

Ab-initio Studies of Polarons, Optical Phonons, and Transport: Case of Complex Oxides

Burak Himmetoglu

ETS & Center for Scientific Computing
University of California Santa Barbara

bhimmetoglu@ucsb.edu



Electron-Phonon interactions

Numerous phenomena, including but not limited to:

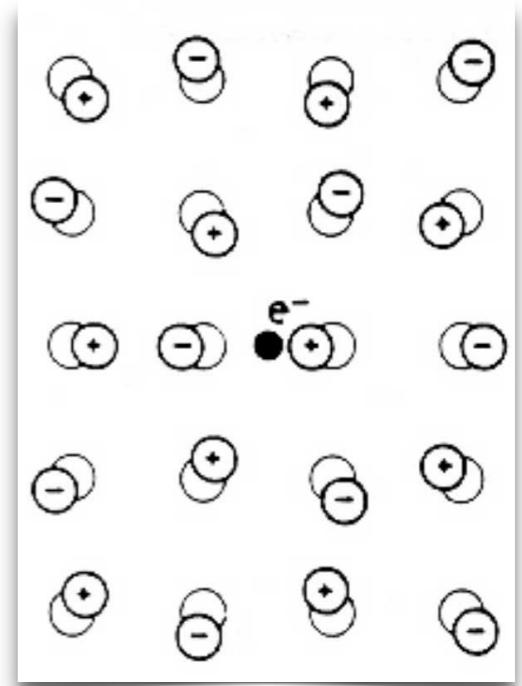
- Temperature dependence of resistivity in metals and mobility in semiconductors
- Superconductivity
- Temperature dependence of band energies, band gaps
- Kohn anomalies, structural transitions
- Polaron formation

Polaron Concept

- One of the simplest, and most widely studied model for interacting electrons and (optical) phonons:

- A conduction electron (or hole) together with its self-induced polarization in a polar semiconductor or ionic crystal:

[Devreese, Polarons,
Encyclopedia of Applied Physics, Vol. 14, pp. 383-409 \(1996\)](#)

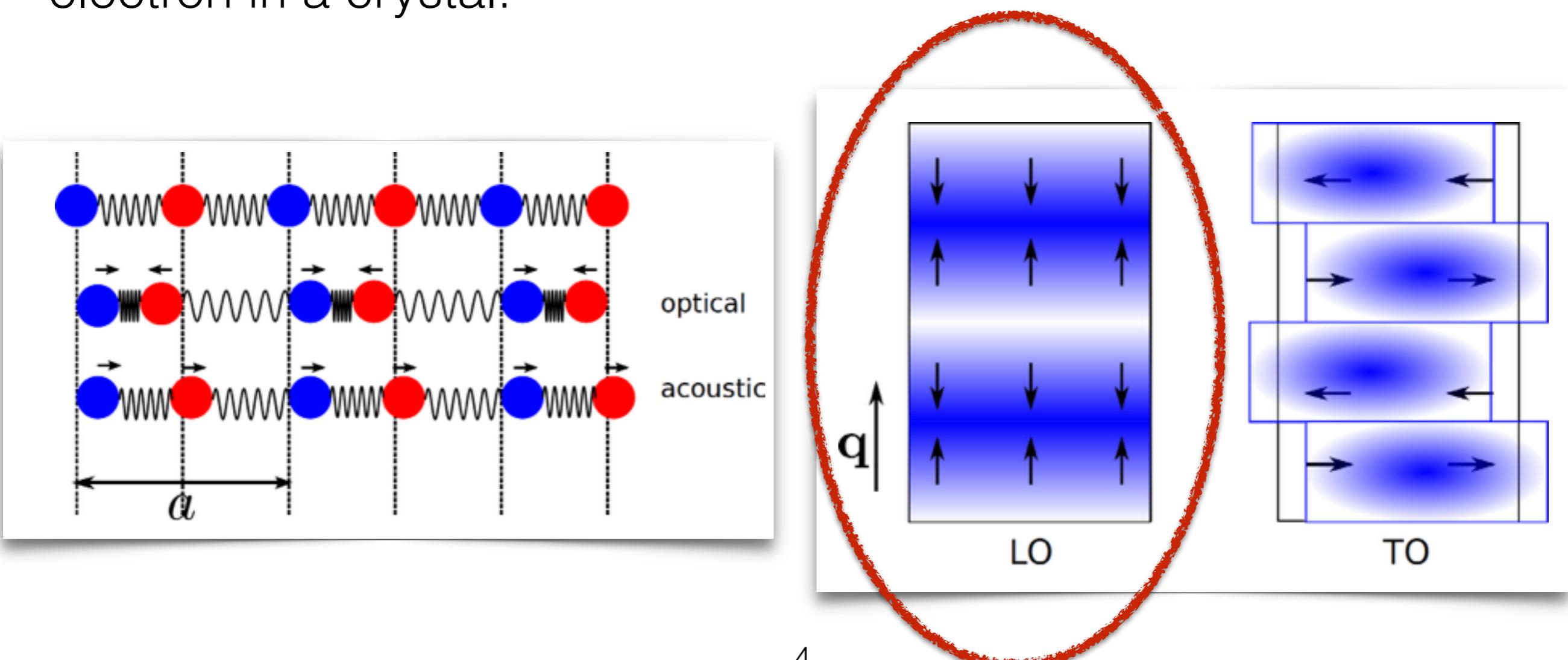


- It is a quasi-particle
- Depending on the radius of the ionic distortion, we can talk about (loosely) two types of polarons i) small ii) large

Weak coupling and large polarons

- Radius of the polaronic state exceeds the lattice constant
- Propagate as free electrons with enhanced effective mass

e.g.: One longitudinal optical (LO) phonon interacting with a band electron in a crystal:



Weak coupling and large polarons

Macroscopic polarization field due to one LO phonon interacting with electron density:

Interaction potential: $V_q = \frac{\hbar\omega_{LO}}{q} \left(\frac{\alpha}{\epsilon_0 V_{cell}} \right)^{1/2} \left(\frac{\hbar}{2m_b \omega_{LO}} \right)^{1/2}$

phonon frequency



phonon wavevector



electron band mass

Coupling constant:

“Fröhlich Coupling”

$$\alpha = \frac{e^2}{\hbar \epsilon_0} \left(\frac{m_b}{2\hbar \omega_{LO}} \right)^{1/2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon} \right)$$



electronic
dielectric
constant

static
dielectric
constant

Fröhlich, Proc. Roy. Soc. A 160, 230 (1937)

Weak coupling and large polarons

- We have an interacting electron-phonon system (non-diagonal Hamiltonian)
- Perform a transformation to obtain the polaron state (diagonalize the Hamiltonian) at linear order in coupling constant:

Polaron mass:

$$m^* \simeq m_b / (1 - \alpha/6)$$



Weak coupling:

$$0 < \alpha < 6$$

- When coupling constant is large, nonlinear effects are important —> **small polarons**

Example Coupling Constants

$$\alpha = \frac{e^2}{\hbar \epsilon_0} \left(\frac{m_b}{2\hbar \omega_{LO}} \right)^{1/2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon} \right)$$

Material	α	Material	α
CdTe	0.31	KI	2.5
CdS	0.52	RbCl	3.81
ZnSe	0.43	RbI	3.16
AgBr	1.6	CsI	3.67
AgCl	1.8	TlBr	2.55
CdF ₂	3.2	GaAs	0.068
InSb	0.02	GaP	0.201
KCl	3.5	InAs	0.052
KBr	3.05	SrTiO ₃	4.5

Word of caution: !

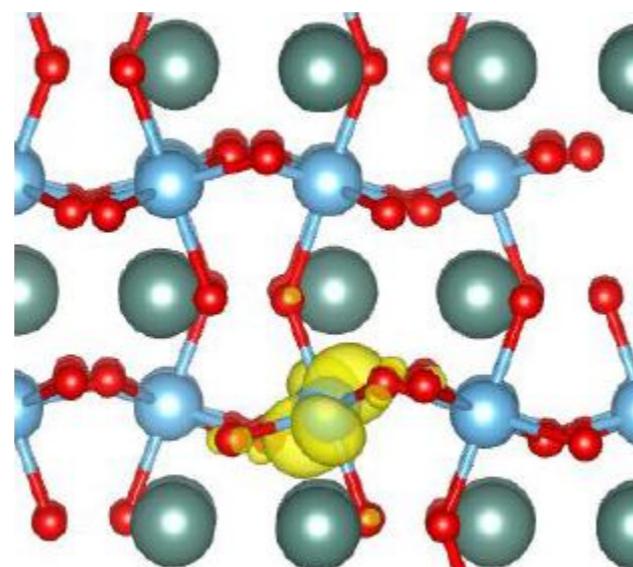
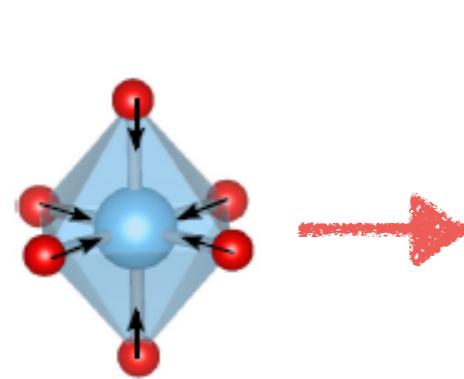
- 3 polar LO modes in STO
- Bands are highly non-parabolic, i.e. m_b energy dependent.

Devreese, Polarons,
Encyclopedia of Applied Physics, Vol. 14, pp. 383-409 (1996)

Strong coupling: small polarons

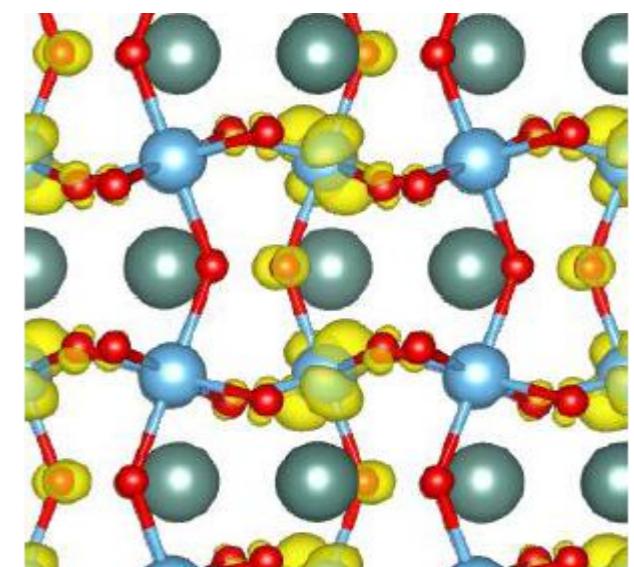
- A macroscopic description of polarization field is invalid
- Typically happens for e-/h⁺ states with small band-widths, i.e. localized states.
- Strong crystal distortion around the localized e-/h⁺ state

e.g.: h⁺ polaron in rare-earth titanates (RTiO₃):



Atomic deformations
around the polaron

vs.



