Electrons, phonons and screening

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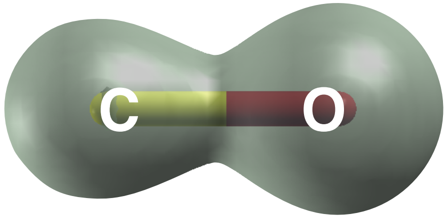
Exciting NEWS 2021
~~HUBerlin July 2020~~
~~Riga June 2021~~
on Zoom June 23rd 2021

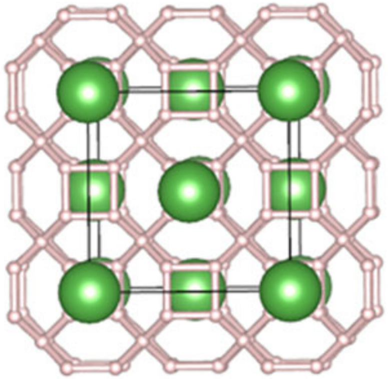
First principles quantum simulations

$$\mathscr{H}\Psi = E\Psi$$



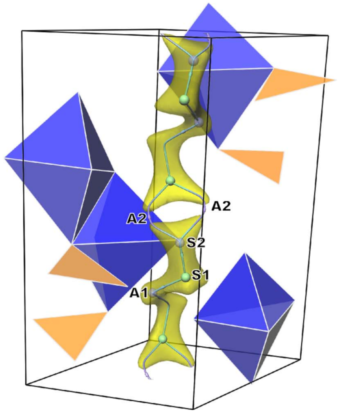
Calculate:

- Structure
- Bonding
- Magnetism
- **Thermodynamics**
- **Kinetics**
- **Superconductivity**
- **Transport**



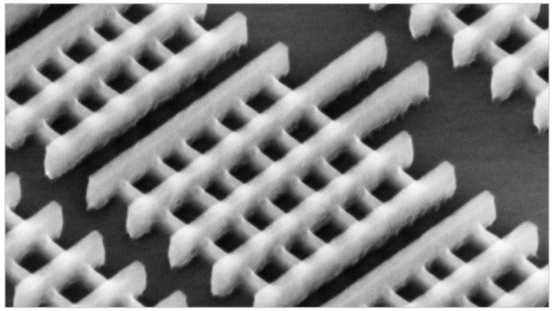
RT superconductor

Drozdov *Nature* 569 528 (2019)

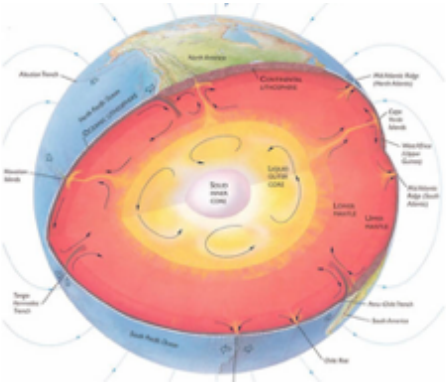


Battery anodes

Kim J. ECS 158 A309 (2011)



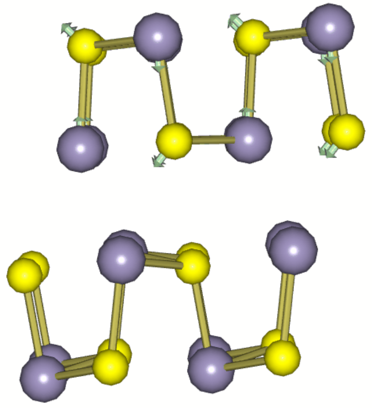
Intel HfO_2 dielectric



Earth's core

Gomi Verstraete et al. PEPI 224 88 (2013)

DPFT refresher



Start from DFT

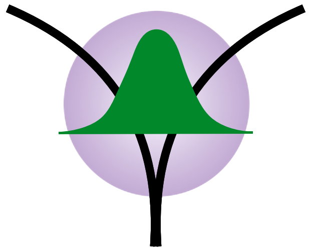
what moves?

- direct
- induced (SCF)
- Pulay/basis set

$$H_k^{(0)}\left|\psi_{ik}^{(0)}\right\rangle = \varepsilon_{ik}^{(0)}\left|\psi_{ik}^{(0)}\right\rangle$$

$$H^{(0)} = T + V_{loc+NL}\underset{\uparrow}{(R)} + V_{Hxc}[n\underset{\uparrow}{(R)}]$$

$$H_k^{\alpha}\left|\psi_{ik}^{\alpha}\right\rangle = \varepsilon_{ik}^{\alpha}\left|\psi_{ik}^{\alpha}\right\rangle$$



Pertrub 1st order

$$\left(H_k^{(0)} - \varepsilon_{ik}^{(0)}\right)\left|\psi_{ik}^{\alpha}\right\rangle = -\left(H_k^{\alpha} - \epsilon_k^{(\alpha)}\right)\left|\psi_{ik}^{(0)}\right\rangle$$

+ choose gauge

$$\left\langle \psi_j^{(0)} \mid \psi_i^{\alpha}\right\rangle = 0 \quad \forall j$$

See lecture on phonons by Fabio Caruso:
https://www2.physik.hu-berlin.de/how-exciting/talk-fabio-caruso.mp4

EPC refresher

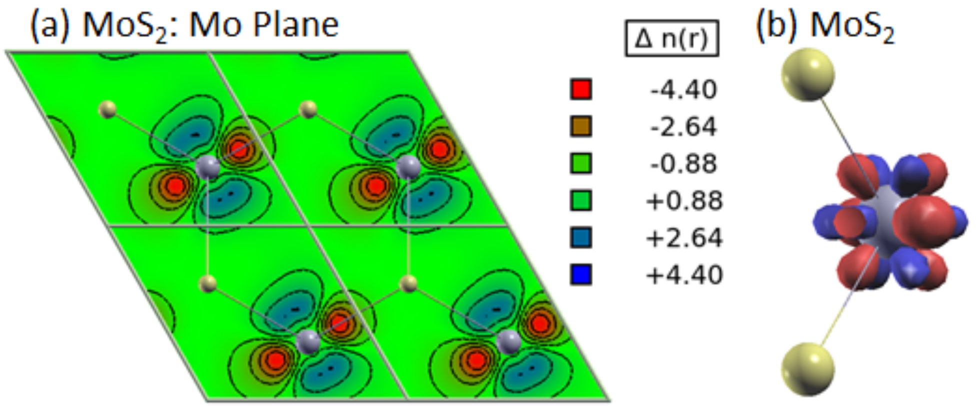
Sternheimer:

- variational SCF
- project on unoccupied states

$$P_{ck}\left(H_k^{(0)} - \varepsilon_{ik}^{(0)}\right) P_{ck} \left|\psi_{ik}^{\alpha}\right\rangle = -P_{ck} H_k^{\alpha} \left|\psi_{ik}^{(0)}\right\rangle$$

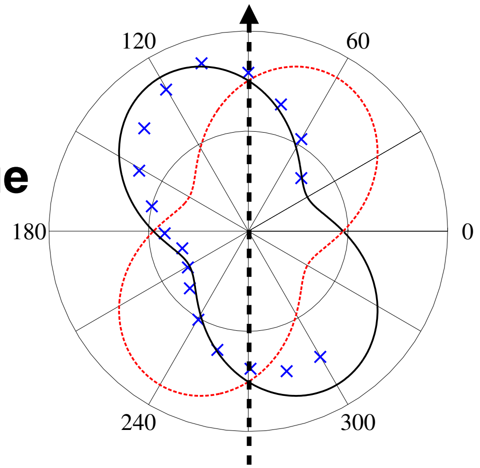
Advantages:

- "easier" than Kohn Sham
- also q dependent (any q!)
- extract coupling: $g_{kij}^{\alpha q} = \left\langle \psi_{ik+q}^{(0)} \middle| H_k^{\alpha q} \middle| \psi_{jk}^{(0)} \right\rangle$



Pike Verstraete PRB 95 201106 (2017)

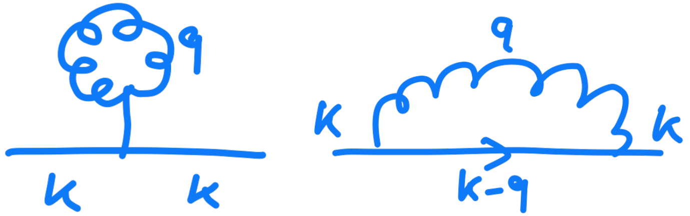
Flipped sign for
Born Effective Charge
Signature in
Polarized Raman

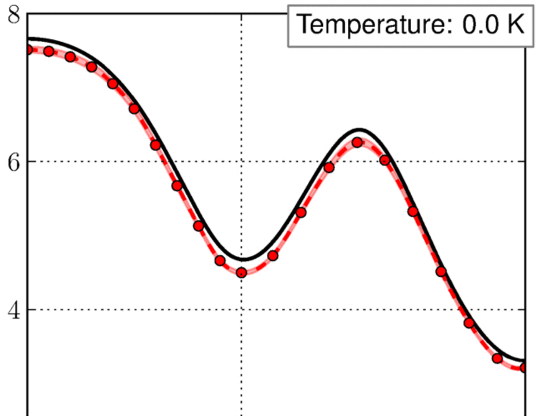


See the lecture on EPC by Sebastian Tillack:
https://www2.physik.hu-berlin.de/how-exciting/talk-sebastian-tillack.mp4

Now what does it do?

