

# Nonequilibrium dynamics of crystal lattices

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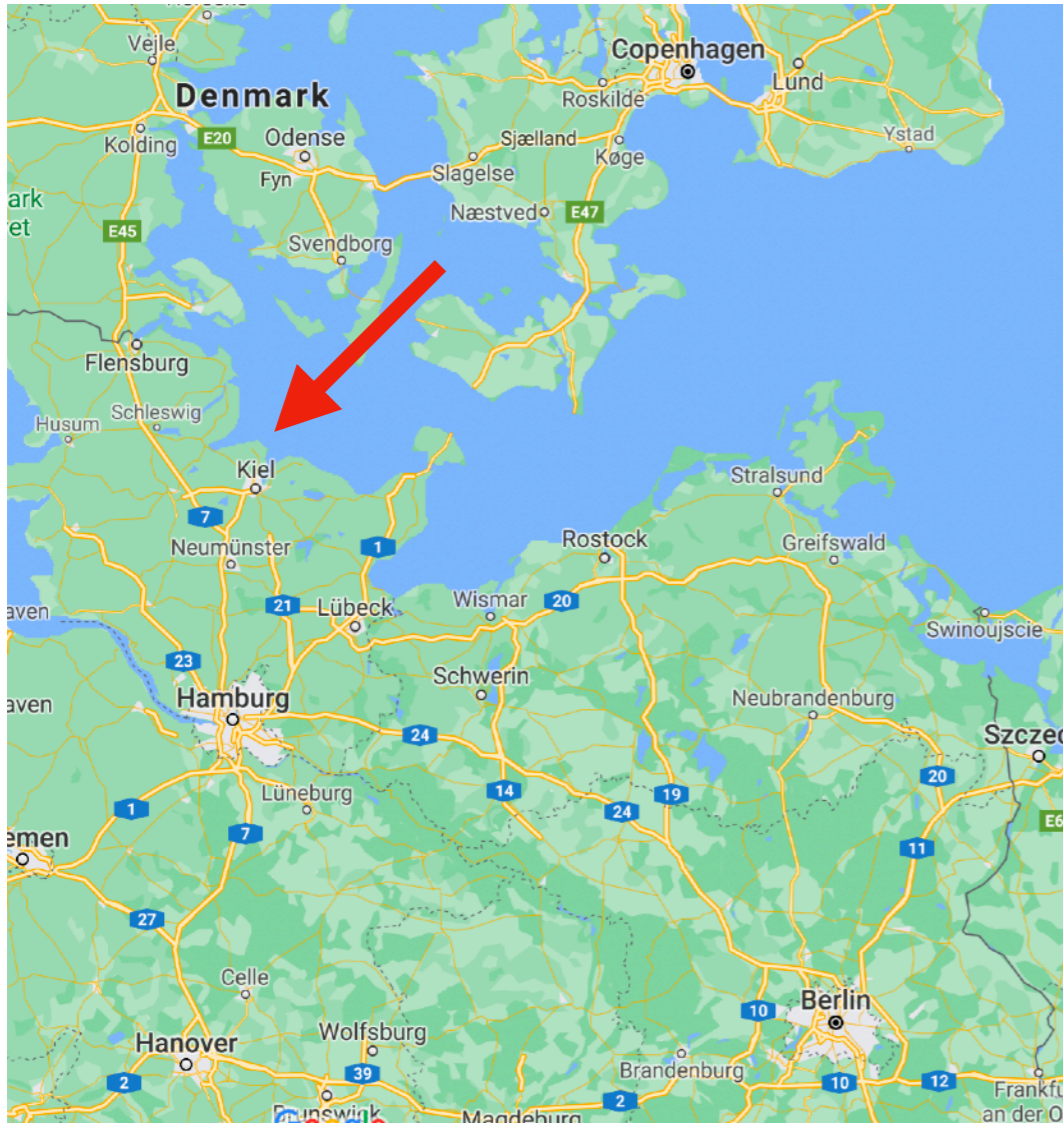
Christian-Albrechts-Universität zu Kiel

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German Research Foundation

# The University of Kiel (founded in 1665)



# The paradigm of first-principles electronic-structure theory

The Schrödinger equation:

$$\hat{\mathcal{H}} \Psi_s(r, R) = E_s \Psi_s(r, R)$$

...a single equation for the whole of matter

1 1A																	18 VIIIA
1 H Hydrogen 1.008																	2 He Helium 4.002602
3 Li Lithium 6.94	4 Be Beryllium 9.0121831											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998403163	10 Ne Neon 20.1797
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 Al Aluminium 26.9815385	14 Si Silicon 28.085	15 P Phosphorus 30.973761998	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.9331954	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.404	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293
55 Cs Caesium 132.90545196	56 Ba Barium 137.327	57 - 71 Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 - 103 Actinoids	104 Rf Rutherfordium (261)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (285)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (289)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)

57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90766	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.0377	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)

Molecules

The chemical universe database (GDB-17) [1]

10<sup>11</sup> entries

(Inorganic) Crystalline solids

The Karlsruhe Inorganic crystal-structure database (ICSD) [2]

200.000 entries

[1] J. Chem. Inf. Model. 52, 2864 (2012)

[2] [icsd.fiz-karlsruhe.de](http://icsd.fiz-karlsruhe.de)

# The paradigm of first-principles electronic-structure theory

electrons + nuclei

The Schrödinger equation:

$$\hat{\mathcal{H}} \Psi_s(r, R) = E_s \Psi_s(r, R)$$

...a single equation for the whole of matter

Hamiltonian operator for coupled electrons and nuclei  
(a differential operator)

Energy of the system in its s-th state  
(a scalar)

Wave function of electrons and nuclei  
(a function of coordinates)

$$\Psi_s(r, R)$$

encodes all information (and all properties) about a system of electrons and nuclei

**Example:** the H atom

$$\psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na_0^*}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) Y_l^m(\theta, \phi)$$

**Any other material: too complex!**



**Approximations are needed!**

# The paradigm of first-principles electronic-structure theory

The Born-Oppenheimer approximation:

$$\Psi_s(r, R) \simeq \psi_\nu(r; R) \chi_{\nu s}(R)$$

electrons (fixed nuclei)

$$\hat{H}^{\text{el}} \psi_\nu(r) = E_\nu^{\text{el}} \psi_\nu(r)$$

nuclei (fixed electrons)

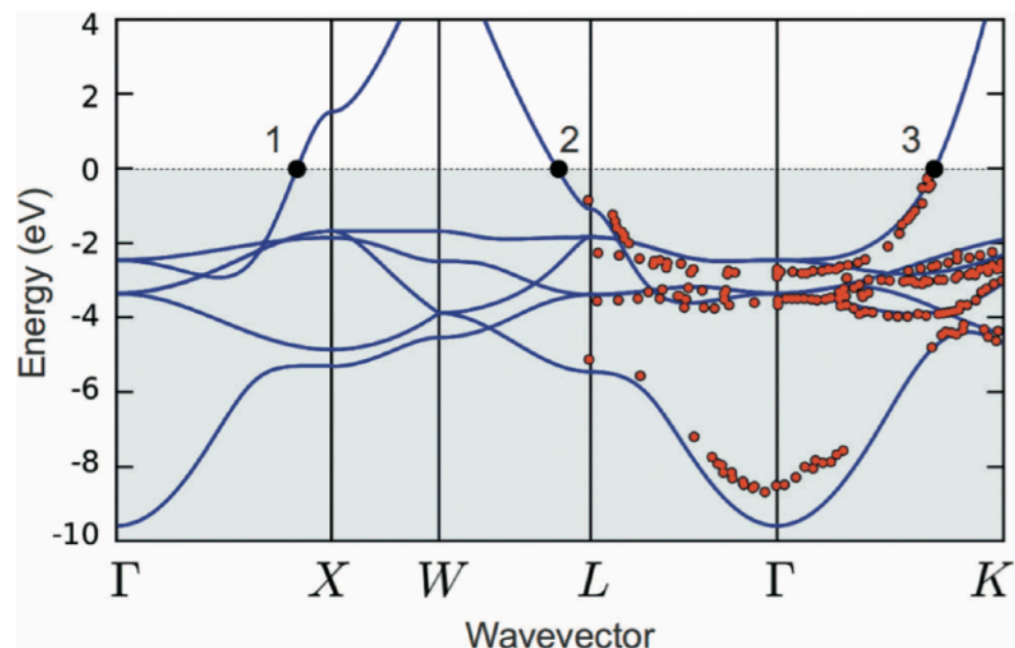
$$\hat{H}^{\text{nuc}} \chi_{\nu s}(R) = E_s \chi_{\nu s}(R)$$

Density functional theory (DFT):

$$n(\mathbf{r}) \iff \Psi$$

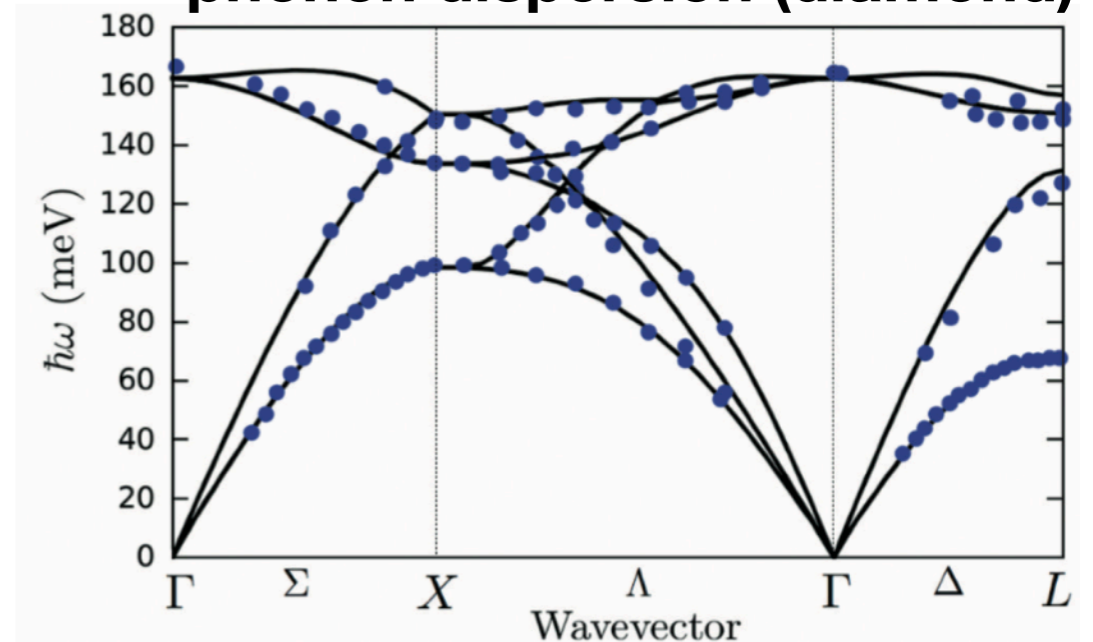
Hohenberg and Kohn, Phys. Rev. (1964)  
Kohn and Sham, Phys. Rev. (1965)

Electron band structure (Copper)



Figs.: Giustino, Materials Modelling using Density Functional Theory (2014)

phonon dispersion (diamond)



Exp.: [1] Courths, and Hübner, Phys. Rep. 112, 53 (1984)  
[2] Warren et al., Phys. Rev. 158, 805 (1967)

# Where do electron-phonon interactions become important?

## Charge transport:

- Ohm's law: dissipation of electronic currents
- Conventional superconductivity: dissipationless conduction

## Energy conversion:

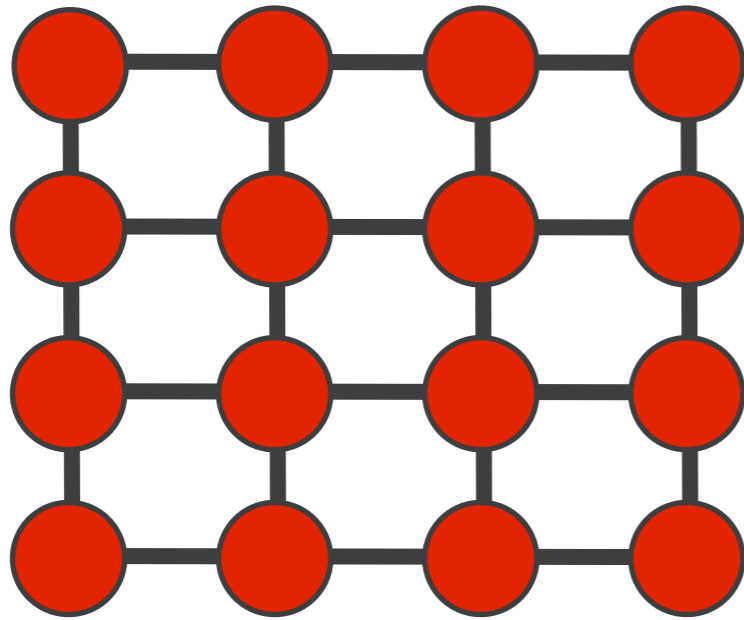
- Phonon assisted optical absorption (silicon photovoltaic)
- Time-scales of hot-carrier dynamics and recombination
- Thermoelectricity (Thermal conductivity)

## Designing and understanding new functions of matter

- Electron-phonon quasiparticles (polarons)
- Ultrafast dynamics of electrons and phonons

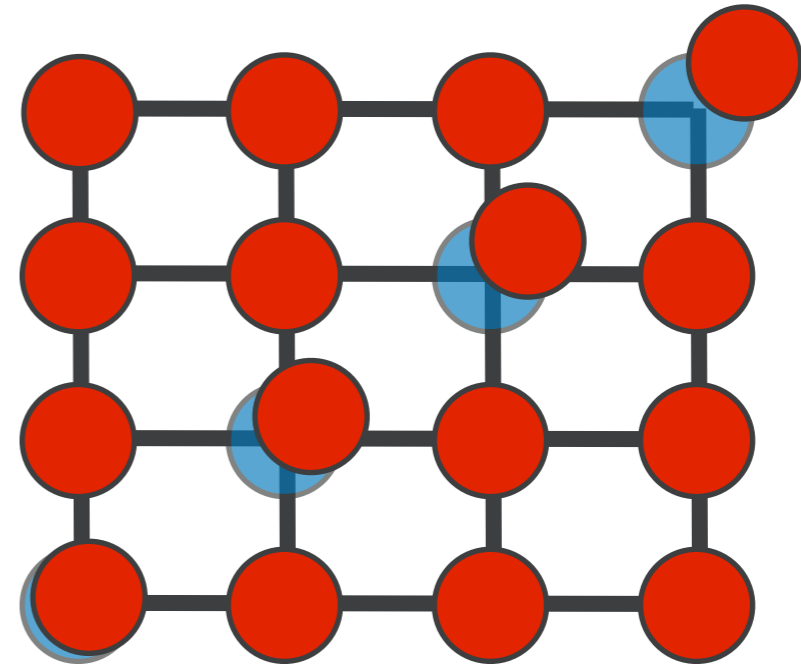
# Electron-phonon interactions in solids

Nuclei at equilibrium



Potential:  $V$

Atomic displacement due to a phonon



Perturbed potential:  $V + \Delta_{\mathbf{q}\nu} V(t)$

**Electron-phonon coupling matrix elements:**

$$g_{mn\nu}^{\text{e-ph}}(\mathbf{k}, \mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} V_{\text{KS}} | \psi_{n\mathbf{k}} \rangle$$

final  
electronic  
state

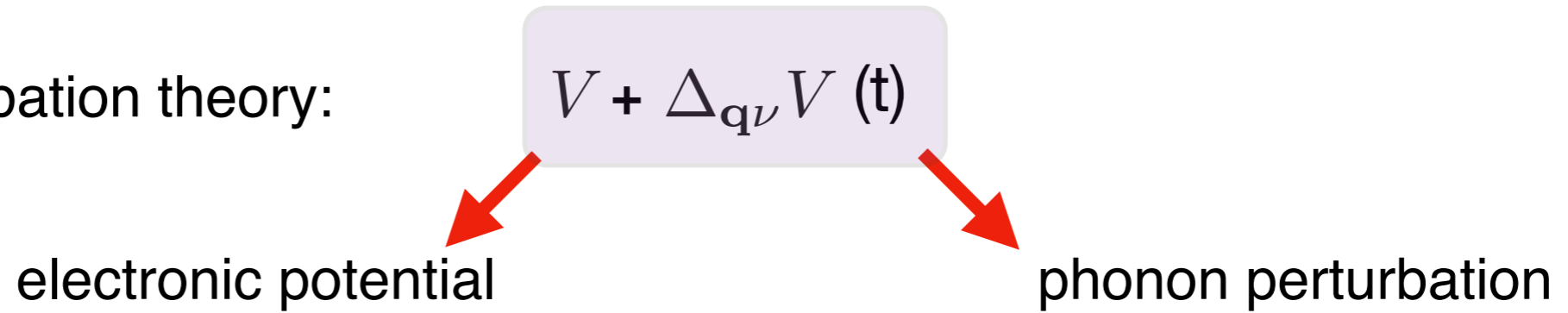
phonon  
perturbation

initial  
electronic  
state

Transition  
probability  
amplitude

# Modern theory of the electron-phonon interaction

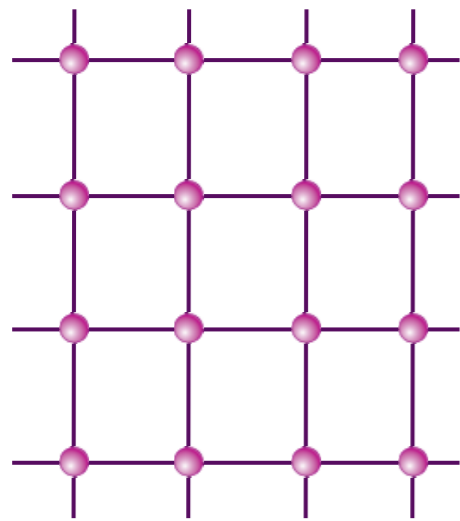
Many-body perturbation theory:



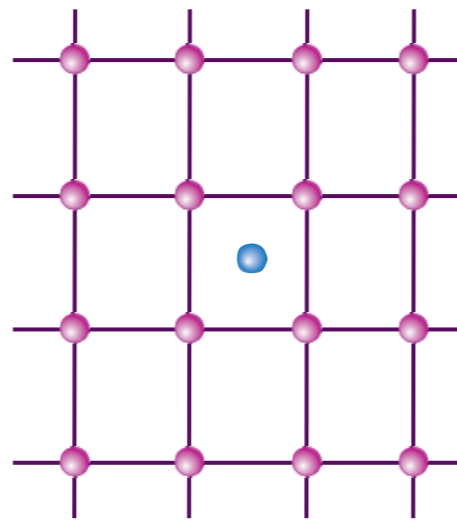
Description	Expression
Electronic charge density	$\langle \hat{n}_e(1) \rangle = -i\hbar \sum_{\sigma_1} G(11^+)$
Nuclear charge density	$\langle \hat{n}_n(\mathbf{r}t) \rangle = n_n^0(\mathbf{r}) - (i\hbar/2) \sum_{\kappa p, \alpha \alpha'} Z_\kappa \partial^2 \delta(\mathbf{r} - \boldsymbol{\tau}_{\kappa p}^0) / \partial r_\alpha \partial r_{\alpha'} D_{\kappa \alpha p, \kappa \alpha' p'}(t^+ t)$
Total electrostatic potential	$V_{\text{tot}}(1) = \int d2v(12) [\langle \hat{n}_e(2) \rangle + \langle \hat{n}_n(2) \rangle]$
Equation of motion, electrons	$[i\hbar \partial / \partial t_1 + (\hbar^2 / 2m_e) \nabla^2(1) - V_{\text{tot}}(1)] G(12) - \int d3 \Sigma(13) G(32) = \delta(12)$
Equation of motion, nuclei	$\sum_{\kappa'' \alpha'' p''} [M_\kappa \omega^2 \delta_{\kappa \alpha p, \kappa'' \alpha'' p''} - \Pi_{\kappa \alpha p, \kappa'' \alpha'' p''}(\omega)] D_{\kappa'' \alpha'' p'', \kappa' \alpha' p'}(\omega) = \delta_{\kappa \alpha p, \kappa' \alpha' p'}$
Electron self-energy	$\Sigma(12) = i\hbar \int d(34) G(13) \Gamma(324) [W_e(41^+) + W_{\text{ph}}(41^+)]$
Screened Coulomb, electrons	$W_e(12) = v(12) + \int d(34) v(13) P_e(34) W_e(42)$
Electronic polarization	$P_e(12) = -i\hbar \sum_{\sigma_1} \int d(34) G(13) G(41^+) \Gamma(342)$
Electronic dielectric matrix	$\epsilon_e(12) = \delta(12) - \int d(3) v(13) P_e(32)$
Vertex	$\Gamma(123) = \delta(12) \delta(13) + \int d(4567) [\delta \Sigma(12) / \delta G(45)] G(46) G(75) \Gamma(673)$
Screened Coulomb, nuclei	$W_{\text{ph}}(12) = \sum_{\kappa \alpha p, \kappa' \alpha' p'} \int d(34) \epsilon_e^{-1}(13) \nabla_{3,\alpha} V_\kappa(\mathbf{r}_3 - \boldsymbol{\tau}_{\kappa p}^0) \times D_{\kappa \alpha p, \kappa' \alpha' p'}(t_3 t_4) \epsilon_e^{-1}(24) \nabla_{4,\alpha'} V_{\kappa'}(\mathbf{r}_4 - \boldsymbol{\tau}_{\kappa' p'}^0)$
Phonon self-energy	$\Pi_{\kappa \alpha p, \kappa' \alpha' p'}(\omega) = \sum_{\kappa'' p''} Z_\kappa Z_{\kappa''} (\partial^2 / \partial r_\alpha \partial r_{\alpha'}) \times [\delta_{\kappa' p', \kappa'' p''} W_e(\mathbf{r}, \mathbf{r}', \omega) - \delta_{\kappa p, \kappa' p'} W_e(\mathbf{r}, \mathbf{r}', 0)]_{\mathbf{r}=\boldsymbol{\tau}_{\kappa p}^0, \mathbf{r}'=\boldsymbol{\tau}_{\kappa' p'}^0}$



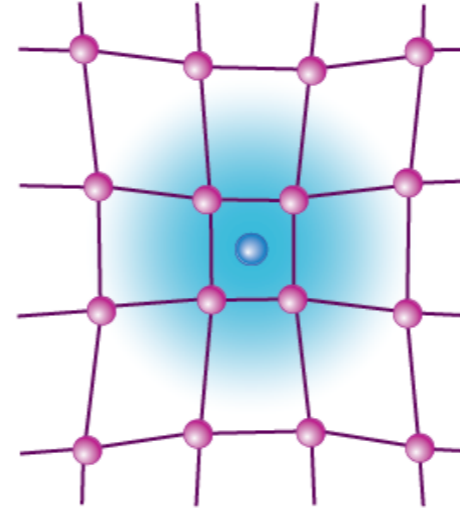
# 1. The concept of quasi-particles



**lattice**



**external particle**



**quasi-particle**

**example:**

electron (hole) +  
lattice distortion  
= **polarons**

Quasi-particle energy:

$$\epsilon_n^{\text{QP}} = \epsilon_n^{\text{NI}} + \Sigma$$

Energy of the  
non-interacting particle

Self-energy



real horse



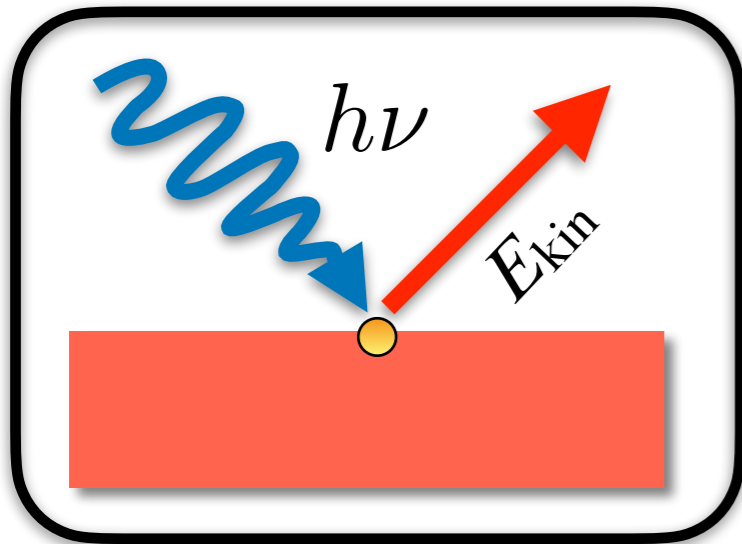
quasi horse

RDM

**R. Mattuck**

## 2. Relation to photoemission spectroscopy

photoemission spectroscopy



Photoelectron current (Fermi's golden rule):

$$J_{\mathbf{k}}(\omega) = \sum_s |\langle \Psi_{\mathbf{k},s} | \Delta | \Psi_i \rangle|^2 \delta(\omega - \varepsilon_{\mathbf{k}} + \varepsilon_s)$$

Diagrammatic labels for the equation above:

- $\Psi_{\mathbf{k},s}$ : final state
- $\Delta$ : perturbation
- $\Psi_i$ : initial state
- $\delta(\omega - \varepsilon_{\mathbf{k}} + \varepsilon_s)$ : energy conservation

$$= \sum_{ij} \Delta_{\mathbf{k}j} A_{ji}(\varepsilon_{\mathbf{k}} - \omega) \Delta_{i\mathbf{k}} \quad [1] \text{ sudden approximation}$$

Spectral function

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi} \sum_n \text{Im} G_{n\mathbf{k}}(\omega)$$

Migdal (diagonal) approximation:

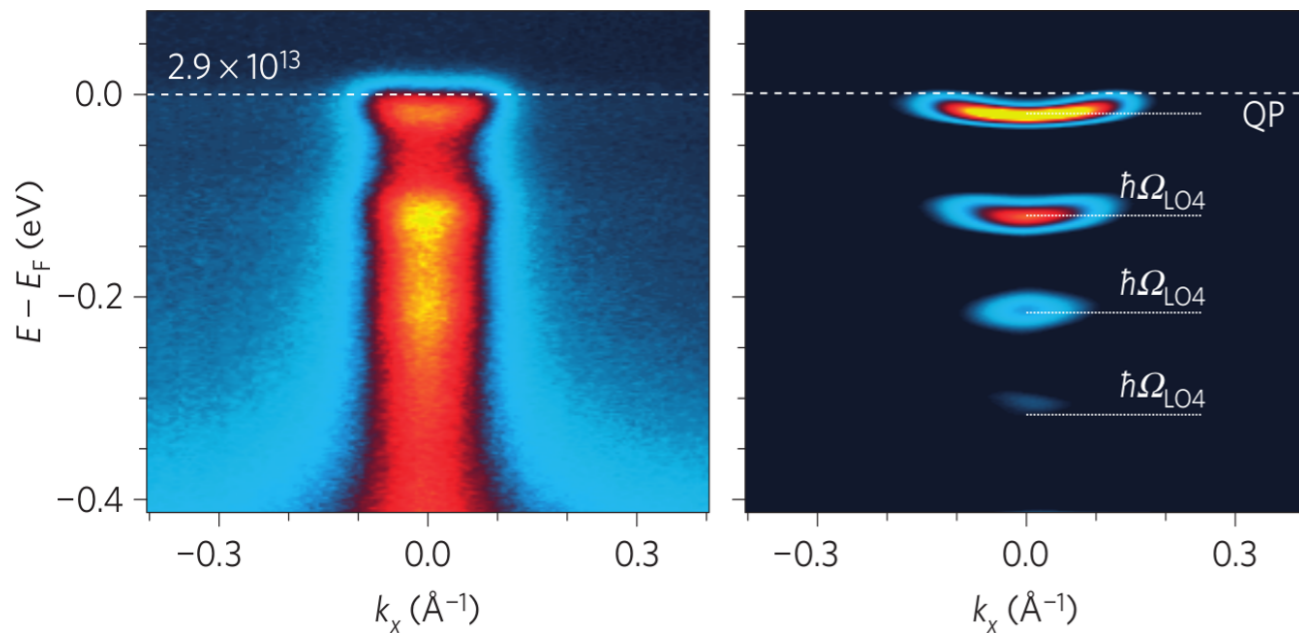
$$= \frac{1}{\pi} \sum_n |\text{Im}[\omega - \varepsilon_{n\mathbf{k}} - \Sigma_{n\mathbf{k}}(\omega)]^{-1}|$$

[1] L. Hedin, et al., Phys. Rev. B **58**, 15565 (1998)

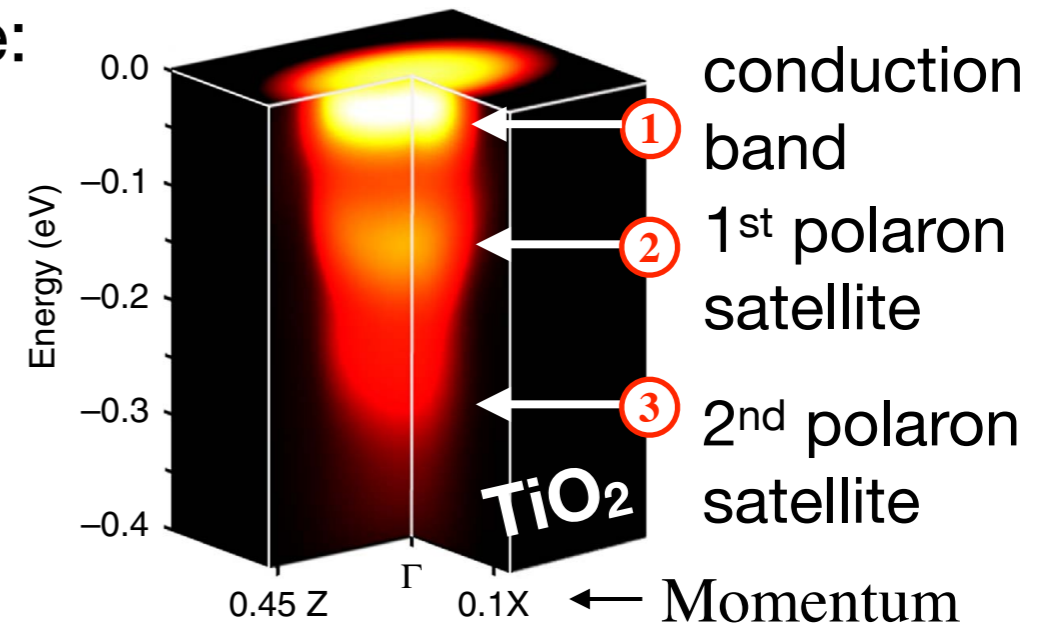
# Polarons in angle-resolved photoemission spectroscopy

**Polaron = electron (hole) dressed by a phonon cloud**

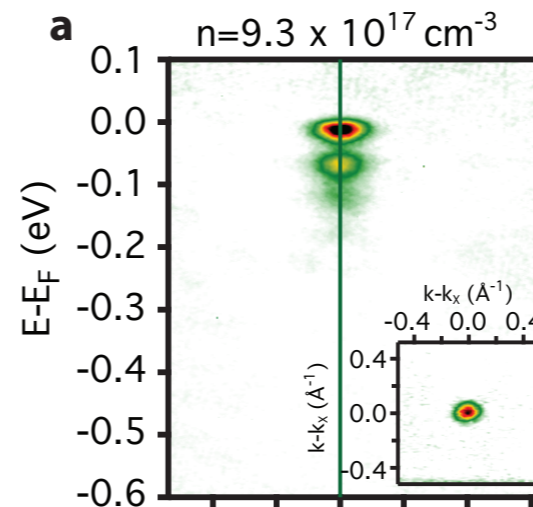
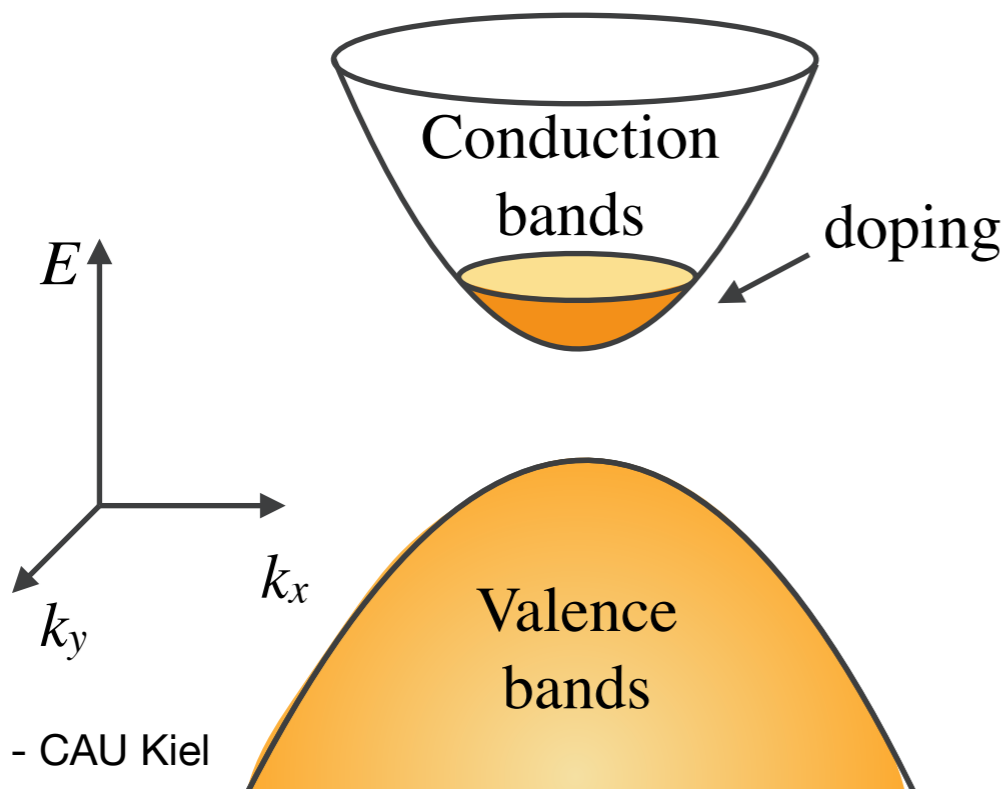
Polarons at the 2DEG at the SrTiO<sub>3</sub>(001) surface:



Wang et al., Nature Mater. **15**, 835 (2016)

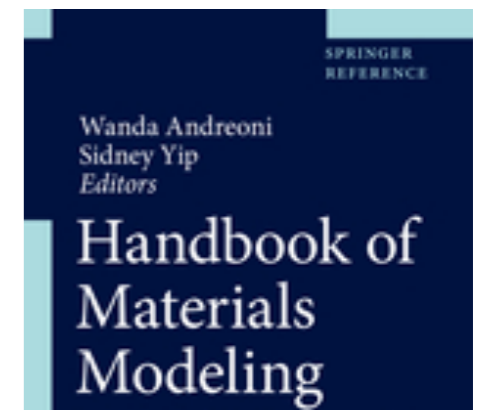


Verdi, FC, Giustino, Nature Comm. **8**, 15769 (2017)



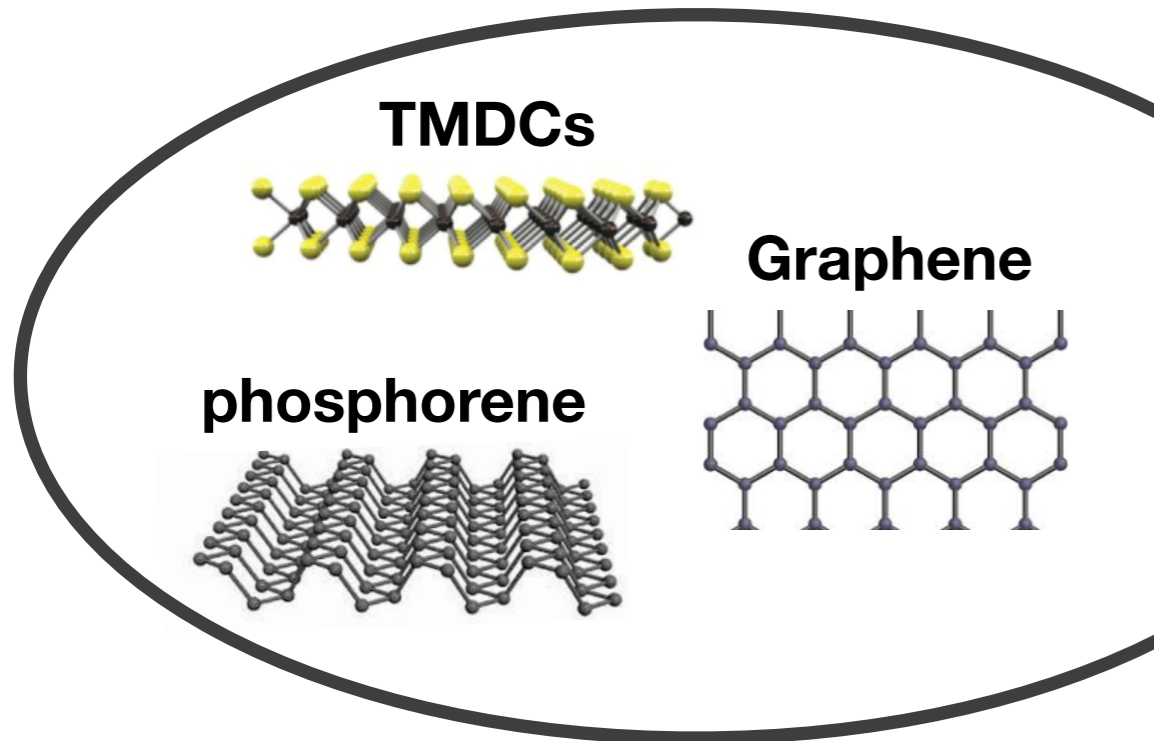
Riley, FC, Verdi, et al. Nature Comm. **9**, 2305 (2018)

FC, Verdi, Giustino, Chapter in Handbook of Materials Modeling (2018)

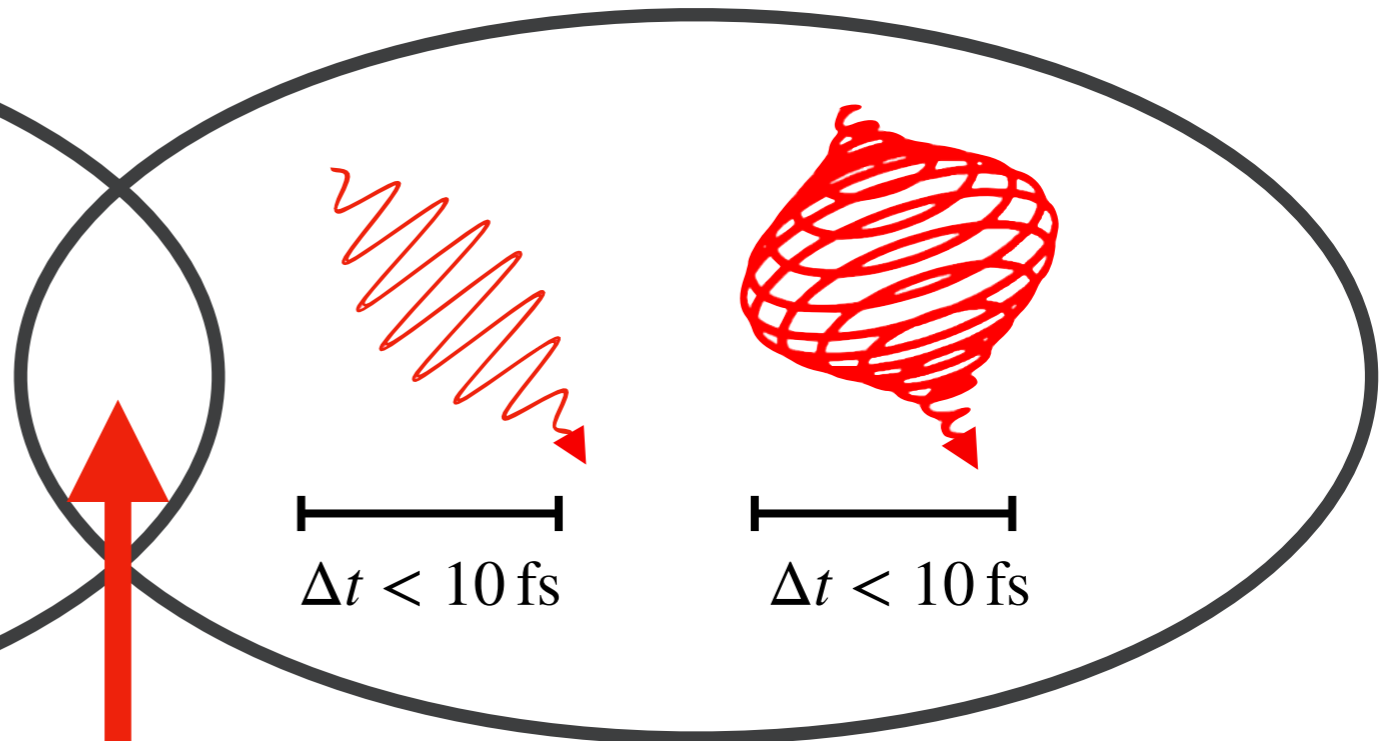


# Nonequilibrium dynamics in two dimensions

## Materials science in 2D



## Advent of femto-second lasers



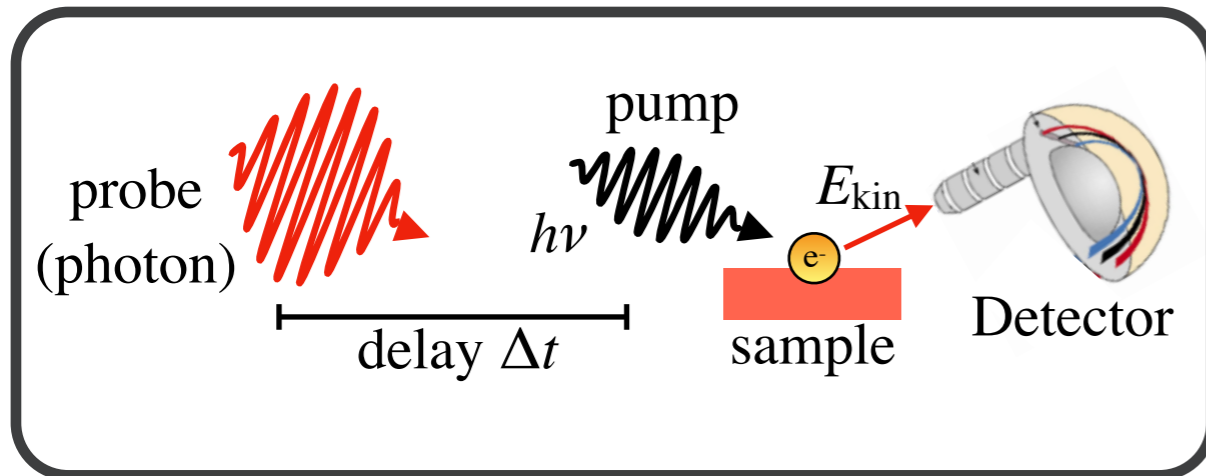
- Reduced dielectric screening
- Quantum-confinement in 2D
- Strong light-matter interactions
- Non-trivial topological properties

- Pump-probe spectroscopies
- Electron and phonon dynamics
- Light-driven phenomena

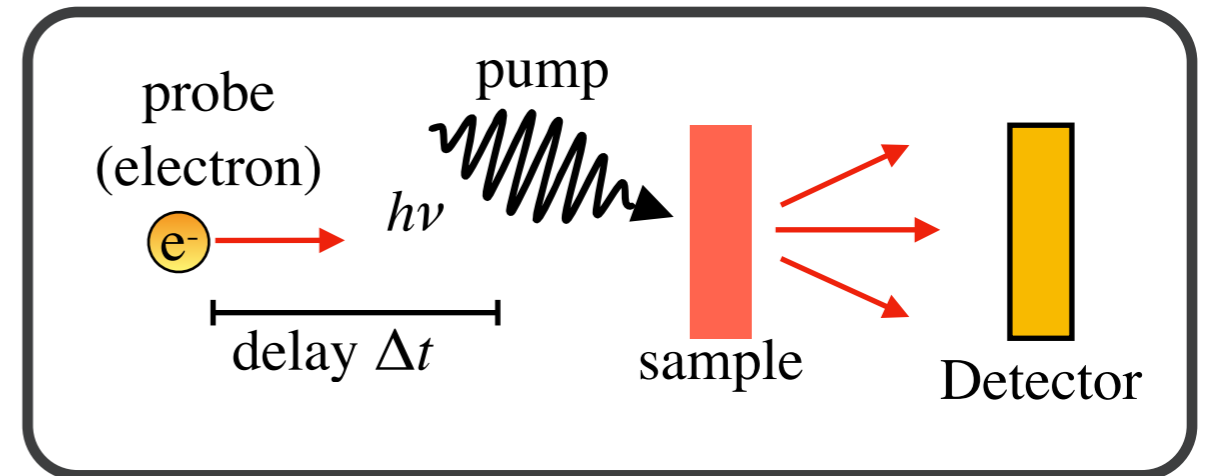
**Properties on-demand  
using light pulses**

# Nonequilibrium dynamics in two dimensions

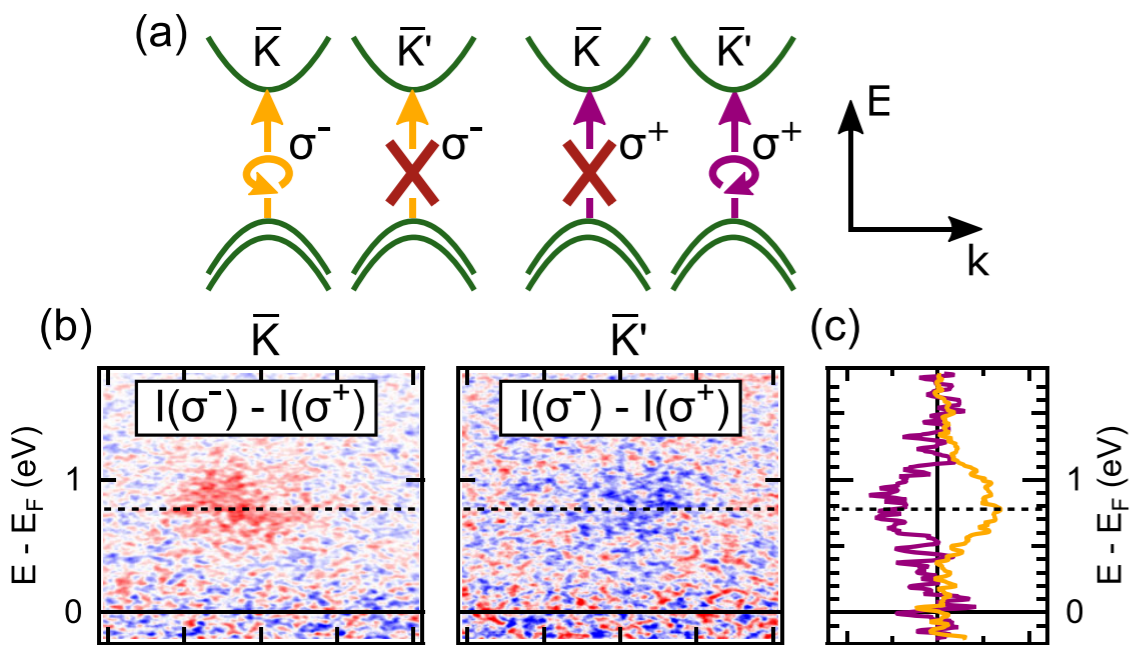
## Time- and angle-resolved photoemission spectroscopy (trARPES)



## Femto-second electron diffuse scattering (FEDS)

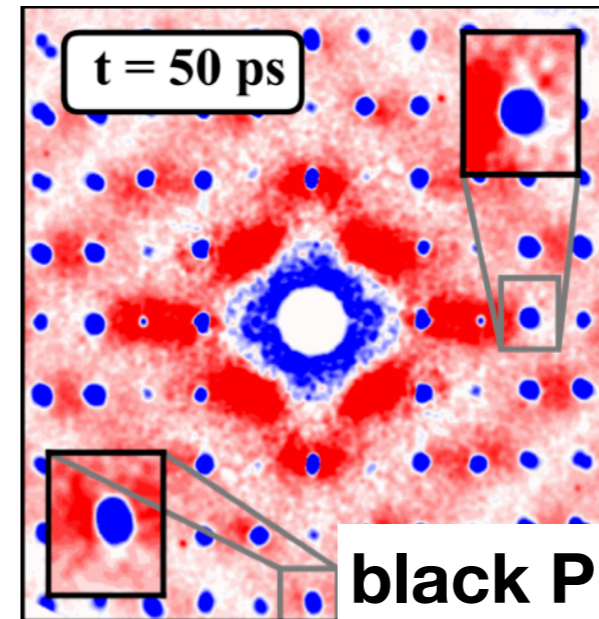


## Circular Dichroism ( $WS_2$ )

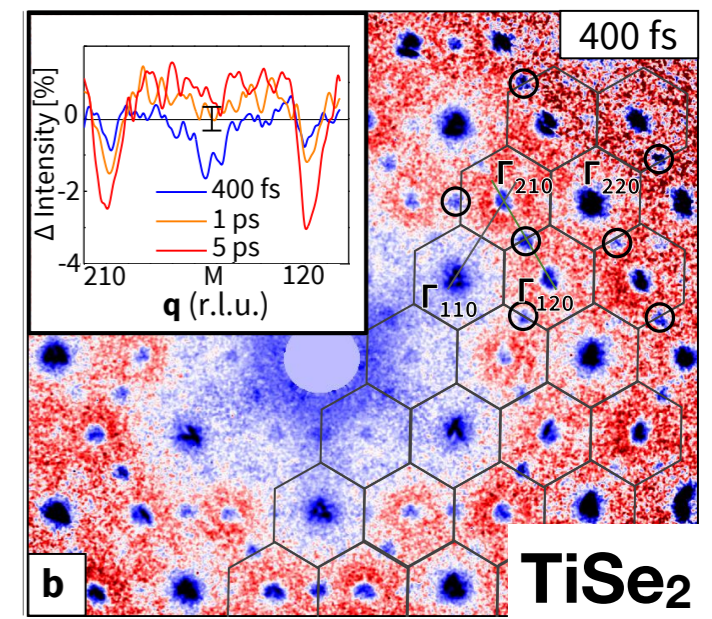


Beyer, Bauer, et al., PRL **123**, 236802 (2019)