Localized h⁺ accompanied
by strong lattice distortion
within a unit cell

Delocalized h⁺ band,
small lattice distortion,
over many unit cells length

Effects on carrier transport

- Large-polarons: More phonons \rightarrow More scattering:

$$n = \frac{1}{e^{\hbar\omega_{\text{LO}}/kT} - 1}$$

Low T: LO phonons
not occupied

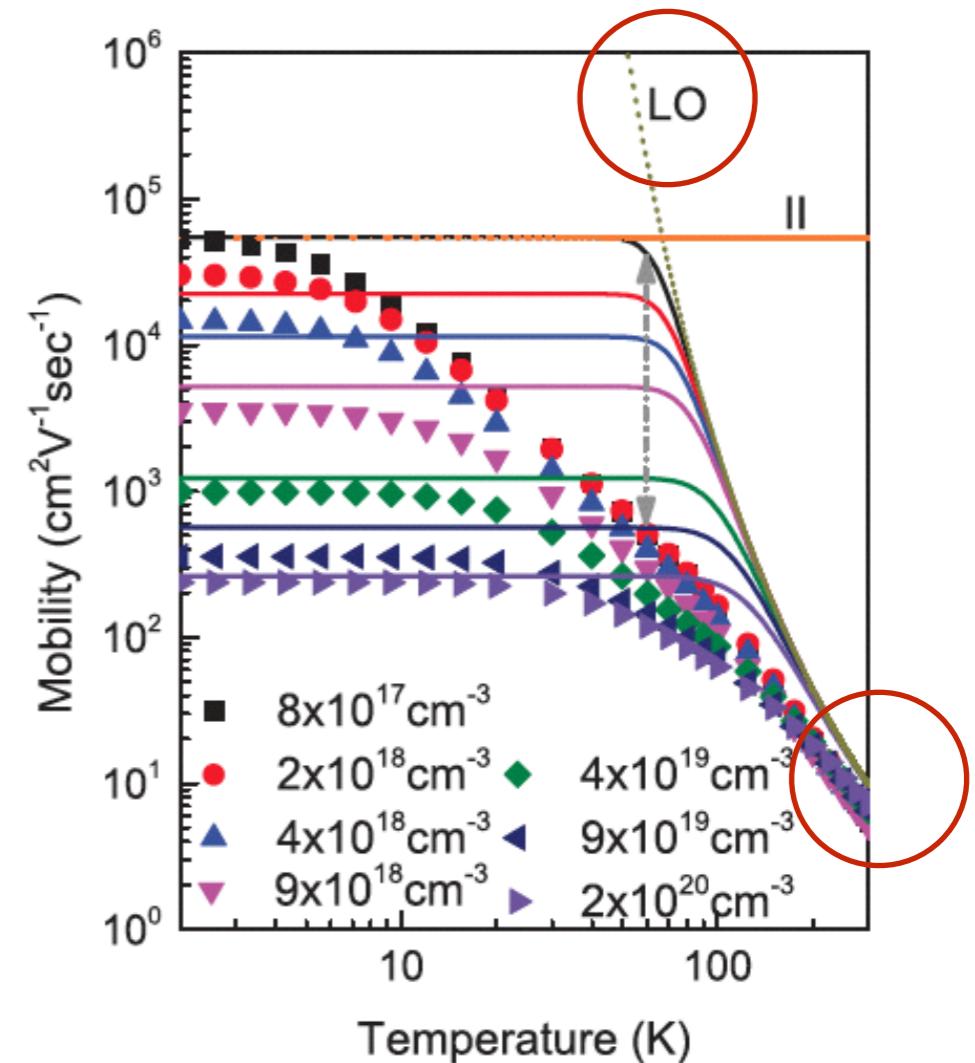
High T: LO phonon scattering
effective

$$\mu_{\text{LO}} \sim 1/n \sim e^{\hbar\omega_{\text{LO}}/kT}$$

$(kT \ll \hbar\omega_{\text{LO}})$

e.g.: n-doped SrTiO₃ thin-films

$$\hbar\omega_{\text{LO}_{\text{max}}} \simeq 0.1 \text{ eV}$$



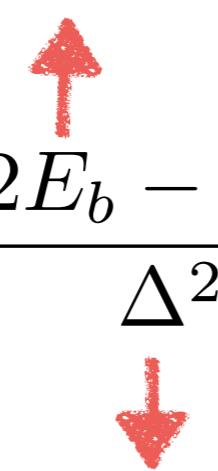
Effects on carrier transport

- Small-polarons: More phonons —> More inter-site hopping:

$$\mu \sim e^{-\hbar\omega_{\text{LO}}/kT} \quad (kT \ll \hbar\omega_{\text{LO}}) \quad (\text{thermally activated})$$

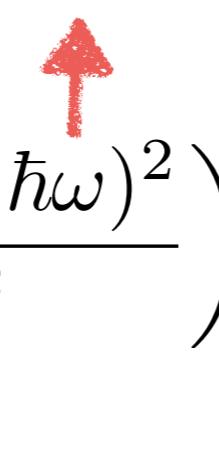
- Optical conductivity (absorption exp.):

polaron
binding energy



$$\sigma(\omega) \propto \exp\left(-\frac{(2E_b - \hbar\omega)^2}{\Delta^2}\right)$$

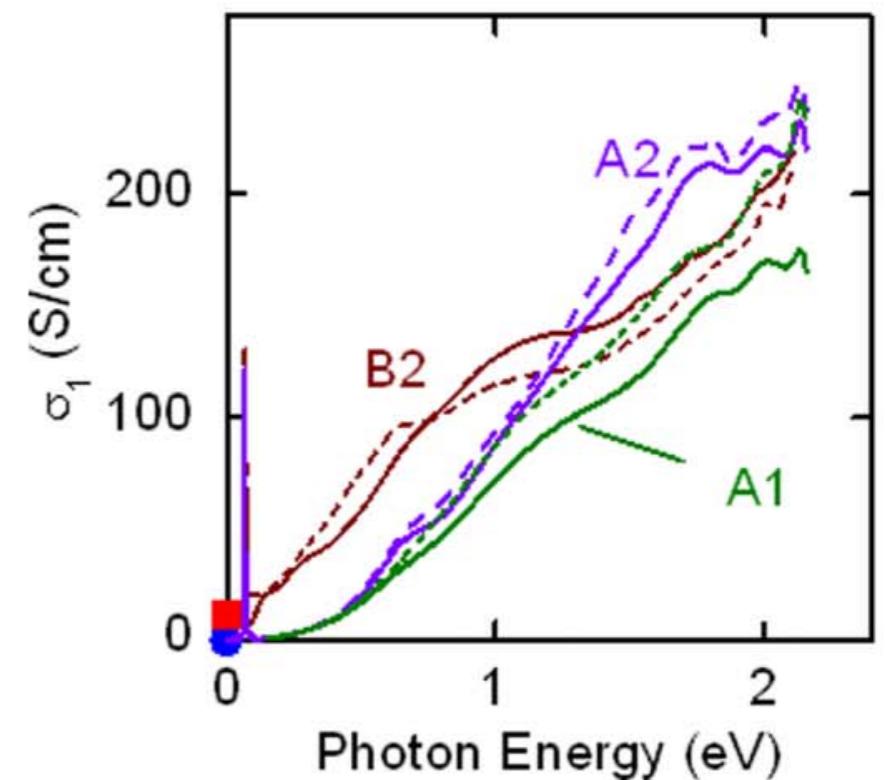
photon
energy



Width: Atom site's zero point energy:

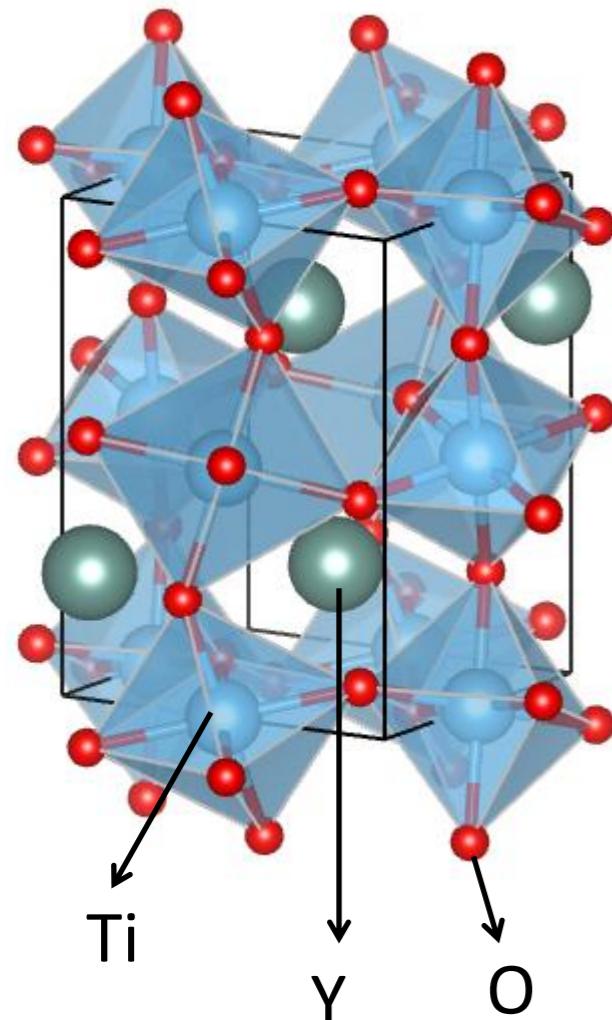
$$\Delta \simeq (4E_b \hbar\omega_{\text{LO}})^{1/2}$$

e.g.: SrTiO₃/GdTiO₃ interface:
p-doping on the GdTiO₃ side



Small Polarons in RTiO₃

- e.g.: YTiO₃



Structure:

- Orthorhombic perovskite with octahedral rotations

Electronic Structure:

- Ferromagnetic ordering of electrons on Ti⁺³
- Mott insulator, **strongly correlated**
- Value of band gap ?
 - Optical absorption features down to ~0.6 eV
Gössling et al. Phys. Rev. B 78, 075122 (2008)
 - Combined photoemission + TiO₆ cluster calculations:
band gap ~ 1.77 eV

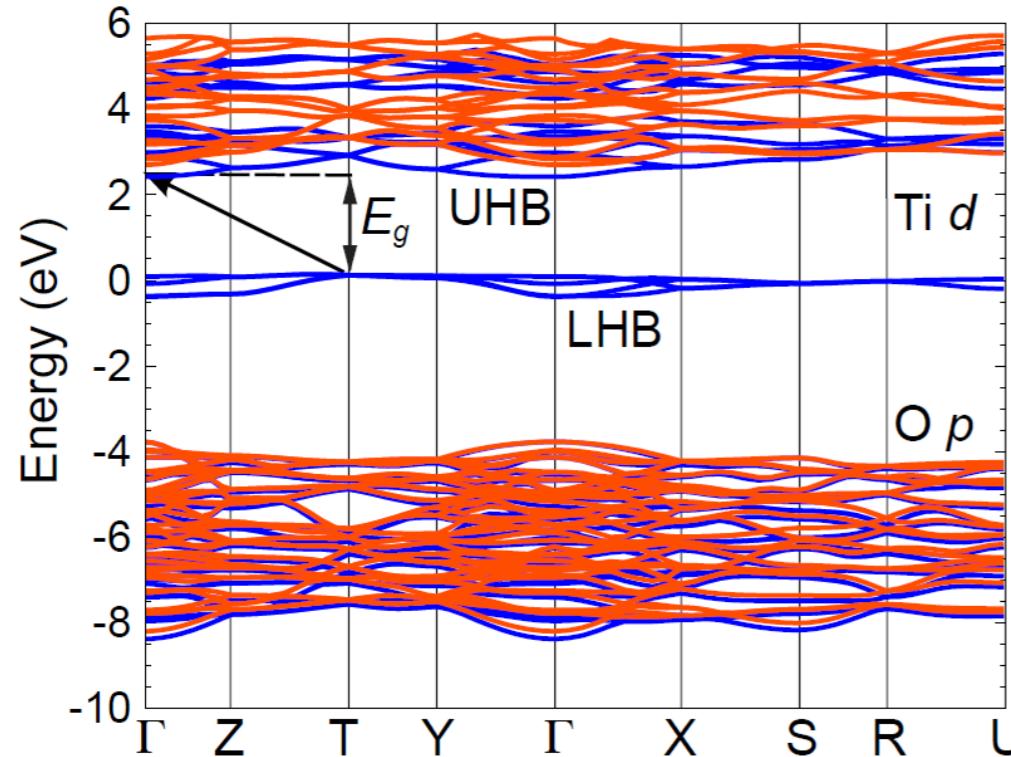
Bocquet et al. Phys. Rev. B 53, 1161 (1996)

DFT based calculations

- Standard approximate DFT functionals (e.g. LDA, GGA)
 - Poor description of e-e interactions
 - Suffer from **self-interaction**
 - Tend to **over-delocalize** electron density
- Hubbard Model based corrective functionals (DFT+U)
 - Effective on-site repulsion parameter U on localized orbitals (e.g. d & f)
Anisimov et al. Phys. Rev. B 44, 943 (1991) and Phys. Rev. B 52, R5467 (1995)
 - U parameter computed self-consistently
Cococcioni et al. Phys. Rev. B 71, 035105 (2005)
Himmetoglu et al. Int. J. Quantum. Chem. 114, 14 (2013)
- Hybrid functionals (e.g. HSE)
 - Partial cancellation of self-interaction
Heyd et al. J. Chem. Phys. 118, 8207 (2003) and J. Chem. Phys. 121, 1187 (2004)

