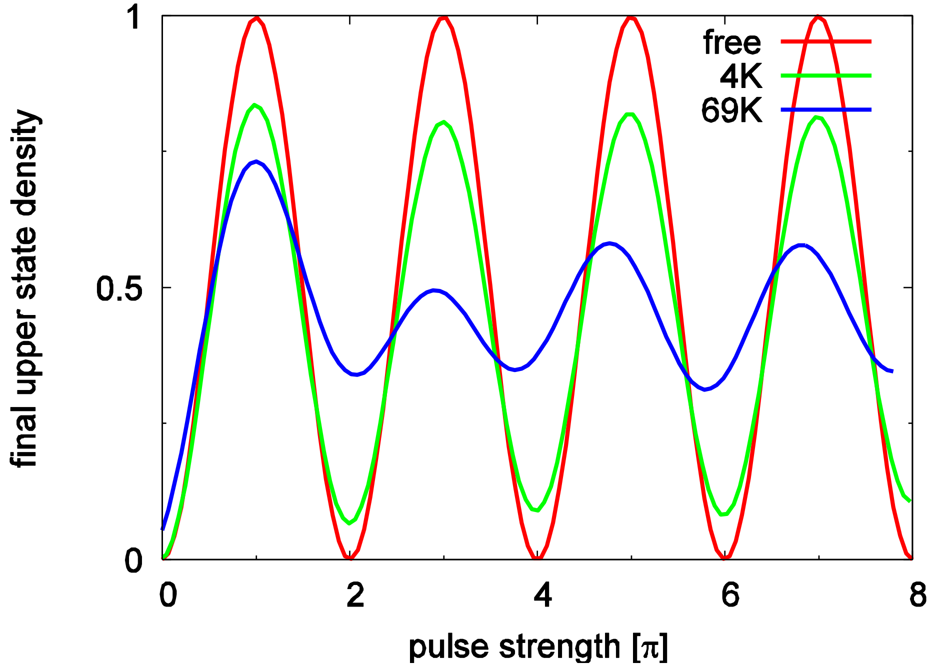


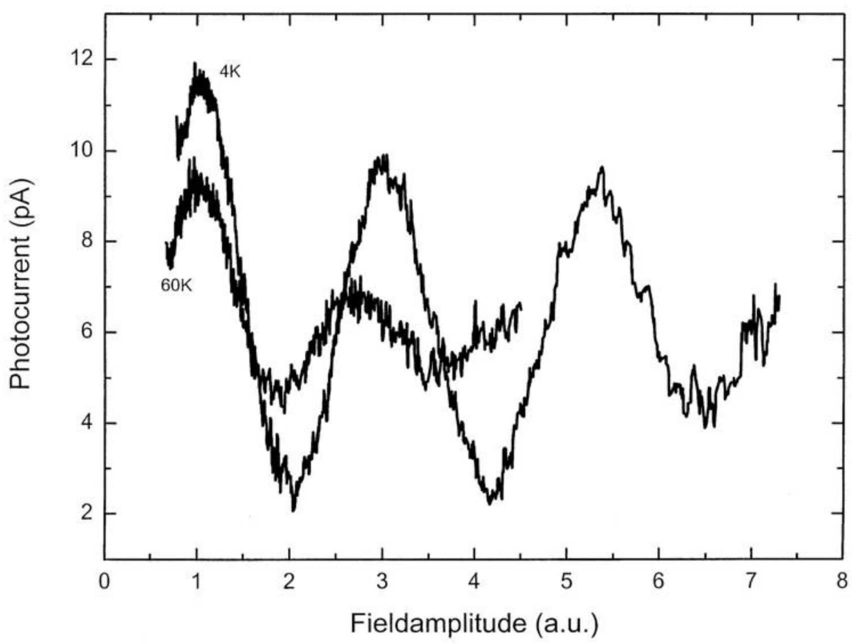
temporal oscillations
of the electron density
with increasing pulse power
(Pauli-blocking!)

system – bath coupling (77K)
phonon-induced damping
in comparison to free dynamics