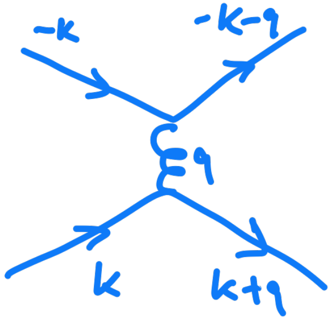
Electron energy renormalization (AHC, polarons)

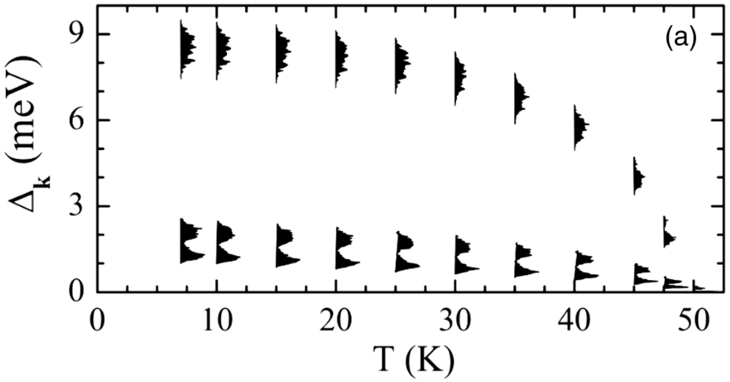




Poncé J Chem Phys 143 102813 (2015)

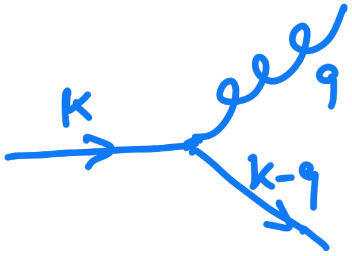
Electron pairing (superconductivity)



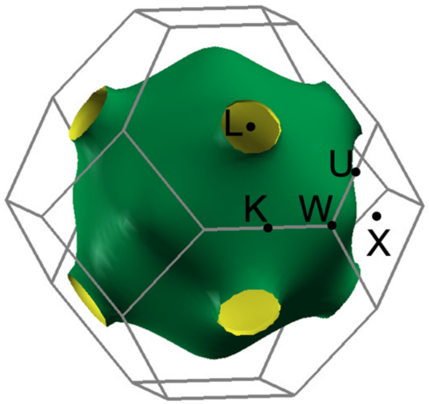


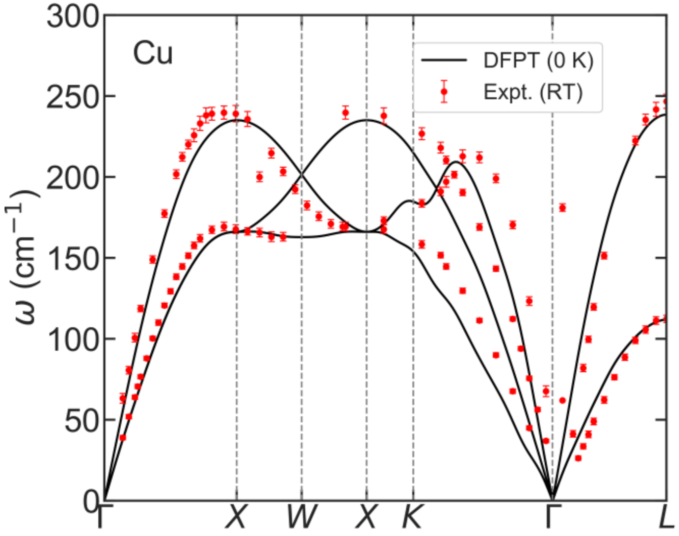
Margine Phys. Rev. B 87 024505 (2013)

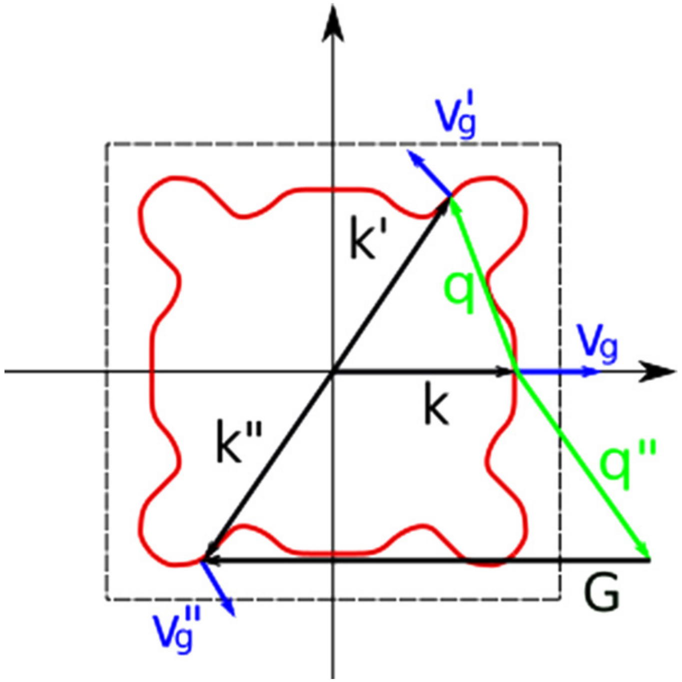
Electron scattering (resistance, Seebeck)

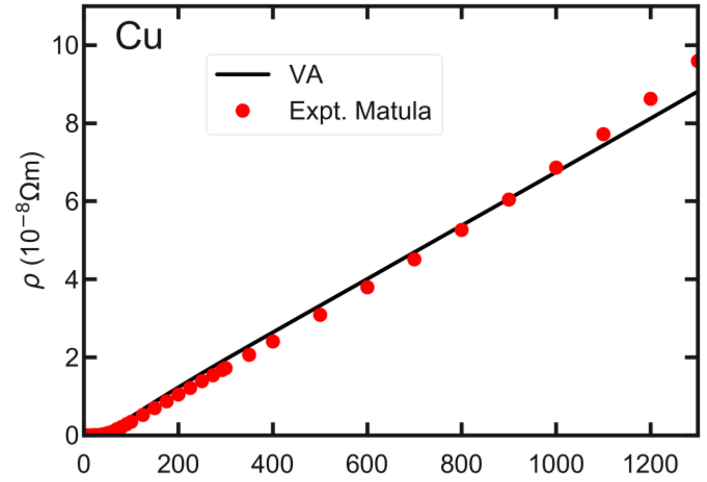


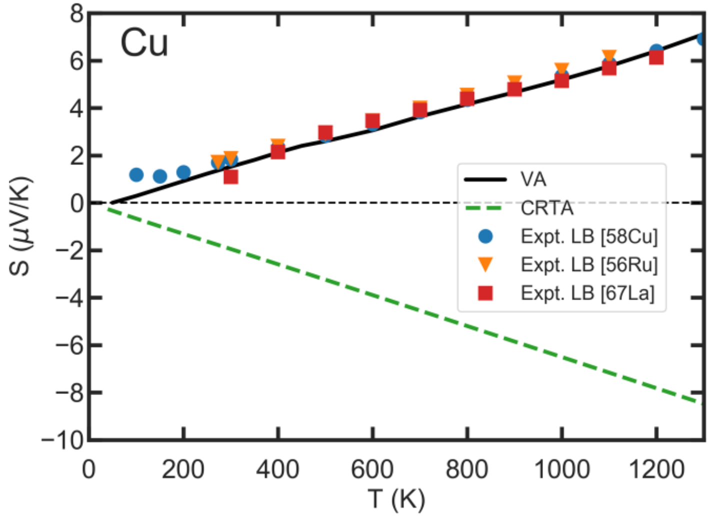
Transport, thermoelectricity



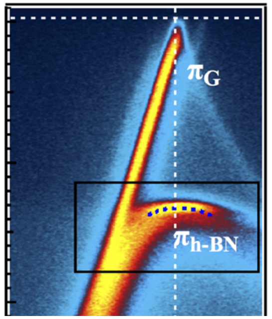




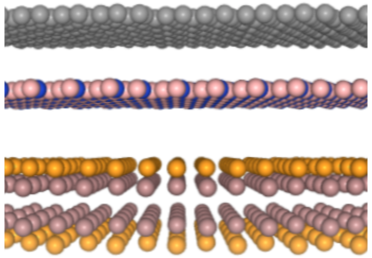




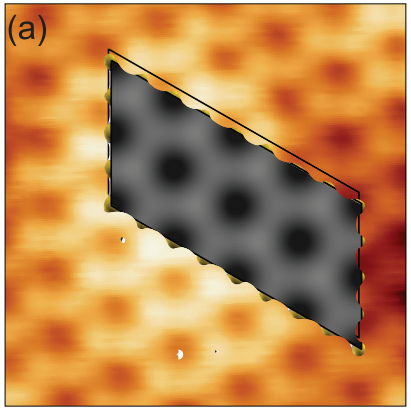
Xu DiGennaro Verstraete PRB 102 155128 (2020)