Electronic Structure of YTiO₃

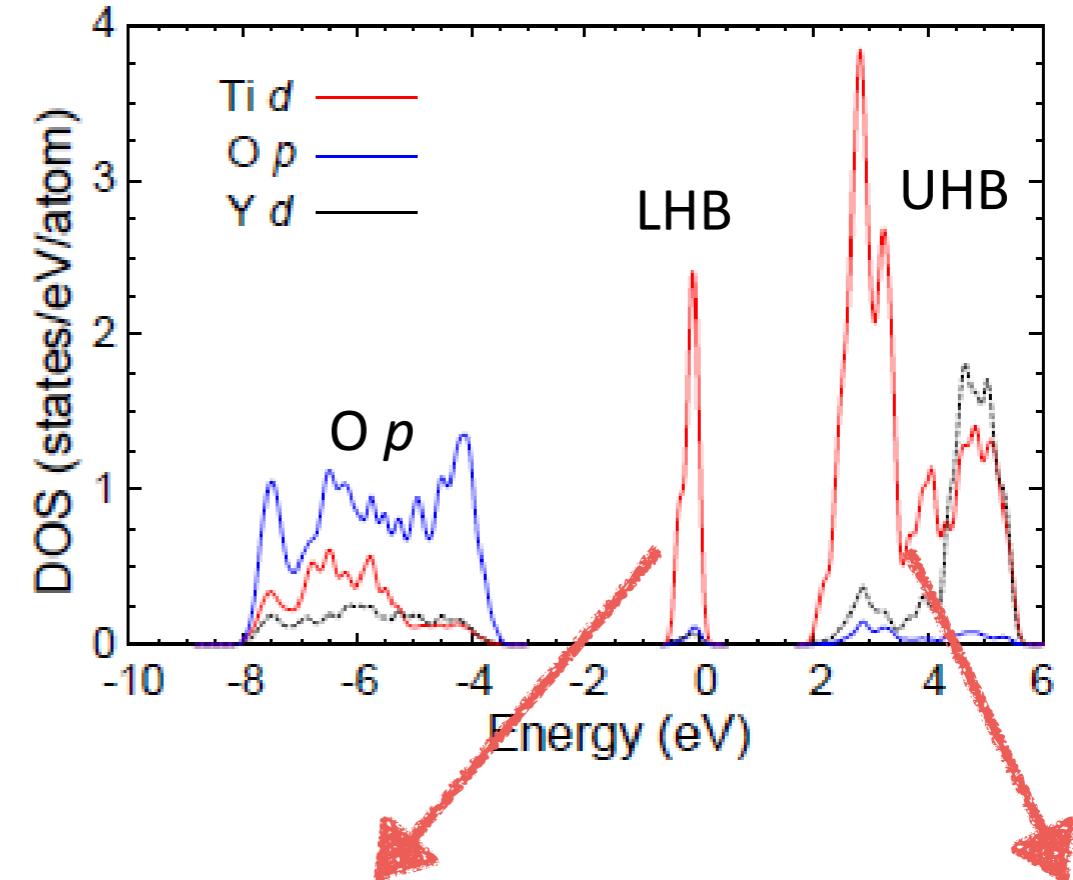
- HSE & DFT+U_{sc} are almost identical.



$$U_{\text{sc}} = 3.70 \text{ eV}$$

$$E_g \simeq 2.20 \text{ eV} \quad (\text{DFT+U}_{\text{sc}})$$

$$E_g \simeq 2.07 \text{ eV} \quad (\text{HSE})$$



d¹ occupied
Ti sites

empty d states

Significantly larger than 0.6 eV gap
Real gap = ? probably in between..

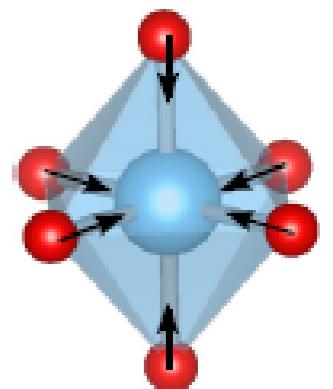
0.6 eV onset: Small Polarons

- Experimental evidence for unintentional p-type doping in RTiO_3

Zhou et al. J. Phys. Condens. Matter.: 17, 7395 (2007)

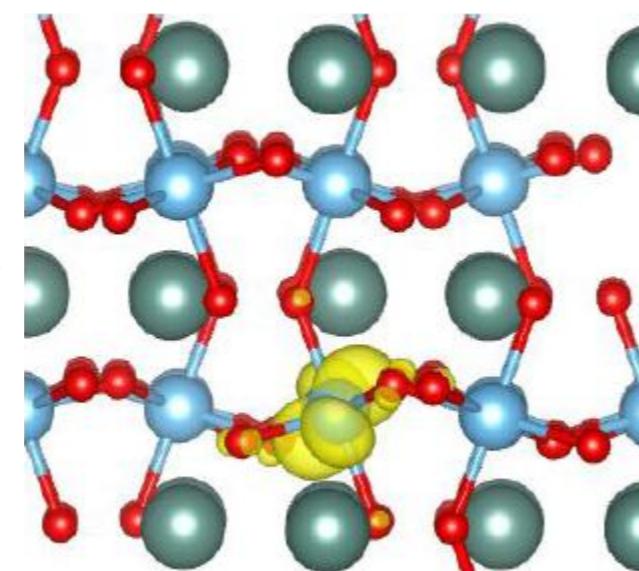
- DFT modeling of small-polarons:

- Supercell calculations with one h^+ (i.e. one e^- missing)
- Optimize electronic and structural d.o.f
- Two possible solutions

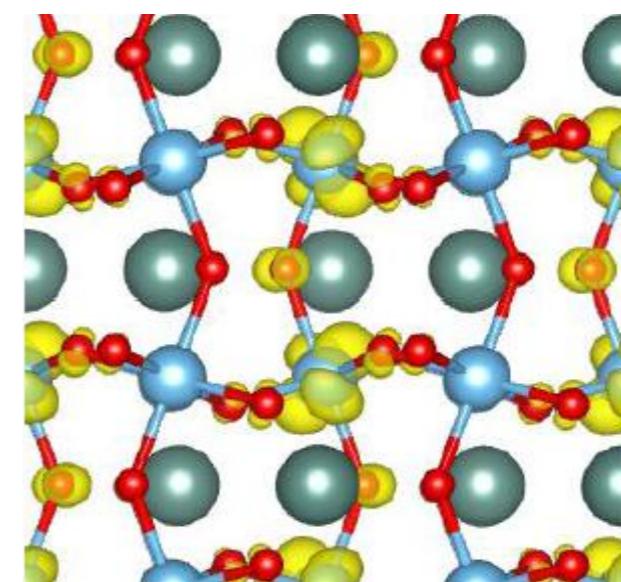


Small polaron

More stable!