Not Quantitative – Still Work to do …



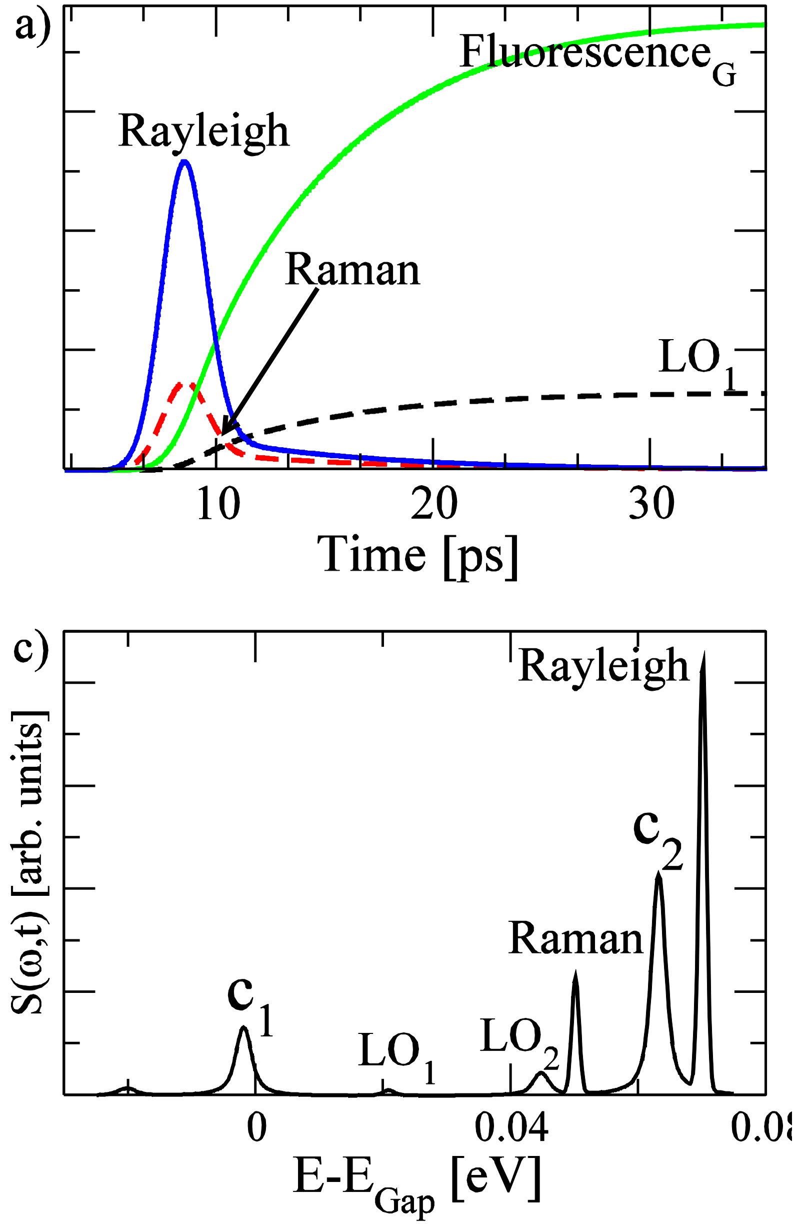


FWHM: 2.3 ps
QD: Elektron: 4.8 nm

M.Hübner,A.Zrenner et al.
(Paderborn)

Also:
hot phonons, coupling to continuum, zero-phonon line ….

Resonant Light Scattering



Julia Kabuß

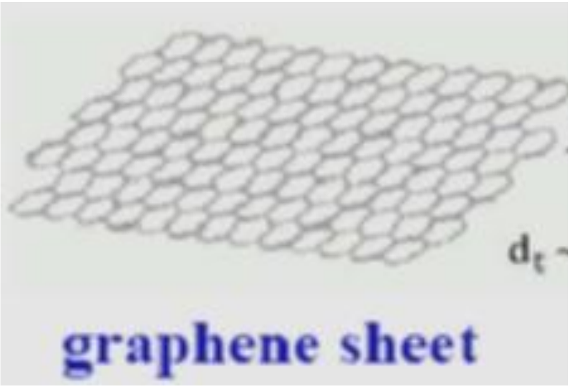
Graphene:
Relaxation of hot electrons
Involvement of hot phonons

Perturbation Theory: Second Order Born, no Memory
However: Phonons are a Dynamical System

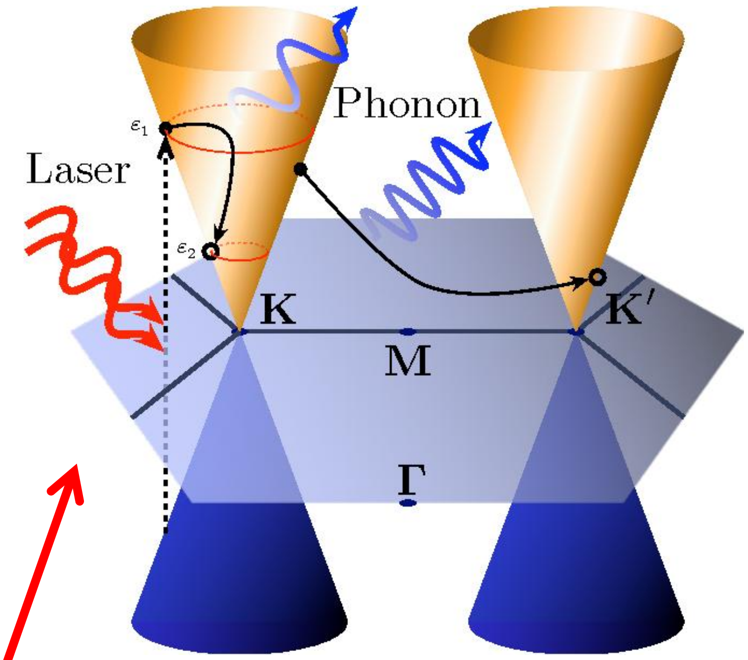
$$\dot{f}^i_{\vec{k}} = \sum_{\pm j,\mathbf{q}} \pm|\Gamma^j_{\mathbf{k},\mathbf{q}}|^2[(n^j_{\mathbf{q}}+1)f^{i\pm}_{\mathbf{k}+\mathbf{q}}f^{i\mp}_{\mathbf{k}} - n^j_{\mathbf{q}}f^{i\pm}_{\mathbf{k}}f^{i\mp}_{\mathbf{k}+\mathbf{q}}],$$