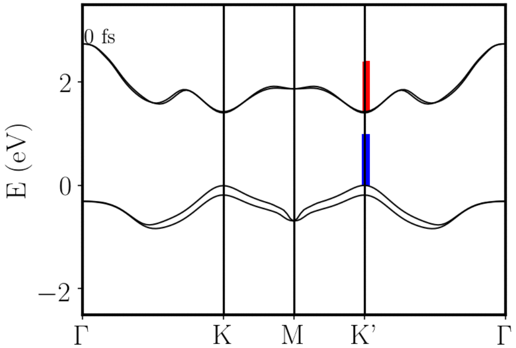
Spectroscopy



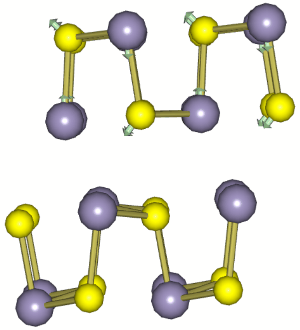
Transport



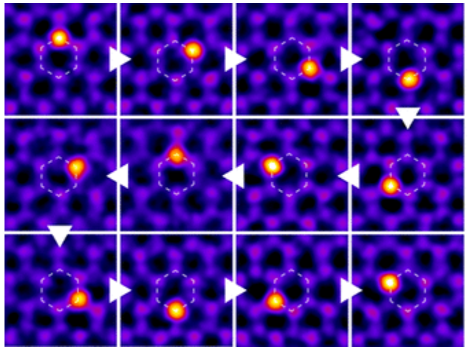
Microscopy



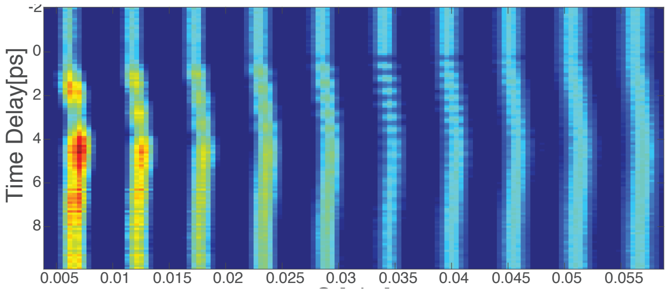
Electrons



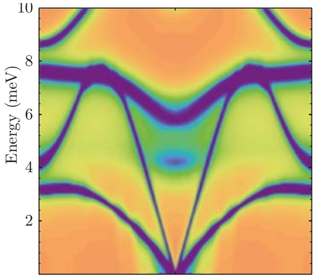
Phonons



Defects

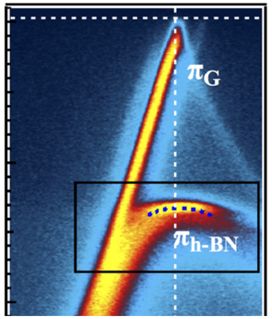


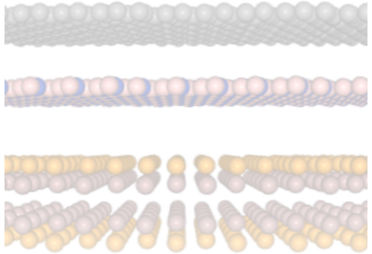
Ultrafast (FEL, pump/probe)

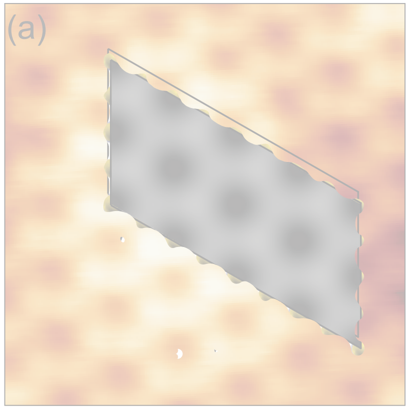


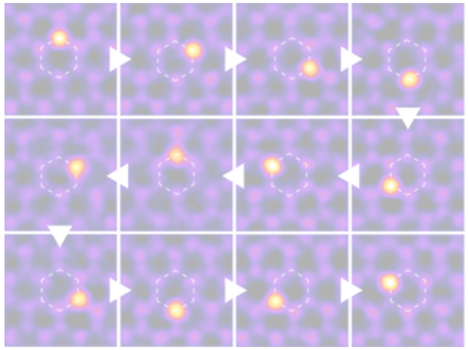
Synchrotrons
neutrons

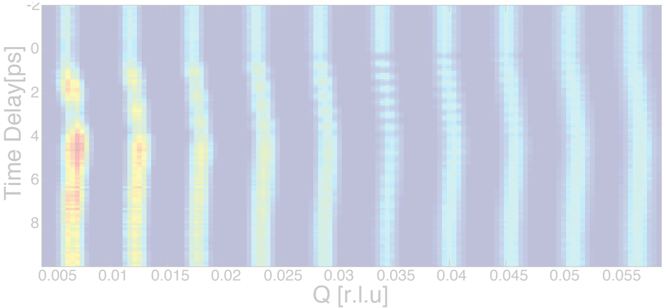
High Throughput Polarons

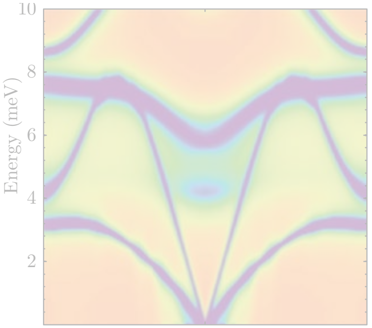








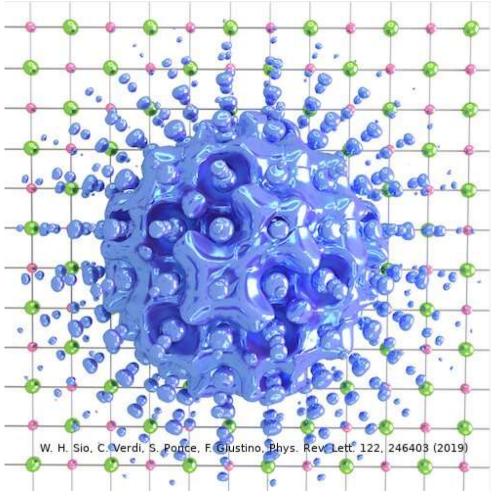




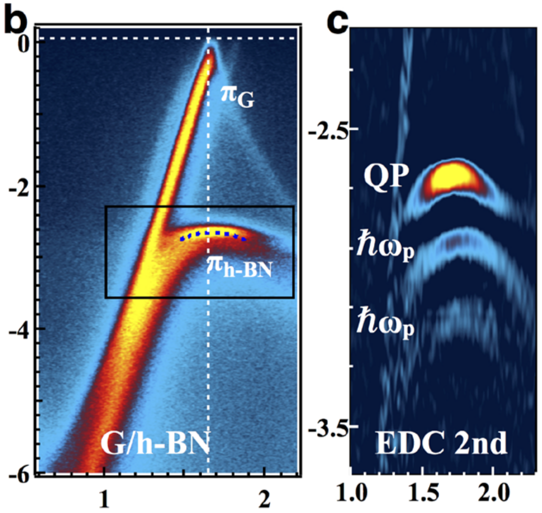
Polaron overview

What is a polaron anyway?

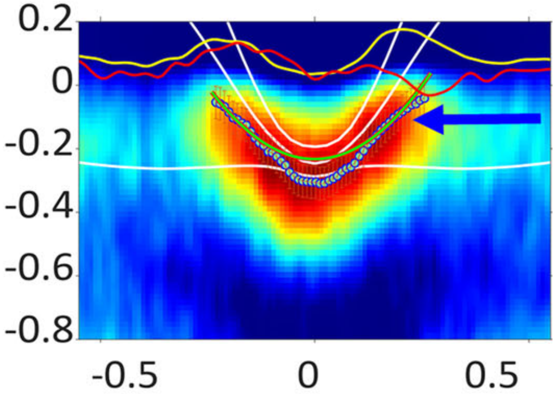
Signatures in optics, transport, superconductivity…



Sio PhysRevLett (2019)



Chen Nano Lett (2018)



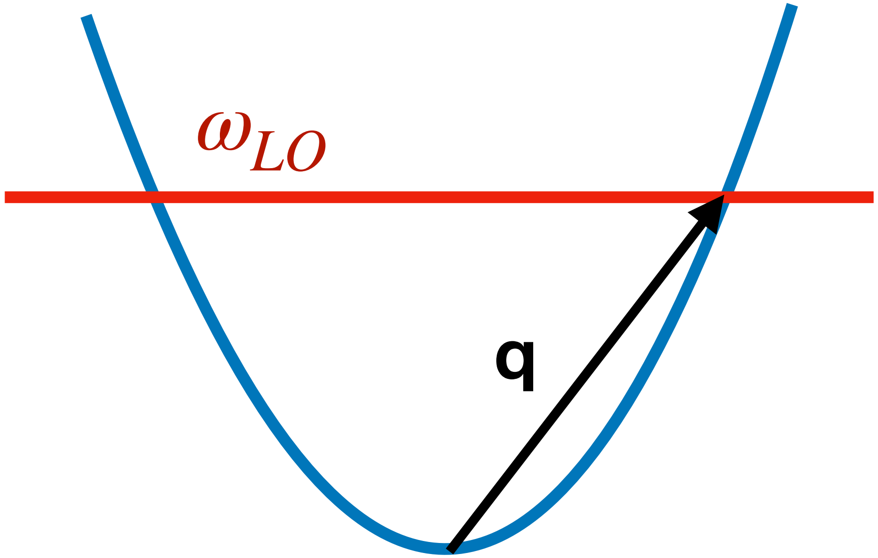
$CaCeMnO_3$

Husanu Nat Comms (2020)

- How common are different types?
- How far can we get with simple models?

See previous lecture on polarons and ARPES by Carla Verdi!