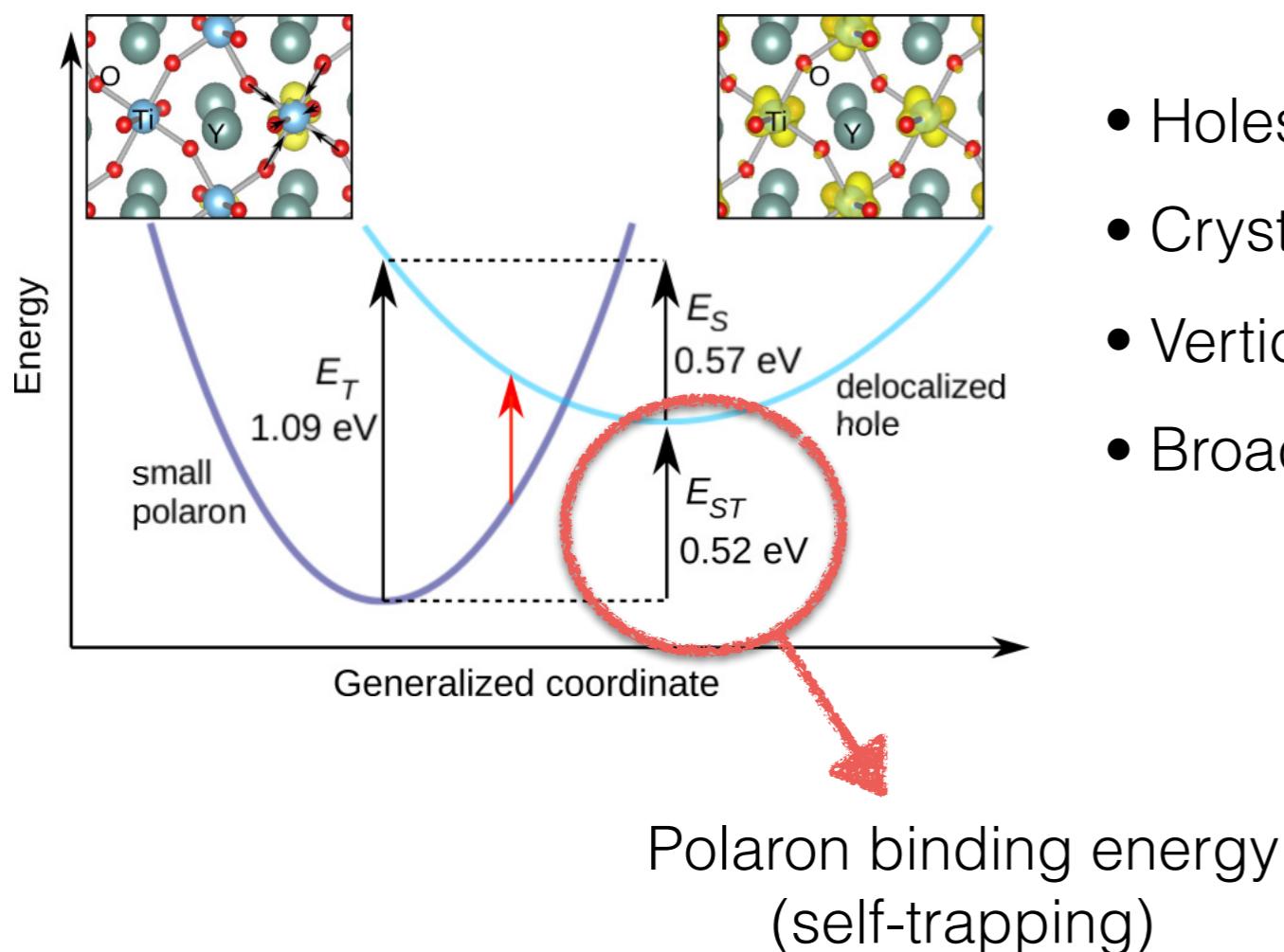
Delocalized hole



Himmetoglu et al. Phys. Rev. B 90, 161102R (2014)
14

Optical absorption

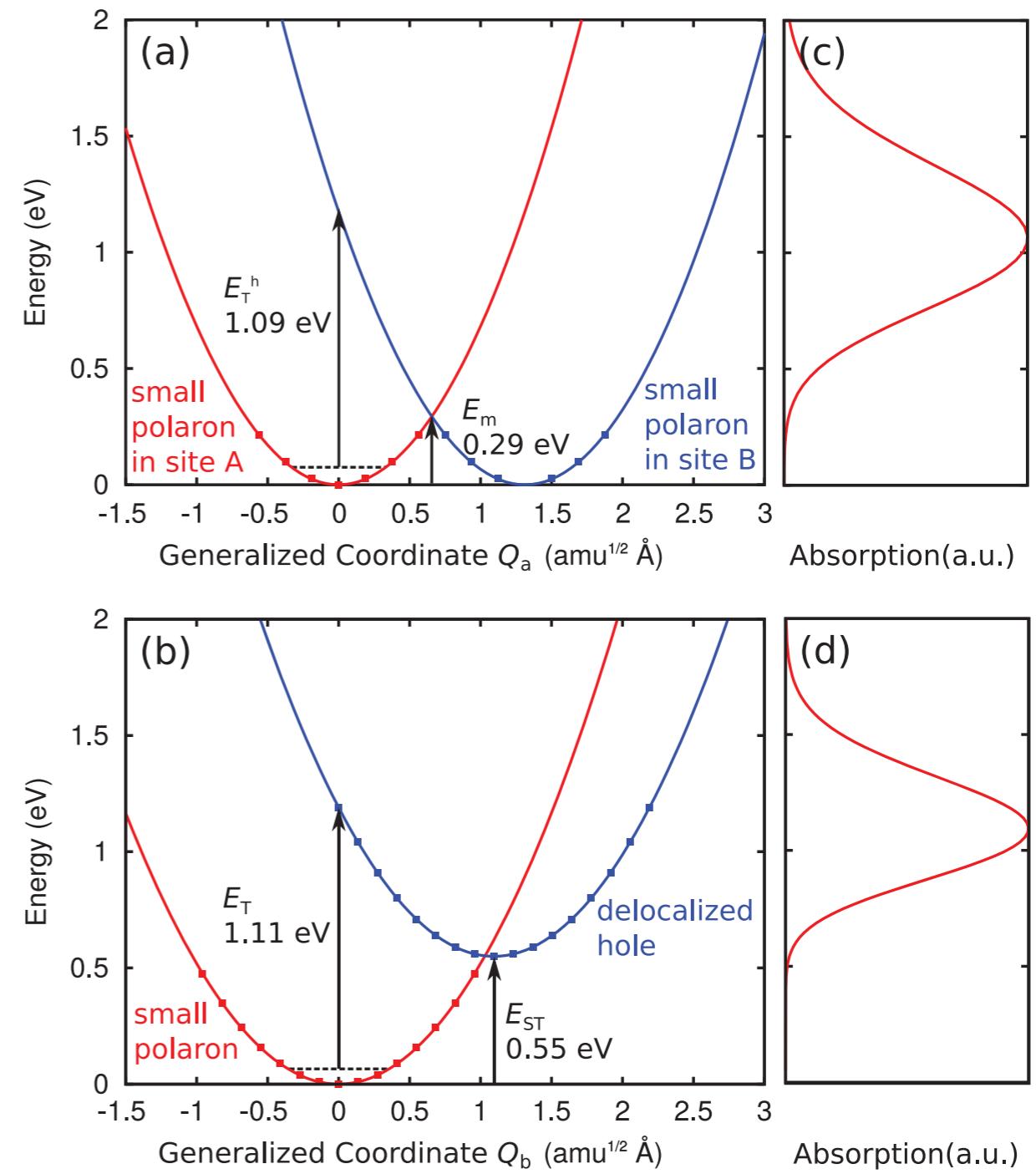
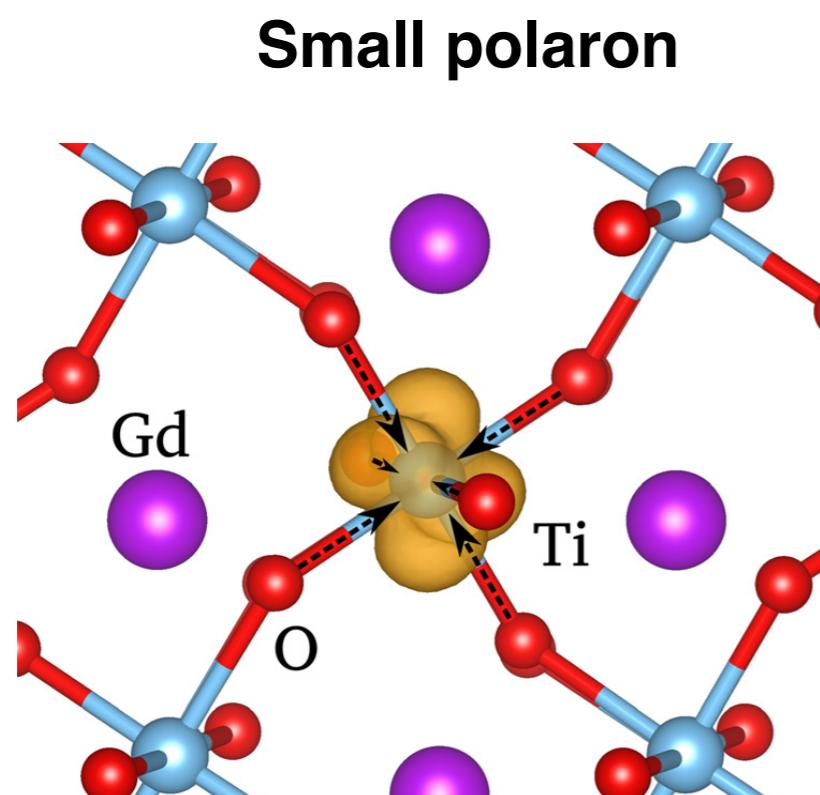
- Site-to-site hopping (mentioned earlier)
- Transition between small polaron and delocalized hole:



- Holes are self-trapped as small polarons
- Crystal strain energy (E_s)
- Vertical transition: polaron to delocalized hole (E_T)
- Broad absorption below the gap

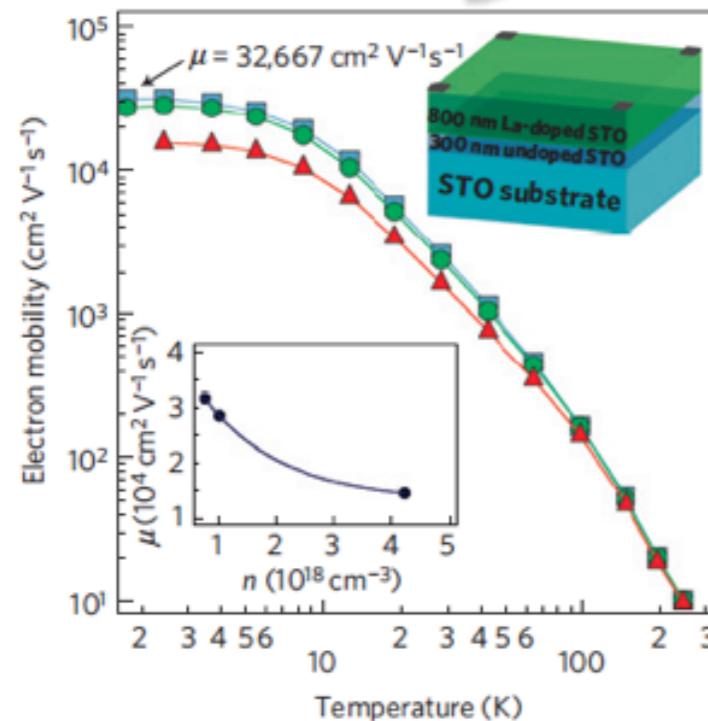
Optical absorption

- Consider both type of processes in GdTiO_3 :
- GdTiO_3 very similar to YTiO_3 (structure, gap)

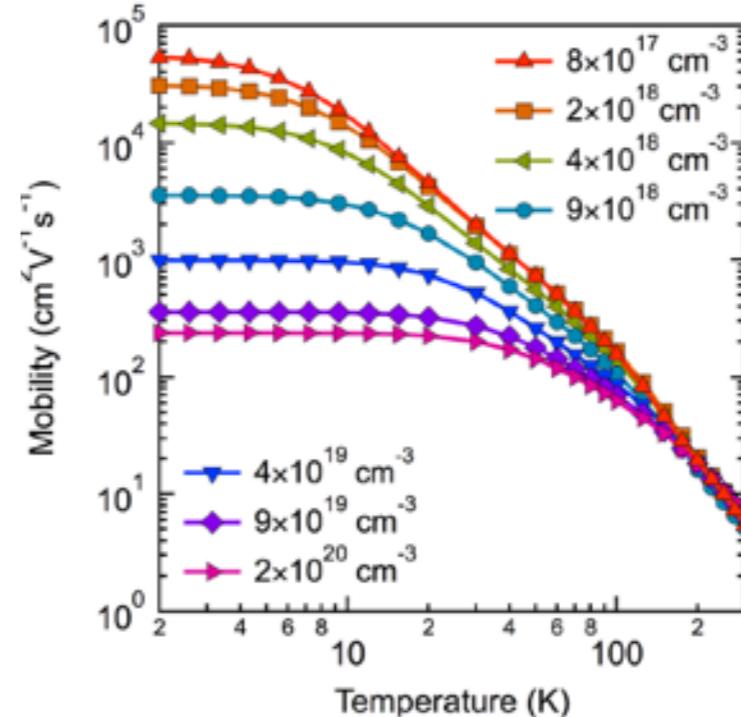


Bjaalie et al. Appl. Phys. Lett. 106, 232103 (2015)

Carrier transport: SrTiO₃ & KTaO₃



Son et al. Nat. Mater. 9, 482 (2010)



Cain et al. Appl. Phys. Lett. 102, 182101 (2013)

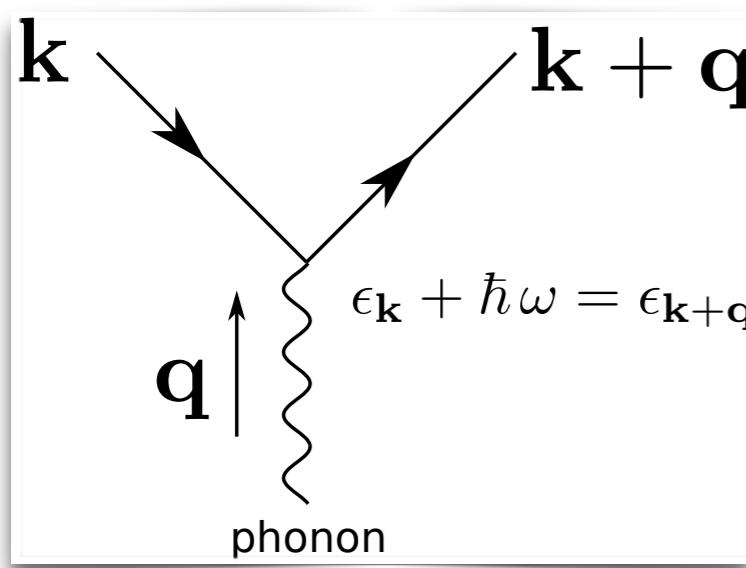
- Discussed in context of device applications
- Rapid fall of mobility at high T in epitaxial STO detrimental

DFT based simulations:

- Scattering mechanisms
- Factors that determine transport properties
- Designing higher mobility oxides

Carrier transport

- Large polarons: can treat e-p interaction at linear order
- Compute carrier lifetimes:

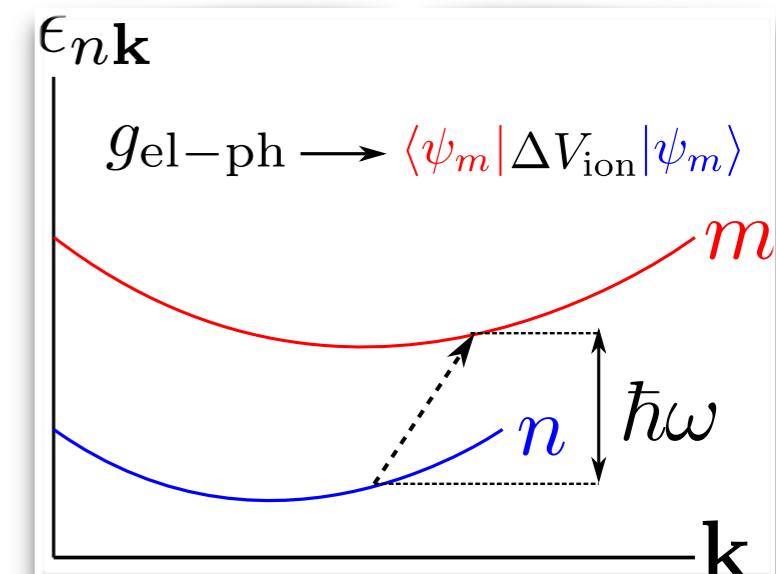


Fermi's Golden Rule:

$$\tau_{nk}^{-1} = \frac{2\pi}{\hbar} \sum_{q\nu,m} |g_{q\nu}|^2 \left\{ (n_{q\nu} + f_{m,k+q}) \delta(\epsilon_{m,k+q} - \epsilon_{nk} - \hbar\omega_{q\nu}) \right. \\ \left. + (1 + n_{q\nu} - f_{m,k+q}) \delta(\epsilon_{m,k+q} - \epsilon_{nk} + \hbar\omega_{q\nu}) \right\}$$