## Anisotropic lattice dynamic



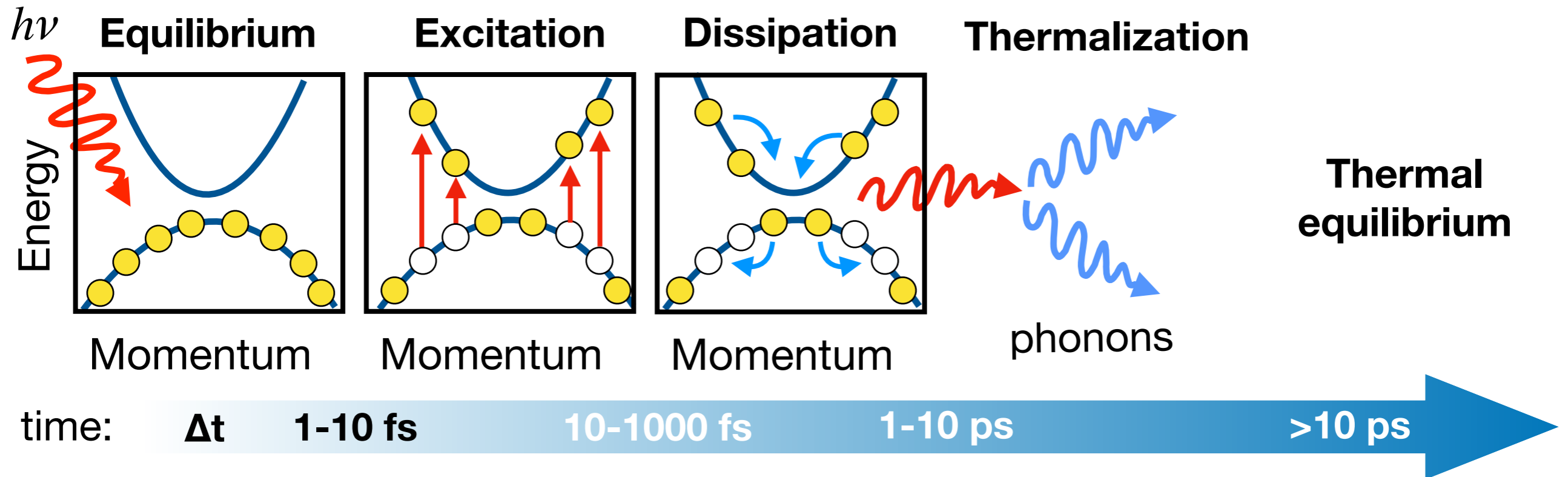
Seiler, FC, et al., arXiv:2006.12873 (2020)



Otto, Siwick, et al., arXiv:1912.03559 (2020)

**What is the influence of phonons and electron-phonon interactions on the nonequilibrium dynamics?**

# Ultrafast dynamics from first principles



## Which level of theory?

- Nonequilibrium Green's functions (& DMFT)
- Time-dependent density-function theory
- Time-dependent Boltzmann equation
- Quantum Master equation
- Molecular dynamics / Path integrals
- Non-thermal lattice models

## Check-list:

- Electron / phonon dynamics
- Electron-phonon coupling
- Full momentum resolution

# Equilibrium and nonequilibrium regimes in a quantum system

**Distribution function (occupation number):**

$f_{n\mathbf{k}}^\sigma$  Number of **electrons** in band  $n$  with momentum  $\mathbf{k}$

$n_{q\nu}$  Number of **phonons** in branch  $\nu$  with momentum  $q$

**Equilibrium:**

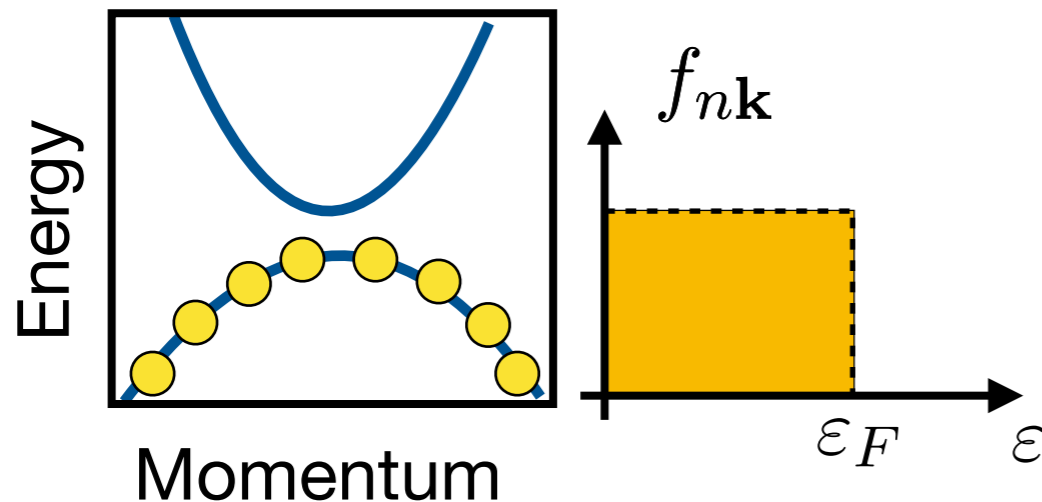
Fermi-Dirac statistics:

Bose-Einstein statistics:

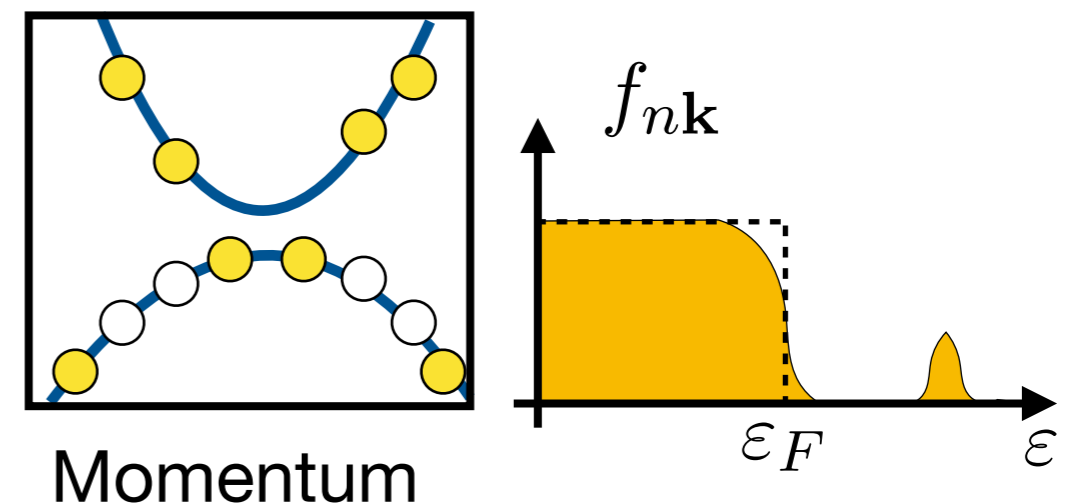
$$f_{n\mathbf{k}}^0(\mu, T) = [e^{(\varepsilon_{n\mathbf{k}} - \mu)/k_B T} + 1]^{-1}$$

$$n_{q\nu}^0(T) = [e^{\hbar\omega_{q\nu}/k_B T} - 1]^{-1}$$

**Equilibrium**



**Excitation**



**Out of equilibrium:**

$$f_{n\mathbf{k}} \neq f_{n\mathbf{k}}^0 \quad \text{and / or} \quad n_{q\nu} \neq n_{q\nu}^0$$

# The Boltzmann equation in solid-state physics



distribution  
function

collision integral

$$\frac{\partial f}{\partial t} = \Gamma_{\text{collisions}}$$

+ other terms  
(fields, etc.)

(In a gas:)

**Equilibrium is  
re-established  
via collisions**

## Books:

Ziman, Electrons and phonons, Oxford University Press (1960)

Hang, Jauho, Quantum Kinetics in Transport and Optics of Semiconductors, Springer (1996)

Bonitz, Quantum Kinetic Theory (1998)

## Charge and thermal Transport:

Poncé, Li, Reichard, Giustino, Rep. Prog. Phys. 83, 036501 (2019)

Li, Carrete, Katcho, Mingo, Comp. Phys. Comm. 185, 1747 (2014)

Mizokami, Togo, Tanaka Phys. Rev. B 97, 224306, (2018)

Chaput, Phys. Rev. Lett 110, 265506 (2013)

Togo, Chaput, Tanaka, Phys. Rev. B 91, 094306 (2015)

## Ultrafast dynamics:

Sadasivam, Chan, Darancet, Phys. Rev. Lett. 119, 136602 (2017)

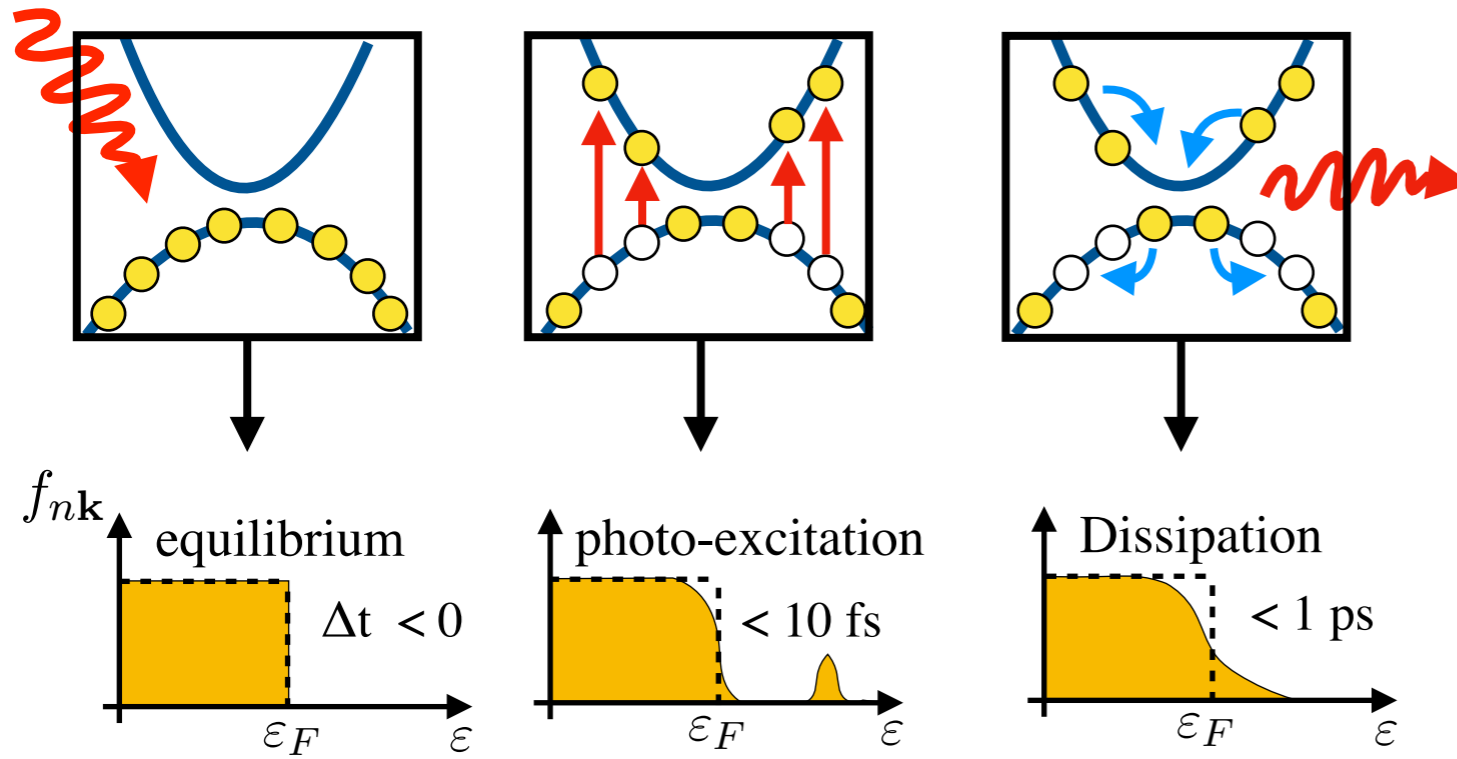
Bernardi, Eur. Phys. J. B 89, 239 (2016)

Jhalani, Zhou, Bernardi, Nano Letters 17, 5012 (2017)

FC, J. Phys. Chem. Lett. 12, 1274 (2021)



# Time-dependent Boltzmann equation



Nonequilibrium states are described by

$$f_{n\mathbf{k}}^\sigma \quad n_{\mathbf{q}\nu}$$

time-dependence of  $f_{n\mathbf{k}}^\sigma$   $n_{\mathbf{q}\nu}$   
 time-dep. Boltzmann eq.:

electron- phonon	electron-photon (dipole int.)	electron- electron
$\swarrow$	$\swarrow$	$\swarrow$
$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I_{n\mathbf{k}}^{\text{e-ph}}[f, n] + \cancel{I_{n\mathbf{k}}^{\text{light}}[f]} + \cancel{I_{n\mathbf{k}}^{\text{e-e}}[f]}$		
$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\text{e-ph}}[f, n] + I_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$		
$\searrow$	$\searrow$	
phonon- electron	phonon- phonon	

# First-principles approach to electron and lattice dynamics

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I_{n\mathbf{k}}^{\text{e-ph}}[f, n]$$

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\text{e-ph}}[f, n] + I_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$$

**Boltzmann equation** for the electron and phonon distribution function

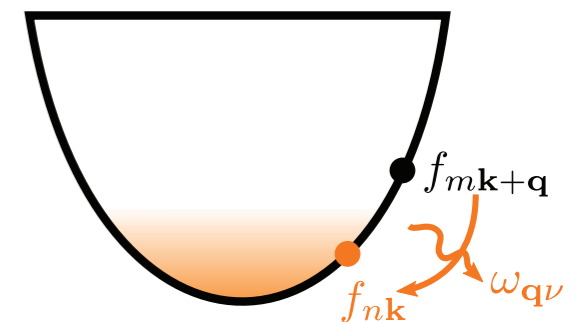
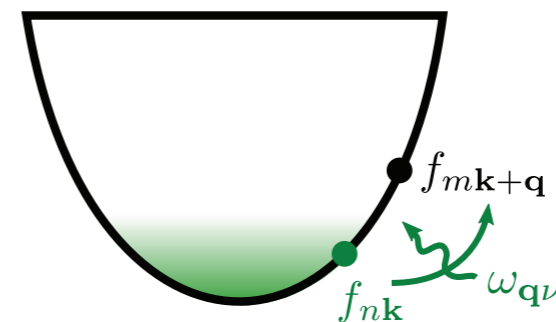
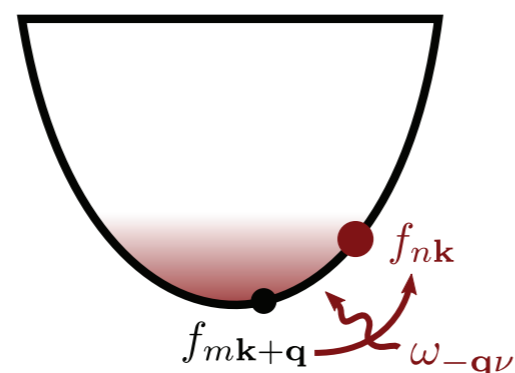
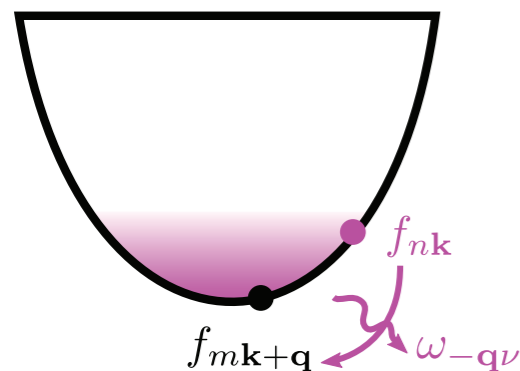
Poncé, et. al, Rep. Prog. Phys. (2019)