Fröhlich model



1 electron 1 polar phonon

Long range electrostatic coupling

Single free parameter α

Binding energy $E_P \simeq -\alpha\omega_{LO}$

aka Zero Point Renormalization (ZPR)

Perturbation theory catastrophe at α=6

Fröhlich Adv. Phys. (1954)
Mishchenko PRB (2000)
Story PRB (2014)
Sjakste PRB (2015)
Verdi PRL (2015)

$$\alpha = \left(\frac{1}{\varepsilon^{\infty}} - \frac{1}{\varepsilon^{0}}\right)\sqrt{\frac{m^*}{2\omega_{LO}}} \qquad \frac{m^*_{\mathrm{P}}}{m^*} \approx \left(1 - \frac{\alpha}{6}\right)^{-1}$$

Methods

Descriptors: m^* ε^∞ ε^0 ω_0

Materials Project databases:

- Intersection of $>$ 1039 materials:
- 9000 m^* : F. Ricci Sci Data (2017)
- 1500 phonons: G. Petretto Sci Data (2018)

Criteria:

- ICSD stable 3D, nonmagnetic, insulators
- 2-5 elements per unit cell

Conduction band minimum (also valence)

pymatgen

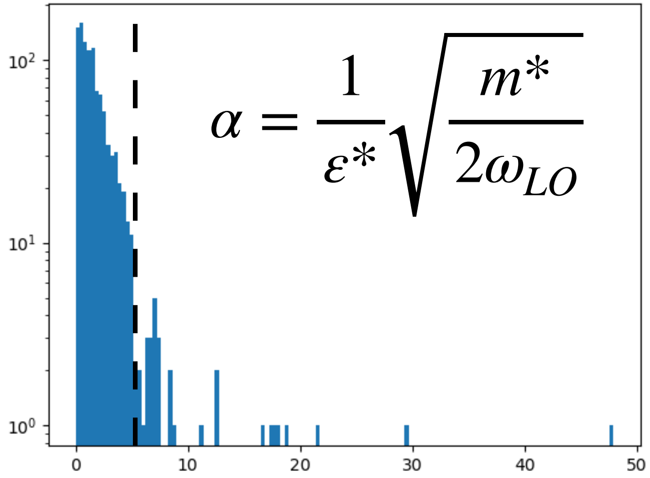
MPContribs

Abinit

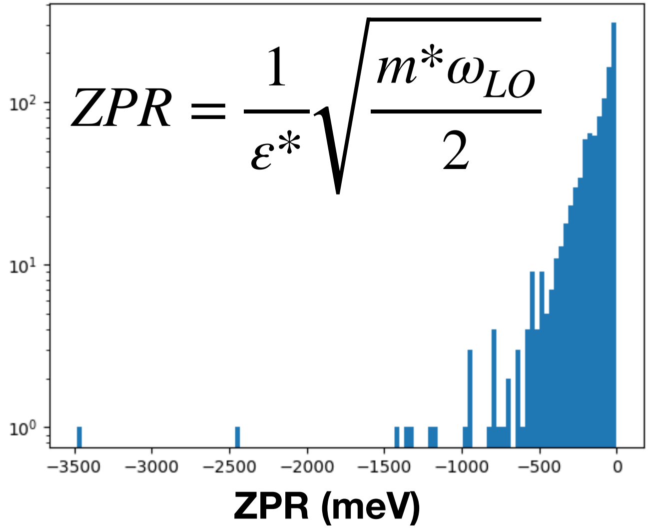
abipy

$$\alpha = \left(\frac{1}{\varepsilon^\infty} - \frac{1}{\varepsilon^0}\right)\sqrt{\frac{m^*}{2\omega_{LO}}}$$

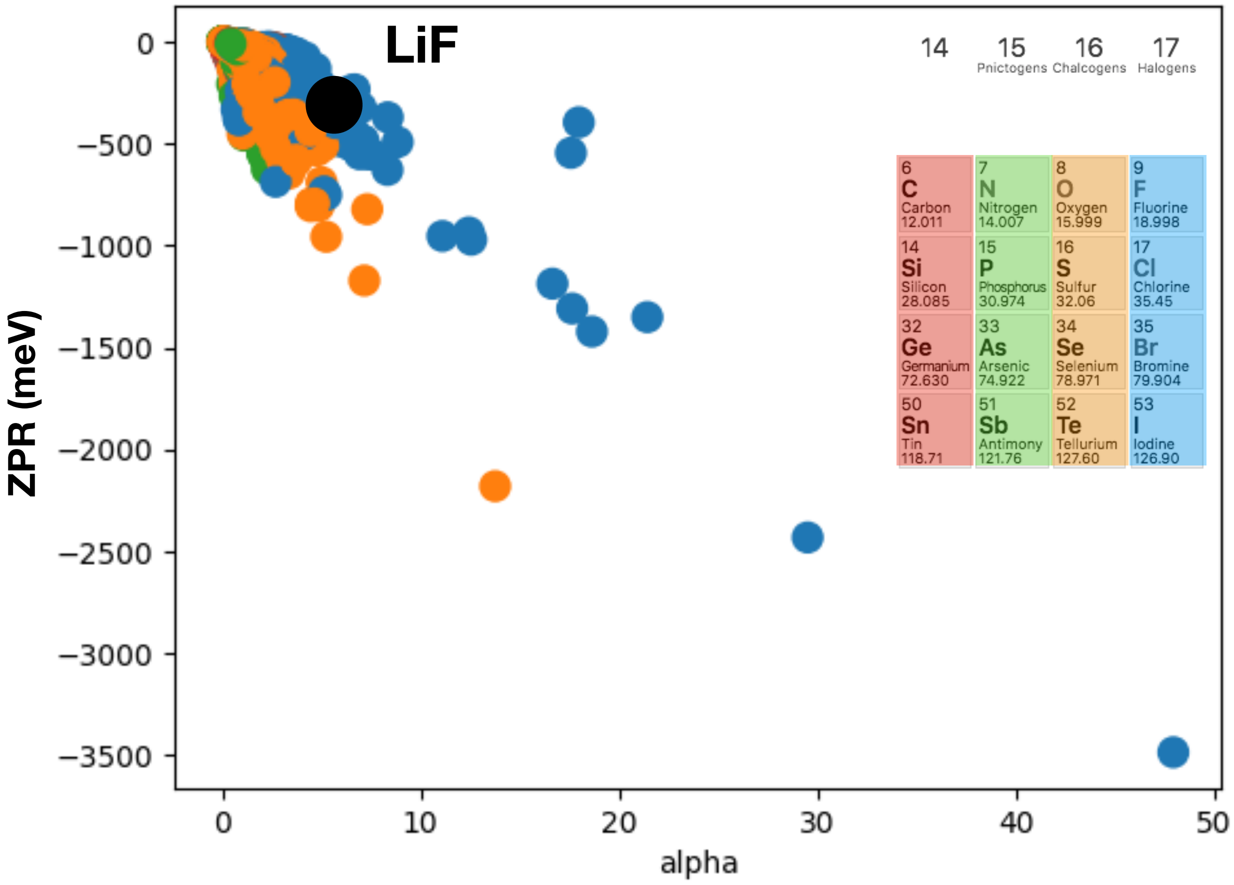
Distribution of alpha and ZPR



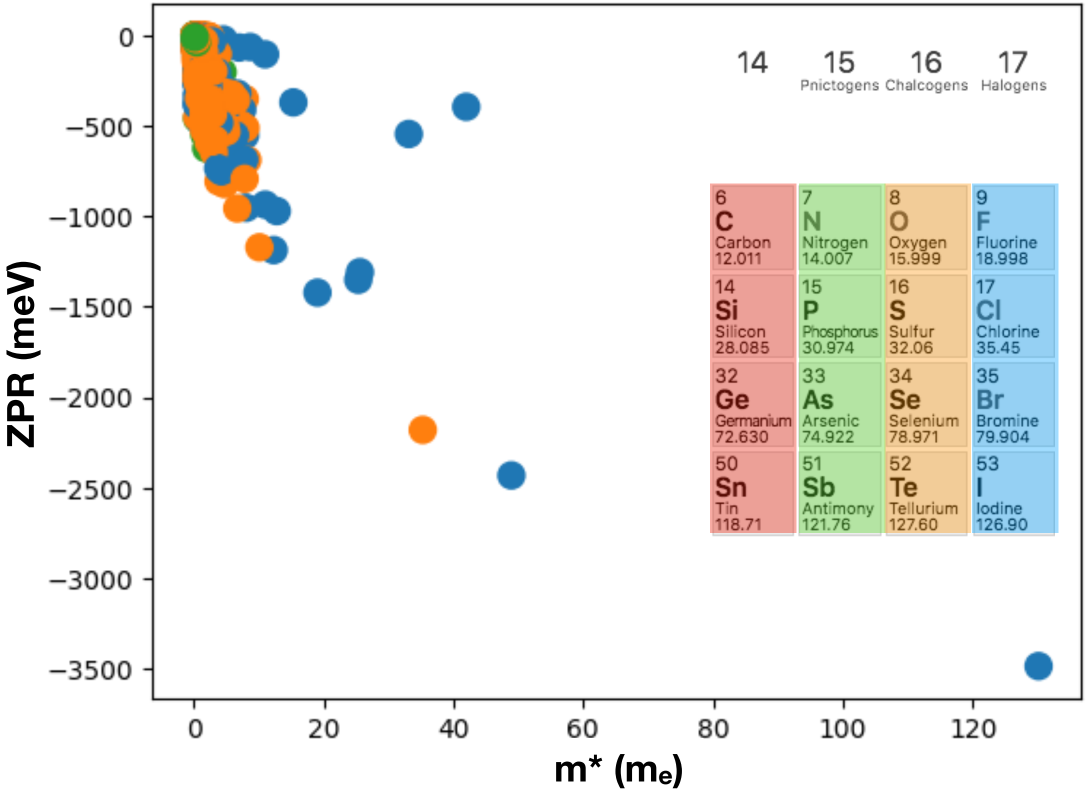
$$\alpha = \frac{1}{\varepsilon^*}\sqrt{\frac{m^*}{2\omega_{LO}}}$$