$$\dot{n}^j_{\mathbf{q}} = \text{similar dynamical equation}$$

Combined Electron and Phonon Dynamics



sheet of carbon atoms
coupled by orbitals of C
(hexagonal honeycomb lattice)

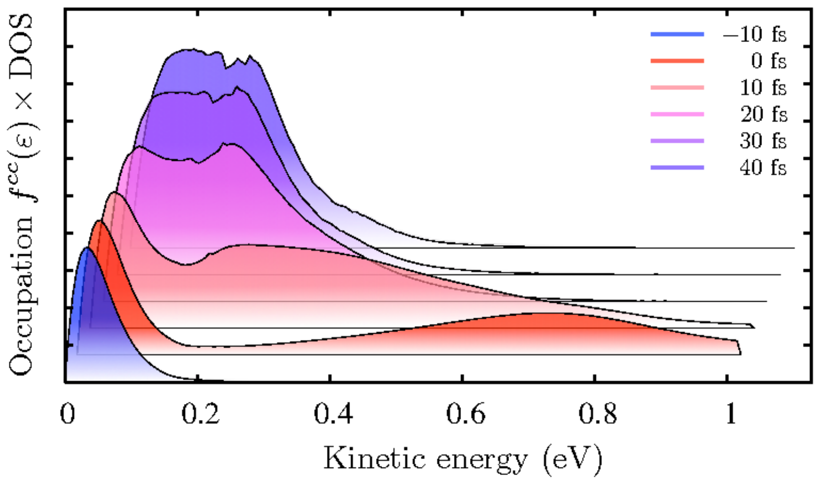


Tight binding band structure:
-p-electrons:
valence/conduction bands
-intersection at K and K‘ points
-linear bandstructure

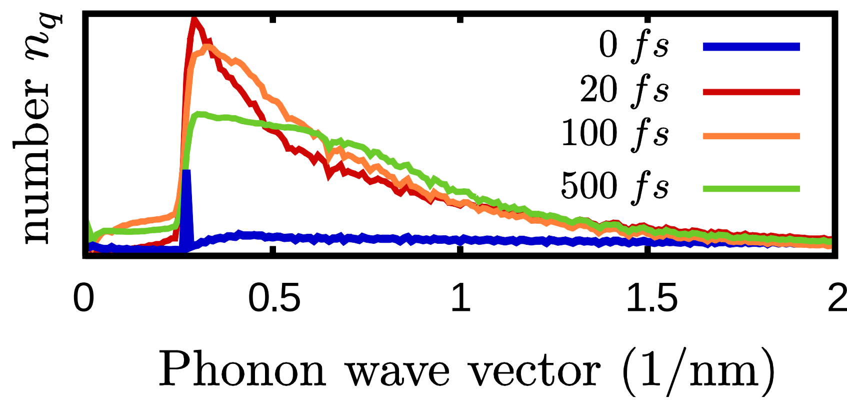
-optical excitation with 10fs pulse
-nonthermal electron distribution
-phonon emission:
intra and intervalley electron cooling

Delayed Electron-Cooling in Graphene

♦ Electron relaxation (phonon emission)



♦ built up non-thermal LO phonons (TO,LO at K, K‘, Gamma point)



-before pulse: thermal distribution

-injection of non-thermal electrons at 800meV

-within 10 fs ultrafast relaxation

-slow down of cooling process (> 20fs)

-> due to band structure (states)

