Electron-phonon interactions

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https://cs2t.de

Computational Solid-State Theory group

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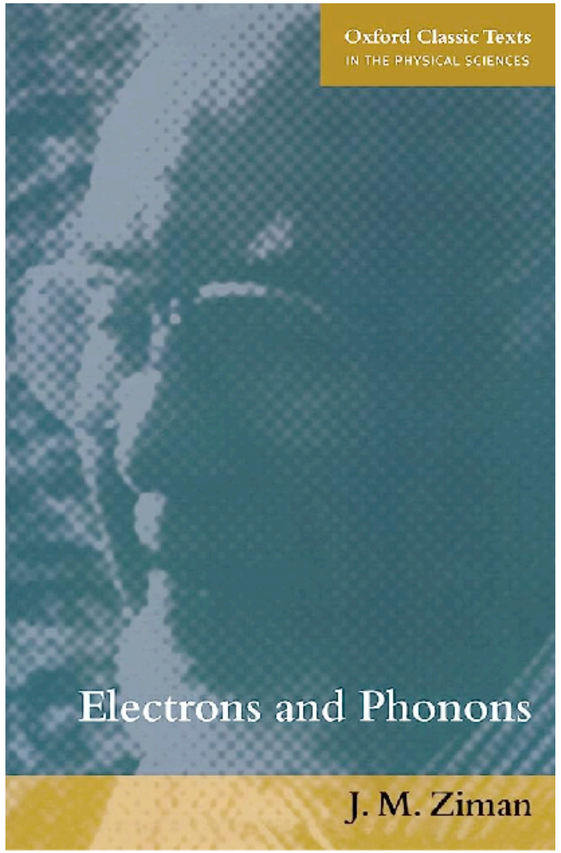
German Research Foundation

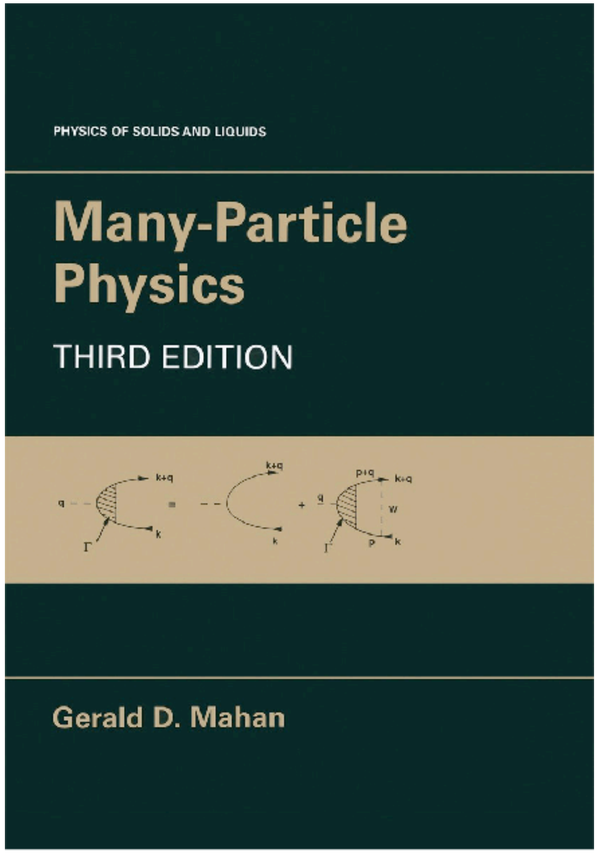
Further readings

Fundamentals



J. M. Ziman,
Electrons and Phonons,
Oxford University Press (1960)

Many-body formalism



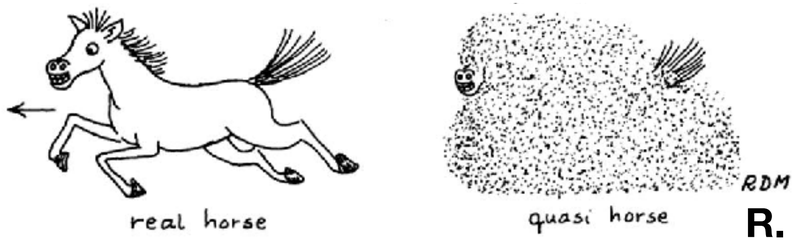
G. D. Mahan,
Many-Particle Physics,
Springer (2000)

Latest developments: Reviews

F. Giustino,
Electron-phonon interactions from first principles
Rev. Mod. Phys. **89**, 015003 (2017)

C. Franchini et al.,
Polarons in Materials,
Nat. Rev. Mater. **6**, 560 (2021)

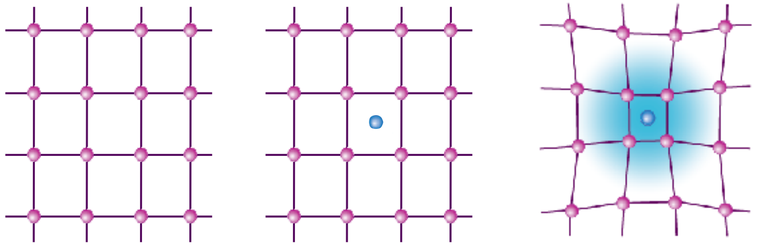
Quasiparticles and phonons



R. Mattuck

L. Landau, Electron motion in crystal lattices,
Phys. Z. Sowjetunion **3**, 664 (1933)

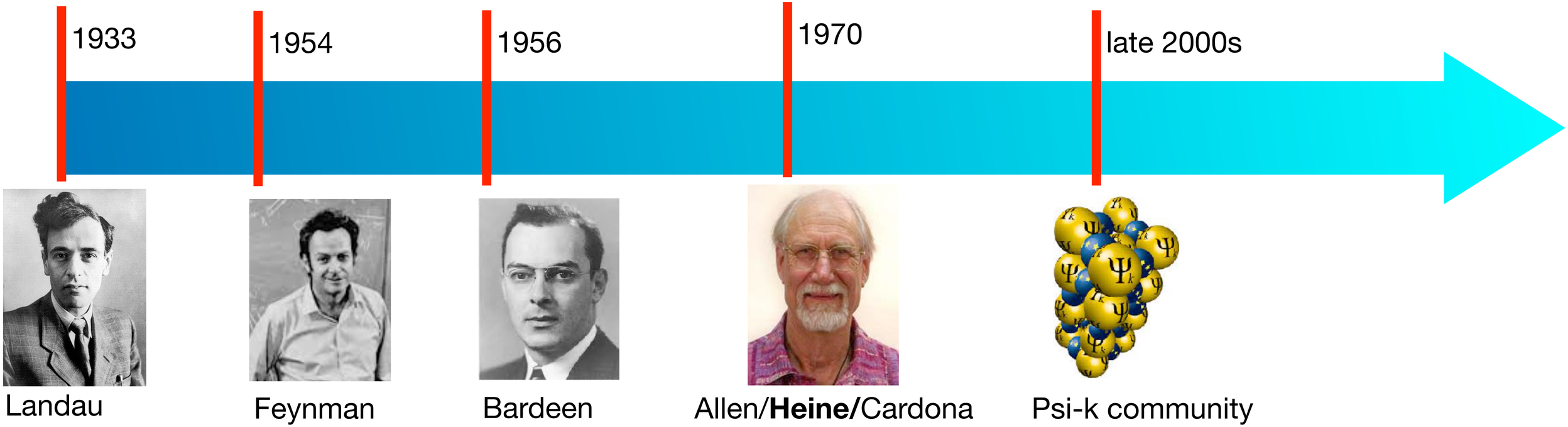
Phonon assisted quasiparticles



example:

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

The timeline of the electron-phonon interaction



(1933) Landau: The polaron problem

(1954) Feynman: Exact solution of the polaron problem via a variational principle

(1956) Bardeen-Cooper-Schrieffer: BCS Theory of superconductivity

(1970) Allen-Heine-Cardona: Theory of the temperature dependence of the band structure

(~2005) Psi-k community: Ab-initio calculation of the electron-phonon interaction

and many more

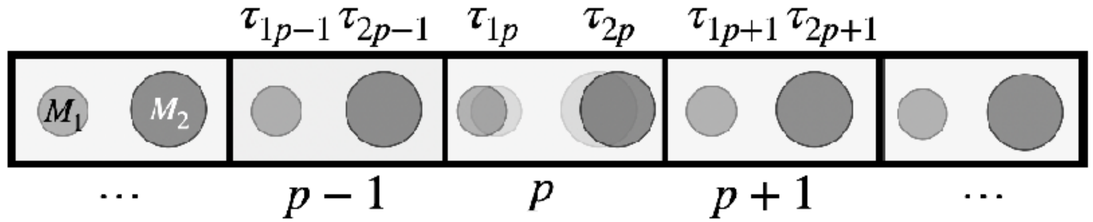
Year	Theoretical and computational models	Polaron properties
1933 (REF.[6])	Dielectric theory: charge moving in a dielectric crystal	Auto-localization due to lattice deformation
1946–1948 (REFS[4,306–308])	Self-consistent theory of a large polaron	Enhancement of effective mass
	Landau–Pekar model	Localization of the wavefunction
1950s[7,8,85,86]	Quantum-mechanical variational theory of large polarons	Effective mass, energy, mobility
	Fröhlich large polaron Hamiltonian (continuum approximation)	Intermediate electron–phonon interaction
1955–2017 (REFS[11,12,93,161,162])	All-coupling continuum polaron theory	Energy, effective mass, mobility (large polaron)
	Feynman variational path-integral formalism	
1956 (REF.[95]), 1980s[94,96]	Monte Carlo calculations	Large polaron ground-state energy
1958 (REFS[309,310]), 1959 (REFS[9,10])	Holstein small polaron theory	Small polaron conduction mechanism
	Holstein small polaron Hamiltonian (lattice approximation)	Effective mass, energy
1963–2000s[87–89,311]	Exact solution of the two-site Holstein polaron	Dynamical characteristics
1969 (REF.[148]), 2000 (REFS[149,150])	Emin–Holstein–Austin–Mott theory	Small polaron hopping
1980 (REF.[146]), 1985 (REFS[119,147])	Marcus theory	Polaron hopping
1994 (REF.[101])	Exact diagonalization	Small polaron frequencies
1997 (REF.[312])	Hartree–Fock	Small polaron density of states
1998–2000 (REFS[58,59])	Diagrammatic Monte Carlo	Energy, effective mass, phonon distribution, spectral density
1999 (REF.[157])	Random walk Monte Carlo	Dispersive transport and recombination
2001 (REF.[104]), 2010 (REF.[56])	Analytical variational approach (variational LDB many-polaron wavefunction)[103]	Many-polaron (large) optical conductivity
2001 (REF.[60])	Path-integral Monte Carlo	Large polaron energy (2D and 3D)
1995 (REF.[65]), 1997 (REF.[66]), 2003 (REF.[67])	Dynamical mean-field theory	Small polaron energy, mass, spectral and transport properties
2010 (REF.[154]), 2018 (REF.[155])	First-principles molecular dynamics of small polarons	Polaron configurations
2002 (REF.[61]), 2006 (REF.[166])	Hybrid functionals	Small polaron spin density
2006 (REF.[92])	Analytical approximation for the Green's function	Energy, mass, dispersion, spectral weight
2006 (REFS[117,118]), 2009 (REF.[313])	DFT+*U*	Small polaron migration, DOS, bipolaron
2007–2010 (REFS[68,69])	Multiscale modelling and kinetic Monte Carlo	Charge transport
2014 (REF.[151])	Random phase approximation	Small energy and hopping
2009 (REF.[62]), 2011 (REF.[132])	Generalized Koopmans' density functional	Small polarons states
2015 (REF.[64])	Density-functional perturbation theory	Fröhlich electron–phonon vertex
2016 (REF.[102])	Renormalization group (large polaron)	Energy, effective mass
2019 (REFS[13,70])	Ab initio theory of polarons	Formation and excitation energies wavefunction (small and large polarons)

Compendium of theoretical works in the study of polarons

Electron-phonon coupling in condensed matter: a very active (and rapidly evolving) field of research

from C. Franchini et al.,Nat. Rev. Mater. 6, 560 (2021)

The electron-phonon coupling



Bare potential:

$$v_{\mathrm{en}}(x,\{\tau_I\}) = -\frac{e^2}{4\pi\epsilon_0}\sum_{I=1}^{2}\sum_{p}^{N_p}\frac{Z_I}{|x-\tau_I|}$$