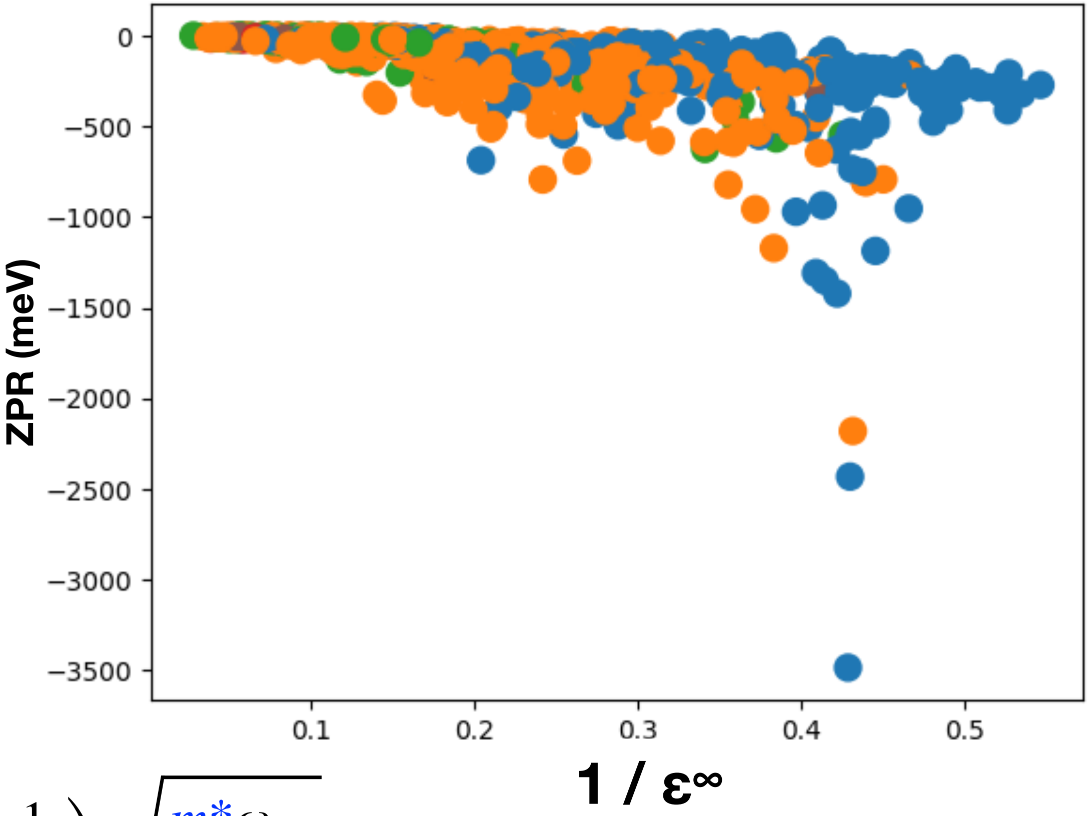


$$ZPR = \frac{1}{\varepsilon^*}\sqrt{\frac{m^*\omega_{LO}}{2}}$$



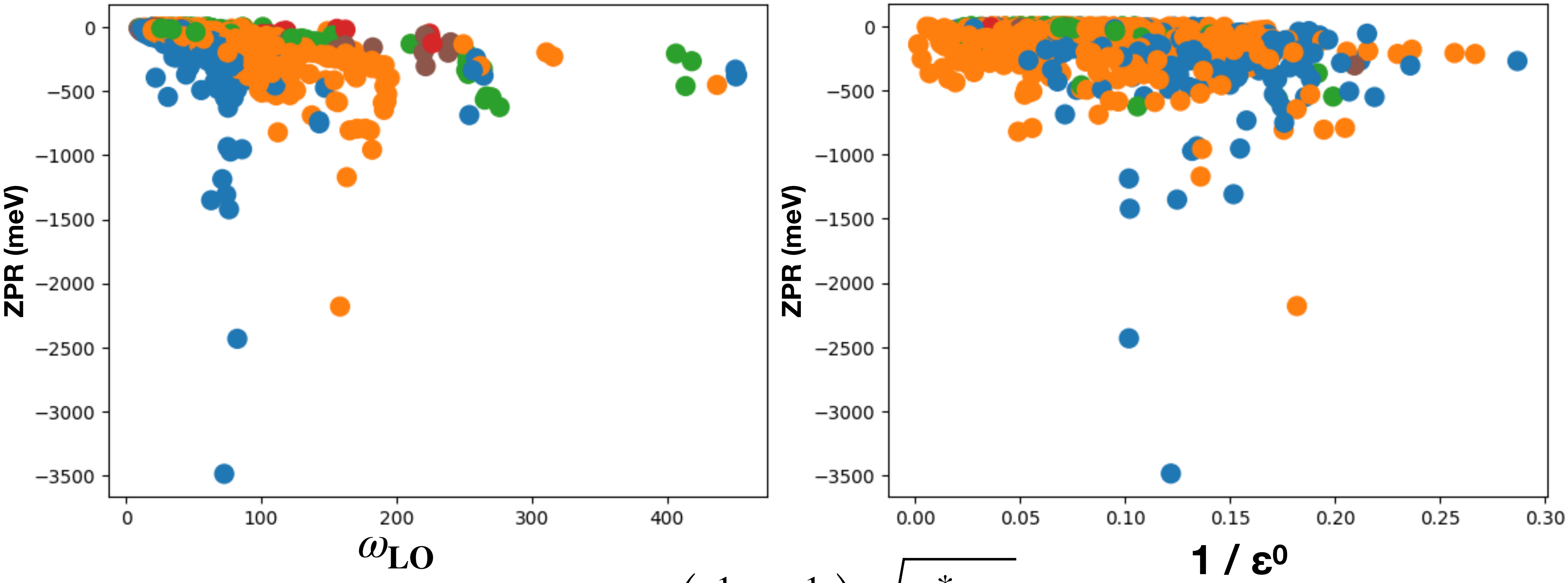
Electron effects





$$ZPR = \left(\frac{1}{\varepsilon^{\infty}} - \frac{1}{\varepsilon^{0}}\right)\sqrt{\frac{m^{*}\omega_{LO}}{2}}$$

Phonon effects



$$ZPR = \left(\frac{1}{\varepsilon^{\infty}} - \frac{1}{\varepsilon^{0}}\right)\sqrt{\frac{m^{*}\omega_{LO}}{2}}$$

Beyond Fröhlich - Generalization

Degenerate bands

All phonon modes

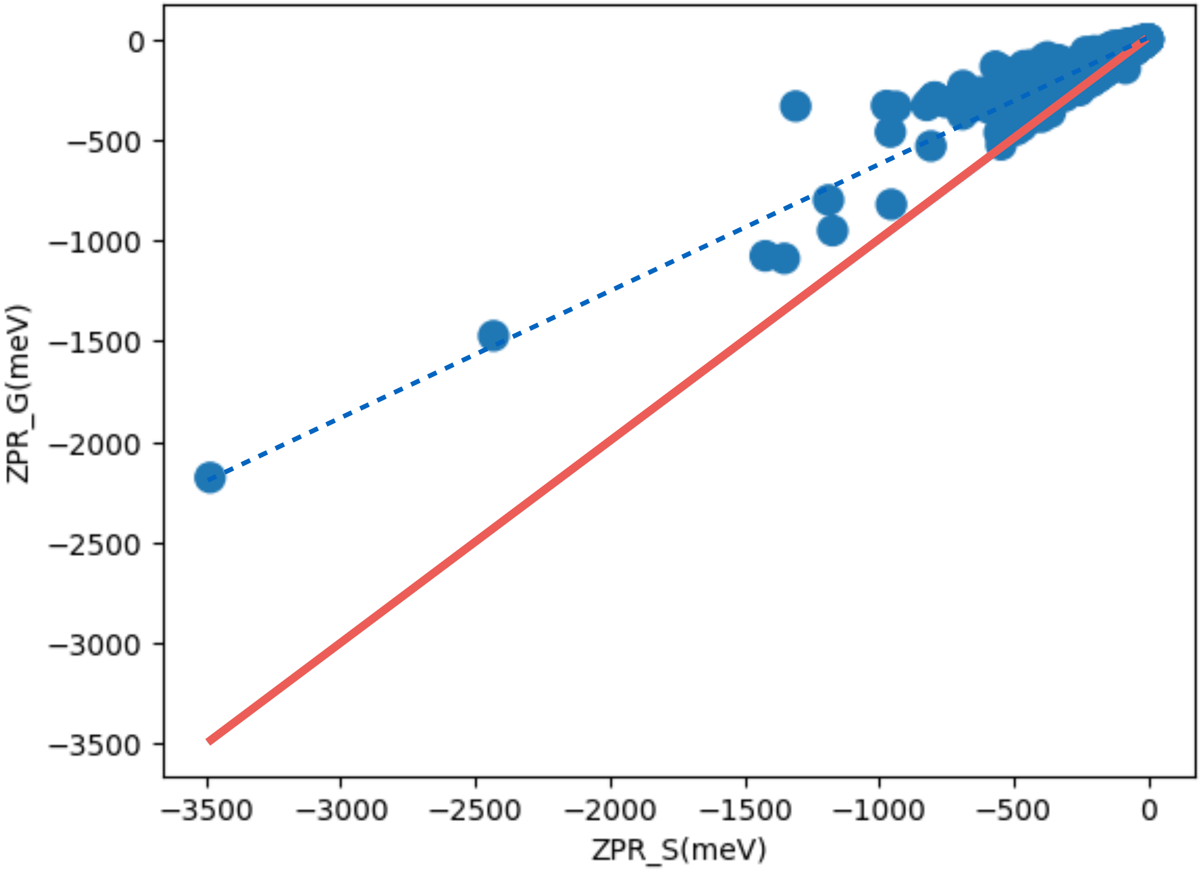
Directional m*

Directional variation of ε and ω

$$\alpha_j = \int d\hat{q} \frac{\langle (m_n^*(\hat{q}))^{1/2} \rangle_n}{\epsilon_j^*(\hat{q}) \sqrt{2\omega_j(\hat{q})}}$$

A. Miglio npj Comp Mater (2020)

Why does Frohlich work so well?



Beyond Fröhlich - validation

How far off are the Fröhlich models?