and nonthermal phonons

-before pulse: no ph-occupation

-phonons fail to act bath-like

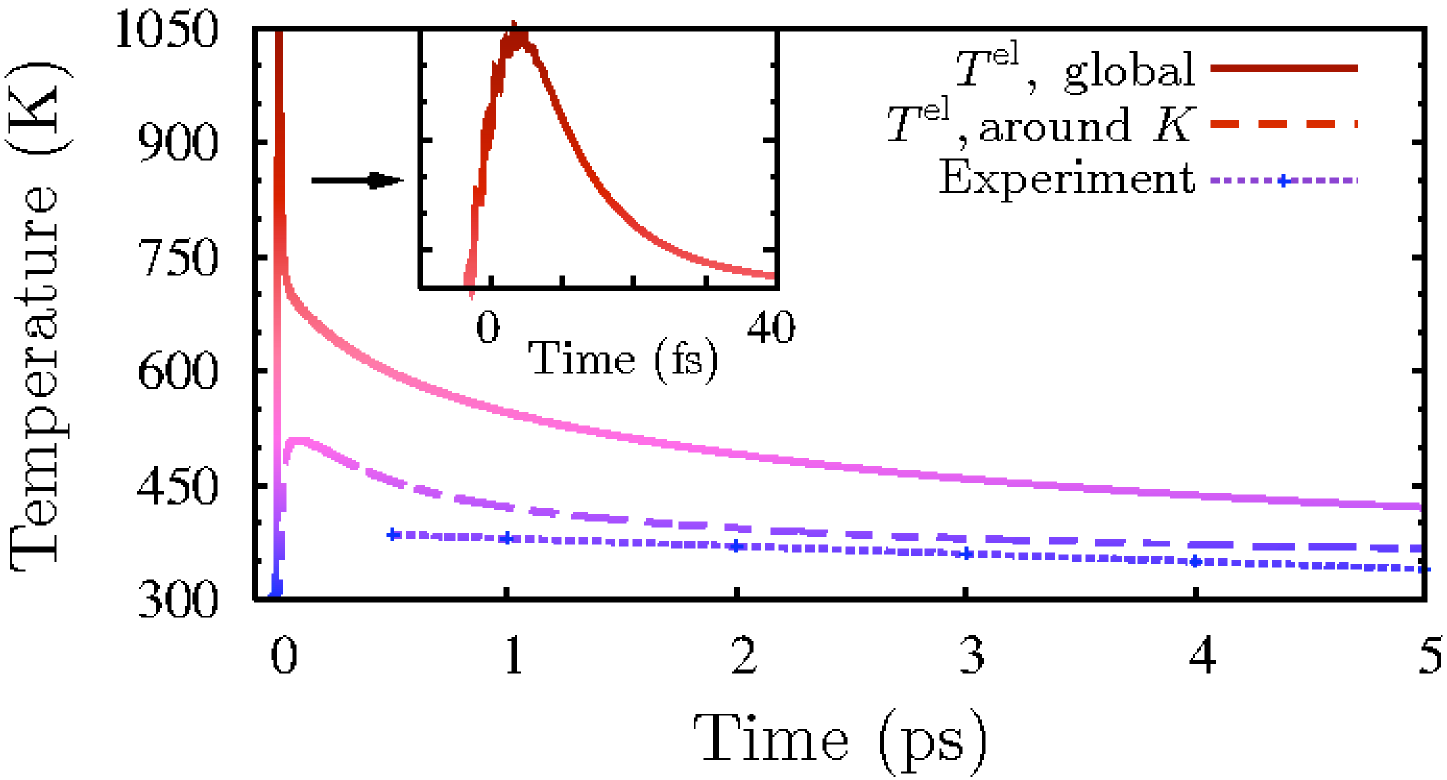
Stefan Butscher

Drawback: constant matrix elements

Comparison with Experiment

pump-test at ultra-thin graphite:
T.Kampfrath, M. Wolf, et al (Free University Berlin) PRL 95, 187403 (2005)

-> fit of electron temperature for electron distribution around the K-point



Theorie: Appl.Phys.Lett.91, 203103 (2007)

Electron Dynamics at a Silicon Surface

Second Order Perturbation, Kohn-Sham-Orbitals

$$w_{i,j} \sim \delta\left(\epsilon_i - \epsilon_j \pm \hbar\omega_{ph}\right)$$

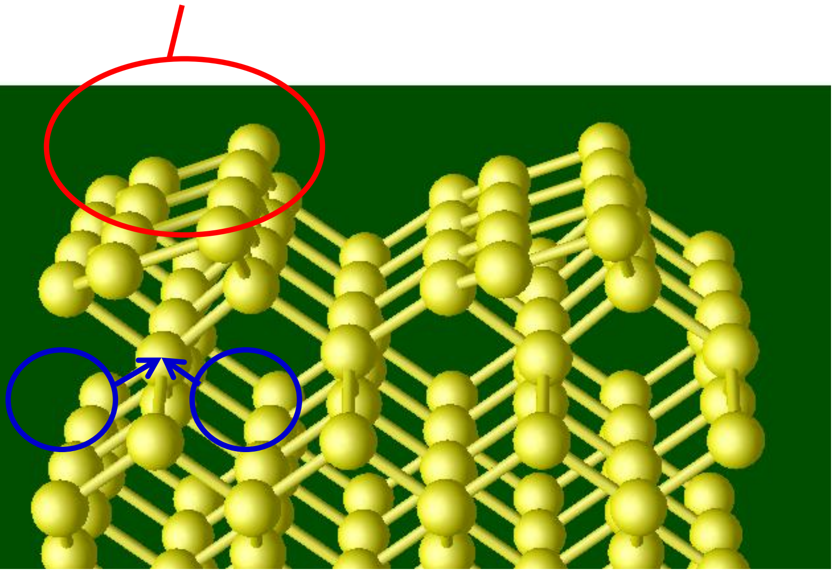
$$\dot{\rho}_{n\vec{k}} = \sum_{m\vec{l}} \left(w_{n\vec{k}}^{m\vec{l}} \rho_{m\vec{l}} (1 - \rho_{n\vec{k}}) - v_{n\vec{k}}^{m\vec{l}} (1 - \rho_{m\vec{l}}) \rho_{n\vec{k}} \right)$$