**Example:** electron-phonon scattering rate

$$I_{n\mathbf{k}}^{\text{e-ph}}[f, n] = \frac{2\pi}{\hbar} \sum_{m\nu} \int \frac{d\mathbf{q}}{\Omega_{\text{BZ}}} |g_{m\nu}(\mathbf{k}, \mathbf{q})|^2$$

electron-phonon coupling matrix element

$$\times \left\{ \begin{aligned} &(1 - f_{n\mathbf{k}}) f_{m\mathbf{k}+\mathbf{q}} \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu}) (1 + n_{\mathbf{q}\nu}) \\ &+ (1 - f_{n\mathbf{k}}) f_{m\mathbf{k}+\mathbf{q}} \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu}) n_{\mathbf{q}\nu} \\ &- f_{n\mathbf{k}} (1 - f_{m\mathbf{k}+\mathbf{q}}) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu}) (1 + n_{\mathbf{q}\nu}) \\ &- f_{n\mathbf{k}} (1 - f_{m\mathbf{k}+\mathbf{q}}) \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu}) n_{\mathbf{q}\nu} \end{aligned} \right\}$$



# Ultrafast dynamics from first principles

WANNIER90

## Wannier-function interpolation

G. Pizzi et al.,  
J. Phys. Cond. Matt. 32, 165902 (2020)



## Electron-phonon coupling

S. Poncé et al.,  
Comp. Phys. Comm. (2017)

## Coupled-dynamics of electrons and phonons

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I_{n\mathbf{k}}^{\text{e-ph}}[f, n]$$
$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\text{e-ph}}[f, n] + I_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$$



## Density functional theory

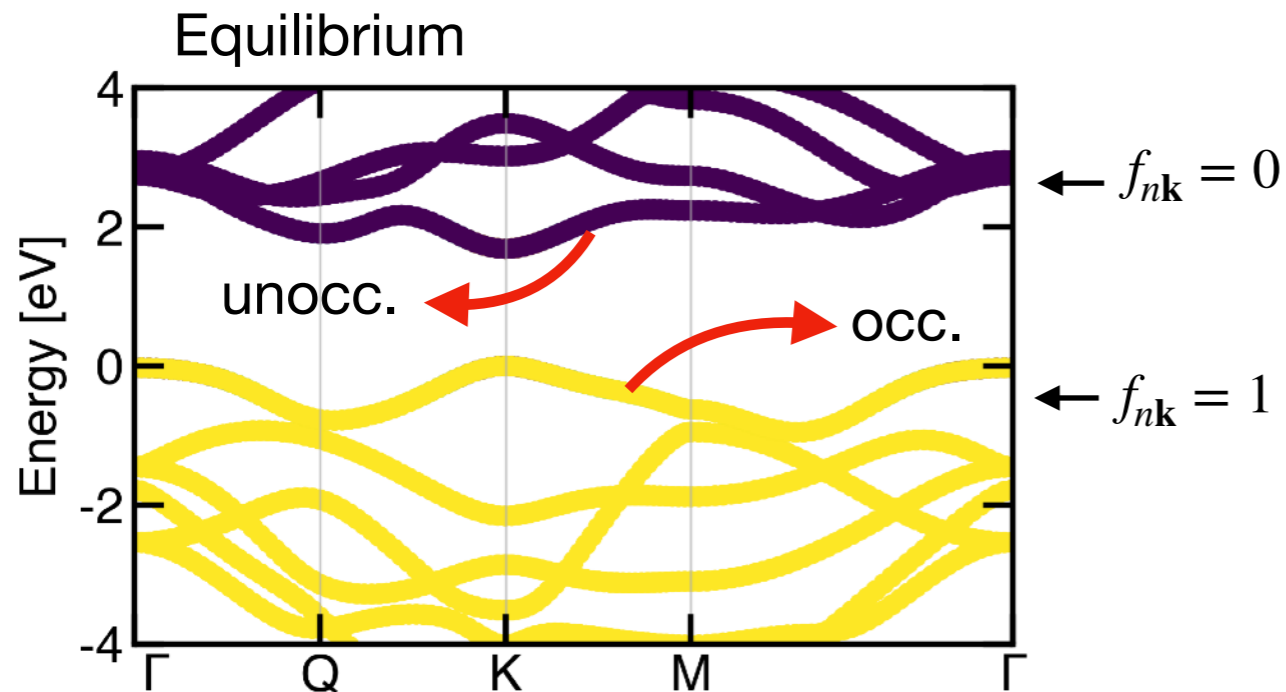
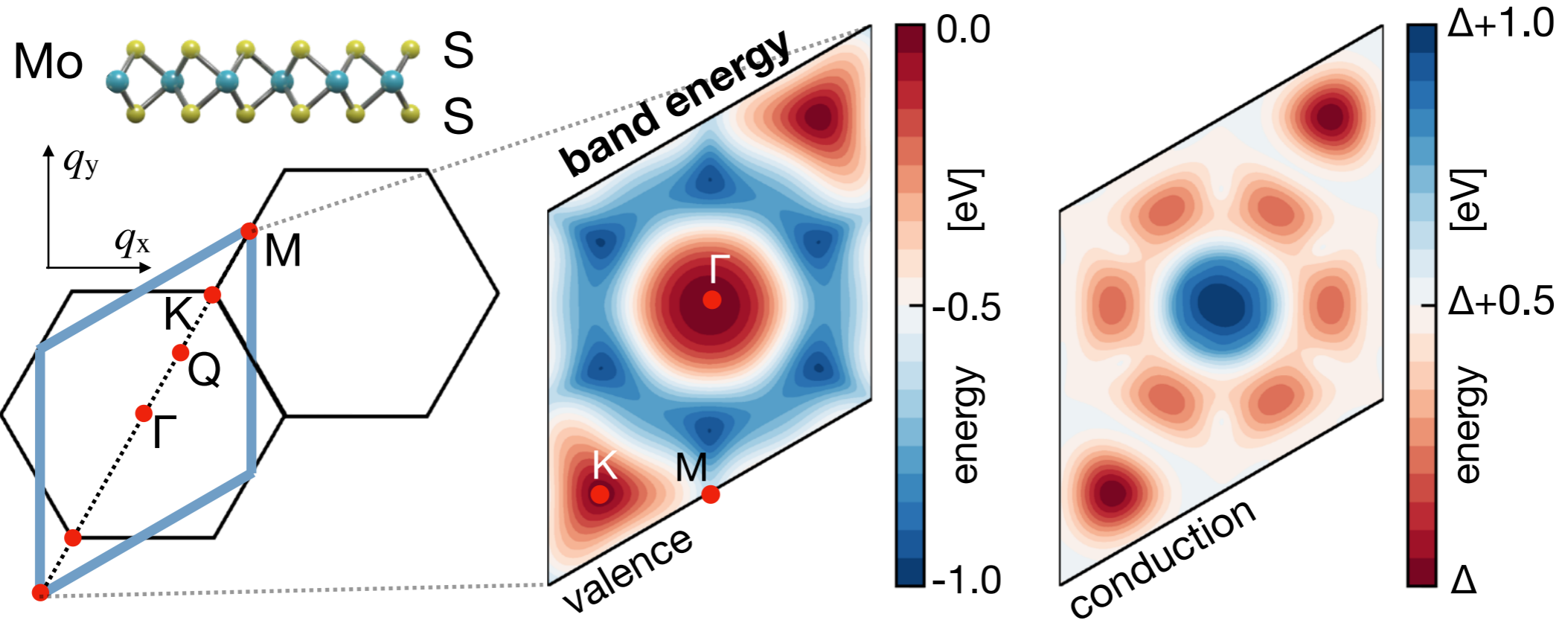
P. Giannozzi et al.,  
J. Phys.: Condens. Matter 29, 465901 (2017)



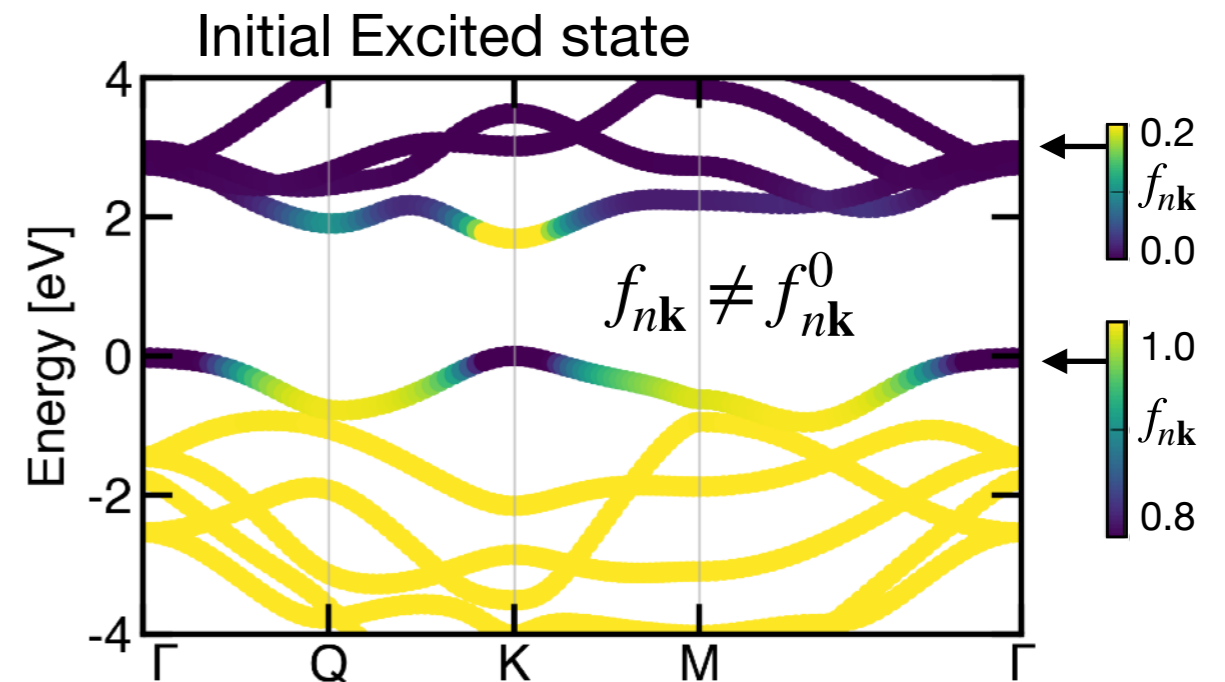
## Third-order force constant

W. Li et al., Comp. Phys. Comm. 185,  
1747 (2014)

# Nonequilibrium electron dynamics in monolayer MoS<sub>2</sub>

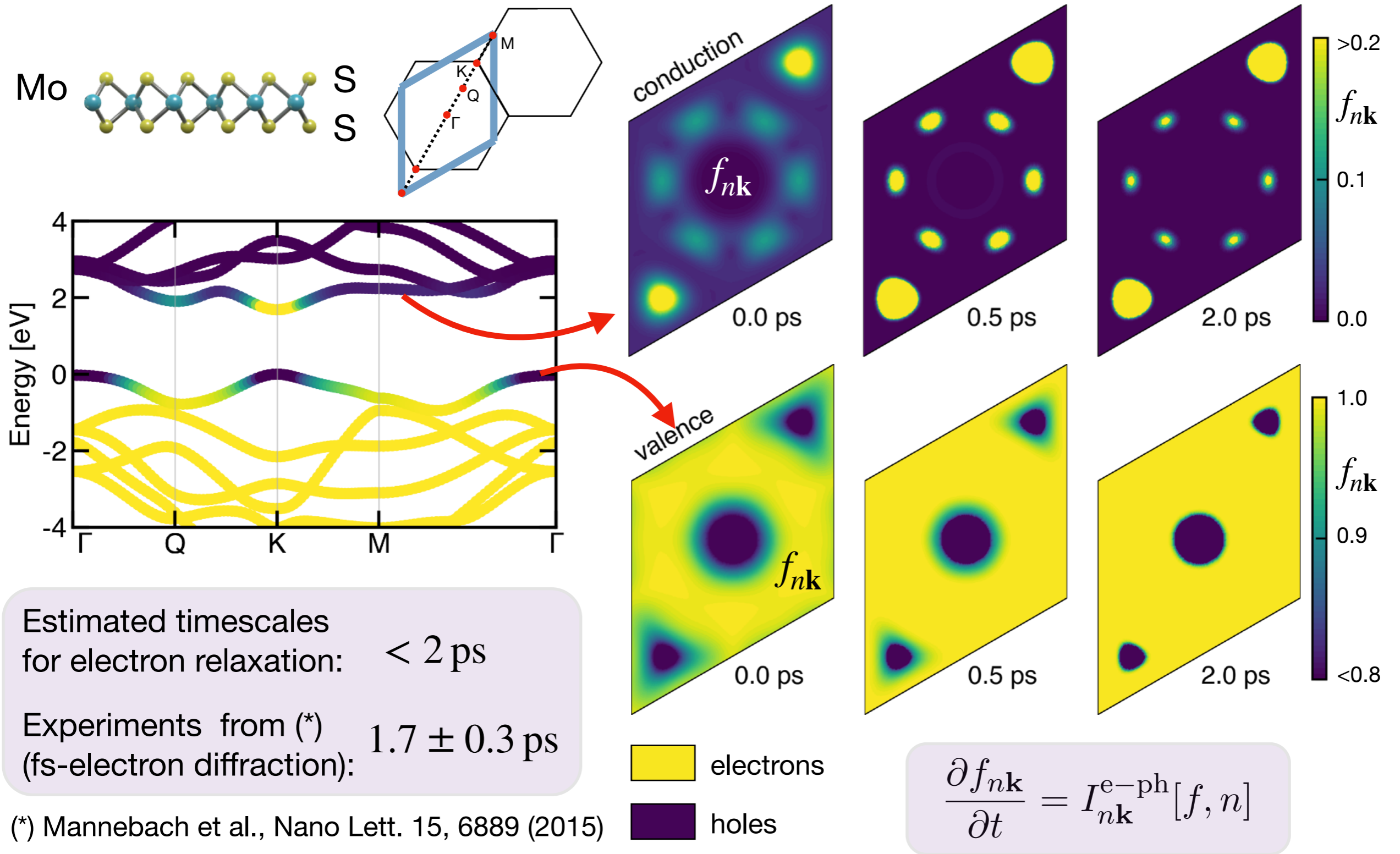


$$f_{n\mathbf{k}}^0(\mu, T) = [e^{(\varepsilon_{n\mathbf{k}} - \mu)/k_B T} + 1]^{-1}$$