- electron-phonon (ep) coupling constant: $g_{q\nu}$

- First-principles density functional theory (DFPT)
- **Model from large polaron theory**



Carrier transport

- Boltzmann Transport + Relaxation time approximation:

$$\sigma_{\alpha\beta} = e^2 \sum_n \int d^3k \tau_{nk} \left(-\frac{\partial f_{nk}}{\partial \epsilon_{nk}} \right) v_{nk,\alpha} v_{nk,\beta}$$



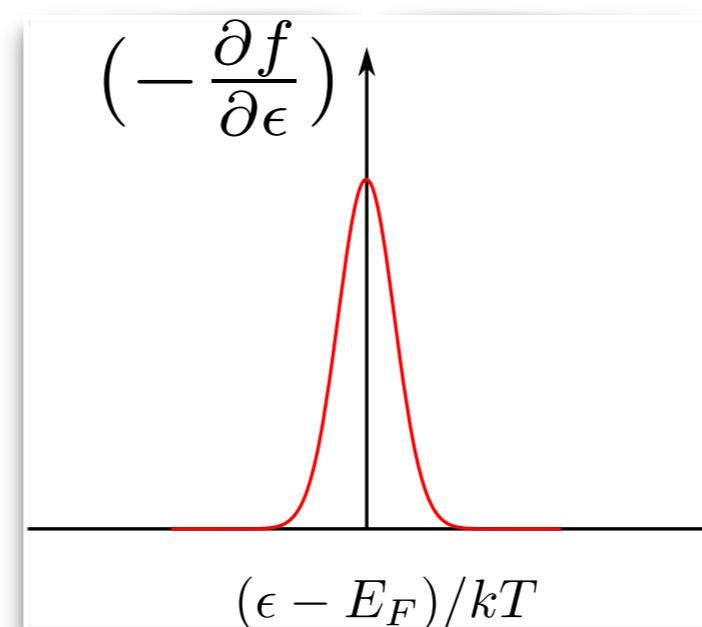
electron
lifetime

derivative of
FD distribution

Band velocities:

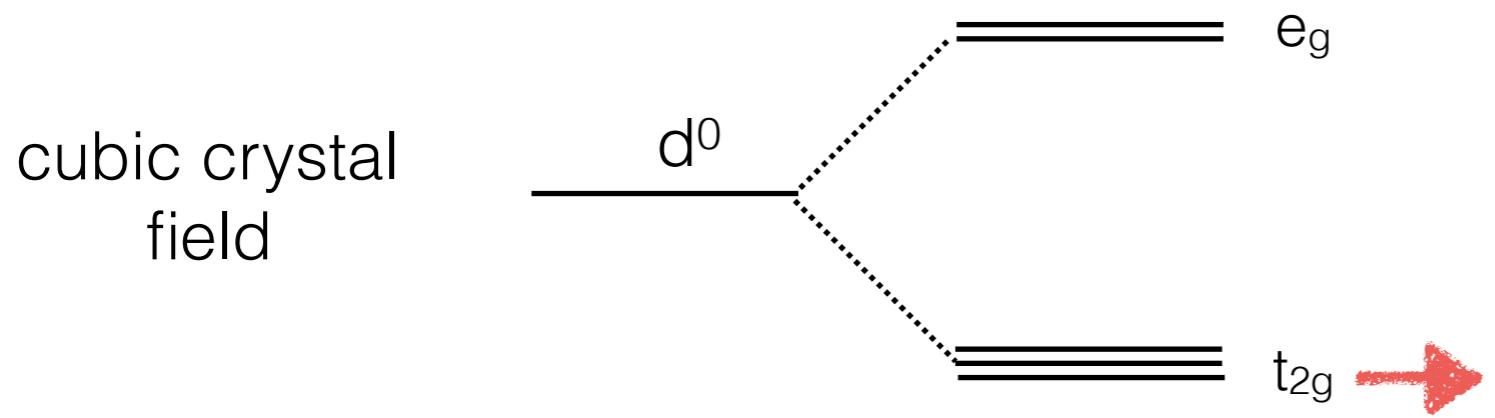
$$v_{nk,\alpha} = \frac{1}{\hbar} \frac{\partial \epsilon_{nk}}{\partial k_\alpha}$$

- All quantities can be calculated from band structure
- Fine sampling of the Brillouin Zone needed for accurate integration



SrTiO₃ & KTaO₃

- Both KTO and STO are cubic perovskites (no rotations) at Room T.
- **d⁰ conduction band:** Do not expect very strong correlation effects.



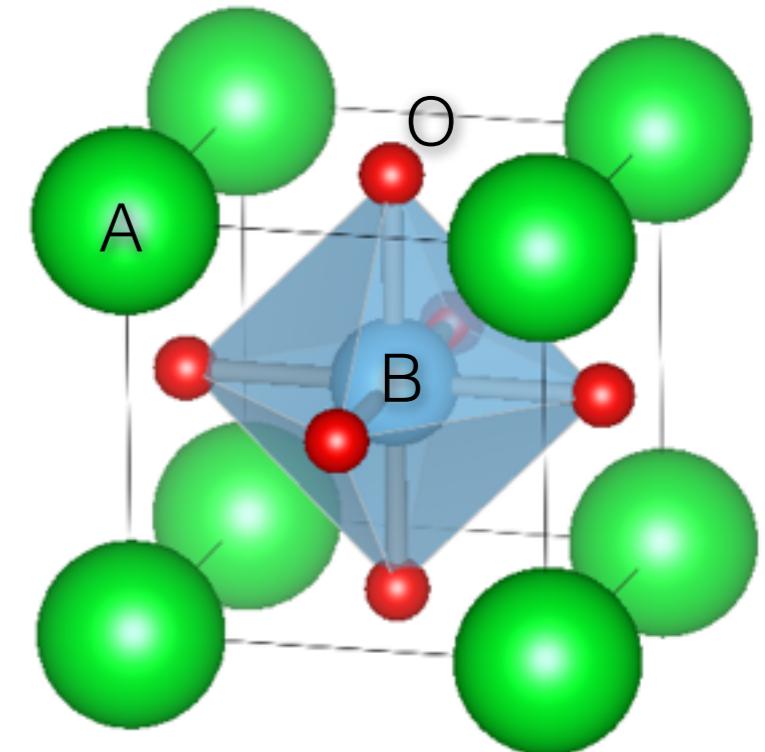
triply degenerate
conduction band*

- Room T mobility of KTO is higher than STO:

$$\text{STO: } \mu_{\text{RT}} \simeq 10 \text{ cm}^2/\text{Vs}$$

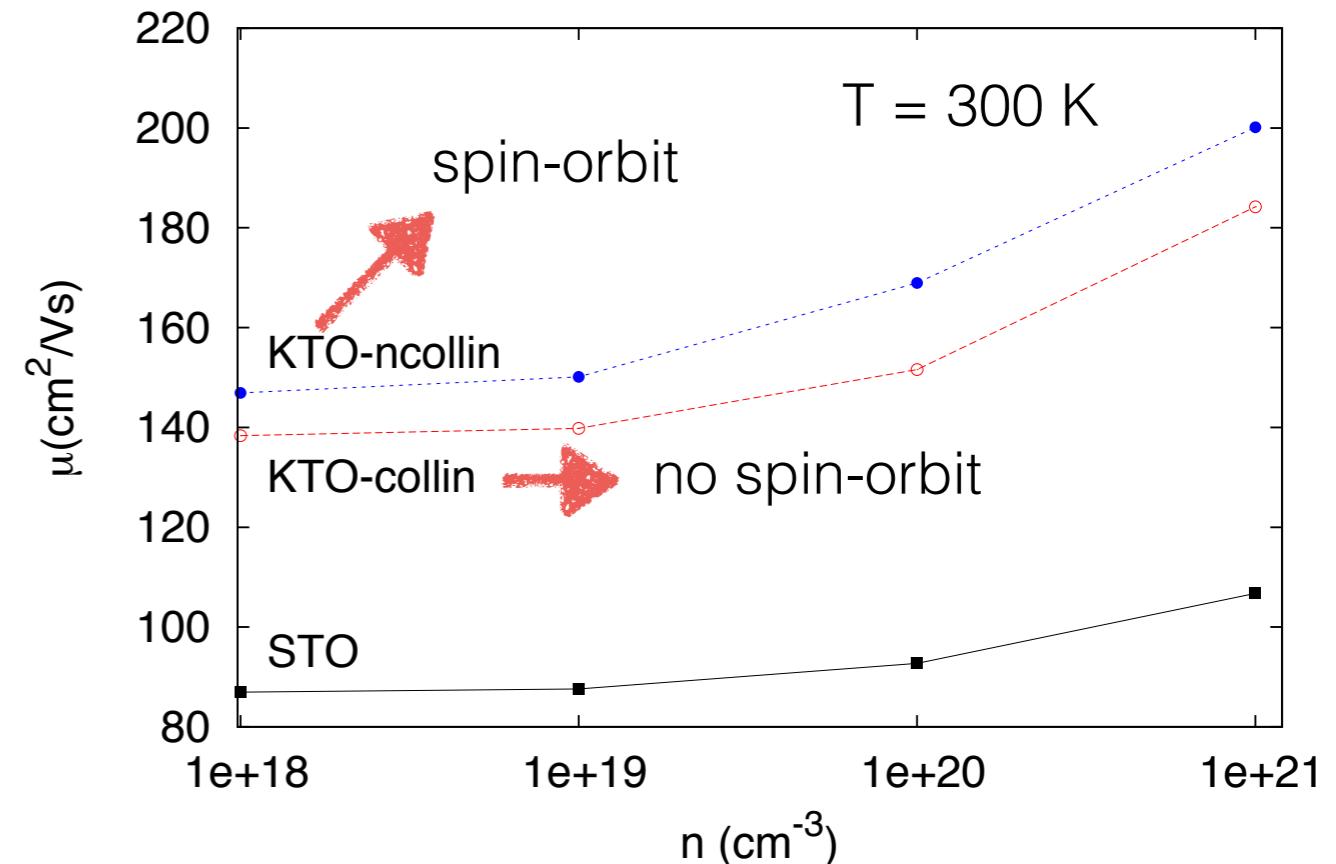
Wemple, Phys. Rev. 137, A1575 (1965)