DFT-DMT Approach: Complex Materials

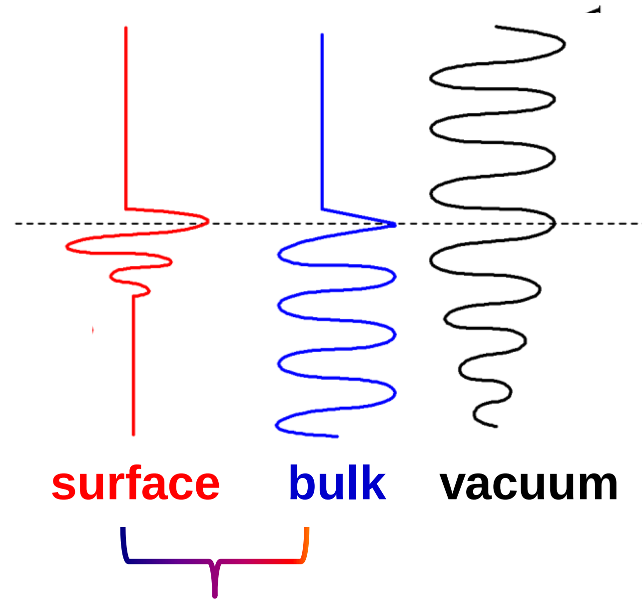
Peter Kratzer   Matthias Scheffler

Example: Si (001) surface

•tilted dimer reconstruction, charge transfer



states →



•2x1: size of reconstruction surface cell
•001: surface orientation

Timescale for electron transfer ?

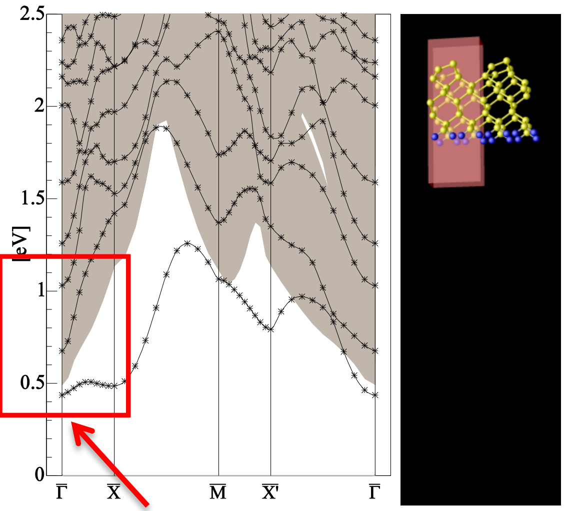
$$n(r,t) = \sum_{i,j} \varphi_i^*(r)\varphi_j(r)\rho_{ij}(t)$$

Kohn-Sham Orbitals from LDA-DFT

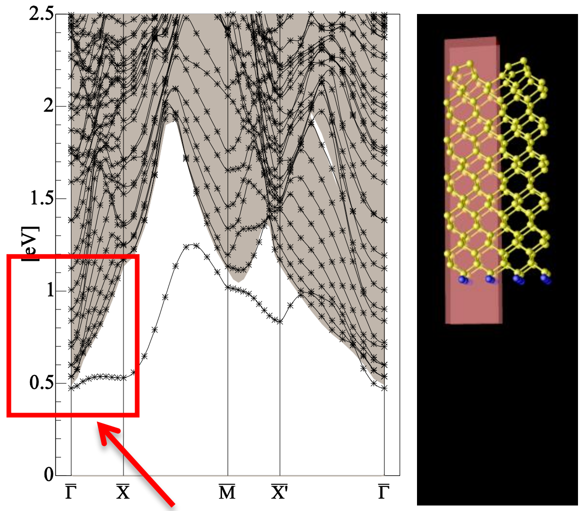
Supercell Band Structure for Different Layer Numbers

Theoretical Physics

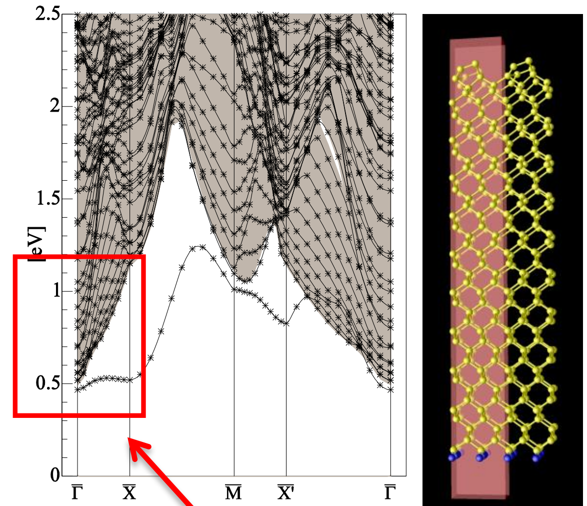
LDA-functional, band-gap of no importance for RWA
number of conduction bands depends on slab thickness



7 layers



22 layers



40 layers

- **high number of layers necessary to treat a „infinite“ surface structure**

- **effective relaxation dynamics only, if: energy distance between bands ~ phonon energy**

relaxation times depend on slab thickness !