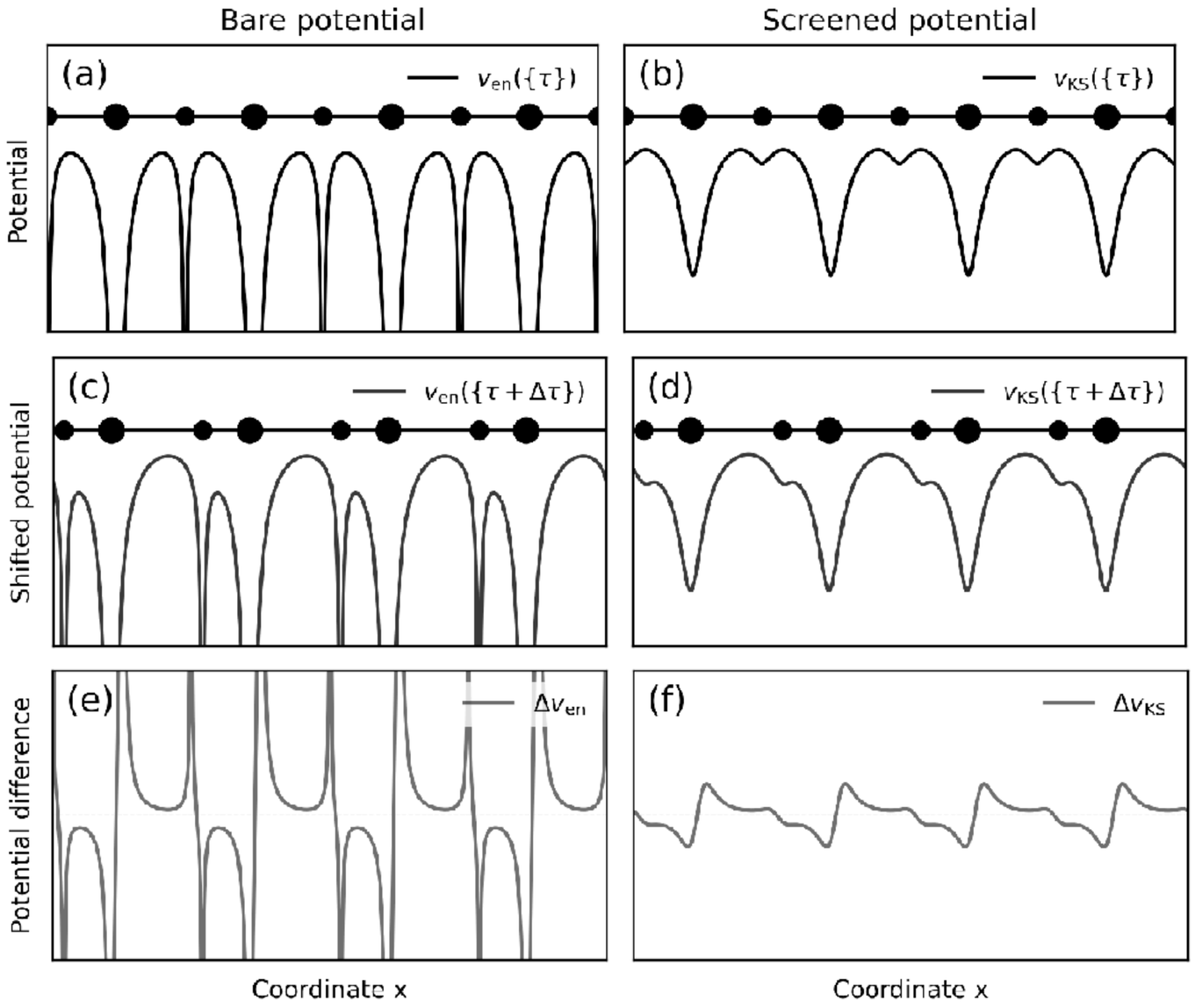
Total potential felt by electrons (**screened potential**):

$$v_{\mathrm{tot}}(x,\{\tau\}) = v_{\mathrm{en}}(x) + v_{\mathrm{eff}}(x)$$

displacement $\{\tau_I\} \rightarrow \{\tau_I + \Delta\tau_I\}$

$$\Delta v_{\mathrm{en}}(x) = v_{\mathrm{en}}(x,\{\tau_I+\Delta\tau_I\}) - v_{\mathrm{en}}(x,\{\tau_I\})$$

$$\Delta v_{\mathrm{tot}}(x) = v_{\mathrm{tot}}(x,\{\tau_I+\Delta\tau_I\}) - v_{\mathrm{tot}}(x,\{\tau_I\})$$



The electron-phonon coupling (EPC) Hamiltonian: DFT as a starting point

The Kohn-Sham equation $$\left[-\frac{\hbar^2\nabla^2}{2m} + v_{\mathrm{KS}}(\boldsymbol{r})\right]\psi_{n\boldsymbol{k}}(\boldsymbol{r}) = \varepsilon\psi_{n\boldsymbol{k}}(\boldsymbol{r})$$

… is a function of the coordinates: $$\hat{h}_{\mathrm{KS}} = -\frac{\hbar^2\nabla^2}{2m} + v_{\mathrm{KS}}(\boldsymbol{r}, \{\boldsymbol{\tau}\})$$

Change of potential due to a phonon: $$v_{\mathrm{KS}} \xrightarrow{\text{phonons}} v_{\mathrm{KS}} + \Delta v_{\mathrm{KS}}$$

Tailor expansion for small displacements: $$v_{\mathrm{KS}}(\mathbf{r}, \{\boldsymbol{\tau}\}) = v^{(0)}_{\mathrm{KS}}(\mathbf{r}) + v^{(1)}_{\mathrm{KS}}(\mathbf{r}) + v^{(2)}_{\mathrm{KS}}(\mathbf{r}) + \cdots$$

First-order EPI Hamiltonian:

$$\hat{H}^{(1)}_{\mathrm{eph}} = v^{(1)}_{\mathrm{KS}}(\mathbf{r}) = \sum_{\kappa p} \left.\frac{\partial v_{\mathrm{KS}}(\mathbf{r}, \{\boldsymbol{\tau}\})}{\partial \Delta\boldsymbol{\tau}_{\kappa p}}\right|_0 \cdot \Delta\boldsymbol{\tau}_{\kappa p}$$

Second-order EPI Hamiltonian:

$$\hat{H}^{(2)}_{\mathrm{eph}} = v^{(2)}_{\mathrm{KS}}(\mathbf{r}) = \frac{1}{2}\sum_{\kappa p}\sum_{\kappa' p'} \left.\frac{\partial^2 v_{\mathrm{KS}}(\mathbf{r}, \{\boldsymbol{\tau}\})}{\partial \Delta\boldsymbol{\tau}_{\kappa p}\partial \Delta\boldsymbol{\tau}_{\kappa' p'}}\right|_0 \Delta\boldsymbol{\tau}_{\kappa p}\Delta\boldsymbol{\tau}_{\kappa' p'}$$

The electron-phonon coupling (EPC) Hamiltonian: second quantization

$$\hat{H}^{(1)}_{\mathrm{eph}} = v^{(1)}_{\mathrm{KS}}(\mathbf{r}) = \sum_{\kappa p} \left.\frac{\partial v_{\mathrm{KS}}(\mathbf{r},\{\boldsymbol{\tau}\})}{\partial \boldsymbol{\Delta\tau}_{\kappa p}}\right|_0 \cdot \boldsymbol{\Delta\tau}_{\kappa p}$$

change of electronic potential
(acts on the Hilbert space of the electrons)

nuclear position operator
(acts on the Hilbert space of the nuclei)

Second quantization (phonon):

$$\boldsymbol{\Delta\tau}_{\kappa p} = \frac{1}{\sqrt{N_p}} \sum_{\mathbf{q}\nu} \mathbf{e}^{\kappa}_{\mathbf{q}\nu} \left(\frac{\hbar}{2M_\kappa \omega_{\boldsymbol{q}\nu}}\right)^{\frac{1}{2}} e^{i\mathbf{q}\mathbf{R}_p} \left(\hat{a}_{\mathbf{q}\nu} + \hat{a}^\dagger_{-\mathbf{q}\nu}\right)$$

expansion in a phonon basis

ladder operators

In the quantum harmonic oscillator:

$$\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (\hat{a} + \hat{a}^\dagger)$$

Second quantization (electorns):

$$\Delta_{\mathbf{q}\nu} v_{\mathrm{KS}}(\mathbf{r}) = \sum_{nm\boldsymbol{k}\boldsymbol{k}'} \langle \psi_{m\boldsymbol{k}'} | \Delta_{\mathbf{q}\nu} v_{\mathrm{KS}}(\mathbf{r}) | \psi_{n\boldsymbol{k}} \rangle_{\mathrm{SC}} \hat{c}^\dagger_{m\boldsymbol{k}'} \hat{c}_{n\boldsymbol{k}}$$

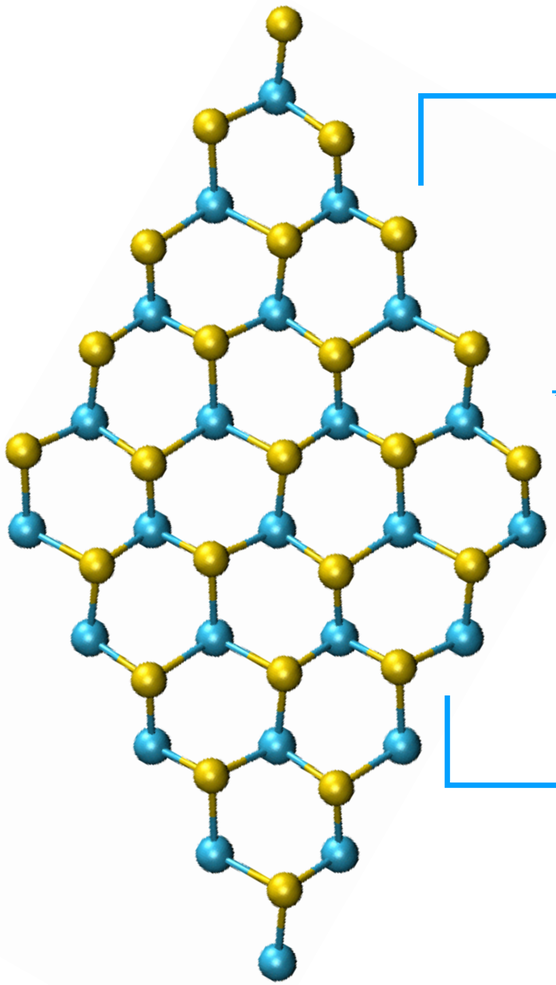
Electron-phonon coupling Hamiltonian:

$$\hat{H}^{(1)}_{\mathrm{eph}} = \frac{1}{\sqrt{N_p}} \sum_{\mathbf{q}\nu} \sum_{mn\boldsymbol{k}} g^{\nu}_{mn}(\boldsymbol{k},\boldsymbol{q}) \hat{c}^\dagger_{m\boldsymbol{k}+\boldsymbol{q}} \hat{c}_{n\boldsymbol{k}} \left(\hat{a}_{\mathbf{q}\nu} + \hat{a}^\dagger_{-\mathbf{q}\nu}\right)$$

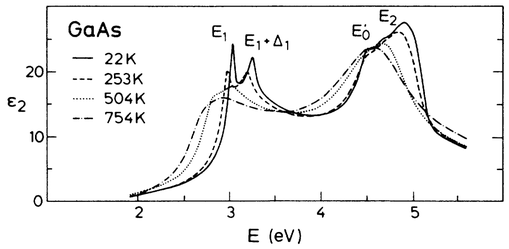
- EPC matrix element. $g^{\nu}_{mn}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta v_{\mathrm{eff}} | \psi_{n\mathbf{k}} \rangle$
- Phonon creation/annihilation operators $\hat{a}^\dagger_{\mathbf{q}\nu}, \hat{a}_{\mathbf{q}\nu}$
- Electron creation/annihilation operators $\hat{c}^\dagger_{n\mathbf{k}}, \hat{c}_{n\mathbf{k}}$

Derivation:
F. Giustino, Rev. Mod. Phys. **89**, 015003 (2017)

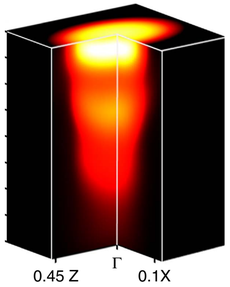
Outline



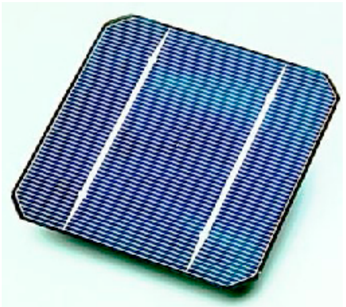
The temperature dependence of the band structure



Polaronic satellites in angle-resolved photoemission spectroscopy (ARPES)



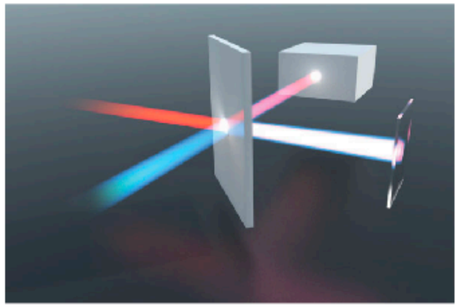
Phonon-assisted optical absorption in semiconductors



Part 1

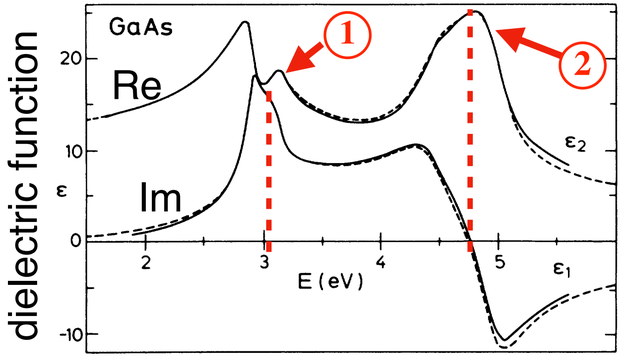
The temperature dependence of the band structure

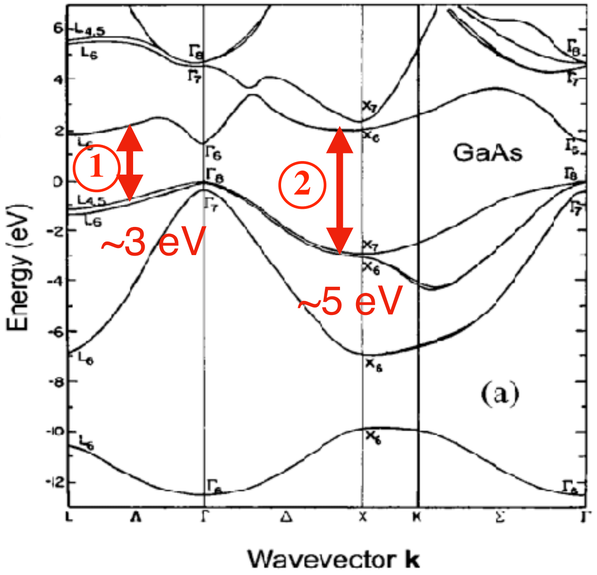
Temperature-depedent of optical measurements of semiconductors