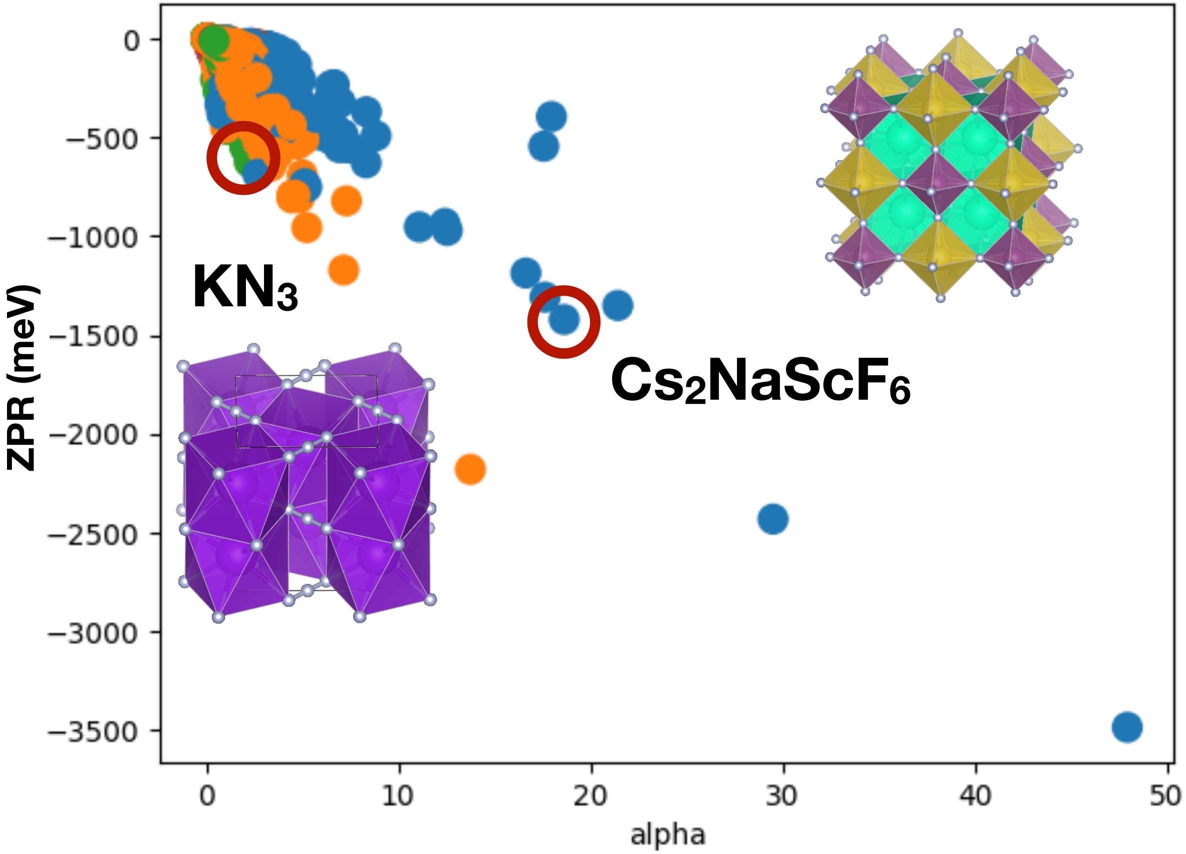
Which modes contribute?

Calculate ZPR with AHC theory

- DFPT Phonons, m*
- Nery PRB (2018)

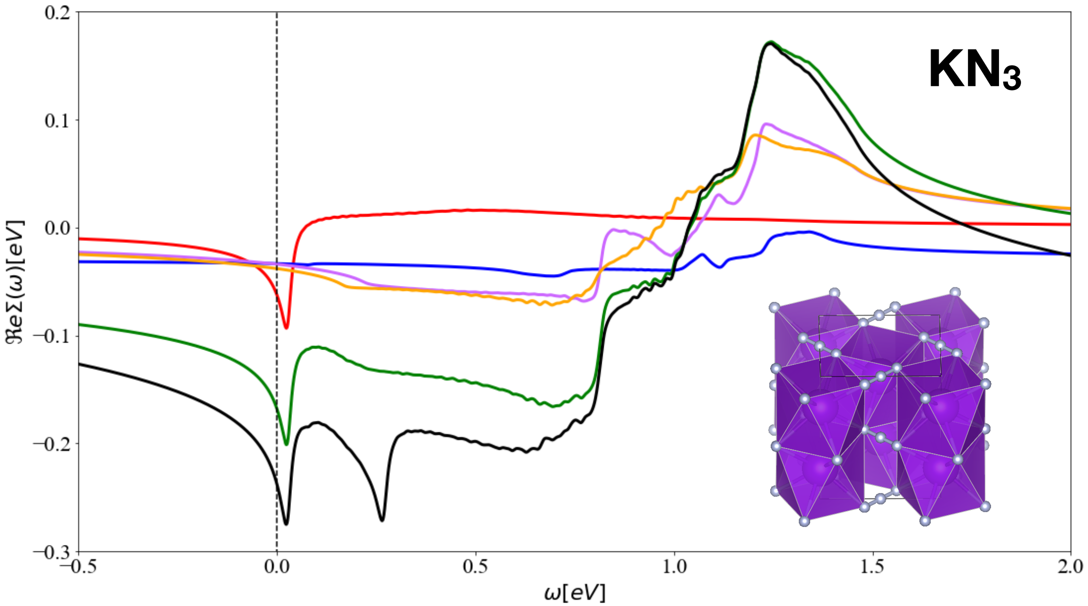
KN_3 : large ZPR small alpha

Cs_2NaScF_6 : large ZPR large alpha

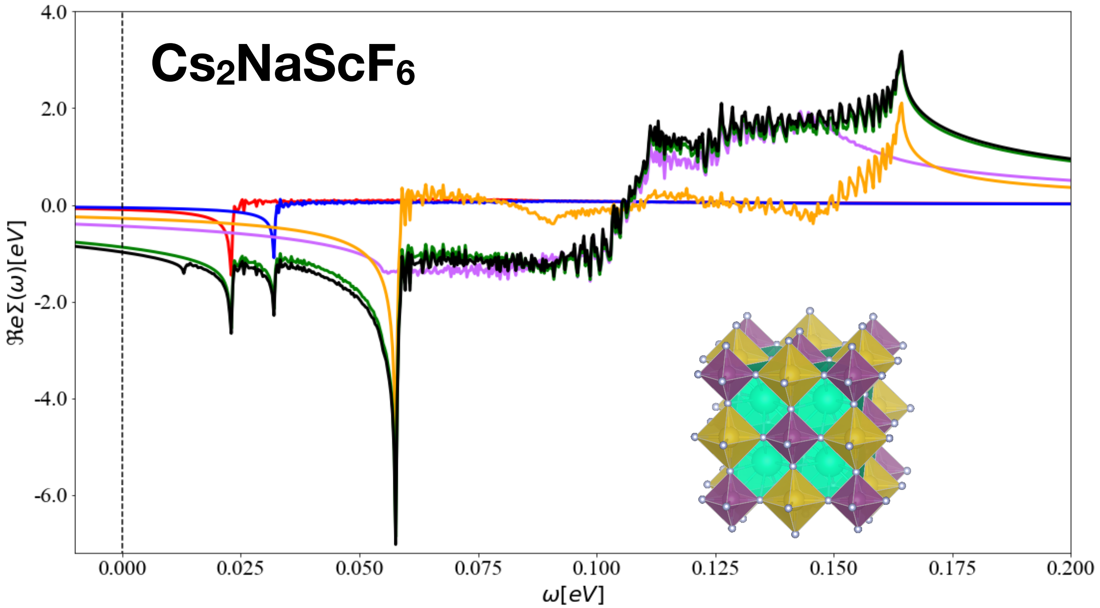


Beyond Fröhlich - validation

$$\Sigma^{\text{Fan}}_{\mathbf{k}nj}(\omega) = \frac{1}{N_q}\sum_{\mathbf{q}}^{\text{BZ}}\sum_{n'}\left|\left\langle \mathbf{k}+\mathbf{q}n' \middle| H^{(1)}_{\mathbf{q}j} \middle| \mathbf{k}n\right\rangle\right|^2 \times \left[\frac{1-f_{\mathbf{k}+\mathbf{q}n'}}{\omega-\varepsilon_{\mathbf{k}+\mathbf{q}n'}-\omega_{\mathbf{q}j}+i\eta} + \frac{f_{\mathbf{k}+\mathbf{q}n'}}{\omega-\varepsilon_{\mathbf{k}+\mathbf{q}n'}+\omega_{\mathbf{q}j}+i\eta}\right]$$



sFr(DB)	sFr(Abinit)	gFr(DB)	**AHC**
-542	-330	-153	**-245**

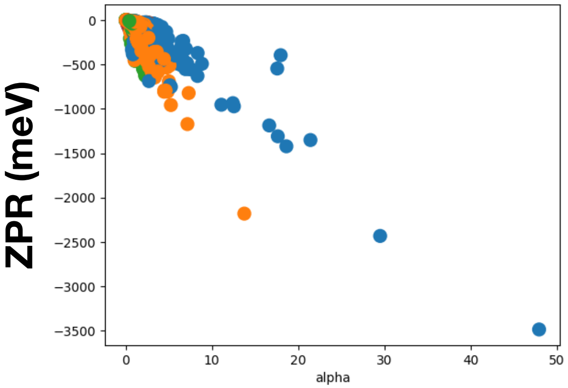


sFr(DB)	sFr(Abinit)	gFr(DB)	**AHC**
-1351	-1241	-1089	**-966**

Polaron takeaway

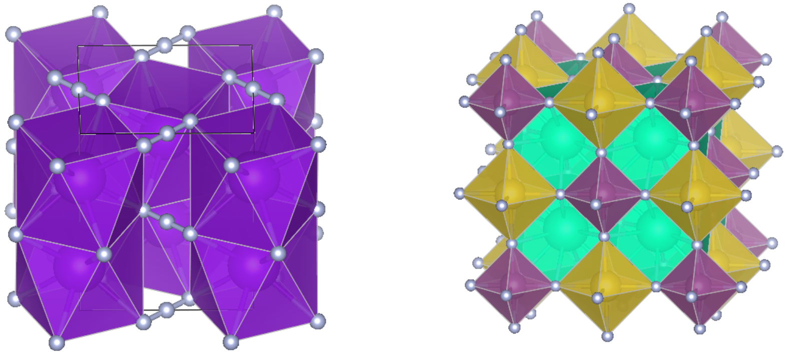
High throughput Fröhlich

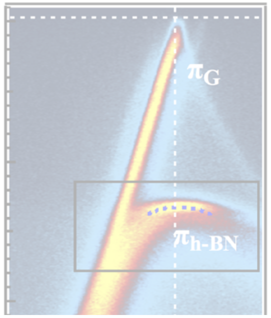
- Clustering by element period/ionicity
- Monotonic electron contribution
- Competing constraints in $\varepsilon_0\ \omega_{LO}\ \varepsilon_\infty\ m^*$
- Valid predictor for order of magnitude