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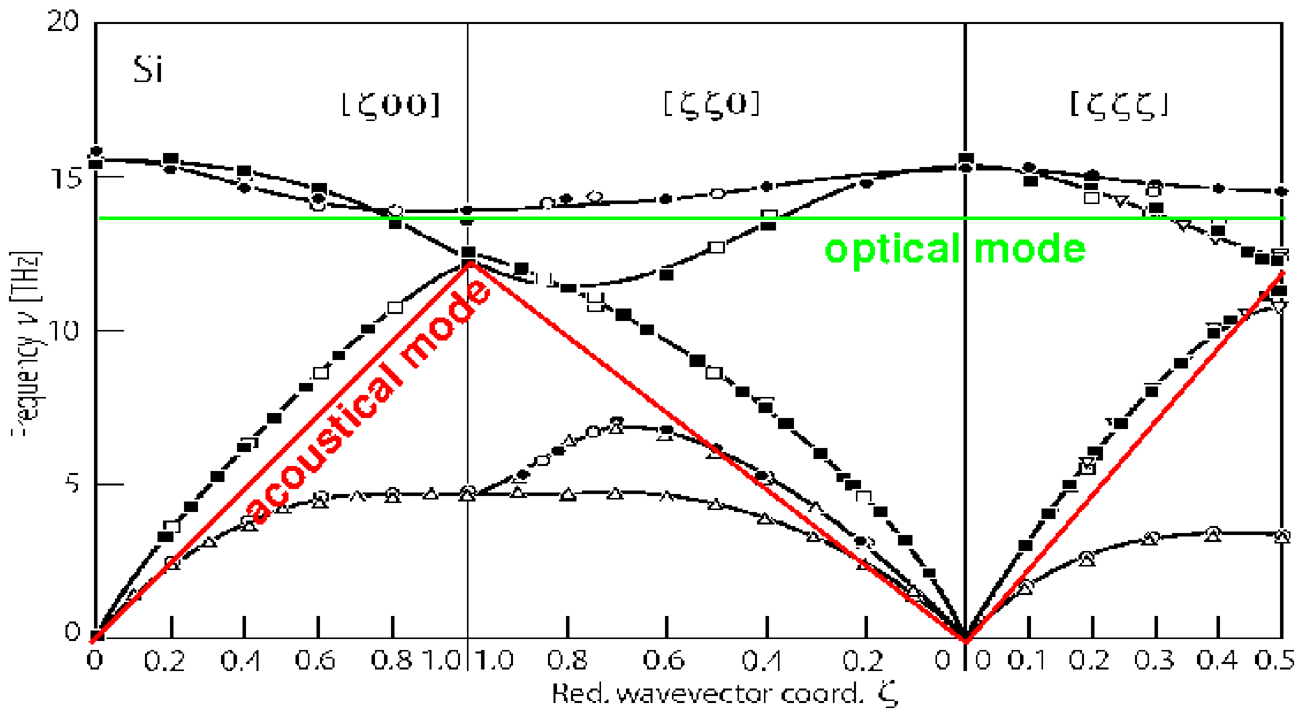
Approximation: bulk phonon modes

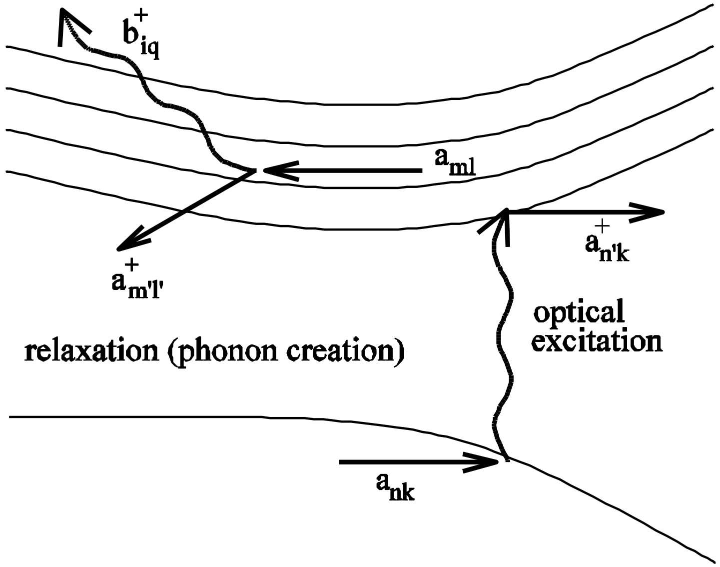


from Landolt-Börnstein, Springer, Berlin

- phonon spectrum similarly elaborate as electronic structure
- calculation computationally demanding, here: bulk phonons
- main features reproduced by 2-bulk mode model

bulk deformation potentials for acoustical and optical phonons

DMT : Markovian Equations, El-Ph Interaction



Equations of motion:

-in-plane wave number k,q and
band number index n,i
-band structure and wave functions
used for coupling -matrix D)

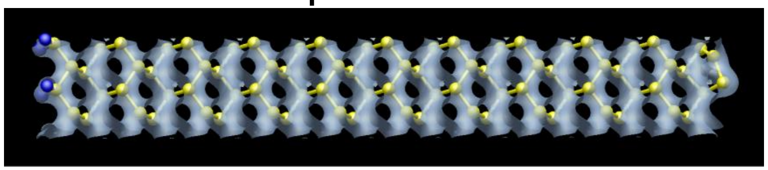
$$\dot{\rho}_{n\vec{k}} = \sum_{m\vec{l}} \Lambda^{\text{in}}_{\substack{m\vec{l}\\ n\vec{k}}} \rho_{m\vec{l}} (1-\rho_{n\vec{k}}) - \Lambda^{\text{out}}_{\substack{m\vec{l}\\ n\vec{k}}} (1-\rho_{m\vec{l}}) \rho_{n\vec{k}}$$

$$\Lambda^{\text{in}}_{\substack{m\vec{l}\\ n\vec{k}}} = \sum_{i\vec{q}} \left| D_{\substack{n\vec{k}\\ m\vec{l}\\ i\vec{q}}} \right| (n_{i\vec{q}}+1)\delta(E_{n\vec{k}} - E_{m\vec{l}} - \hbar\omega_{i\vec{q}}) + n_{i\vec{q}}\delta(E_{n\vec{k}} - E_{m\vec{l}} + \hbar\omega_{i\vec{q}})$$

Surface Electron Dynamics

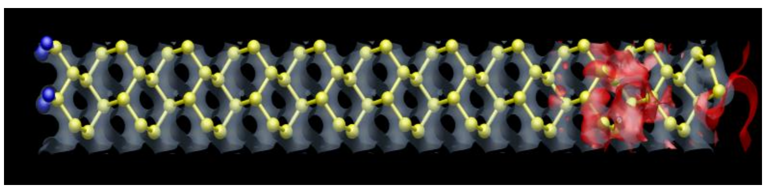
$$n(r,t) = \sum_{i,j} \varphi_i^*(r)\varphi_j(r)\rho_{ij}(t)$$