Excited carrier density:  $n=10^{14} \text{ cm}^{-2}$

# Nonequilibrium electron dynamics



# Nonequilibrium phonon dynamics

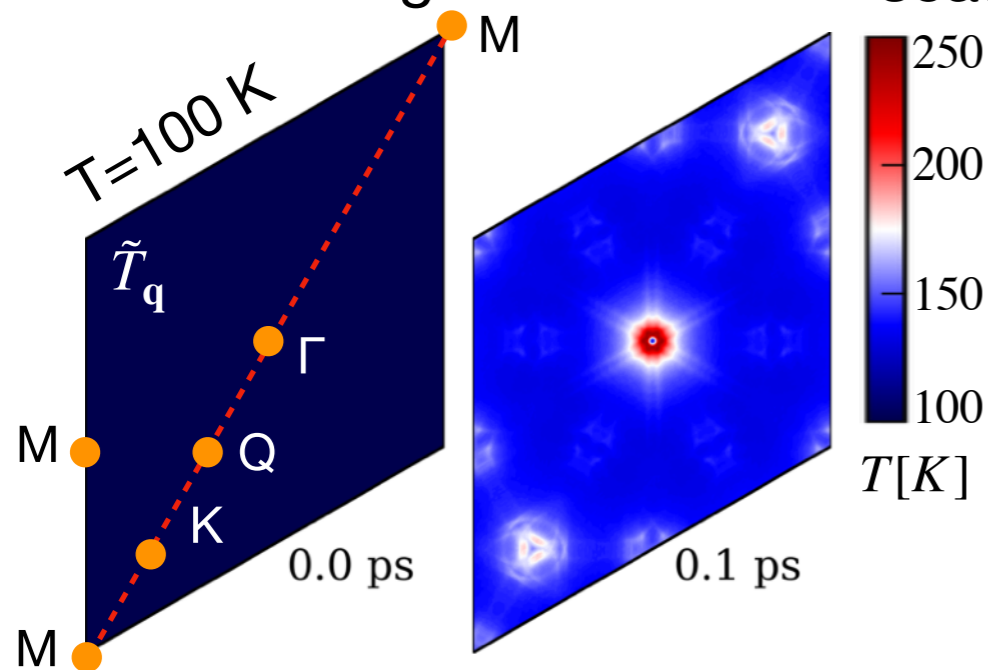
$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\text{e-ph}}[f, n] + I_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$$

effective vibrational temperature

$$T_{\mathbf{q}\nu} = \hbar\omega_{\mathbf{q}\nu} [k_B \ln(1 + n_{\mathbf{q}\nu})]^{-1}$$

electron-phonon scattering

phonon-phonon scattering

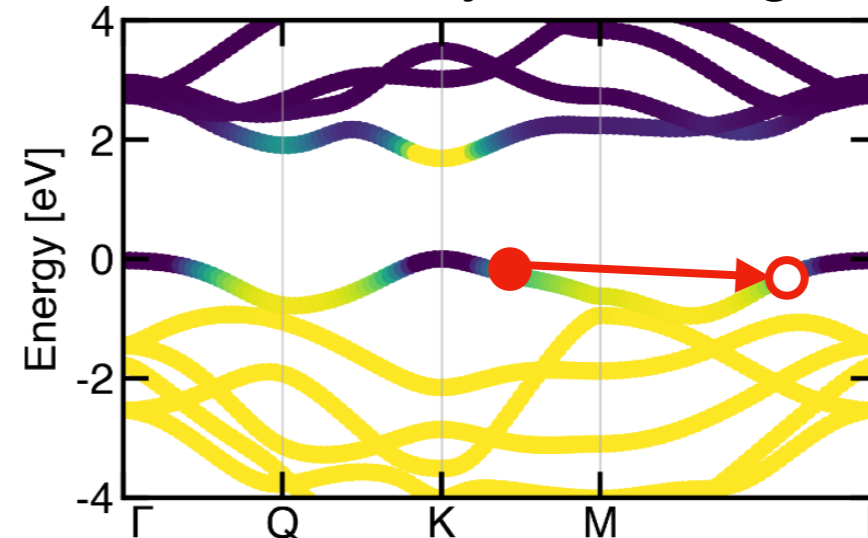


**vibrational temperature**

Energy cons.:  $\hbar\omega_{\mathbf{q}\nu} = \varepsilon_{n\mathbf{k}} - \varepsilon_{n\mathbf{k}'}$

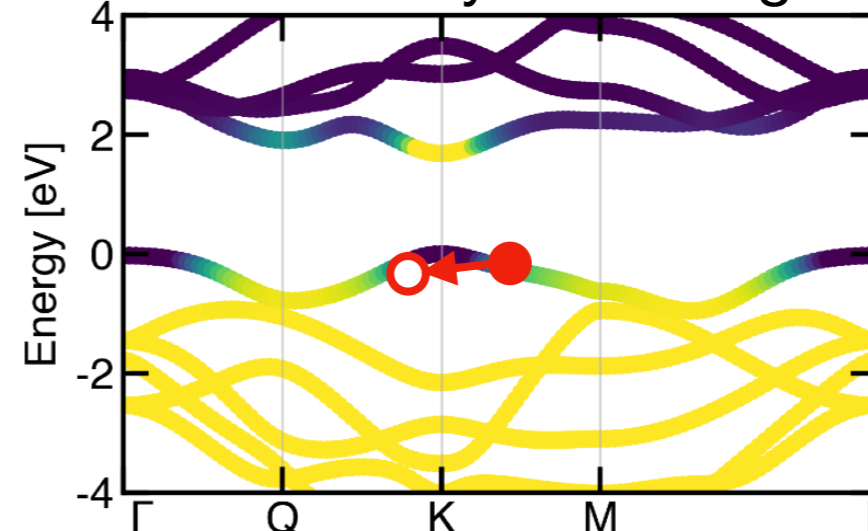
Momentum cons.:  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$

**Intervalley scattering**



allowed phonon momenta:  
 $\mathbf{q} \simeq \mathbf{K}$

**Intravalley scattering**



allowed phonon momenta:  
 $\mathbf{q} \simeq \Gamma$

# Nonequilibrium phonon dynamics

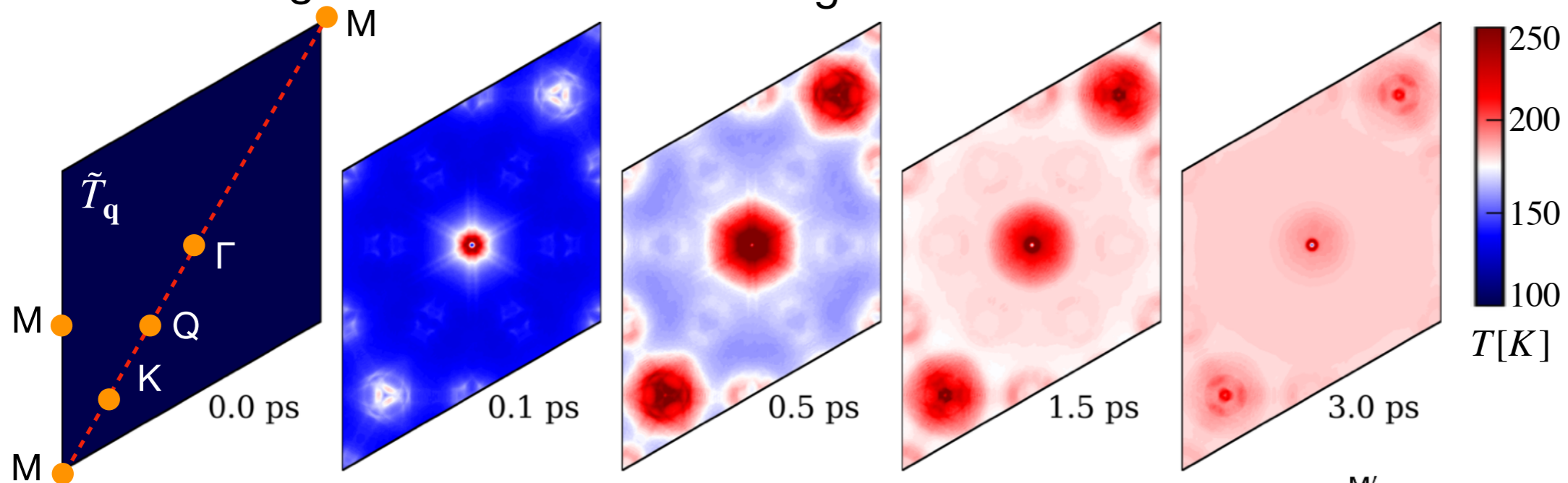
$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\text{e-ph}}[f, n] + I_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$$

effective vibrational temperature

$$T_{\mathbf{q}\nu} = \hbar\omega_{\mathbf{q}\nu} [k_B \ln(1 + n_{\mathbf{q}\nu})]^{-1}$$

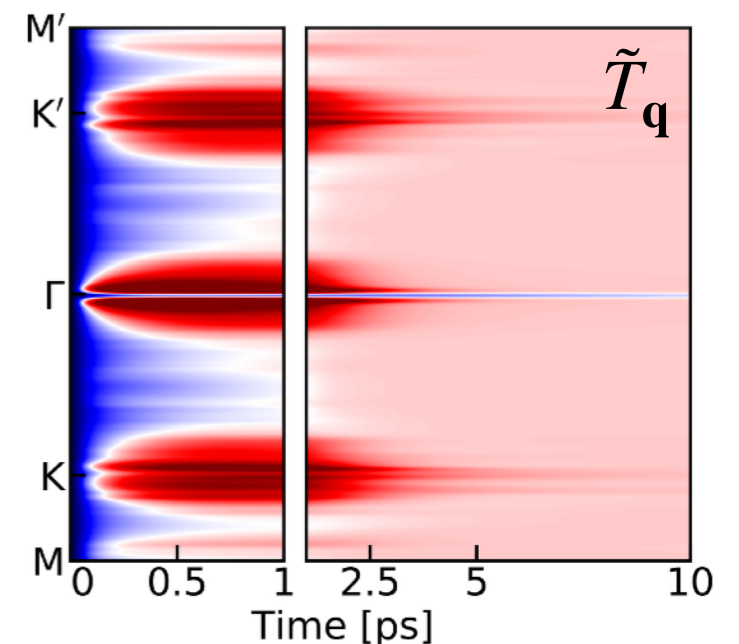
electron-phonon scattering

phonon-phonon scattering

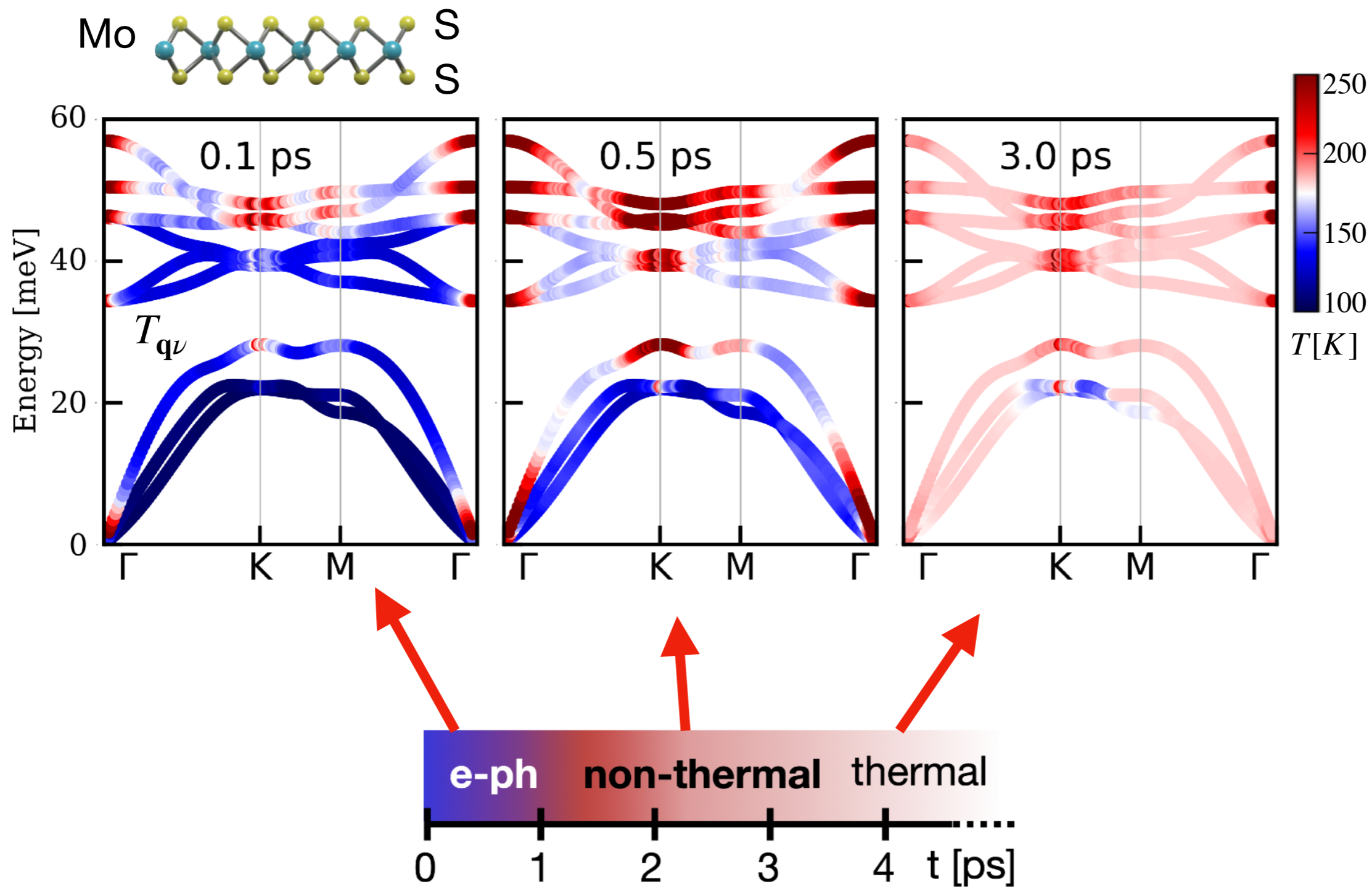


Energy cons.:  $\hbar\omega_{\mathbf{q}\nu} = \varepsilon_{n\mathbf{k}} - \varepsilon_{n\mathbf{k}'}$

Momentum cons.:  $\mathbf{q} = \mathbf{k}' - \mathbf{k}$



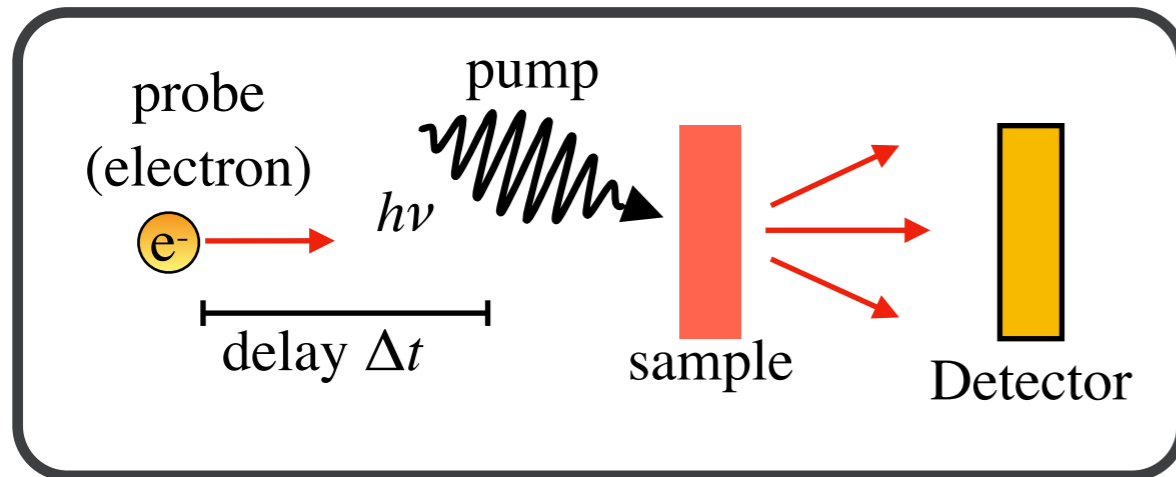
# Regimes of nonequilibrium phonon dynamics