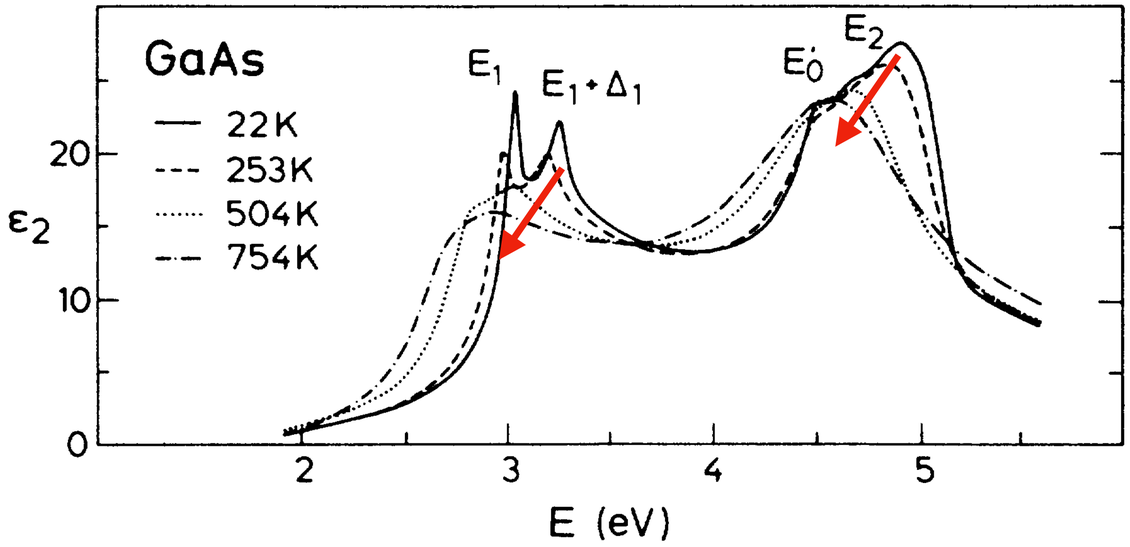
Signatures of electron-phonon coupling in optical measurements

Dielectric function of GaAs
(from ellipsometry measurement





Temperature dependence of the dielectric function



$$\mathrm{Im}\,\epsilon(\omega) \sim \mathrm{JDOS}(\omega) = N_k^{-1} \sum_{nm\mathbf{k}} \delta(\omega - (\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}}))$$

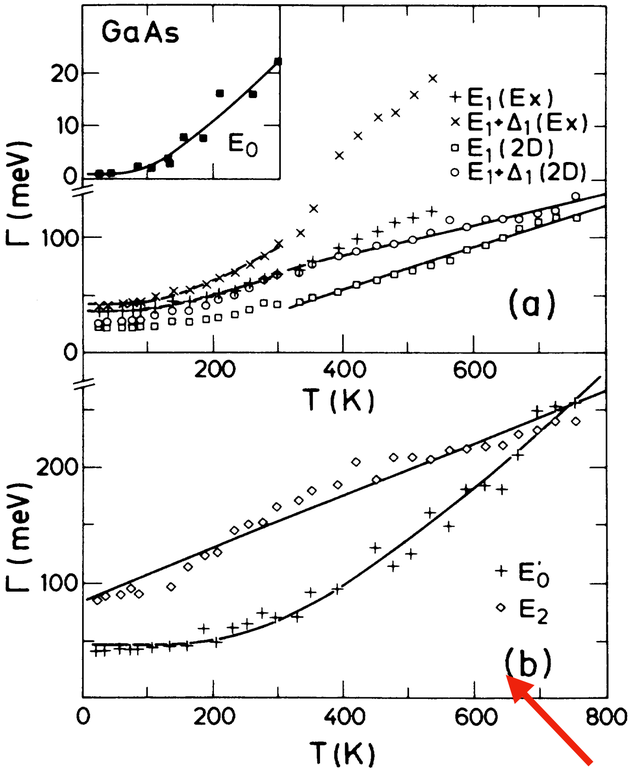
peaks in $\mathrm{Im}\,\epsilon$ → transitions from occupied to empty states

Temperature dependence of the band structure

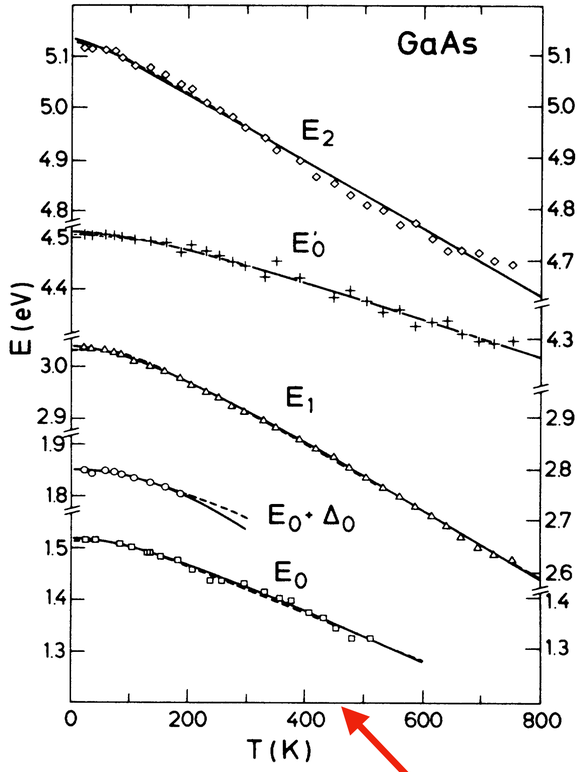
Lautenschlager et al., Phys. Rev. B **35**, 9173 (1987)

Temperature-depedent of optical measurements of semiconductors

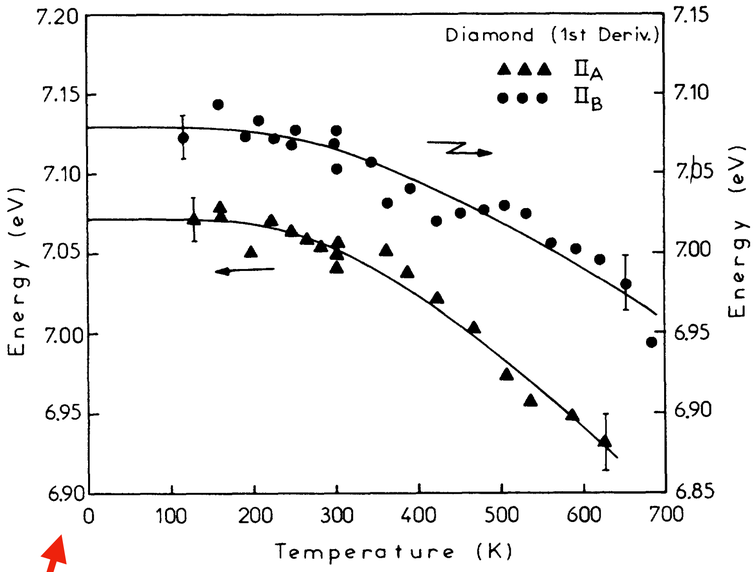
Peak broadening
(lifetime)



Critical points
(peaks in the Joint DOS)



Fundamental gap



Strong temperature dependent renormalization of the band structure

Temperature dependence

$$\Gamma(T)=\Gamma_1+\frac{\Gamma_0}{e^{\Theta/T}-1}$$

$$E(T)=E_B-a_B\left[1+\frac{2}{e^{\Theta/T}-1}\right]$$

- **Not explained by the thermal expansion (TE):**
  Measured shifts **~0.2 meV / K**
  Expected shifts (from TE) **~0.004 meV / K**
- **Depends on T as the Bose Einstein distribution**

Electron-phonon interaction

Lautenschlager et al., Phys. Rev. B **35**, 9173 (1987)
Logothetidis et al., Phys. Rev. B **46**, 4483 (1992)

Perturbative treatment of the electron-phonon interaction: the Fan-Migdal term

$$\hat{H}_{e-ph} = \sum_I \left.\frac{\partial v_{\text{eff}}}{\partial u_I}\right|_{u=0} u_I$$

electrons phonons

Hamiltonian: $\hat{H} = \hat{H}_0 + \Delta\hat{H}$

Perturbation: $\Delta\hat{H} \equiv \hat{H}_{e-ph}$

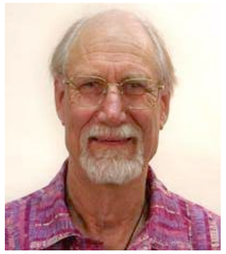
Rayleigh-Schrödinger perturbation theory

Perturbative expansion

$$\varepsilon_{n\mathbf{k}} = \varepsilon^{(0)}_{n\mathbf{k}} + \varepsilon^{(1)}_{n\mathbf{k}} + \varepsilon^{(2)}_{n\mathbf{k}} + \dots$$

$$\psi_{n\mathbf{k}} = \psi^{(0)}_{n\mathbf{k}} + \psi^{(1)}_{n\mathbf{k}} + \psi^{(2)}_{n\mathbf{k}} + \dots$$


Phil Allen


Volker Heine


Manuel Cardona

Allen-Heine-Cardona theory
- Apply second-order perturbation-theory to the electrons
- Treat the phonons via a thermal average

First-order perturbation theory

$$\varepsilon^{(1)}_{n\mathbf{k}} = \langle\psi^{(0)}_{n\mathbf{k}}|\hat{H}_{e-ph}|\psi^{(0)}_{n\mathbf{k}}\rangle = 0 \quad \leftarrow \langle u_I\rangle_T = 0$$

$\langle u_I\rangle_T$ average displacement at temperature T

Second-order perturbation theory

$$\varepsilon^{(2)}_{n\mathbf{k}} = \sum_{m\neq n}\sum_{\mathbf{q}} \frac{|\langle\psi^{(0)}_{m\mathbf{k}+\mathbf{q}}|\hat{H}_{e-ph}|\psi^{(0)}_{n\mathbf{k}}\rangle|^2}{\varepsilon^{(0)}_{n\mathbf{k}} - \varepsilon^{(0)}_{m\mathbf{k}+\mathbf{q}}} \quad \leftarrow \langle u_I^2\rangle_T \neq 0$$

$\langle u_I^2\rangle_T$ mean squared displacement

... some algebra:

$$\varepsilon^{\text{FM}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu}\sum_{m\neq n} |g^{\nu}_{mn}(\mathbf{k},\mathbf{q})|^2 \frac{2n_{\mathbf{q}\nu}(T)+1}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}}$$

Fan-Migdal term
Phonon-assisted renormalization of the electron energy levels

Perturbative treatment of the electron-phonon interaction: the Debye-Waller term

$$v_{\text{eff}}(\{R_I + u_I\}) = v_{\text{eff}}(\{R_I\}) + \Delta^{(1)} v_{\text{eff}} + \Delta^{(2)} v_{\text{eff}} + \dots$$

Debye-Waller term

quadratic change of v_{eff} treated at 1st order in perturbation theory — **... also quadratic in the perturbation**

linear change of v_{eff} treated at 2nd order in perturbation theory — **quadratic dependence on the phonon displacement (the perturbation)**

Fan-Migdal term

Debye-Waller term

$$\varepsilon_{n\mathbf{k}}^{\text{DW}} = \langle \psi_{n\mathbf{k}}^{(0)} | \Delta^{(2)} v_{\text{eff}} | \psi_{n\mathbf{k}}^{(0)} \rangle$$

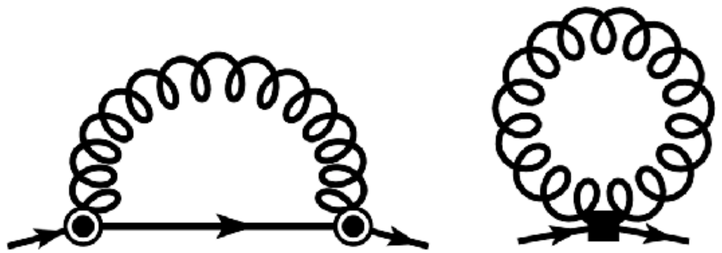
some algebra →

second-order

$$\Delta\varepsilon_{n\mathbf{k}}^{(2),\text{DW}} = \frac{1}{N_p} \sum_{\mathbf{q}\nu} \tilde{g}_{nn}^{\nu\nu}(\mathbf{k}, \mathbf{q}, -\mathbf{q})(2n_{\mathbf{q}\nu} + 1)$$

Temperature dependence of the band structure in Allen-Heine-Cardona theory

$$\Delta\varepsilon_{n\mathbf{k}}^{\text{AHC}} = \Delta\varepsilon_{n\mathbf{k}}^{\text{FM}}(T) + \Delta\varepsilon_{n\mathbf{k}}^{\text{DW}}(T)$$



Review: X. Gonze et al., Ann. Phys. (Berlin) 523, 168 (2011)

Temperature-dependence of the AHC correction to the bands and zero-point motion renormalization

$$\Delta\varepsilon_{n\mathbf{k}}^{\mathrm{AHC}} = \Delta\varepsilon_{n\mathbf{k}}^{\mathrm{FM}}(T) + \Delta\varepsilon_{n\mathbf{k}}^{\mathrm{DW}}(T)$$

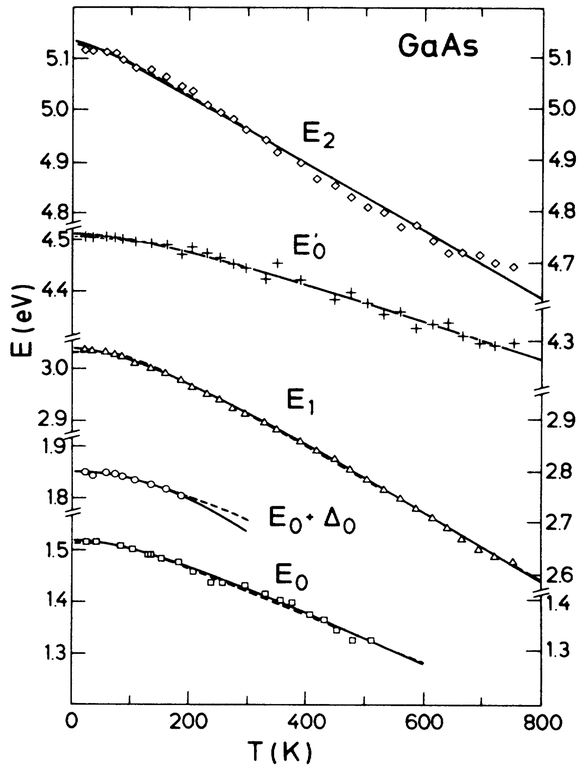
$$\varepsilon_{n\mathbf{k}}^{\mathrm{FM}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu}\sum_{m\neq n} |\, g_{mn}^{\nu}(\mathbf{k},\mathbf{q})\,|^2 \frac{2n_{\mathbf{q}\nu}(T)+1}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}} \qquad \varepsilon_{n\mathbf{k}}^{\mathrm{DW}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu} \tilde{g}_{nn}^{\nu\nu}(\mathbf{k},\mathbf{q},-\mathbf{q})(2n_{\mathbf{q}\nu}+1)$$

Consider a materials with only one vibrational frequency ($n_{\mathbf{q}\nu}(T) \simeq n(T)$):

number of phonons at temperature T

$$\varepsilon_{n\mathbf{k}}^{\mathrm{FM}} = [2n(T)+1]\frac{1}{N_p}\sum_{m\neq n} |\, g_{mn}^{\nu}(\mathbf{k},\mathbf{q})\,|^2 \frac{1}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}} = \alpha[2n(T)+1]$$

$$E(T) = E_B - a_B\left[1 + \frac{2}{e^{\Theta/T}-1}\right]$$



① Fully captures the temperature-dependence of bands determined in experiments.