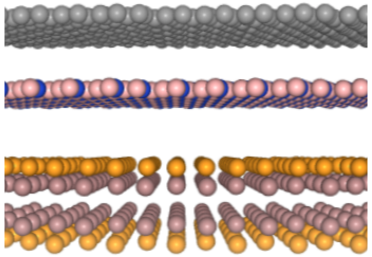


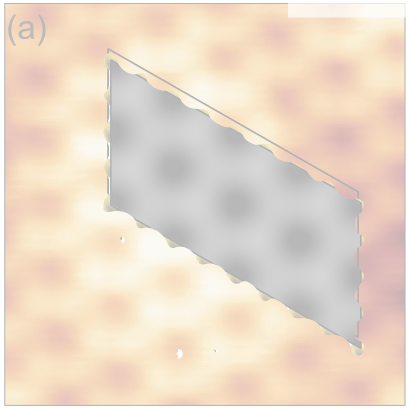
Comparison with full DFPT + AHC theory:

- Many phonons intervene
- Highest LO does not dominate
- Fröhlich ZPR 30-50% overestimation

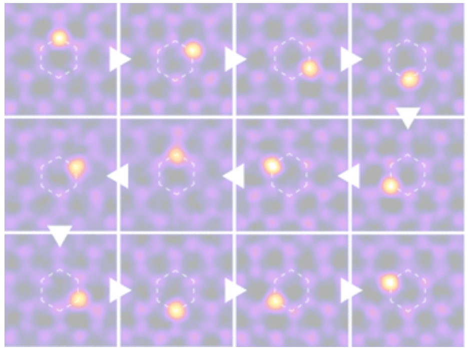


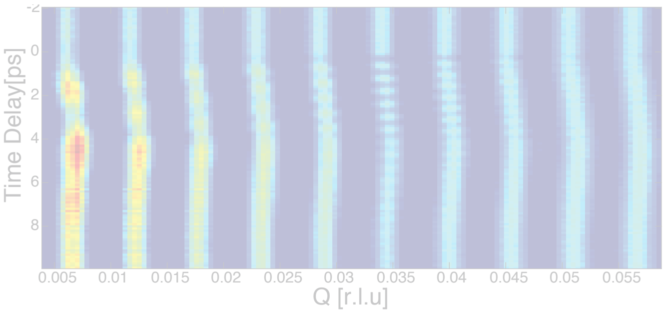


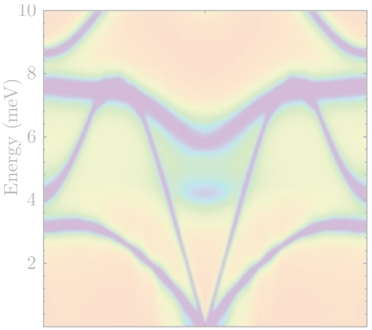




Dielectric nano-engineering







2D Electronics

Goal: maximize electron mobility

Also for opto- or spintronics

Issues for 3D materials @ nanoscale:

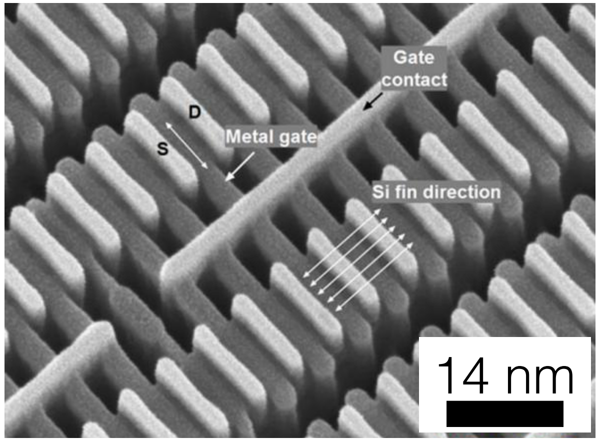
leakage, heat, fabrication, cost

What changes in 2D?

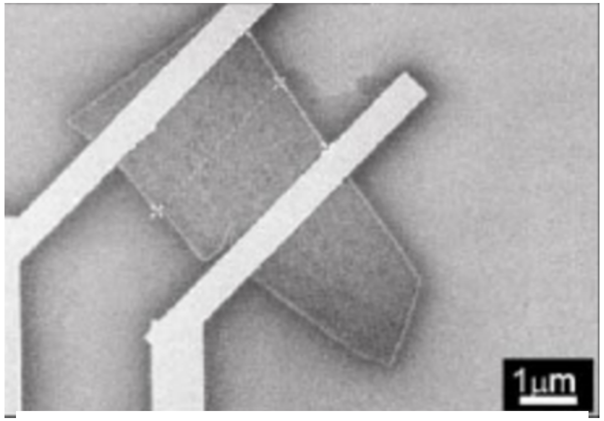
+ low mass
+ low operational voltage
+ easy assembly

+/- environment sensitive

Find optimal material (combination)

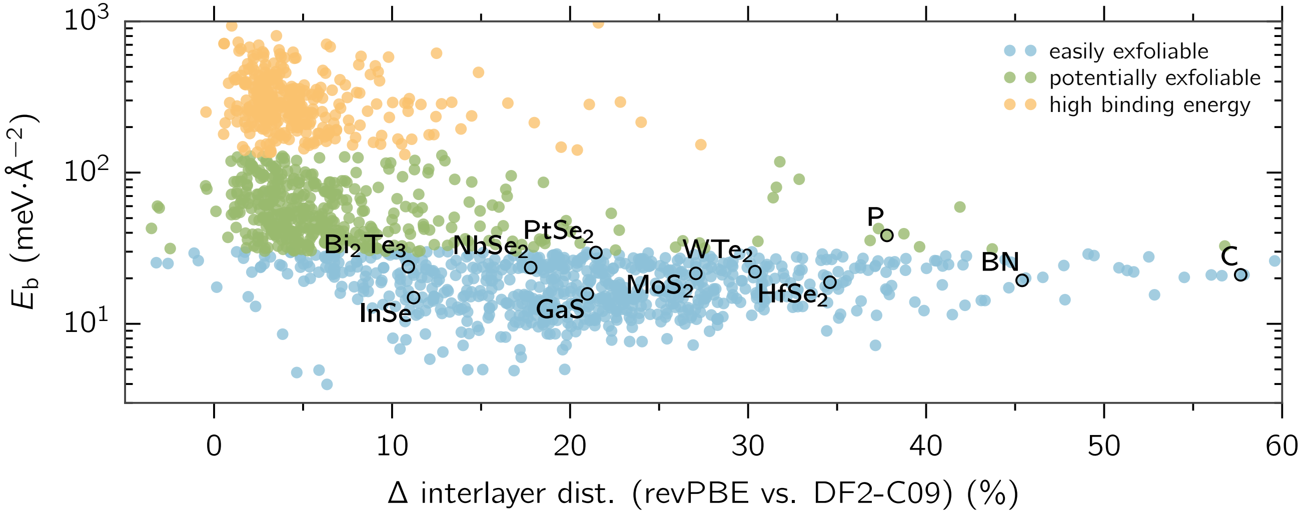


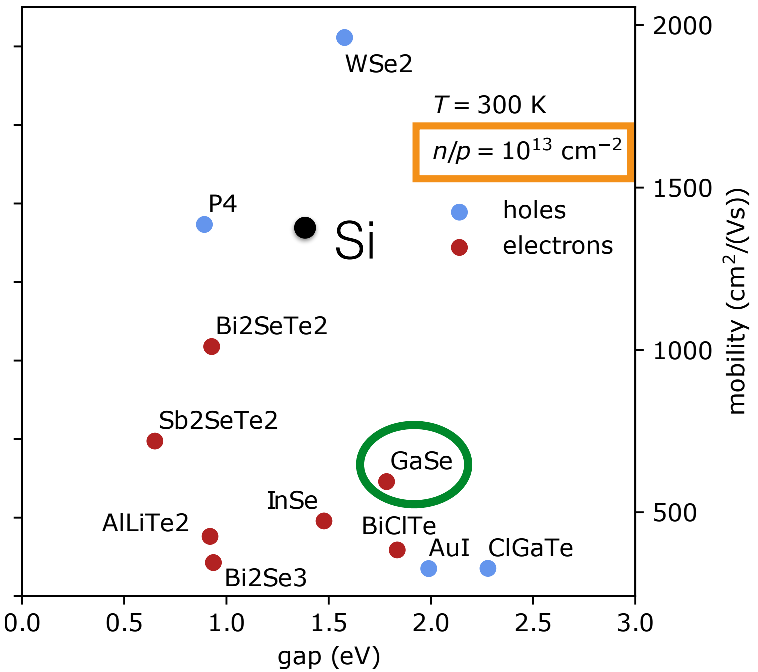
3D Si FinFET
Samsung (2020)