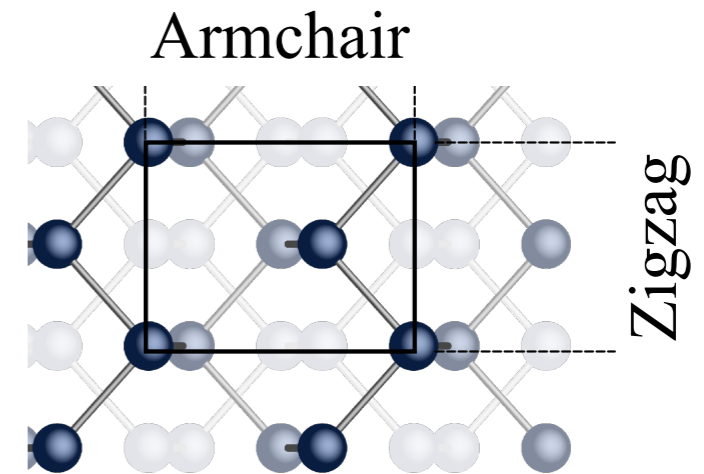


# Electron diffuse scattering: black Phosphorus

## Femto-second electron diffuse scattering (FEDS)



## Black phosphorus



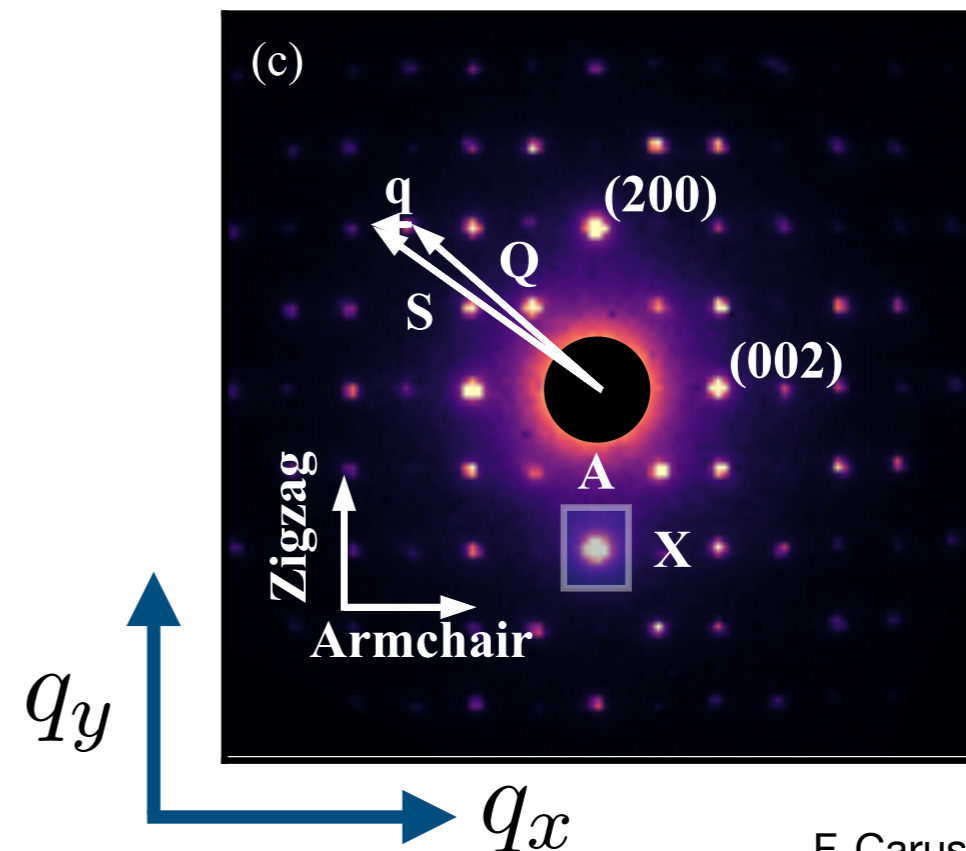
## Experiments: FHI Berlin



Helene Seiler



Ralph Ernstorfer

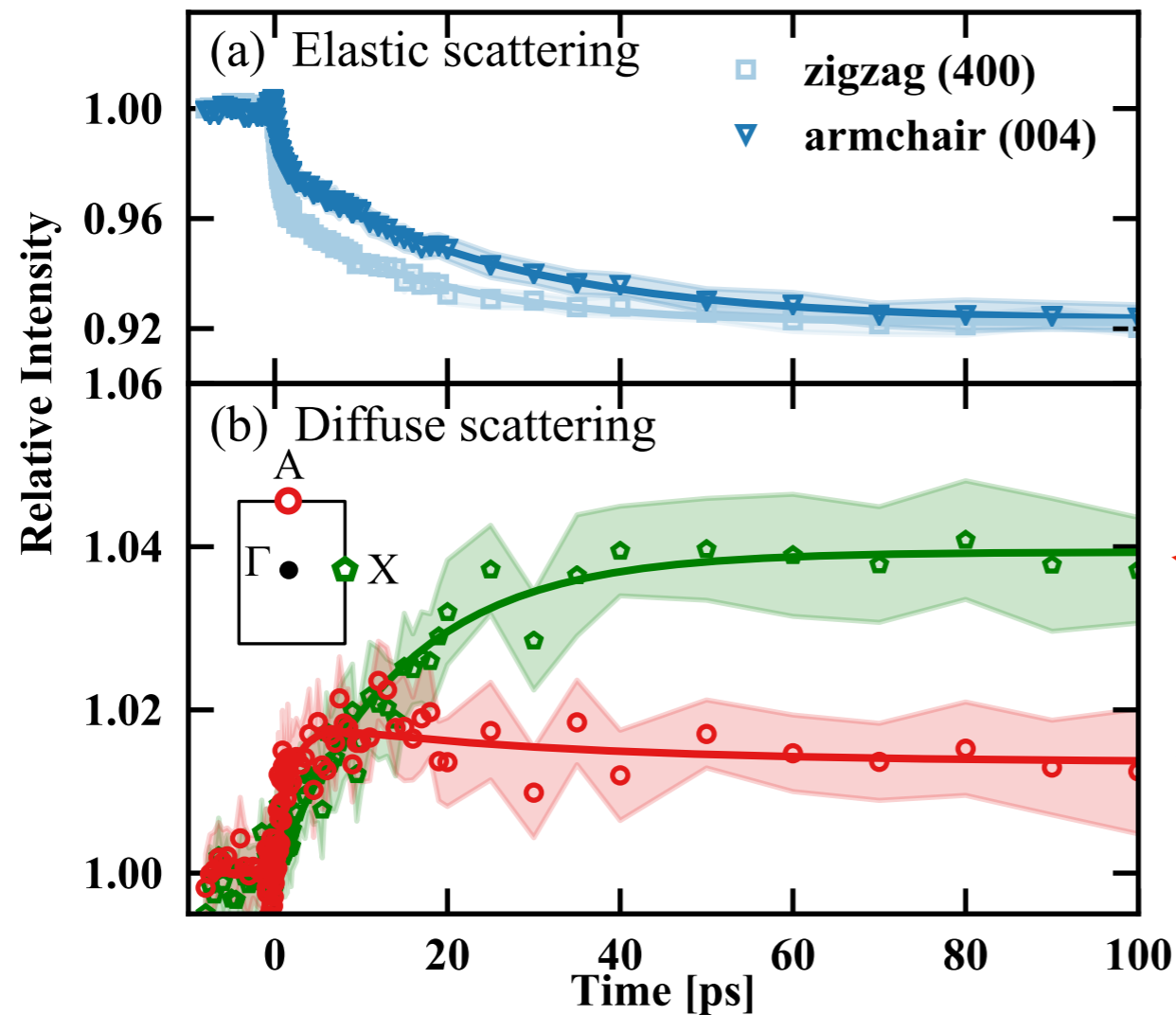
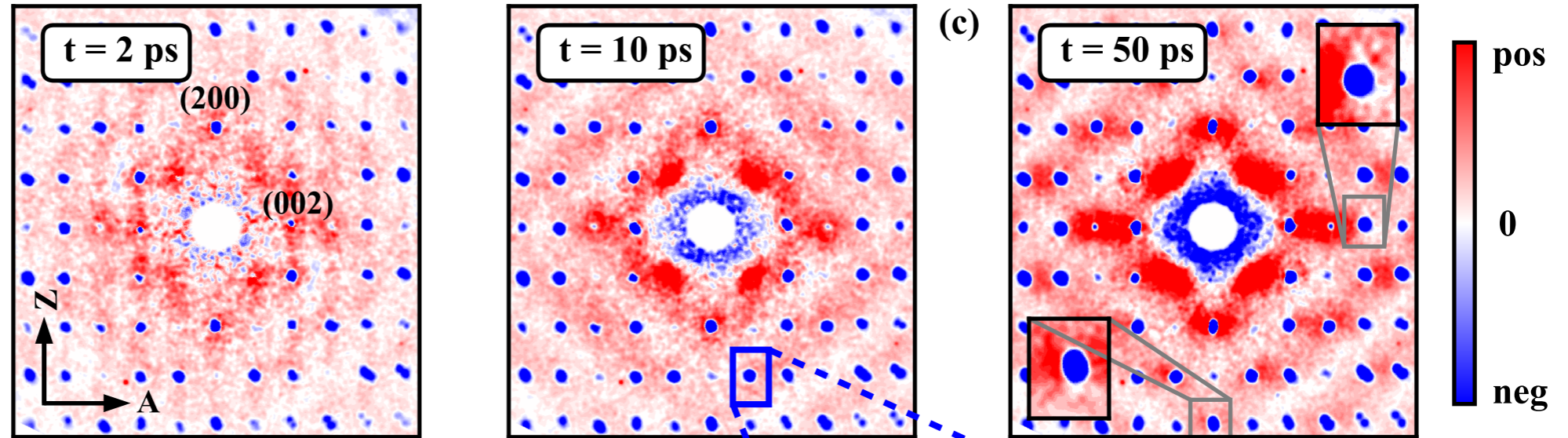


# Anisotropic non-equilibrium lattice dynamics in bP

**Experiment:**

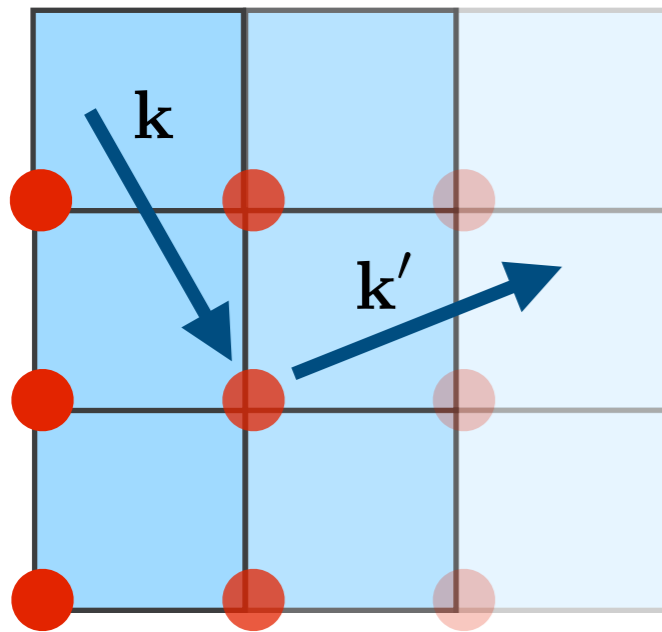
Intensity difference:

$$I(\mathbf{S}, t) - I(\mathbf{S}, t < t_0)$$



**Highly-anisotropic  
lattice dynamics**

# Diffraction from a lattice



Bragg's law for interference condition:

$$A(\mathbf{q}) = \sum_p^{N_p} f_0 \exp [i\mathbf{q} \cdot \mathbf{R}_p]$$

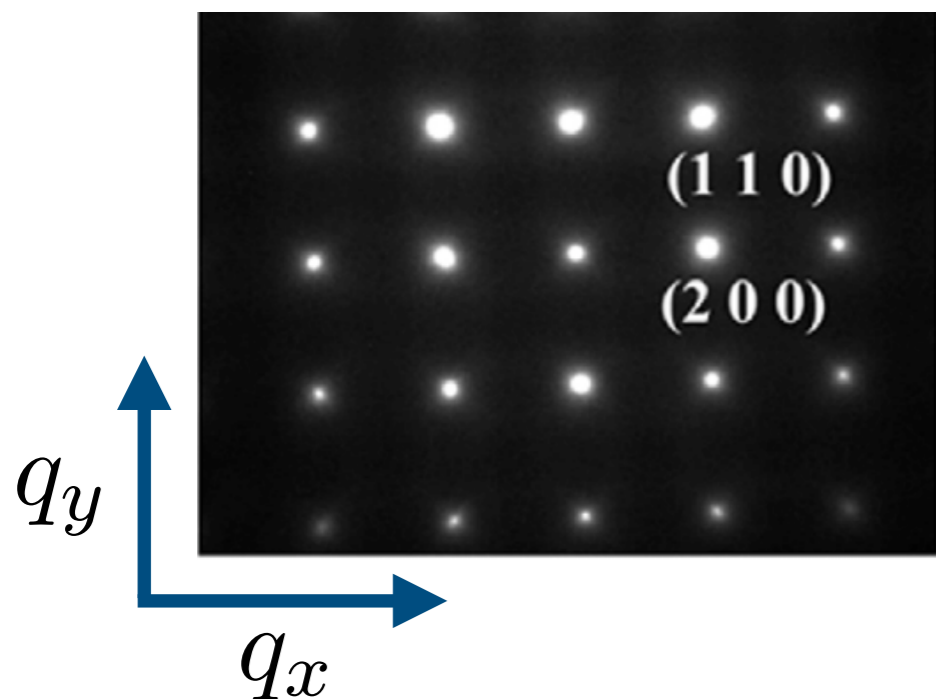
amplitude

Scattering  
cross section

$\mathbf{q} = \mathbf{k}' - \mathbf{k}$   
Transferred  
momentum

Lattice  
vector

example: Cubic lattice

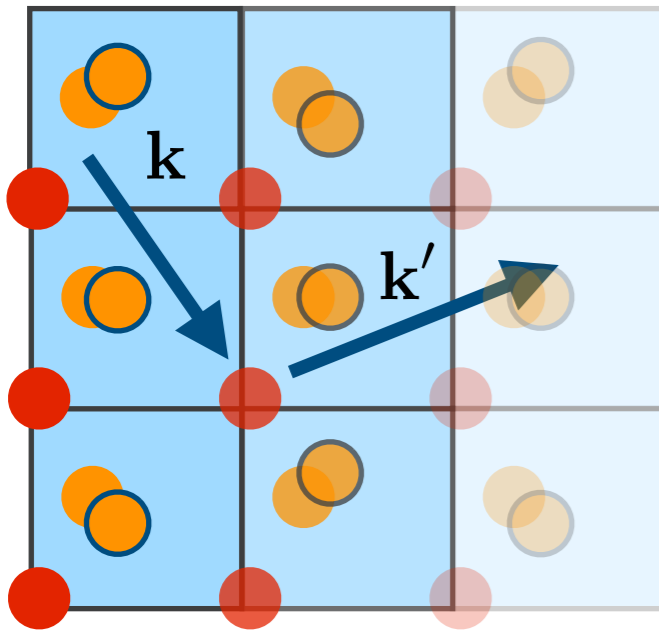


Scattering intensity for a perfect lattice:

$$I(\mathbf{q}) = |A(\mathbf{q})|^2 \simeq \delta_{\mathbf{q},\mathbf{G}}$$

Reciprocal  
lattice vector

# Diffraction from a vibrating lattice



## Zero-phonon term:

$$\langle I_0(\mathbf{S}) \rangle_T = N_p^2 |f_0|^2 \exp(-2W_T) \delta_{\mathbf{S}, \mathbf{G}}$$

## Debye-Waller factor:

$$2W_T = \frac{1}{M_\kappa N_p} \sum_{\mathbf{q}\nu} \left[ \sum_{\alpha\alpha'} S_\alpha S_{\alpha'} e_{\kappa\alpha}^\nu(\mathbf{q}) e_{\kappa\alpha'}^{\nu*}(\mathbf{q}) \right] E_{\mathbf{q}\nu, T}$$

## One-phonon (dynamical) structure factor

$$\begin{aligned} \langle I_1(\mathbf{S}, E) \rangle_T &= |f_0|^2 \exp(-2W_T) \frac{\hbar^2 N_p}{2M_\kappa} \sum_{\mathbf{q}\nu} \left[ \sum_{\alpha\alpha'} S_\alpha S_{\alpha'} e_{\kappa\alpha}^\nu(\mathbf{q}) e_{\kappa\alpha'}^{\nu*}(\mathbf{q}) \right] \frac{1}{\hbar\omega_{\mathbf{q}\nu}} \quad (16) \\ &\times \left[ \delta(\mathbf{S} + \mathbf{q}) n_{\mathbf{q}\nu, T} \delta(E + \hbar\omega_{\mathbf{q}\nu}) + \delta(\mathbf{S} - \mathbf{q}) (n_{\mathbf{q}\nu, T} + 1) \delta(E - \hbar\omega_{\mathbf{q}\nu}) \right]. \end{aligned}$$