② At T=0, $n(T) = 0$ however $\varepsilon_{n\mathbf{k}}^{\mathrm{AHC}} \neq 0$

Renormalization of the bands even in absence of phonons

Zero-point motion effect (purely quantum)

The Allen-Heine-Cardona theory in ab-initio calculations

$$\Delta\varepsilon^{\mathrm{AHC}}_{n\mathbf{k}} = \Delta\varepsilon^{\mathrm{FM}}_{n\mathbf{k}}(T) + \Delta\varepsilon^{\mathrm{DW}}_{n\mathbf{k}}(T)$$

$$\varepsilon^{\mathrm{FM}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu}\sum_{m\neq n} |\, g^{\nu}_{mn}(\mathbf{k},\mathbf{q})\,|^2 \frac{2n_{\mathbf{q}\nu}(T)+1}{\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}}} \qquad \varepsilon^{\mathrm{DW}}_{n\mathbf{k}} = \frac{1}{N_p}\sum_{\mathbf{q}\nu} \tilde{g}^{\nu\nu}_{nn}(\mathbf{k},\mathbf{q},-\mathbf{q})(2n_{\mathbf{q}\nu}+1)$$

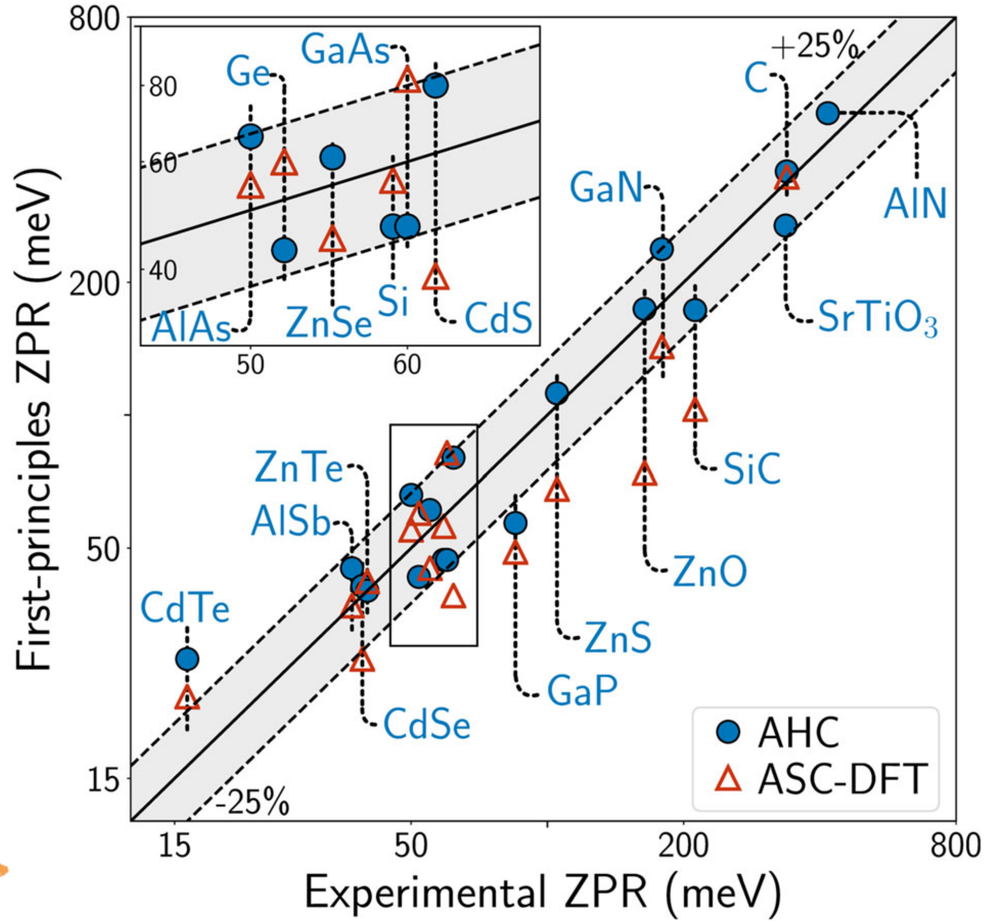
- $g^{\nu}_{mn}(\mathbf{k},\mathbf{q})$: electron-phonon matrix elements → from DFPT
- $\varepsilon_{n\mathbf{k}}$: single particle energy → from DFT
- $n_{\mathbf{q}\nu}(T) = [e^{\hbar\omega_{\mathbf{q}\nu}/k_BT} - 1]^{-1}$: Bose-Einstein distribution

Fully ab-initio have only "recently" become accessible

- Calculations require very dense grids to sample the integrals over the Brillouin zone (denser than 30×30×30)
- Interpolation using Maximally-localized Wannier function is required for $g^{\nu}_{mn}(\mathbf{k},\mathbf{q})$

Available in many ab-initio codes:

EPW, exciting, Yambo, Abinit



Miglio, et al., npj Comput. Mater. **6**, 167 (2020)

Marzari et al., Rev. Mod. Phys. **84**, 1419 (2012)
Giustino et al., Phys. Rev. B **76**, 165108 (2007)

Many-body perturbation theory (MPBT) of electron-phonon coupling

Consider a perturbation acting on the electron Hamiltonian : $\hat{H}^{el} = \hat{H}_0^{el} + \Delta\hat{V}$

Consider a perturbation acting on the **lattice** Hamiltonian : $\hat{H}^{ph} = \hat{H}_0^{ph} + \Delta\hat{V}$

Electron Green's function

$$G_{ij}(t_1, t_2) = -i\hbar^{-1}\langle\Psi\,|\,\hat{T}[\hat{\psi}_i(t_1)\hat{\psi}_j^{\dagger}(t_2)]\,|\,\Psi\rangle$$

$\|\Psi\rangle$:	electron ground-state wave function
$\hat{\psi}^{\dagger}, \hat{\psi}$:	creation/annihilation operators
$\hat{T}$:	Wick's time-ordering operator

Phonon Green's function

$$D_{\alpha\beta}(t_1, t_2) = -i\hbar^{-1}\langle\Phi\,|\,\hat{T}\Delta\hat{\tau}_{\alpha}(t_1)\Delta\hat{\tau}_{\beta}(t_2)\,|\,\Phi\rangle$$

$\|\Phi\rangle$:	**phonon** ground-state wave function
$\Delta\hat{\tau}_{\alpha}$:	displacement operator
$\hat{T}$:	Wick's time-ordering operator

Direct access to physical properties (spectral function, observables, total energy, ect)

Formally exact treatment of the perturbation

G: the (exact) Green's function.

G_0: the non-interacting Green's function.

Σ: the electron self-energy

The Dyson equation

$$G = G_0 + G_0\Sigma G$$

coupled by the electron-phonon interactions

Perturbative treatment of the phonon Green's function

D: the (exact) **phonon** Green's function.

D_0: the non-interacting **phonon** Green's function.

$\Pi^{(na)}$: the non-adiabatic phonon self-energy

The Dyson equation

$$D = D_0 + D_0\Pi^{(na)}D$$

Exact self-consistent equations for the electron and phonon Green's functions

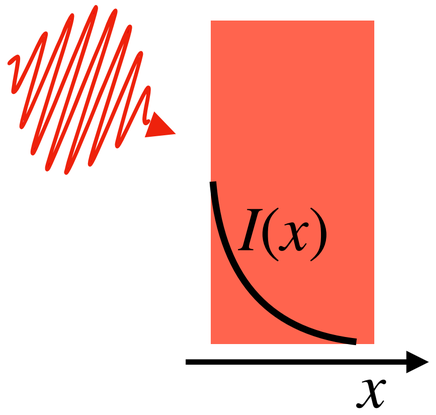
Description	Expression
Electronic charge density	$\langle \hat{n}_{\mathrm{e}}(1) \rangle = -i\hbar \sum_{\sigma_1} G(11^+)$
Nuclear charge density	$\langle \hat{n}_{\mathrm{n}}(\mathbf{r}t) \rangle = n^0_{\mathrm{n}}(\mathbf{r}) - (i\hbar/2) \sum_{\kappa p, \alpha\alpha'} Z_\kappa \partial^2 \delta(\mathbf{r} - \boldsymbol{\tau}^0_{\kappa p}) / \partial r_\alpha \partial r_{\alpha'} D_{\kappa\alpha p, \kappa\alpha' p}(t^+ t)$
Total electrostatic potential	$V_{\mathrm{tot}}(1) = \int d2 v(12) [\langle \hat{n}_{\mathrm{e}}(2) \rangle + \langle \hat{n}_{\mathrm{n}}(2) \rangle]$
Equation of motion, electrons	$[i\hbar \partial/\partial t_1 + (\hbar^2/2m_{\mathrm{e}}) \nabla^2(1) - V_{\mathrm{tot}}(1)] G(12) - \int d3 \Sigma(13) G(32) = \delta(12)$
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	$\Sigma(12) = i\hbar \int d(34) G(13) \Gamma(324) [W_{\mathrm{e}}(41^+) + W_{\mathrm{ph}}(41^+)]$
Screened Coulomb, electrons	$W_{\mathrm{e}}(12) = v(12) + \int d(34) v(13) P_{\mathrm{e}}(34) W_{\mathrm{e}}(42)$
Electronic polarization	$P_{\mathrm{e}}(12) = -i\hbar \sum_{\sigma_1} \int d(34) G(13) G(41^+) \Gamma(342)$
Electronic dielectric matrix	$\epsilon_{\mathrm{e}}(12) = \delta(12) - \int d(3) v(13) P_{\mathrm{e}}(32)$
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	$W_{\mathrm{ph}}(12) = \sum_{\kappa\alpha p, \kappa' \alpha' p'} \int d(34) \epsilon^{-1}_{\mathrm{e}}(13) \nabla_{3,\alpha} V_\kappa(\mathbf{r}_3 - \boldsymbol{\tau}^0_{\kappa p}) \times D_{\kappa\alpha p, \kappa' \alpha' p'}(t_3 t_4) \epsilon^{-1}_{\mathrm{e}}(24) \nabla_{4,\alpha'} V_{\kappa'}(\mathbf{r}_4 - \boldsymbol{\tau}^0_{\kappa' p'})$
Phonon self-energy	$\Pi_{\kappa\alpha p, \kappa' \alpha' p'}(\omega) = \sum_{\kappa'' p''} Z_\kappa Z_{\kappa''} (\partial^2/\partial r_\alpha \partial r'_{\alpha'}) \times [\delta_{\kappa' p', \kappa'' p''} W_{\mathrm{e}}(\mathbf{r}, \mathbf{r}', \omega) - \delta_{\kappa p, \kappa' p'} W_{\mathrm{e}}(\mathbf{r}, \mathbf{r}', 0)]_{\mathbf{r} = \boldsymbol{\tau}^0_{\kappa p}, \mathbf{r}' = \boldsymbol{\tau}^0_{\kappa'' p''}}$

Giustino, Rev. Mod. Phys. (2017)

Part 3

Phonon-assisted optical absorption in semiconductors

Optical absorption in semiconductors

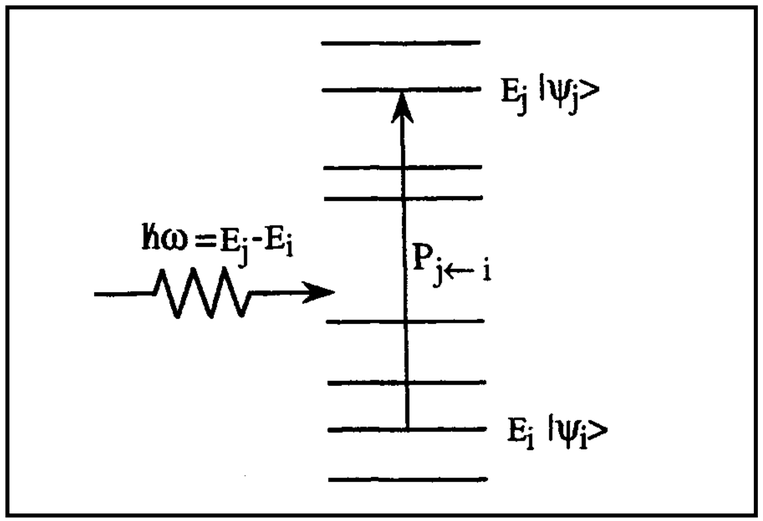


Intensity of radiation propagating through the sample

$$I(\omega, x) = I_0\, e^{-\alpha(\omega)x}$$

α : absorption coefficient

Quantum picture of the absorption process



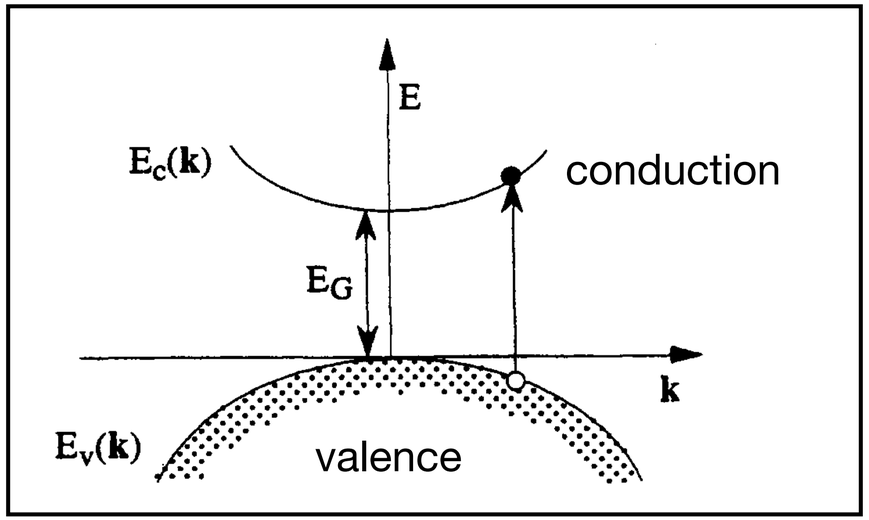
Why is it important?