$$\text{KTO: } \mu_{\text{RT}} \simeq 30 \text{ cm}^2/\text{Vs}$$

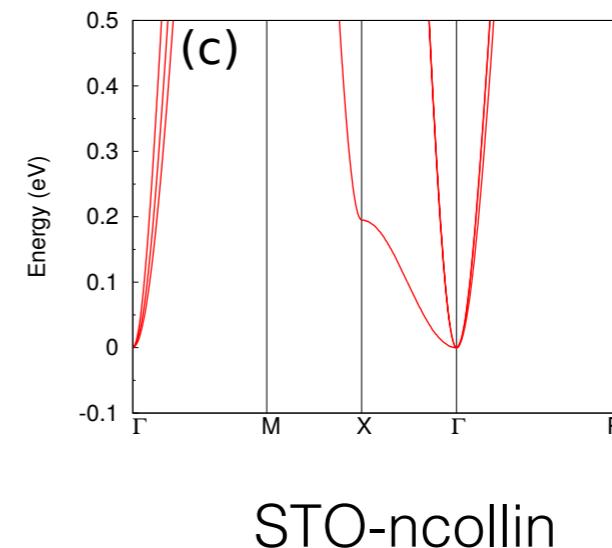
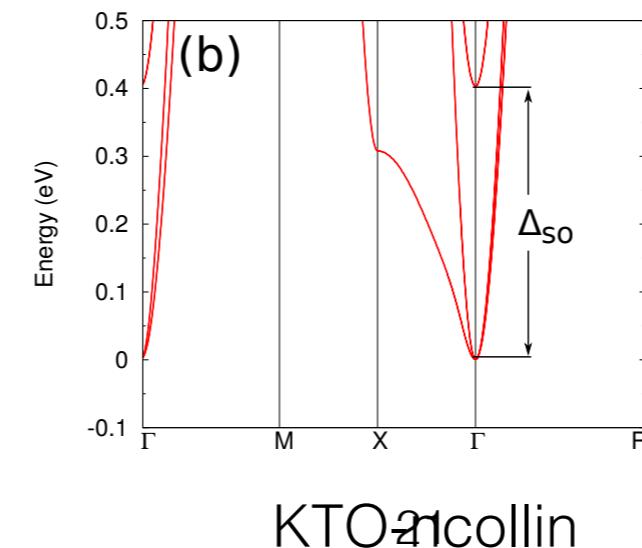
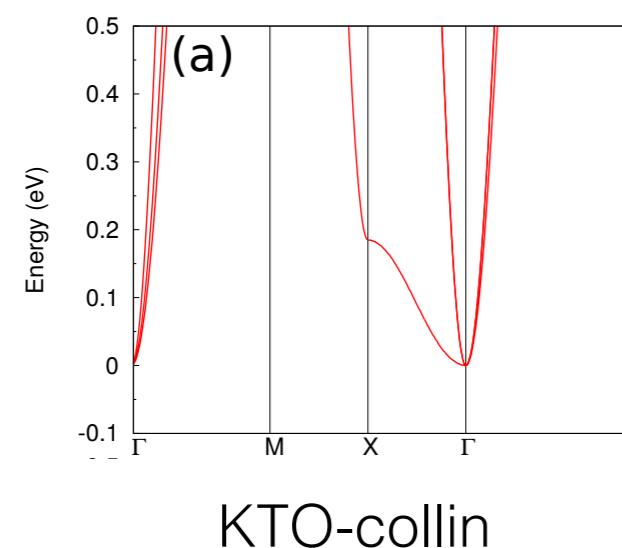


SrTiO₃ & KTaO₃

- KTO has higher mobility
- Spin-orbit interaction relevant for KTO
- Calculations involving spin-orbit lead to higher mobility
- Predicted mobilities higher than experiment

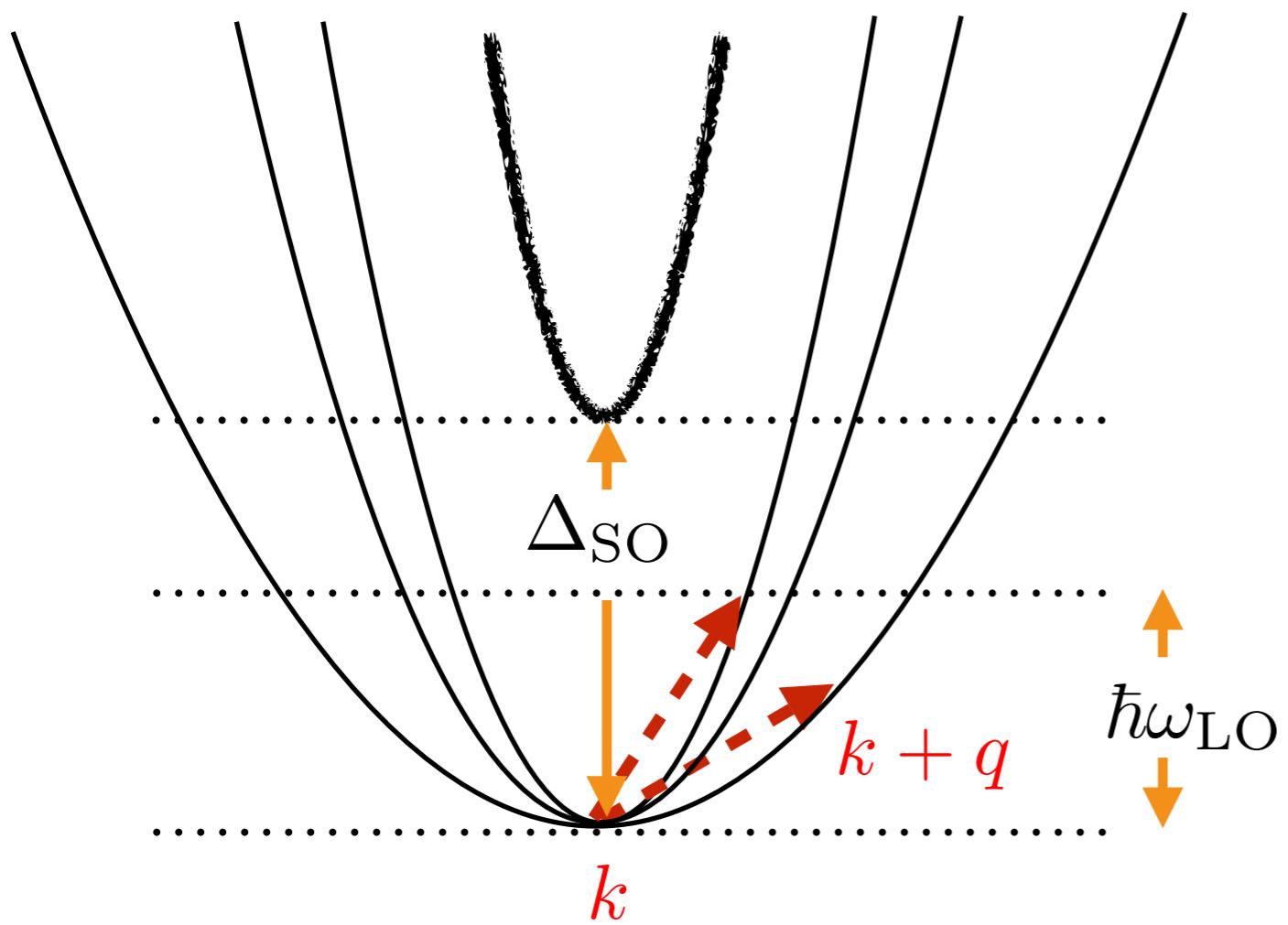


Himmetoglu et al. J. Phys. Condens. Matter.:
28, 065502 (2016)



SrTiO₃ & KTaO₃

- Effective number of conduction bands:



- Recall the energy conserving terms:

$$\delta(\epsilon_{m,k+q} - \epsilon_{nk} \pm \hbar\omega_{q\nu})$$
- Inter-band scattering forbidden for split-off band ($\Delta_{SO} \gg \hbar\omega_{LO}$)
- Ta is heavier than Ti, stronger spin-orbit splitting.
- KTO is effectively 2-band, while STO is 3-band.

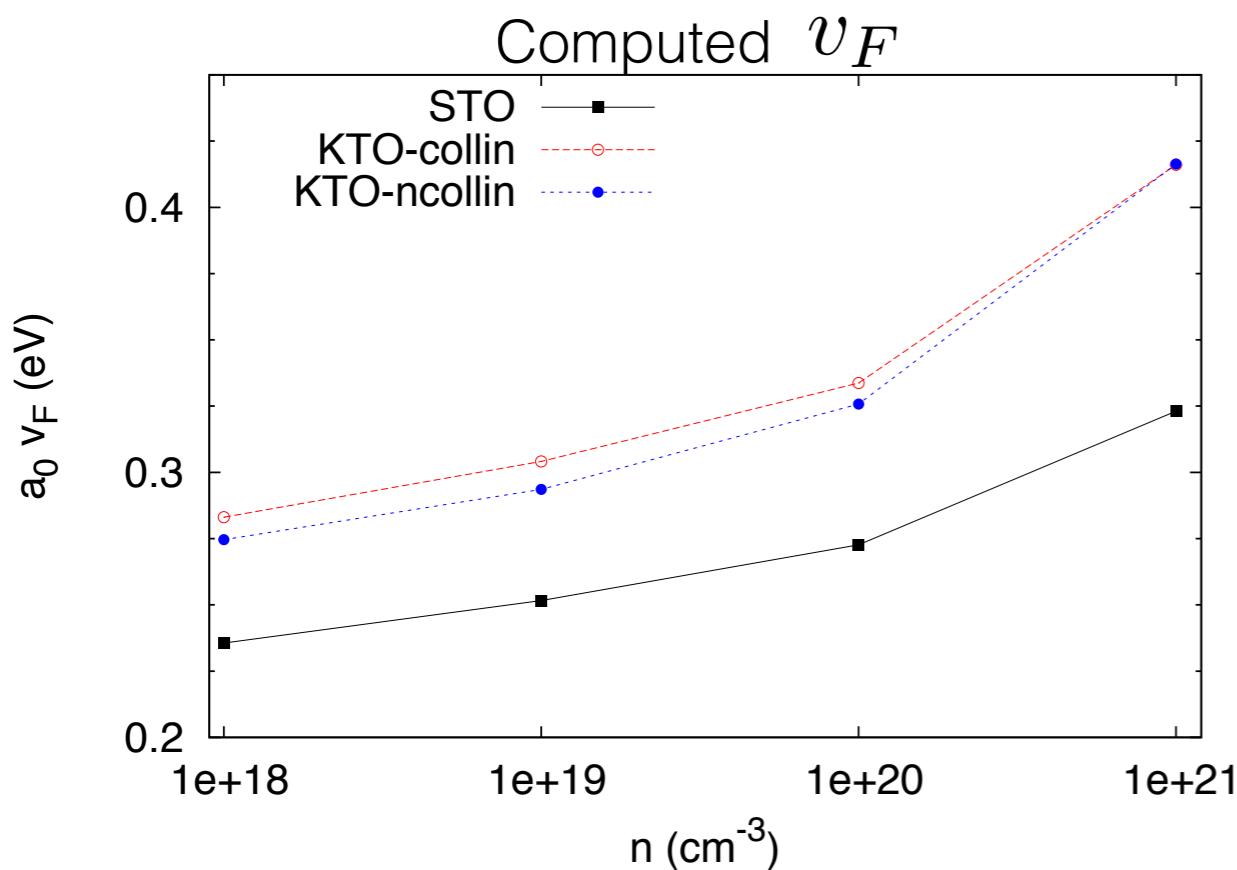
- Can **strain** be used to split bands or modify LO phonon frequencies?