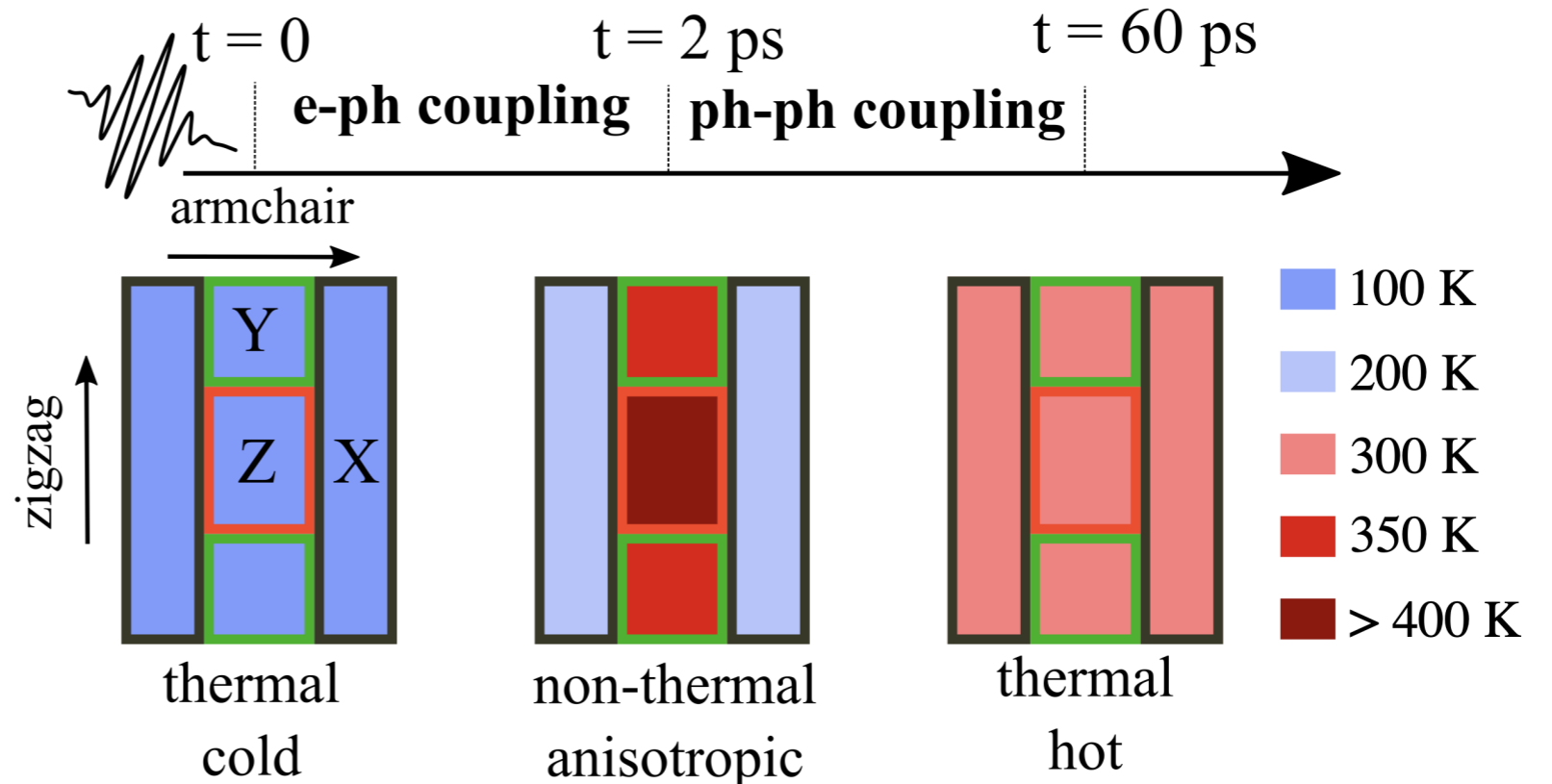
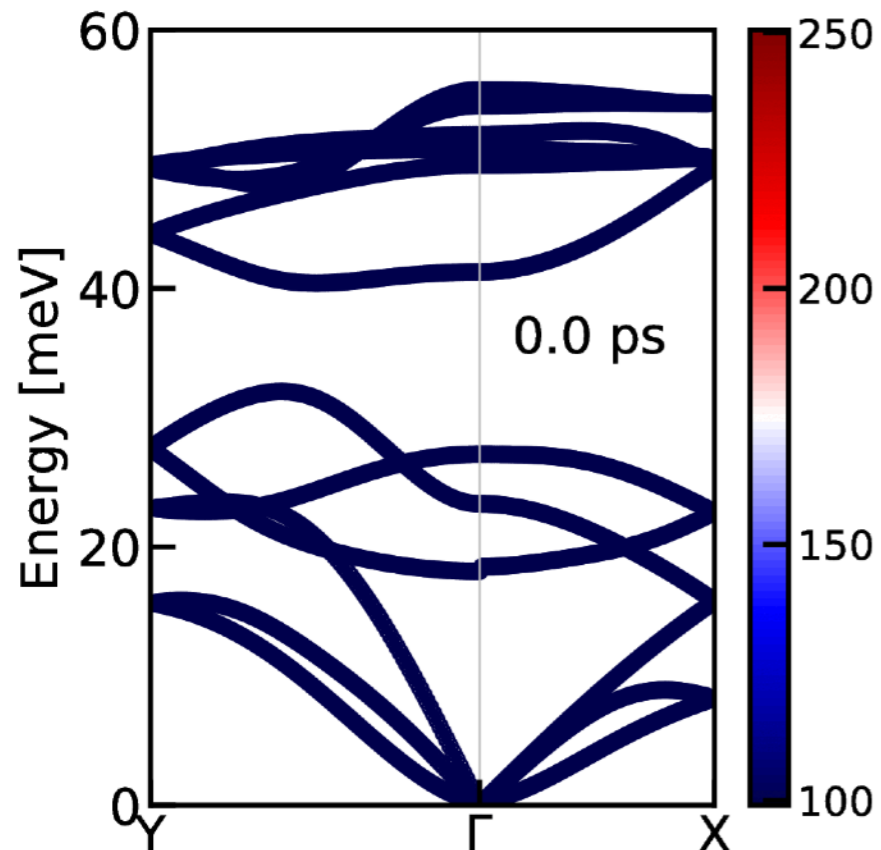
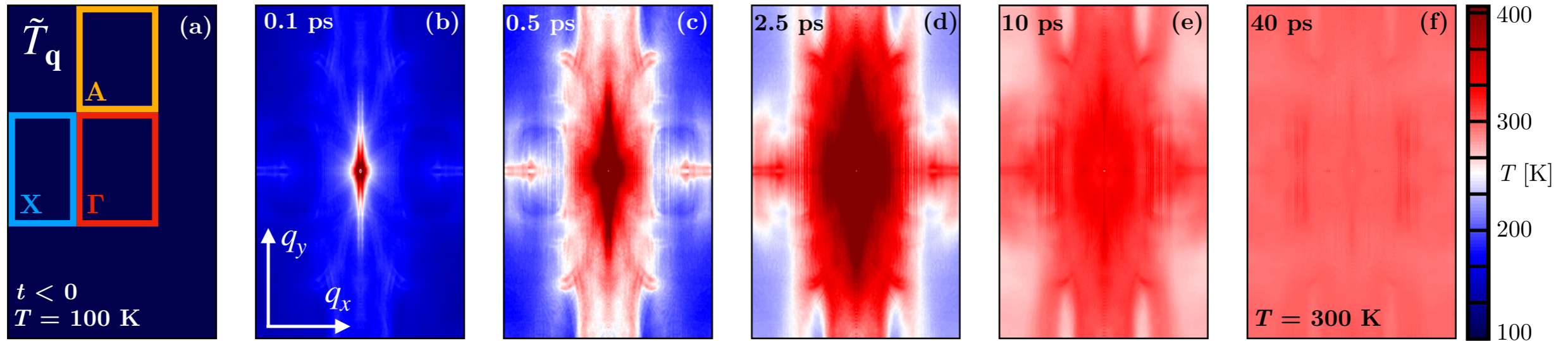
from the time-dependent Boltzmann equation

First-principles approach to Femto-second electron diffuse scattering (FEDS)

# Non-equilibrium lattice dynamics in bP from first-principles

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\text{e-ph}}[f, n] + I_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$$

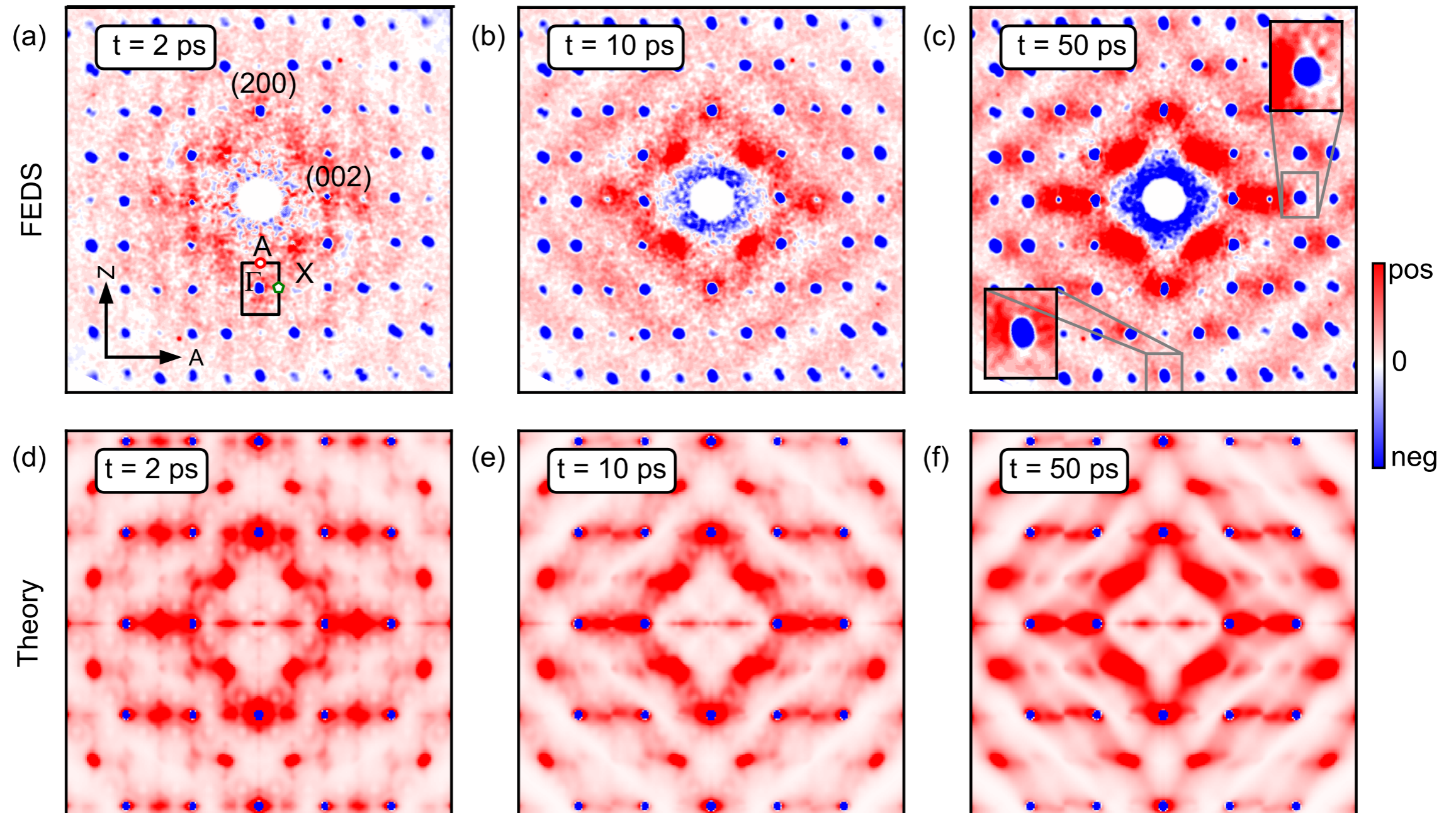
Effective vibrational temperature



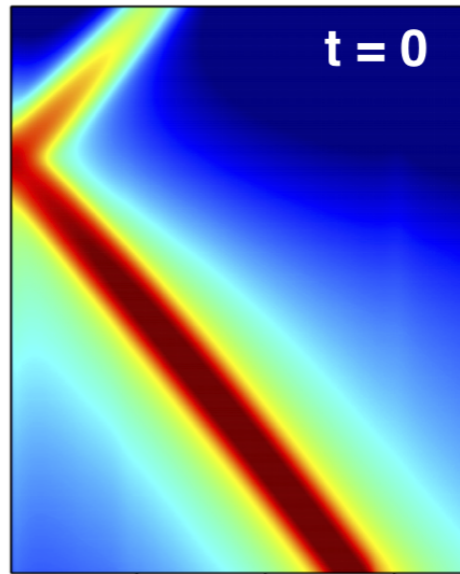
# Non-equilibrium lattice dynamics in bP from first-principles

Intensity difference:

$$I(\mathbf{S}, t) - I(\mathbf{S}, t < t_0)$$

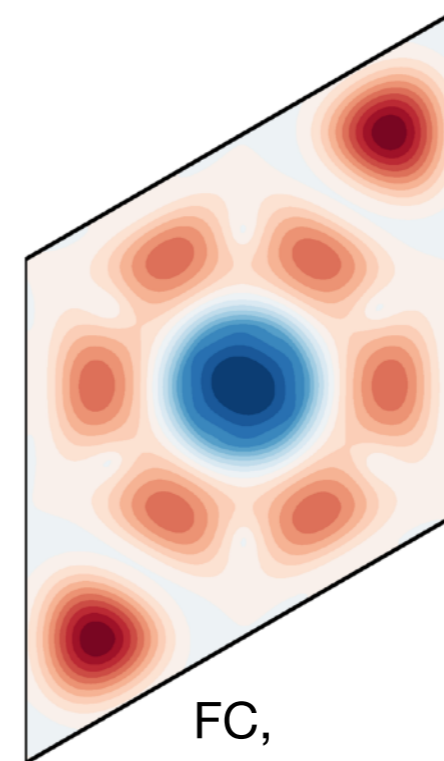


# Ultrafast dynamics of electrons and phonons



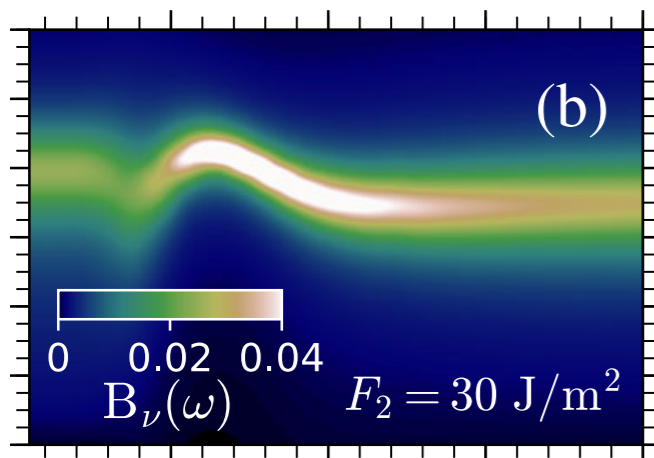
Nonequilibrium carrier dynamics in graphene

FC, Novko, Draxl, Phys. Rev. B **101** 035128 (2020)



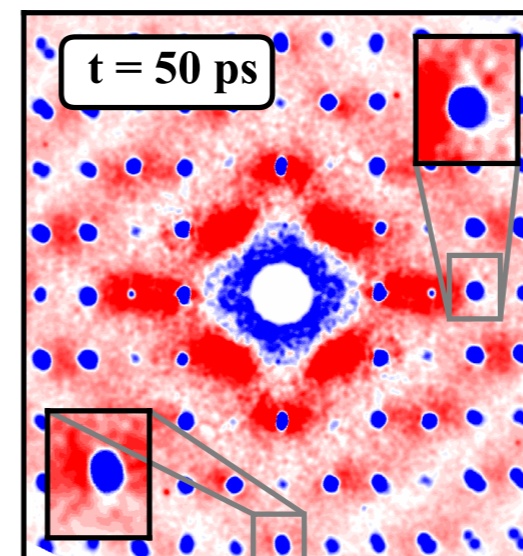
Nonequilibrium lattice dynamics in MoS<sub>2</sub>

FC, J. Phys. Chem. Lett. **12**, 1274 (2021)



Transient phonon renormalization in MgB<sub>2</sub>

Novko, FC, Draxl, Cappelluti, Phys. Rev. Lett. **124** 077001 (2020)



Signatures of nonequilibrium lattice dynamics in phosphorene

Seiler, Zahn, Zacharias, et al. arXiv (2020)

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## THEORY

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- Christoph Emeis

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### Fritz Haber Institute, Berlin

- Helene Seiler
- Daniela Zahn
- Ralph Ernstorfer



#### EPW:

S. Poncé et al.,  
Comp. Phys. Comm. (2017)



#### Quantum Espresso:

P. Giannozzi et al., J. Phys.:  
Condens. Matter 29, 465901 (2017)



Wannier90: G. Pizzi et al., J. Phys.  
Cond. Matt. 32, 165902 (2020)



#### ShengBTE:

W. Li et al., Comp. Phys.  
Comm. 185, 1747 (2014)