- powerful characterization technique
- fundamental principle underlying solar energy conversion

In this lecture:
What is the role of phonons in the absorption of light in solids?

Phonon-assisted optical absorption in semiconductors

(direct) optical absorption



The absorption coefficient:

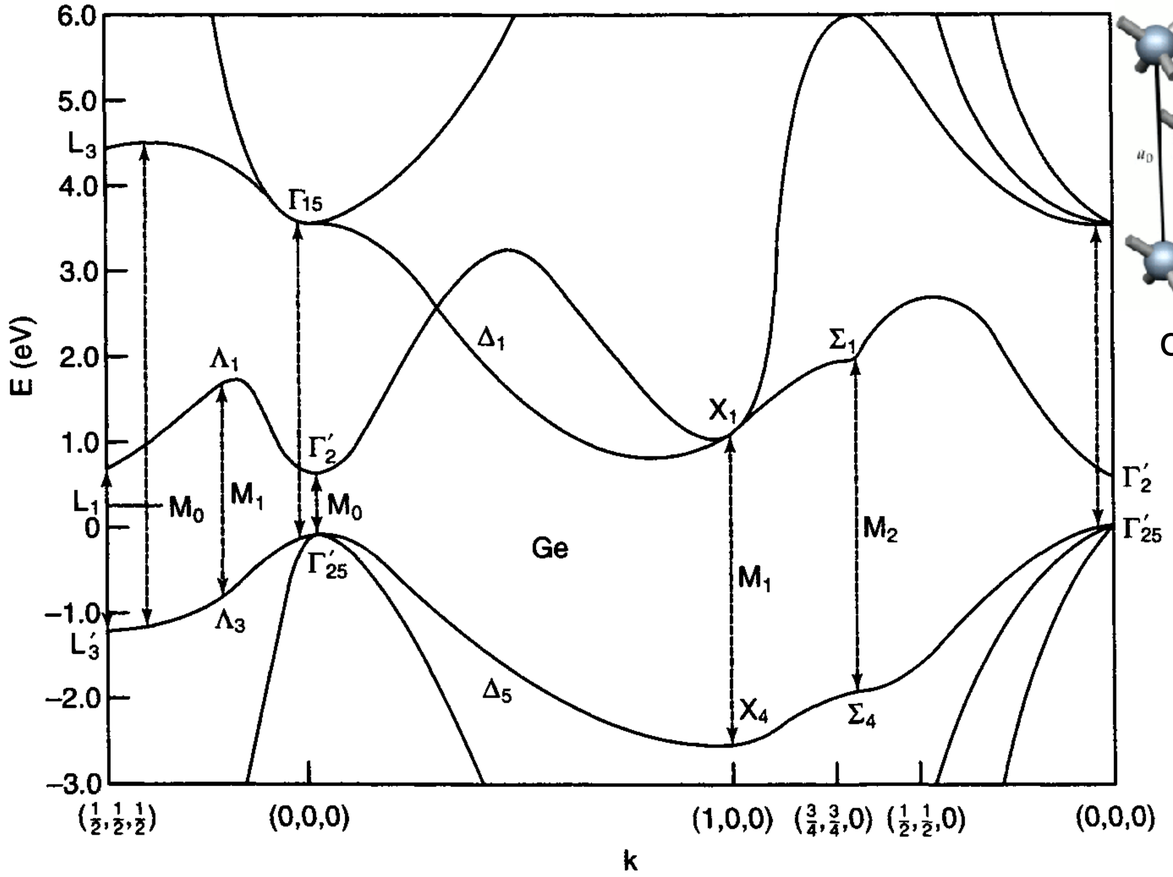
$$\alpha(\omega) = \frac{\omega}{c\, n(\omega)} \varepsilon_2(\omega)$$

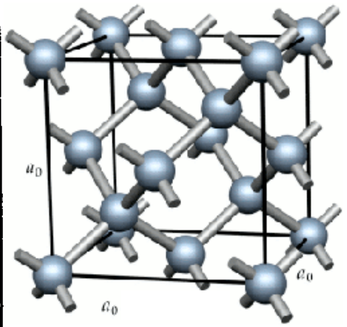
speed of light

refractive index

dielectric fn.

Band structure of Germanium





diamond-like structure

Brust et al., Phys. Rev. Lett **9**, 94 (1962)

Theory optical absorption in the indipendent particle approximation

In presence of an electromagnetic field: $\mathbf{p} \rightarrow \mathbf{p} - e \cdot \mathbf{A}$ (Peierls substitution)

Kinetic energy: $$\hat{T} = \frac{p^2}{2m} \rightarrow \frac{(p - e\mathbf{A})^2}{2m} = \frac{p^2}{2m} - \frac{e\mathbf{p} \cdot \mathbf{A}}{m} + \frac{e^2 A^2}{2m}$$

Perturbation: $$\hat{H}_{e-light} = -\, e\mathbf{p} \cdot \mathbf{A}/m$$

Fermi golden rule: $$\Gamma = \frac{2\pi}{\hbar} \sum_{in,fin} |\langle \Psi_{fin} | \hat{H}_{int} | \Psi_{in} \rangle|^2 \delta(E_{fin} - E_{in})$$

proportional to the absorption coefficient

Phonon-assisted optical absorption in semiconductors

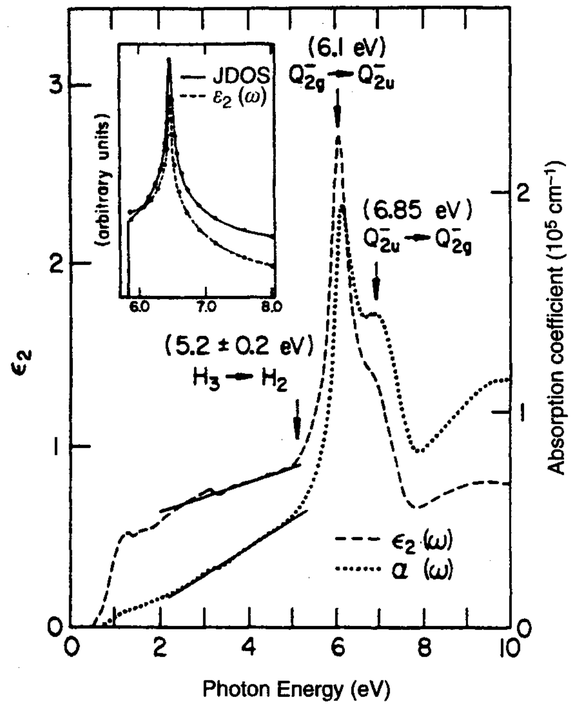
The absorption coefficient:

$$\alpha(\omega) = \frac{\omega}{c\, n(\omega)} \varepsilon_2(\omega)$$

speed of light

refractive index

dielectric fn.



Hoffman et al., Phys. Rev. B **30**, 6051 (1984)

The dielectric function independent particle approximation (IPA):

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{m^2\omega^2} \frac{1}{V} \sum_{cv} \sum_{\mathbf{k}} |\langle \psi_{c\mathbf{k}} | \mathbf{e}\cdot\mathbf{p} | \psi_{v\mathbf{k}} \rangle|^2 \, \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

matrix elements of the momentum operator

delta function for energy conservation

$\langle \psi_{c\mathbf{k}} | \mathbf{e}\cdot\mathbf{p} | \psi_{v\mathbf{k}} \rangle$: typically a slowly varying function

The joint density of states:

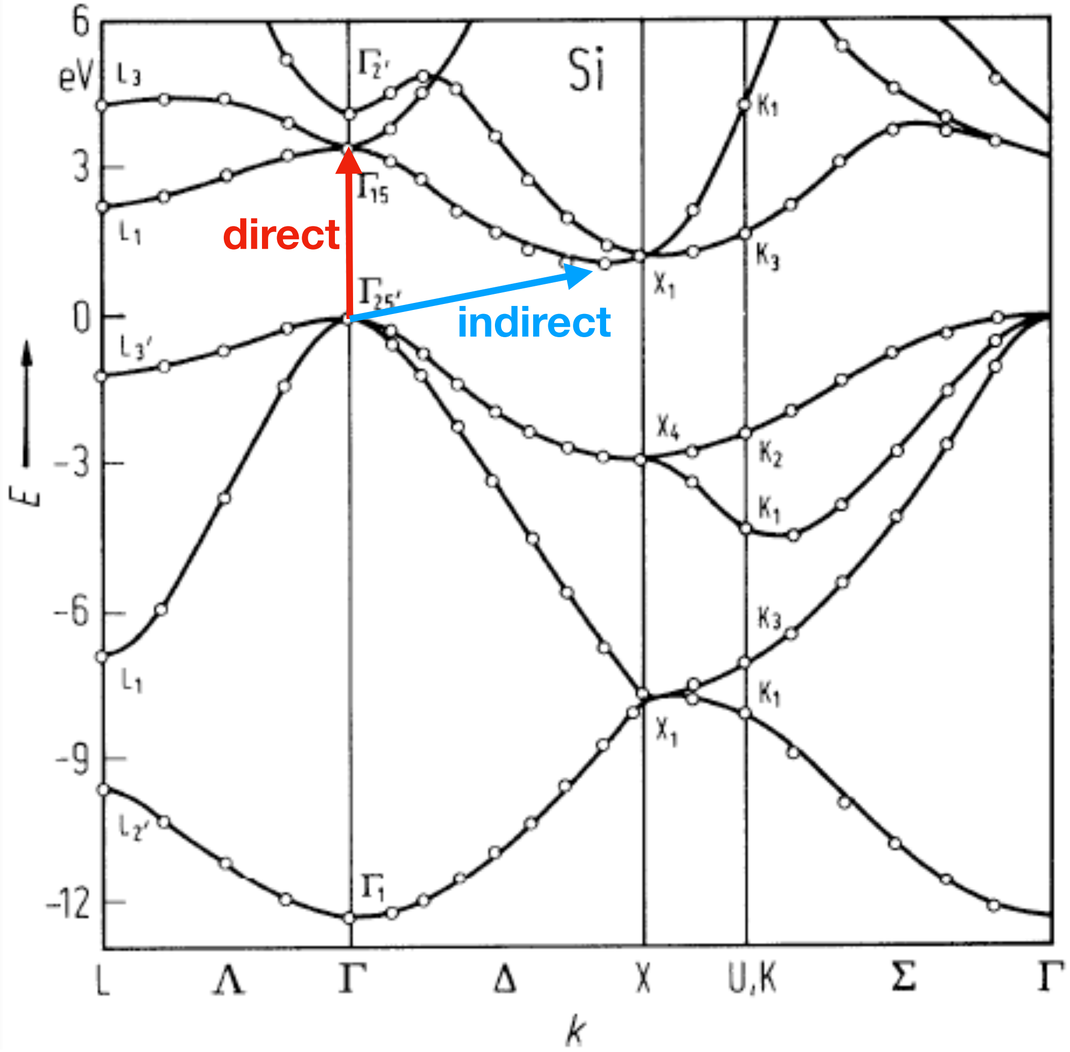
$$J_{cv}(\omega) = \int_{B.Z.} \frac{d\mathbf{k}}{(2\pi)^3} \, \delta(E_{c\mathbf{k}} - E_{v\mathbf{k}} - \hbar\omega)$$

1. Structures in the absorption spectrum arise from peaks in the joint DOS
(exceptions: excitons, phonon assisted transitions)

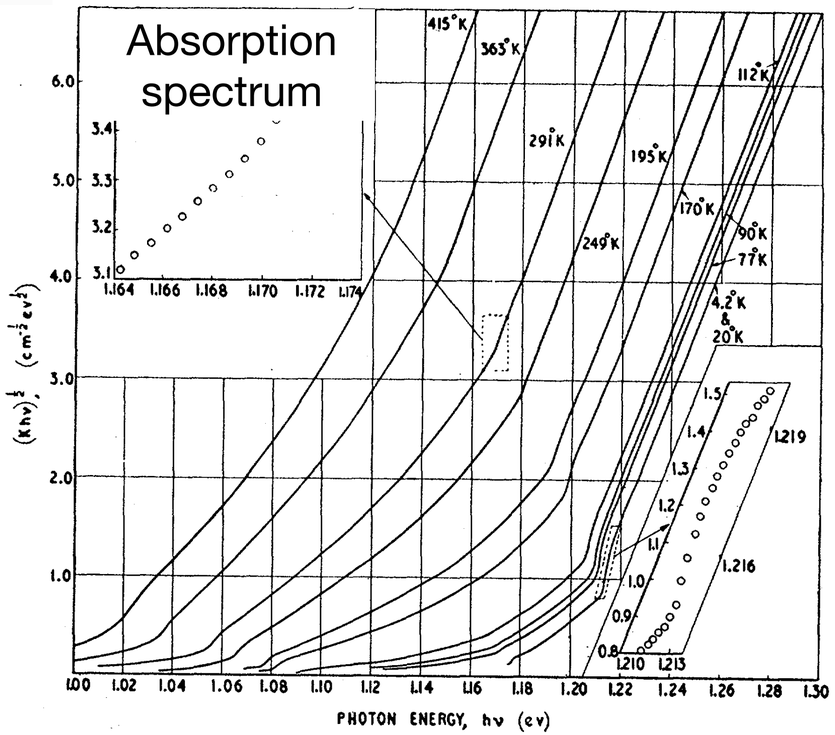
2. No absorption for photon energies smaller than the band gap (exceptions: excitons)

Optical absorption in INDIRECT-gap semiconductors: silicon

Band structure



Direct band gap: 3.5 eV **= minimum energy for direct transitions**
Indirect band gap: 1.12 eV



Absorption of light occurs already for energy comparable with the indirect gap.