before the pulse



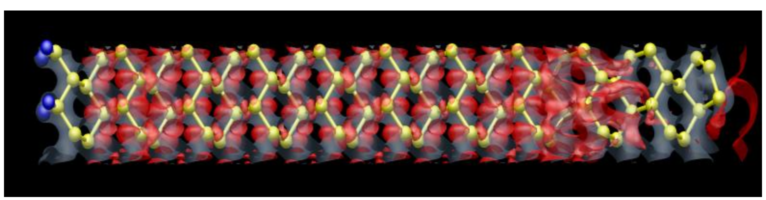
population at surface

t=0fs



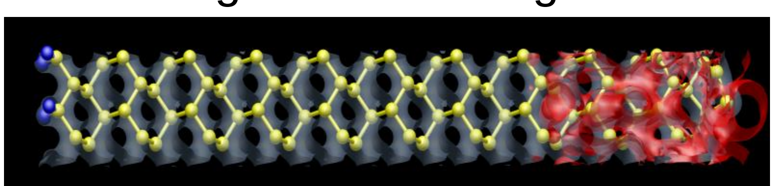
distribution over slab

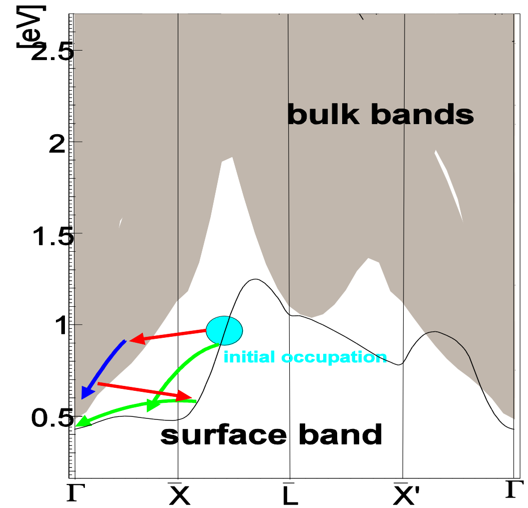
t=2ps



finding the surface again

t>50ps



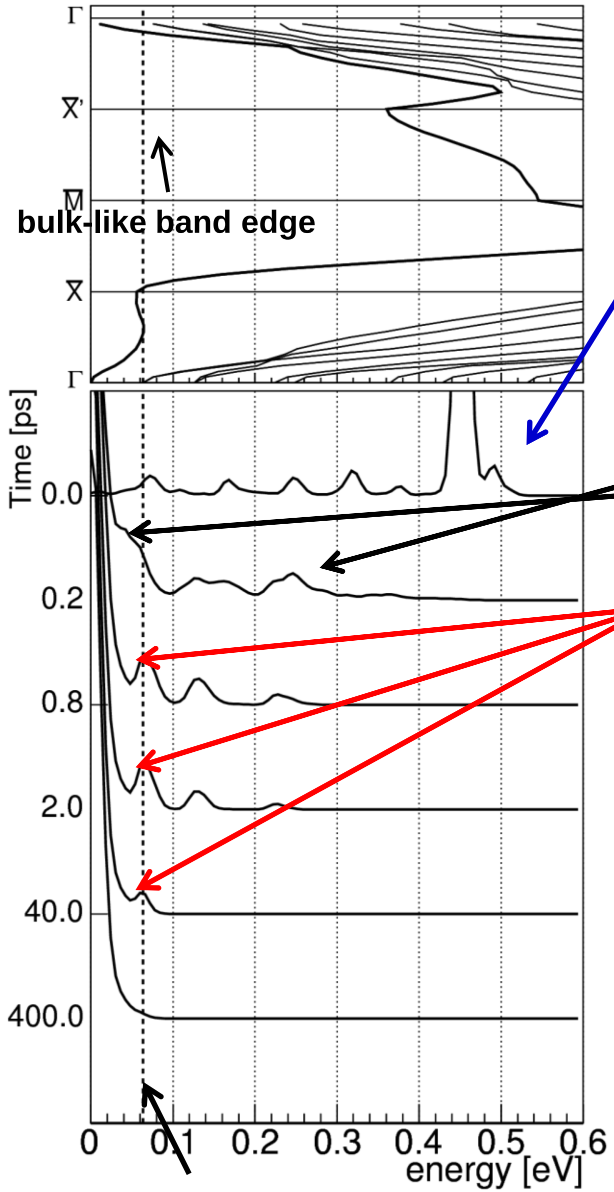


initial preparation in surface states

•surface-surface scattering:
fast cooling due to optical phonons

•surface-bulk-surface scattering:
Initially fast,
later slow due to acoustic phonons

Relaxation via electron-phonon scattering: 40 layers



band structure: surface and bulk bands

•**initial condition:** optical excitation with 1.69 eV above valence bands.

•**t<2ps:**
fast relaxation inside surface band,
fast relaxation inside bulk bands

•population is trapped at bulk band minimum: 0.06 eV (t=0-40ps)

•slow transfer from bulk to surface band (t ~ 50ps)

• two time scales !!!

N.B. et al., Phys. Rev B 77, 233305 (2008)

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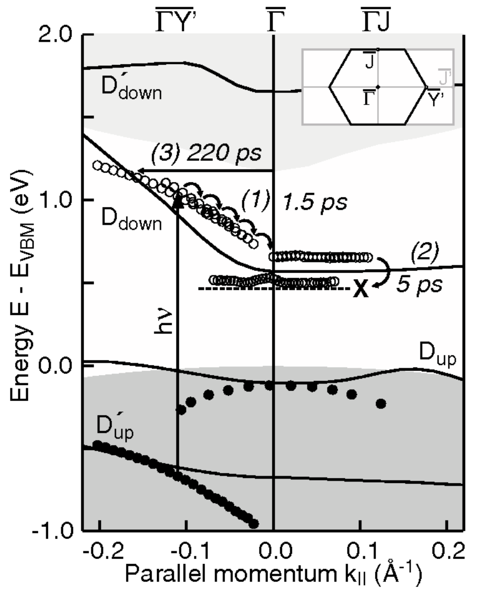
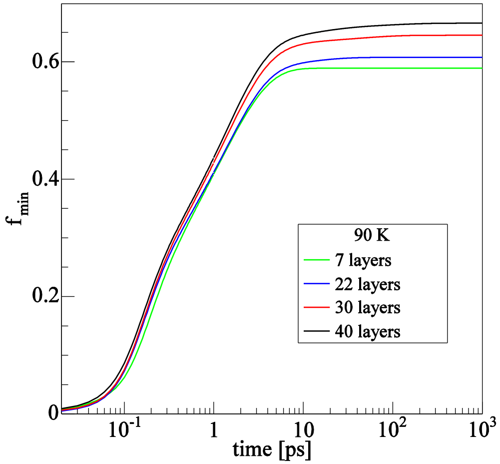
Experimental Results: Times Scales in 2-Photon-Emission

2PPE experiment on Si (001) probing the surface state minimum





M.Weinelt et al. (Erlangen, MBI Berlin), PRL 92,126801

- relaxation observed experimentally: bulk-surface 220 ps, surface-surface 1.5 ps

- two timescales found, reproduced by theory:
  - -short = good agreement (1-2ps),
  - -long = qualitative agreement (50ps)

third time scale: exciton formation, here not included