SrTiO₃ & KTaO₃

- Band velocities (near E_F) and/or band masses:

e.g.: Parabolic bands: $\epsilon_{nk} = \frac{\hbar^2 k^2}{2 m_b}$ $v_{nk,\alpha} = \frac{\hbar k_\alpha}{m_b}$

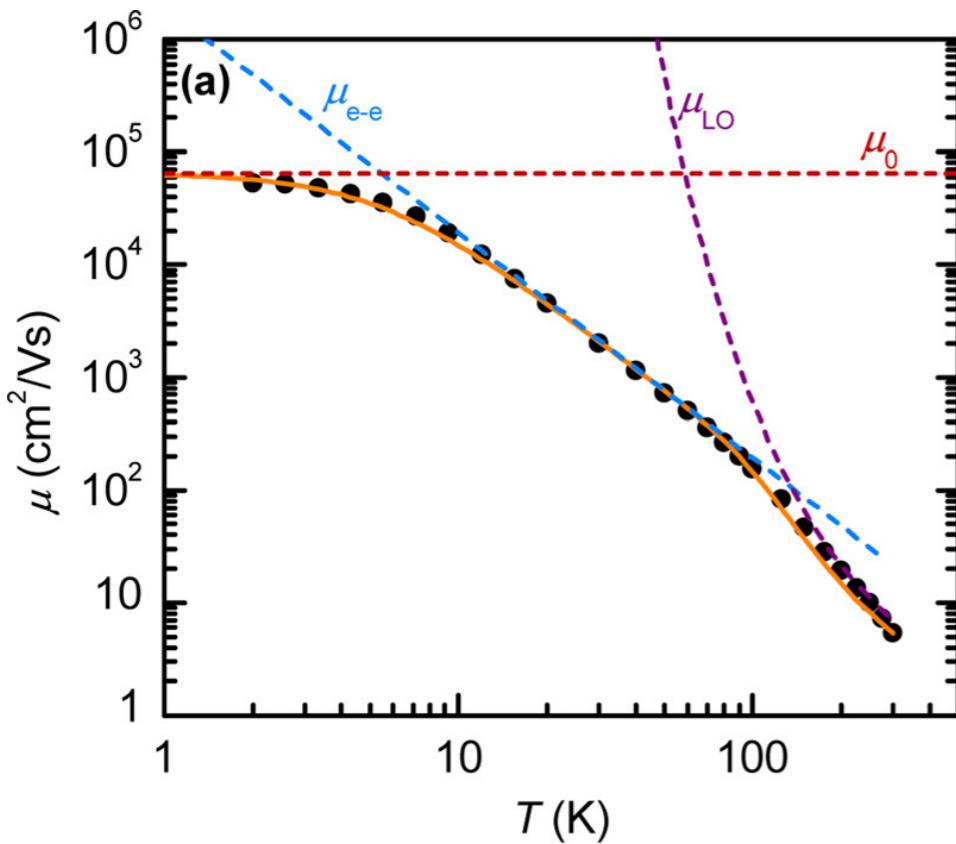
Smaller mass, larger mobility (but d⁰ perovskites have highly non-parabolic bands)



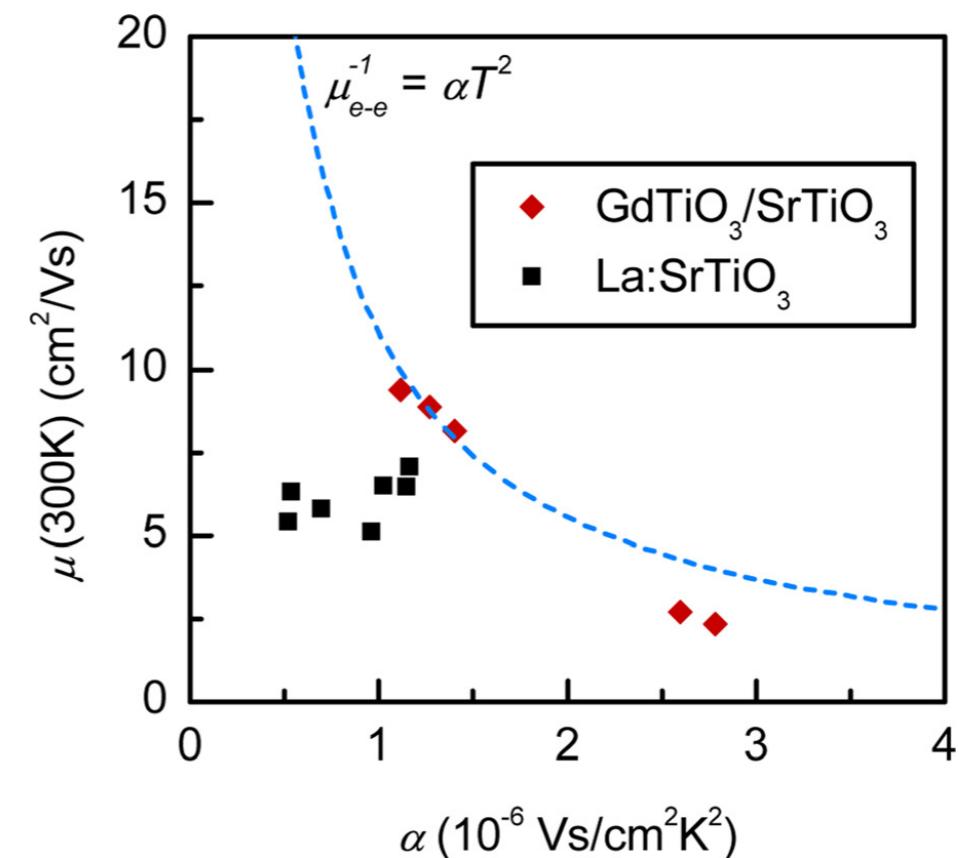
- 5d states of Ta have larger band-width than 3d of Ti
- Leads to higher band velocities
- Can **strain** be used to modify band masses/velocities ?
- Can we use even **heavier** atoms ?

2DEGs & screening LO modes out

Mikheev et al. Appl. Phys. Lett. 106, 062102 (2015)



Bulk doped STO



2DEG on STO thin-film

- Mobility fits to a quadratic T dependence instead of exponential in 2DEG
- High density 2DEG could screen the polarization field and remove the LO modes

Summary & Outlook

- Polarons (small & large) are ubiquitous in many perovskite oxide systems.
- Impact carrier transport, optical properties
- DFT based calculations give good insight

- Boltzmann transport + relaxation time approximation yield good qualitative description
- Code available (model e-p + transport)

https://github.com/bhimmetoglu/transport_new

- Development: Full e-p + other scattering mechanisms

LO phonon interaction

- Fröhlich interaction for multiple modes (using Born effective charges):

$$g_{\mathbf{q}\nu} \equiv \frac{e^2}{\epsilon_0 V} \sum_{s, \alpha, \beta, \lambda} \left(\frac{\hbar}{2 M_s \omega_{L\nu}} \right)^{1/2} \frac{1}{q} \hat{q}_\alpha (\epsilon_\infty^{-1})^{\alpha\beta} Z_s^{*\beta\lambda} e_{s\lambda}(\mathbf{q}; \nu)$$

- Simplifications:

$$|g_{\mathbf{q}\nu}|^2 = \frac{1}{q^2} \left(\frac{e^2 \hbar \omega_{L\nu}}{2\epsilon_0 V_{\text{cell}} \epsilon_\infty} \right) \frac{\prod_{j=1}^N \left(1 - \frac{\omega_{Tj}^2}{\omega_{L\nu}^2} \right)}{\prod_{j \neq \nu} \left(1 - \frac{\omega_{Lj}^2}{\omega_{L\nu}^2} \right)}$$

- For a single mode, the above expression is equivalent to Fröhlich.

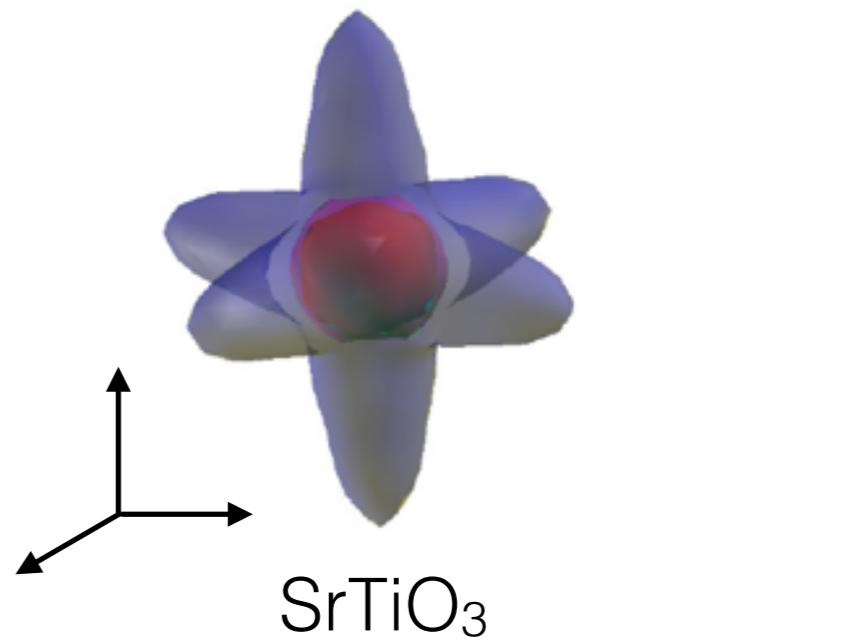
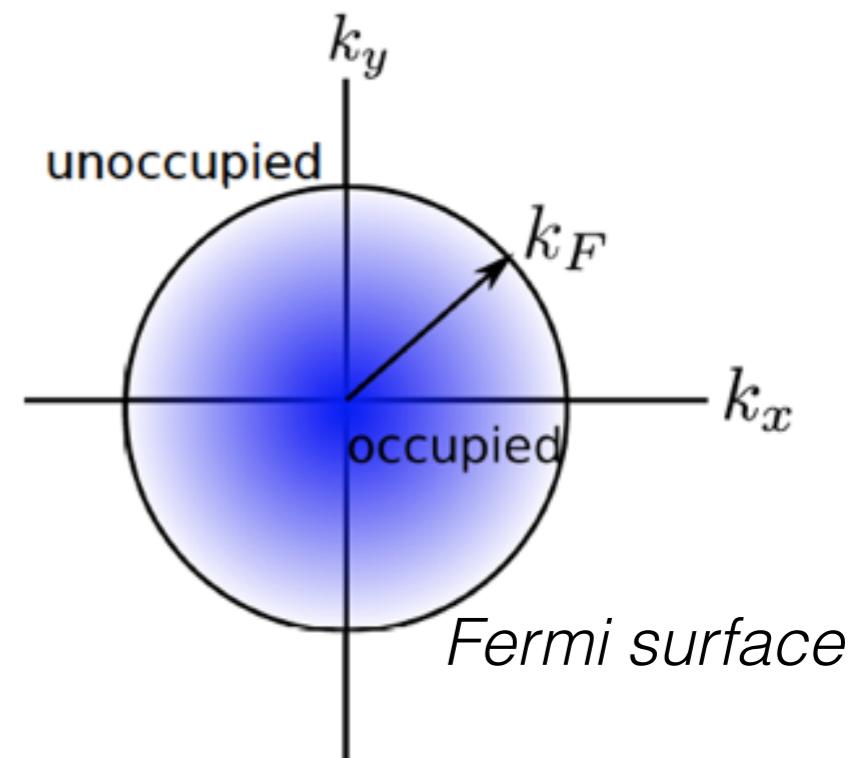
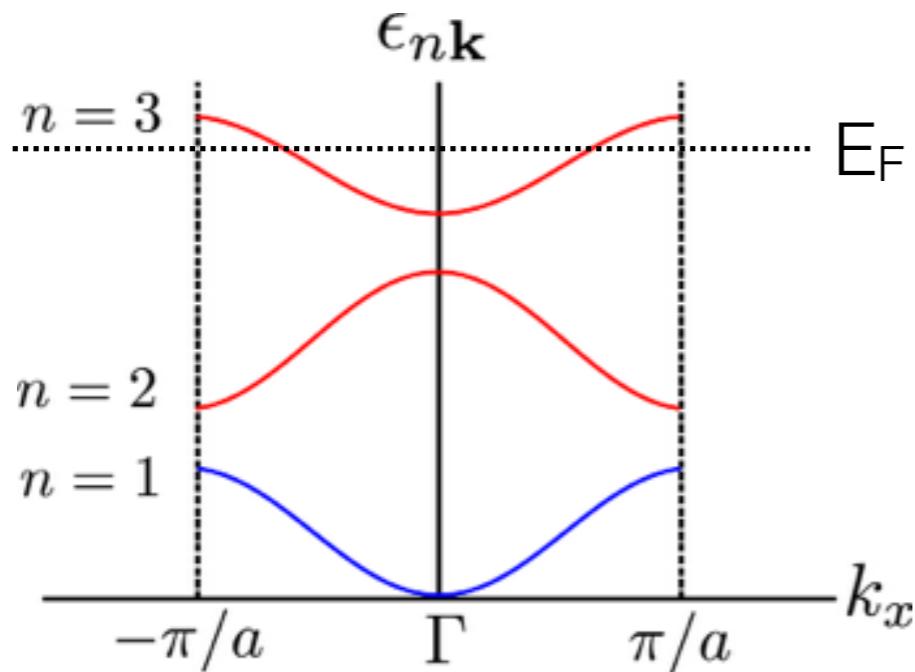
Transport

- Evolution of the distribution function f under applied \mathbf{E} -field:

$$f(\mathbf{r}, \mathbf{k}, t) d^3r d^3k$$

- Equilibrium distribution:

$$f_{n\mathbf{k}}^{(0)} = \frac{1}{e^{(\epsilon_{n\mathbf{k}} - E_f)/kT} + 1} \quad (\text{Fermi-Dirac})$$