With strong temperature dependence (phonons?)

$1.0 < E < 1.3$ eV

Due to momentum conservation: only possible if a phonon is absorbed or emitted in the absorption process

Phonon assisted optical absorption

Macfarlane et al., Phys. Rev. **111**, 1245 (1958)

Phonon-assisted optical absorption in semiconductors

$$\hat{H} = \hat{H}_{el} + \hat{H}_{e-ph} + \hat{H}_{e-light} = \hat{H}_{el} + \hat{H}_{int}$$

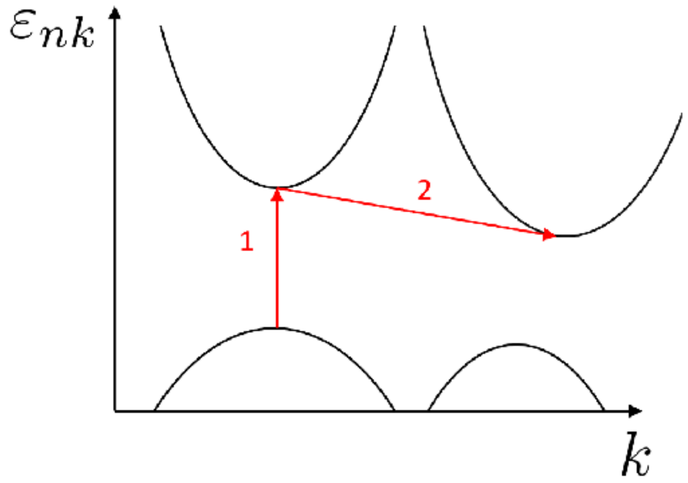
Fermi golden rule

$$\Gamma = \frac{2\pi}{\hbar} \sum_{in,fin} |\langle \Psi_{fin} | \hat{H}_{int} | \Psi_{in} \rangle|^2 \delta(E_{fin} - E_{in})$$

One perturbation at a time. Either:
(i) light-absorption OR (ii) electron-scattering due to phonon absorption
Insufficient!!

Second order Fermi golden rule:

$$\Gamma = \frac{2\pi}{\hbar} \left| \sum_{n} \frac{\langle \Psi_{fin} | H_{int} | \Psi_n \rangle \langle \Psi_n | H_{int} | \Psi_{in} \rangle}{E_{in} - E_n + i\eta} \right|^2 \delta\left(E_{fin} - E_{in}\right)$$



Phonon-assisted indirect optical absorption (emission)

Two possible processes:

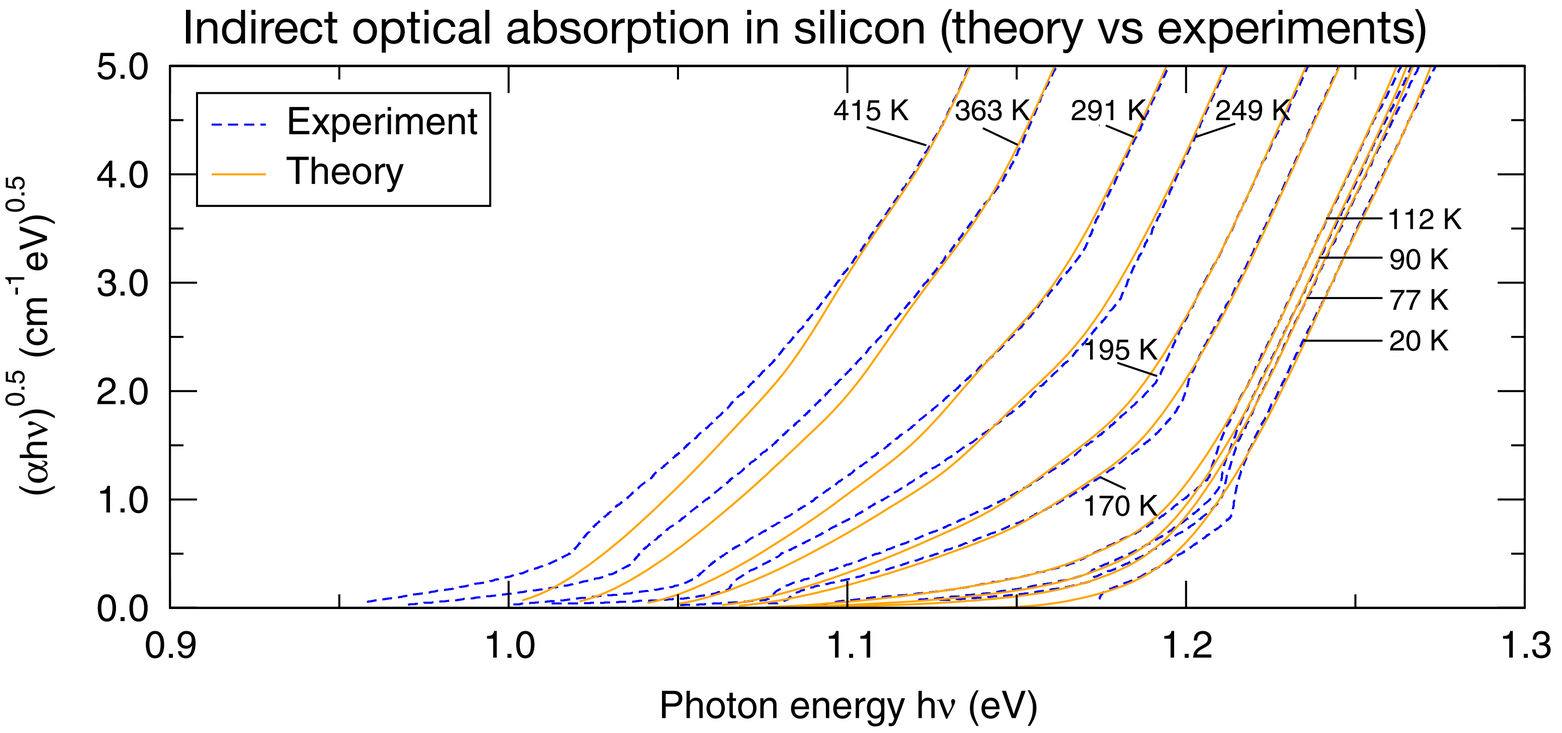
1. One photon absorbed (emitted) & one phonon is absorbed
2. One photon absorbed (emitted) & one phonon is emitted

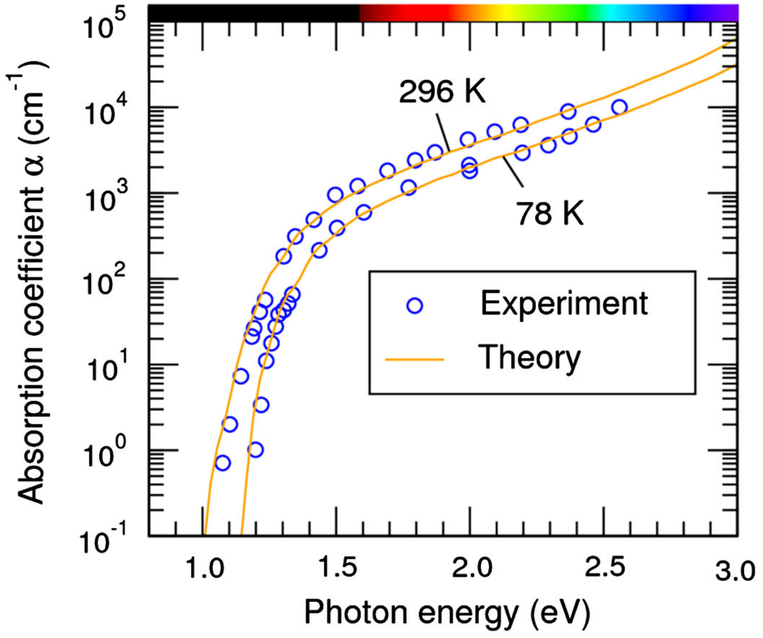
Theory: 2nd order Fermi golden rule + electron-phonon coupling

$$\alpha(\omega) = 2\frac{4\pi^2 e^2}{\omega c n_r(\omega)}\frac{1}{V_{\text{cell}}}\frac{1}{N_k N_q}\sum_{\nu ijkq}|\boldsymbol{\lambda}\cdot(\boldsymbol{S}_1+\boldsymbol{S}_2)|^2\ '\delta(\epsilon_{j,k+q}-\epsilon_{ik}-\hbar\omega\pm\hbar\omega_{\nu q})$$

generalized matrix elements

delta function for energy conservation



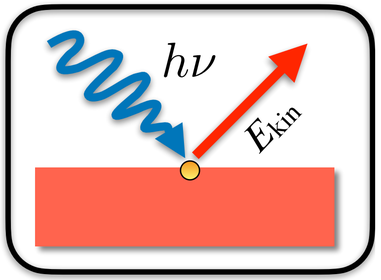


Noffsinger et al., Phys. Rev. Lett. **108**, 167402 (2012)

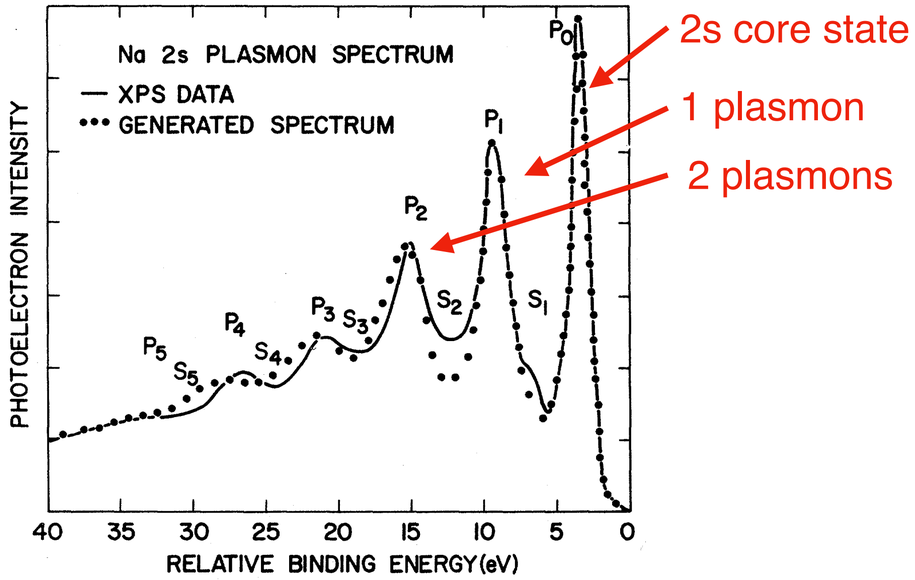
Part 2

Polaronic satellites in angle-resolved photoemission spectroscopy (ARPES)

Satellites in photoemission: a hallmark of electron-boson interaction

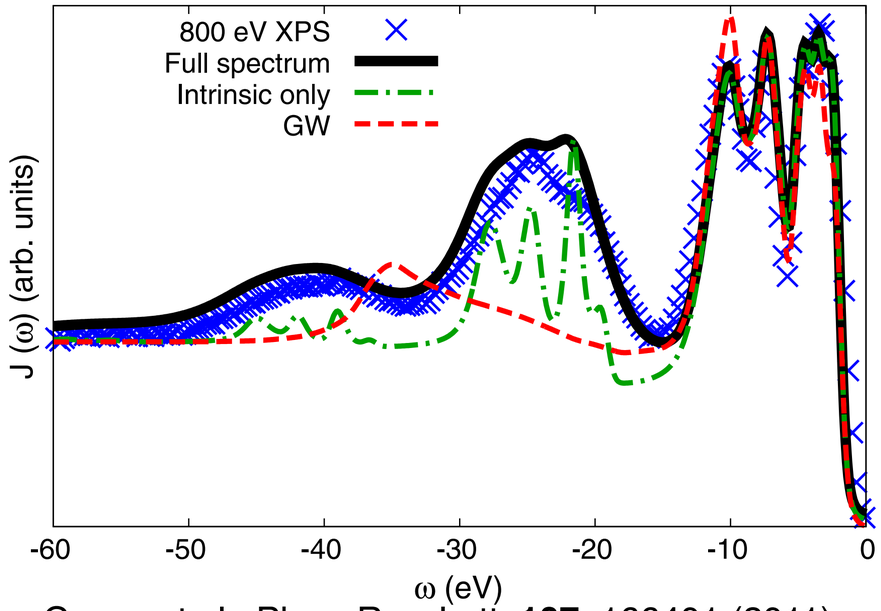


Metals



Pardee et al., Phys. Rev. B **11**, 3614 (1975)

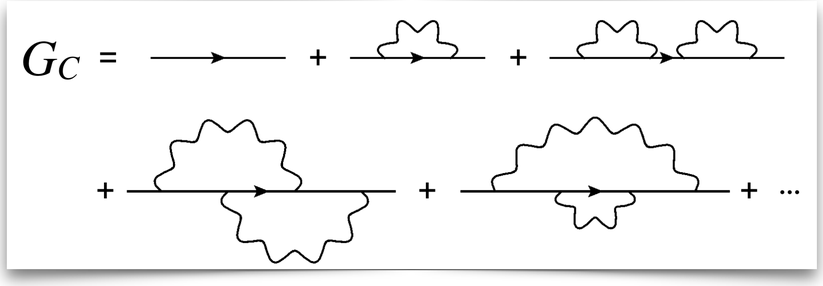
Semiconductors



Guzzo et al., Phys. Rev. Lett. **107**, 166401 (2011)

A strong stimulus for the development of (ab-initio) theories of the electron-boson interaction

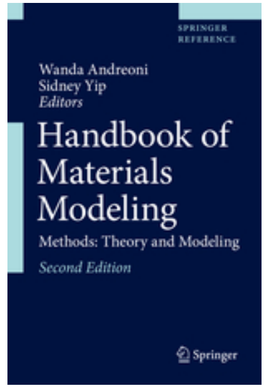
Example: the cumulant expansion approach