Transport

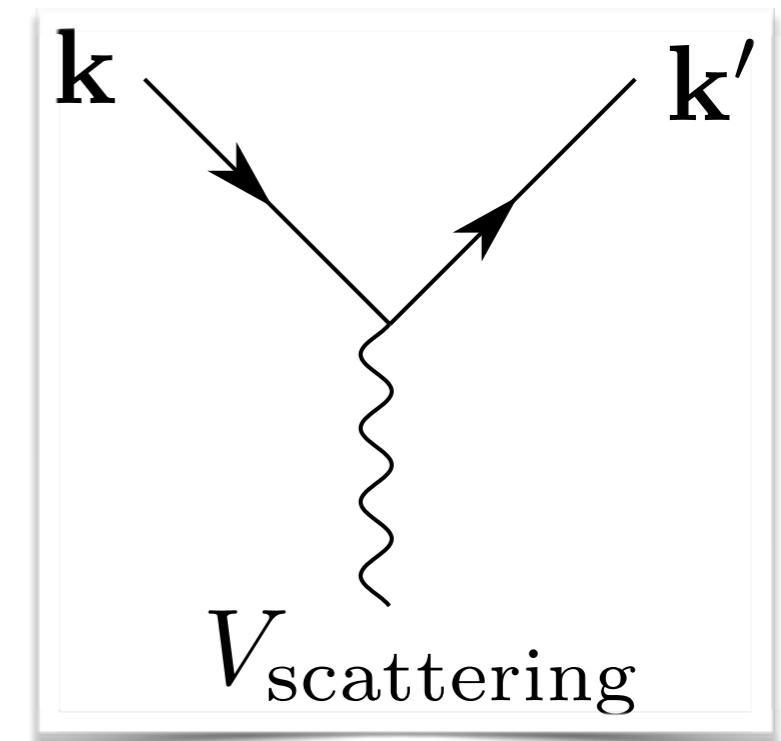
- **Boltzmann Transport Equation**
- Solution in terms of transport integrals \Rightarrow Conductivity:

$$\sigma_{\alpha\beta} = e^2 \sum_n \int d^3k \tau_{n\mathbf{k}} \left(-\frac{\partial f_{n\mathbf{k}}^{(0)}}{\partial \epsilon_{n\mathbf{k}}} \right) v_{n\mathbf{k},\alpha} v_{n\mathbf{k},\beta}$$

Band velocities: $v_{n\mathbf{k},\alpha} = \frac{1}{\hbar} \frac{\partial \epsilon_{n\mathbf{k}}}{\partial k_\alpha}$

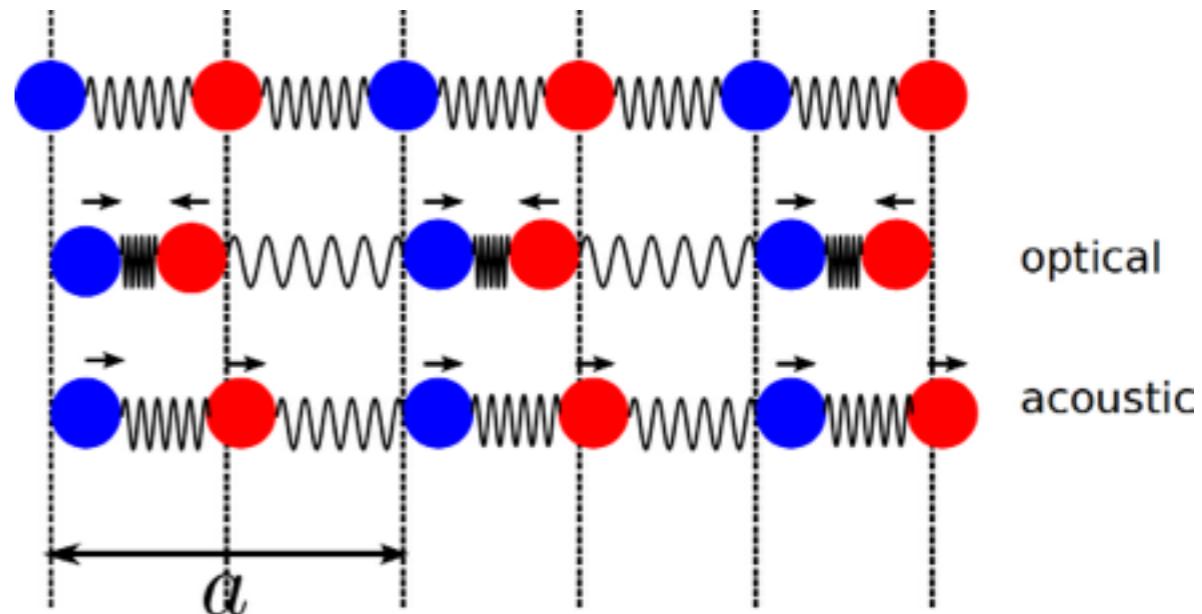
Scattering rates: $\tau_{n\mathbf{k}}^{-1}$

- Scattering times/rates determined by collisions:
 - Electron-defect
 - Electron-electron
 - **Electron-phonon**

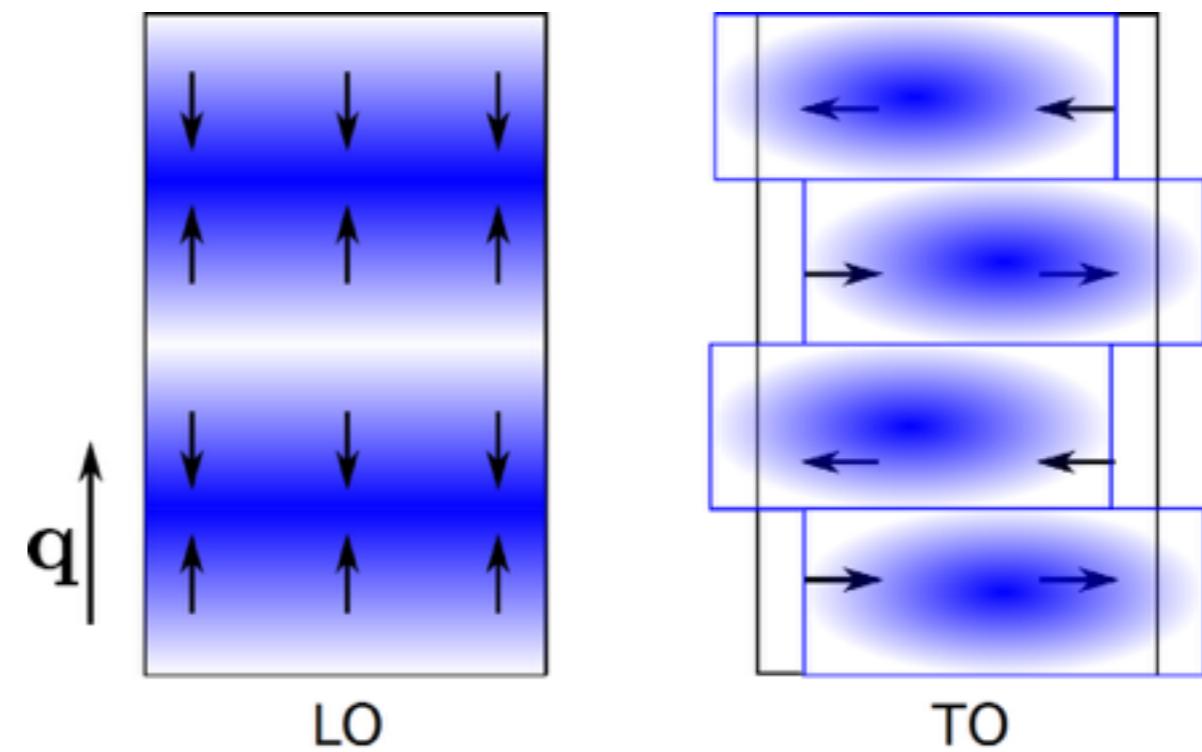


Phonon scattering

- A specific type of phonon scattering dominates at RT
- ***Longitudinal Optical (LO)*** phonons:



- Transverse vs longitudinal
- TO modes \Rightarrow charged planes slide
- ***LO modes \Rightarrow charge accumulation***
 - **Strong Coulomb scattering!**
 - **Dominant for materials with polar LO modes.**



Strongly correlated systems

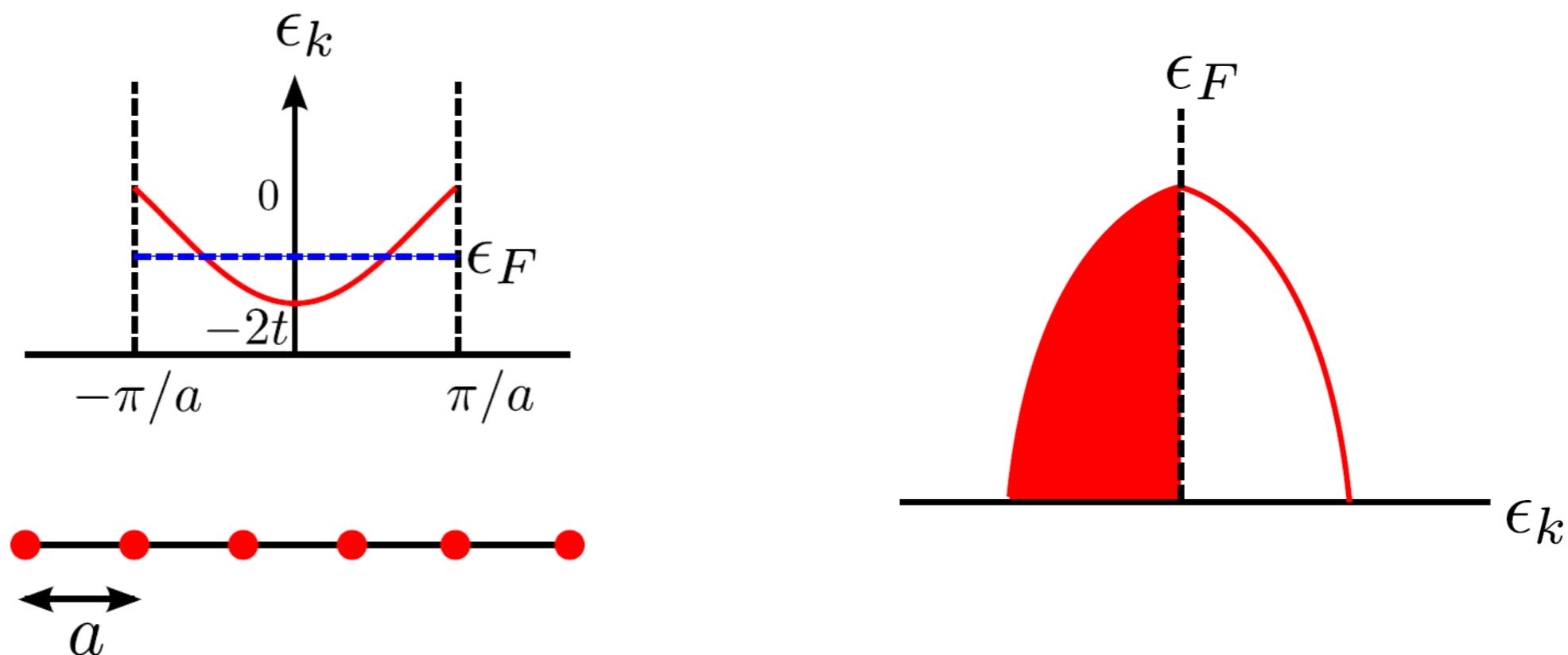
$$\mathcal{H} = \boxed{-t \sum_{\langle i,j \rangle, \sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c)} + \textcolor{red}{U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}$$

Independent e^-

$e^- - e^-$ interaction

$t \gg U$

Small Coulomb repulsion: **U** large hopping amplitude: **t**



Strongly correlated systems

$$\mathcal{H} = -t \sum_{\langle i,j \rangle, \sigma} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

Independent e^-

$e^- - e^-$ interaction

$t \ll U$

Large Coulomb repulsion: **U** small hopping amplitude: **t**