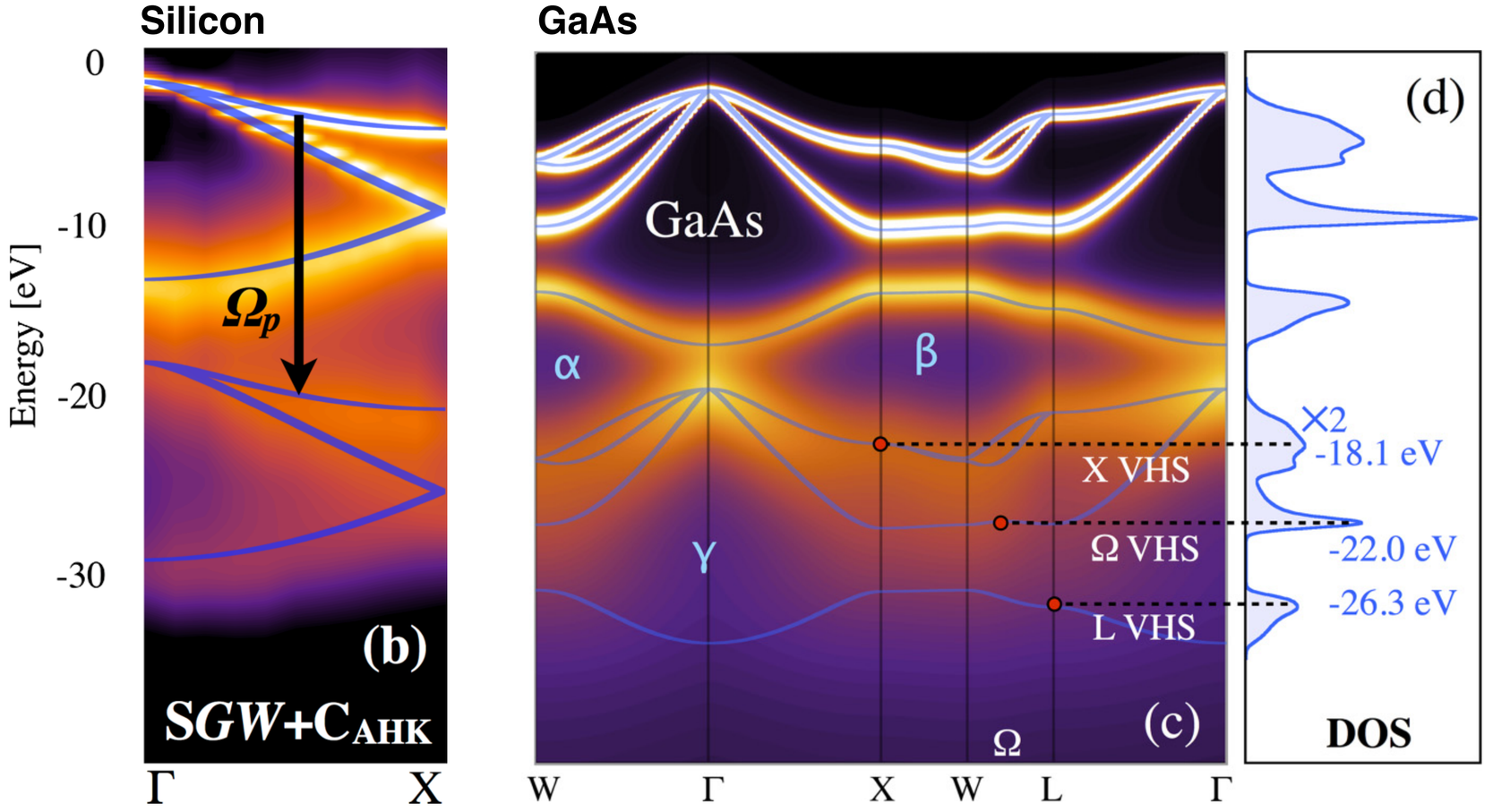
Cumulant representation of the spectral function

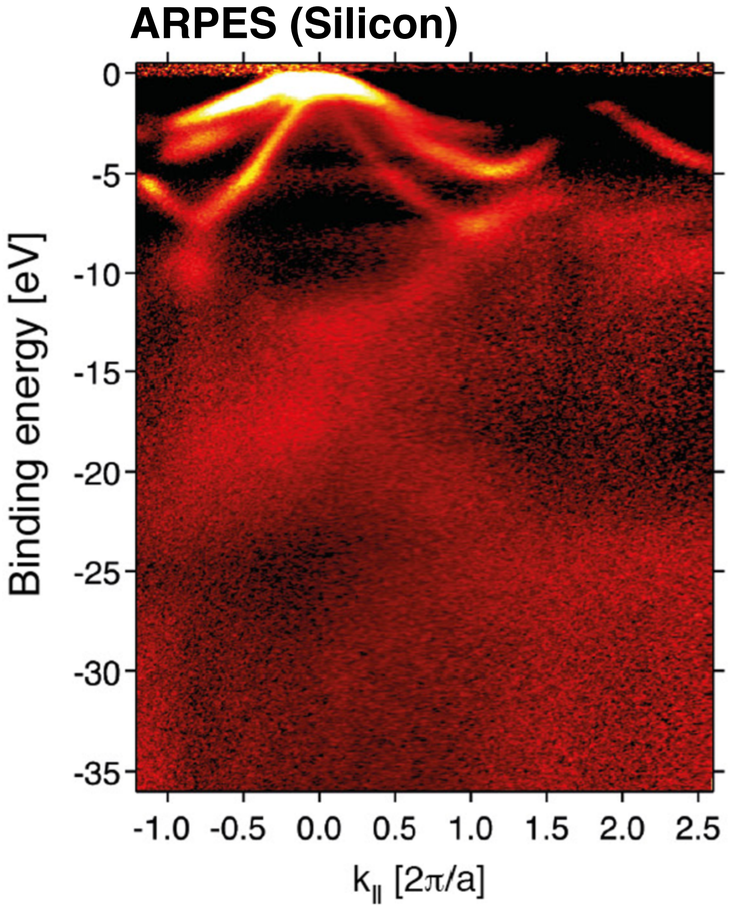
$$A(\mathbf{k},\omega) = \sum_n e^{A^{\mathrm{S1}}_{n\mathbf{k}}(\omega)} * A^{\mathrm{QP}}_{n\mathbf{k}}(\omega)$$

Caruso, Verdi, Giustino,
Handbook of Materials Modeling
Springer (2018)



Band structures of plasmonic polarons



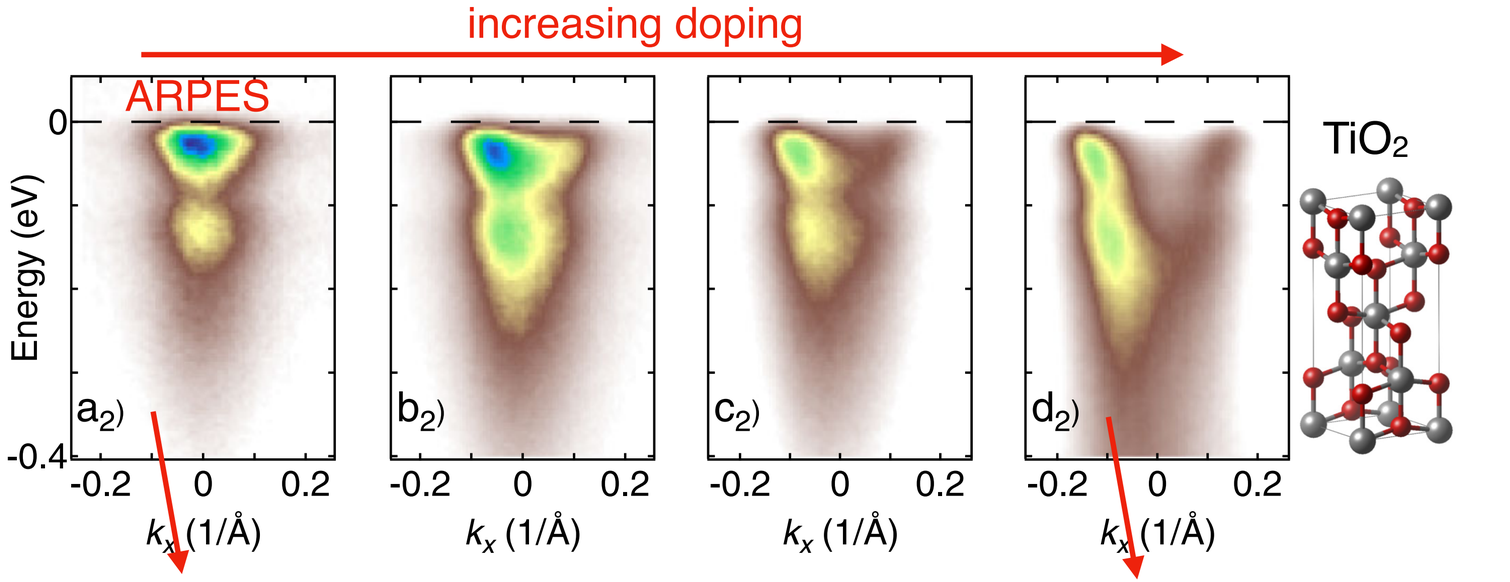


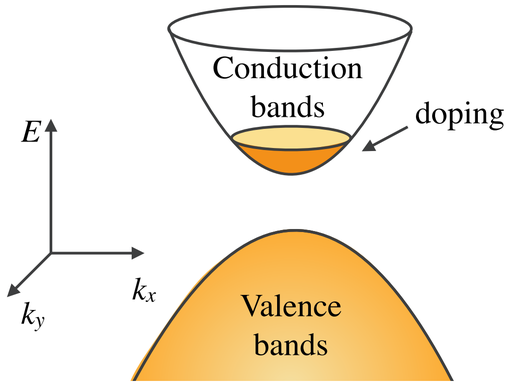
Full replicas of the band structure due to the electron-plasmon interactions

Caruso et al., Phys. Rev. Lett. **114**, 146404 (2015)
Caruso et al., Phys. Rev. B, **92**, 045123 (2015)

Lischner et al., Phys. Rev. B, **91,** 205113 (2015)

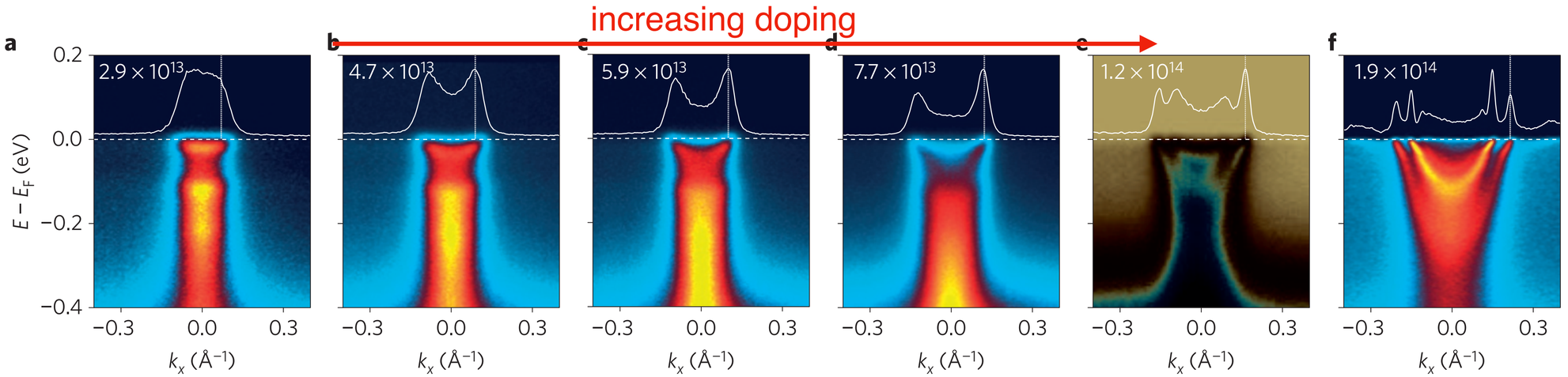
Satellites due to the electron-phonon coupling: highly-doped polar semiconductors



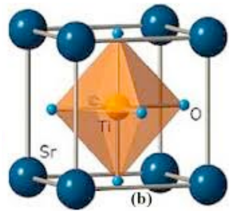


Moser et al., Phys. Rev. Lett. **110,** 196403 (2013)

What is the origin of polaronic satellites?
What is the influence of doping?



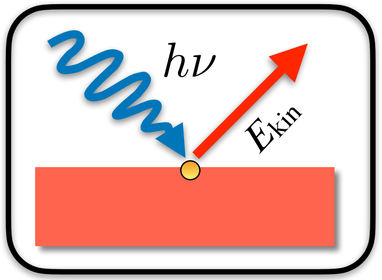
2D electron gas
at the surface of $SrTiO_3$



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

First-principles theory of photoemission spectroscopy

photoemission spectroscopy



Photoelectron current (Fermi's golden rule):

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

final state · perturbation · initial state · energy conservation

$$= \sum_{ij} \Delta_{\mathbf{k}j} A_{ji}(\varepsilon_k - \omega) \Delta_{i\mathbf{k}}$$

[1] sudden approximation

Spectral function

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

Migdal (diagonal) approximation:

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

Phonons: $\omega^{\mathrm{b}}_{\mathbf{q}\nu} = \omega_{\mathbf{q}\nu}$

$$g^{\text{e-ph}}_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \partial_{\mathbf{q}\nu} V | \psi_{n\mathbf{k}} \rangle$$

C. Verdi, F. Giustino, Phys. Rev. Lett. **115**, 176401(2015)

Fröhlich (polar) coupling:

$$g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q}) \propto \sum_{\kappa} \frac{\mathbf{Z}^*_{\kappa} \cdot \mathbf{e}_{\kappa\nu}(\mathbf{q})}{(\mathbf{q}+\mathbf{G})}$$

Electron-Phonon coupling with Wannier function (EPW)

Electron-boson coupling self-energy (Fan-Migdal):

$$\Sigma_{n\mathbf{k}}(\omega) = \frac{1}{N_{\mathbf{q}}} \sum_{m\nu\mathbf{q}} |g^{\text{e-b}}_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \left[\frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} + \omega^{\mathrm{b}}_{\mathbf{q}\nu} - i\eta} + \frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} - \omega^{\mathrm{b}}_{\mathbf{q}\nu} - i\eta} \right]$$

+

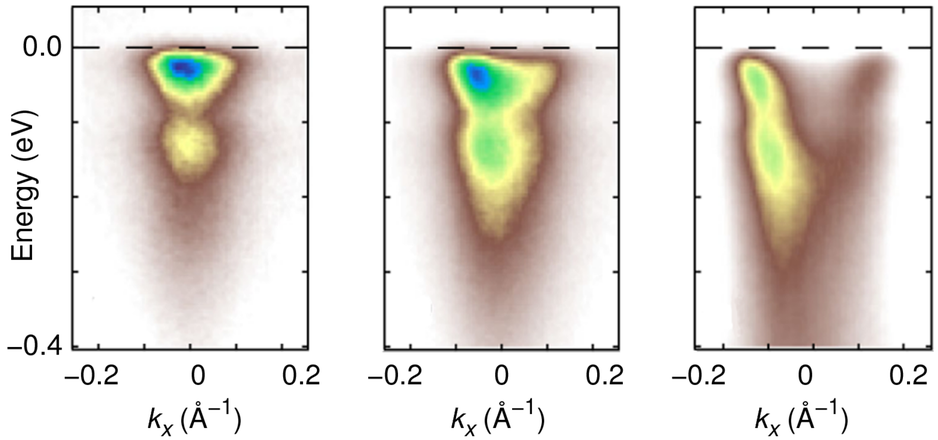
Cumulant expansion approach

$$A(\mathbf{k},\omega) = \sum_n e^{A^{\mathrm{S1}}_{n\mathbf{k}}(\omega)} * A^{\mathrm{QP}}_{n\mathbf{k}}(\omega)$$

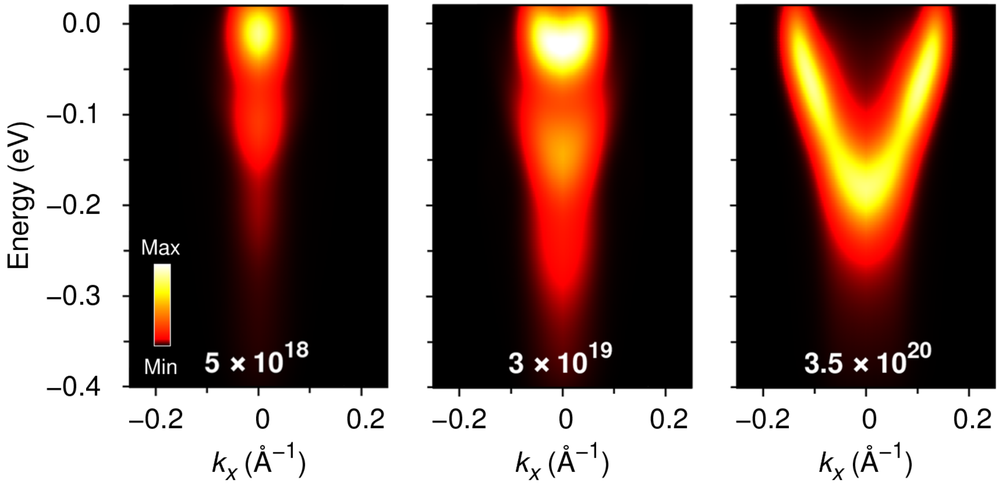
[1] L. Hedin, et al., Phys. Rev. B **58**, 15565 (1998)

Satellites due to the electron-phonon coupling: highly-doped polar semiconductors

ARPES measurements of highly-doped TiO_2



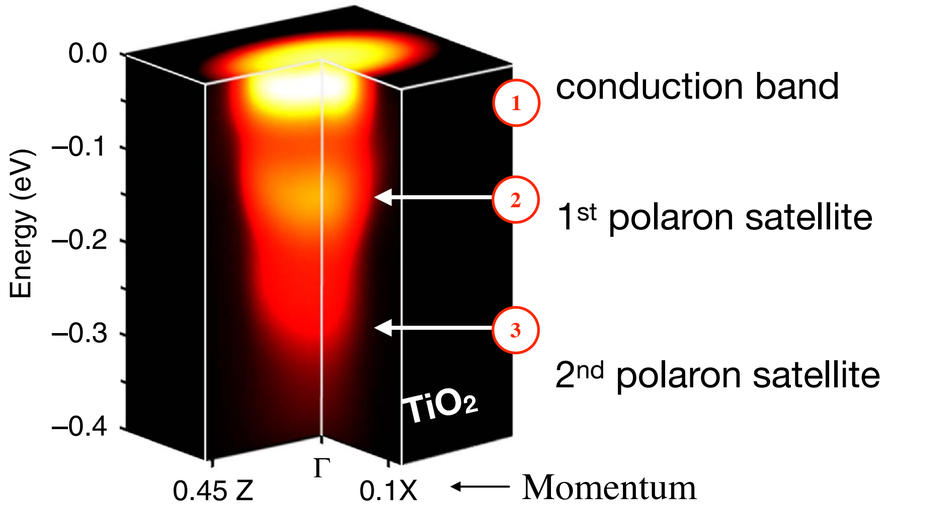
Spectral function including electron-phonon interactions:



ARPES: Moser et al., Phys. Rev. Lett. **110**, 196403 (2013)
Theory: Verdi, Caruso, Giustino, Nature Comm. **8**, 15769 (2017)

Free carriers screen the electron-phonon interactions
(progressively reduce the coupling at higher doping)

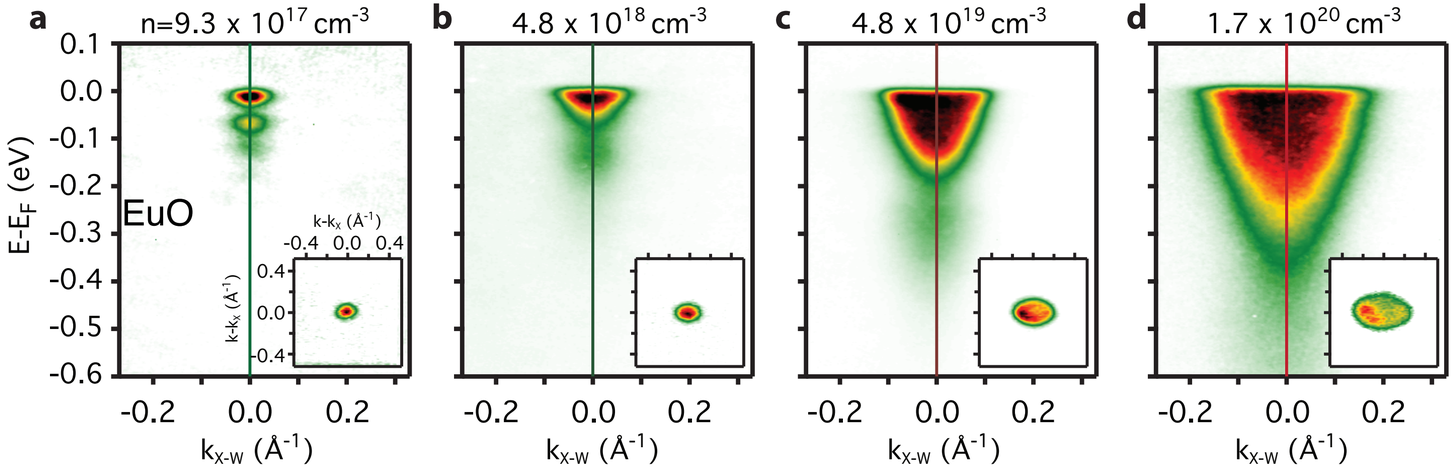
Doping-induced polaronic to Fermi liquid transition




Carla Verdi

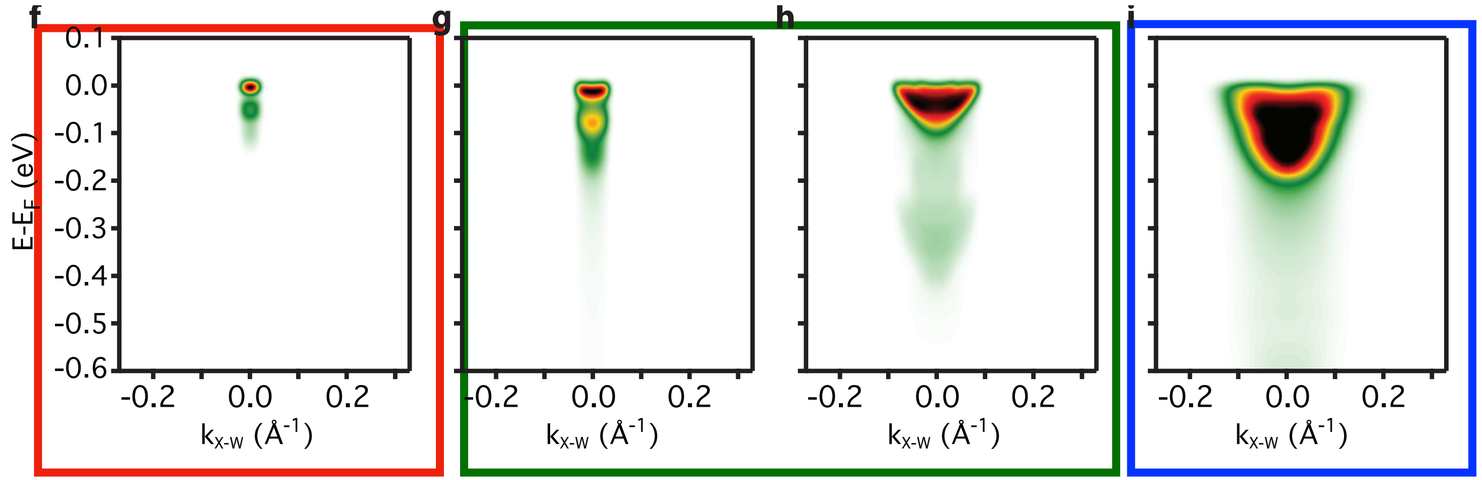

Feliciano Giustino

Doping-induced crossover from lattice to plasmonic polarons

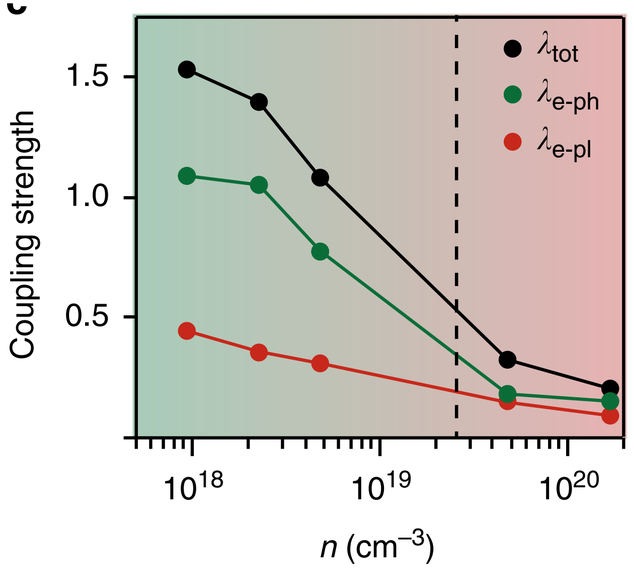


Spectral function with: $\Sigma(\mathbf{k},\omega) = \Sigma^{\mathrm{eP}} + \Sigma^{\mathrm{e-ph}}$

F. Caruso, F. Giustino,
Phys. Rev. B **94**, 115208 (2016)

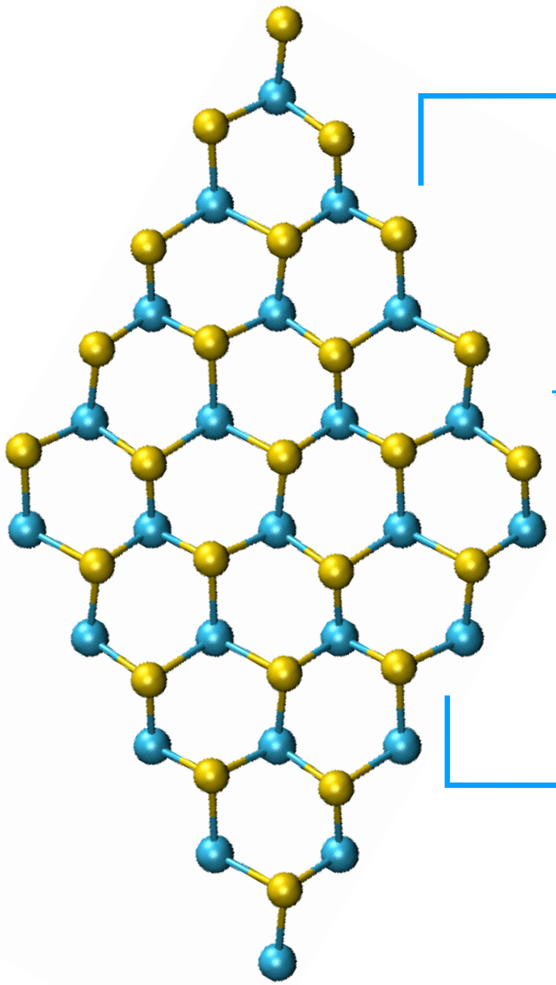


phonons **phonons + plasmons** **plasmons**

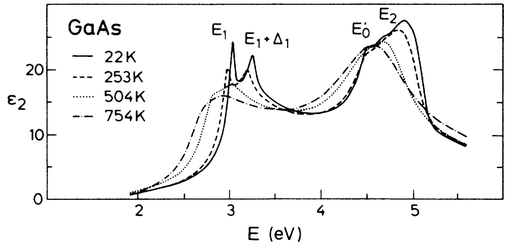


J. Riley, F. Caruso, C. Verdi, et al. Nature Comm. **9**, 2305 (2018)

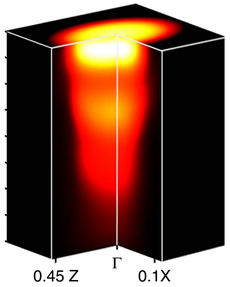
Outline



The temperature dependence of the band structure



Polaronic satellites in angle-resolved photoemission spectroscopy (ARPES)



Phonon-assisted optical absorption in semiconductors