2D graphene
Chen IBM (2008)

Filter the interesting candidates





100 000 3D parents

2000 easily exfoliable

250 small unit cells

12 mobility calculation

Mounet Nat. Nano 13 246 (2018)

Sohier 2D Mater. 8 015025 (2020)

QUANTUMESPRESSO

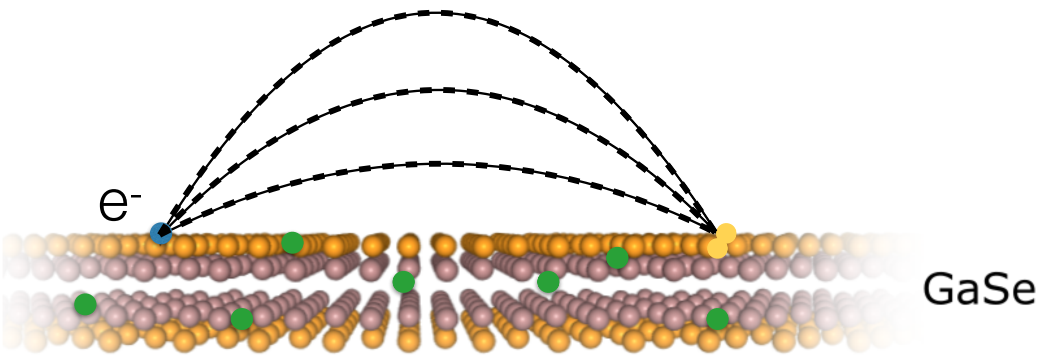
Competitive with Silicon

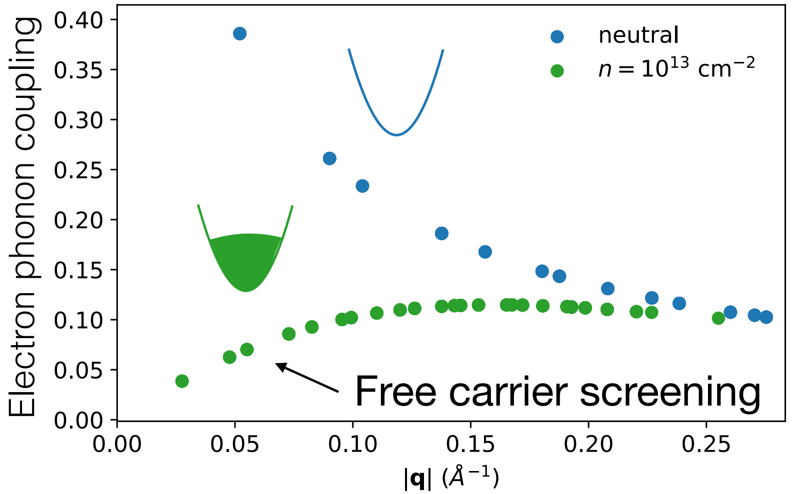
Good mobility only at high doping

High mobility without doping?

Let's look at GaSe

Transport in 2D





Mobility limited by phonon scattering

Polar mode coupling strongest (Fröhlich)

2D screening geometrical factor 1/|q|

$$\mathbf{D}(\mathbf{q}) = \frac{e^2}{\Omega} \sum_a \mathbf{Z}_a \cdot \mathbf{u}^a_{\mathrm{LO}}(\mathbf{q})$$

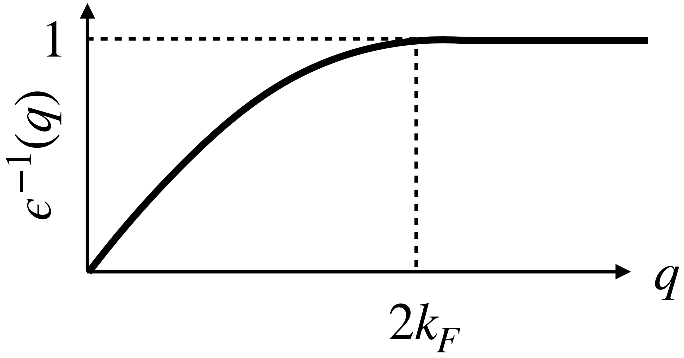
$$\mathbf{E}(\mathbf{q}) = -\, W_c(\mathbf{q})\ [\mathbf{q} \cdot \mathbf{D}(\mathbf{q})]\ \mathbf{q}$$

$$W_c(\mathbf{q}) = \begin{cases} \dfrac{4\pi}{|\mathbf{q}|^2 \epsilon} & \text{(3D)} \\[2ex] \dfrac{2\pi}{|\mathbf{q}|\epsilon} & \text{(2D)} \end{cases}$$

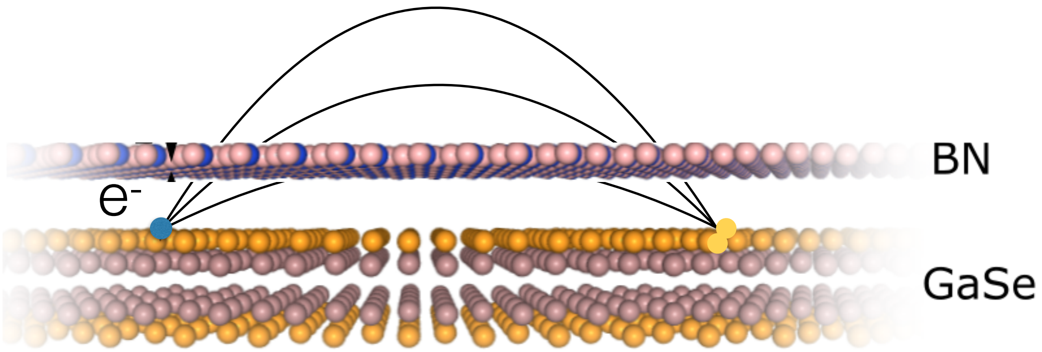
ε also depends on phonon wavevector q

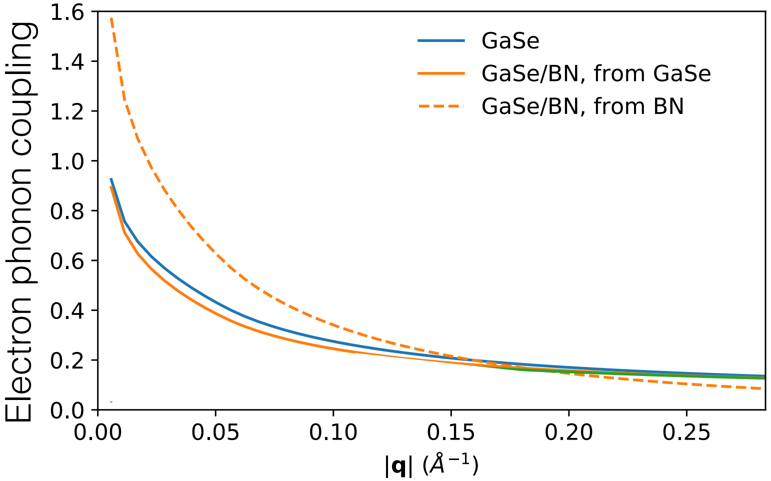
Free carriers → Drude ε → kill EPC

But now it's metallic w/ large voltages



Engineering GaSe

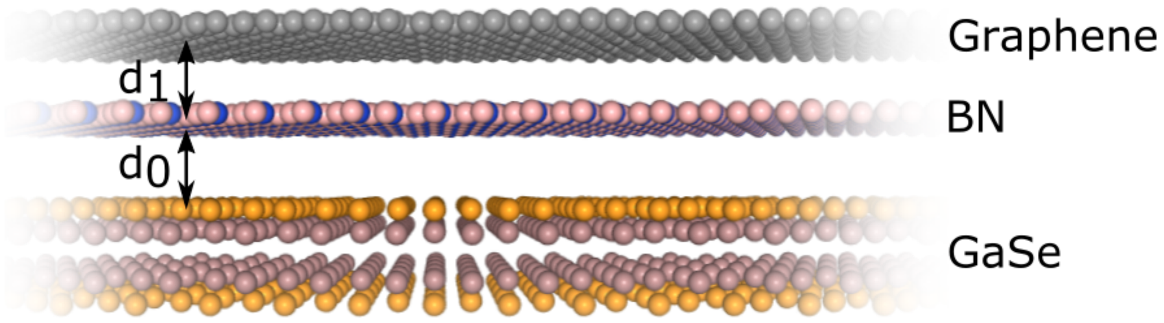


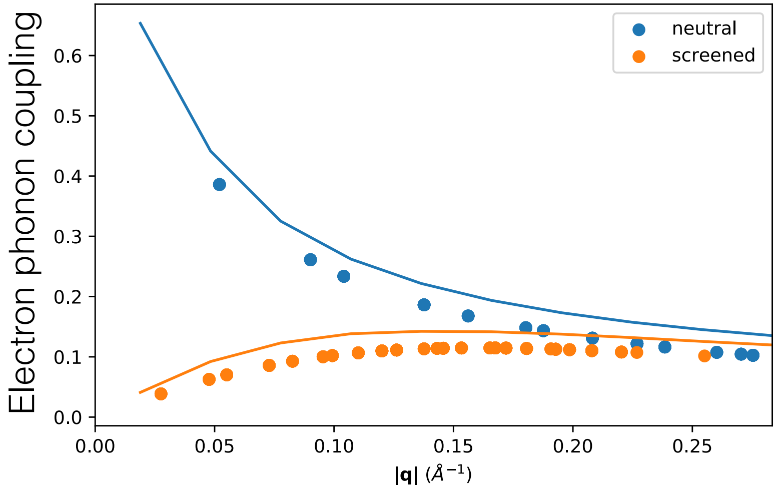


Real device will be encapsulated

Coupling screened remotely with BN (a bit)

Engineering GaSe





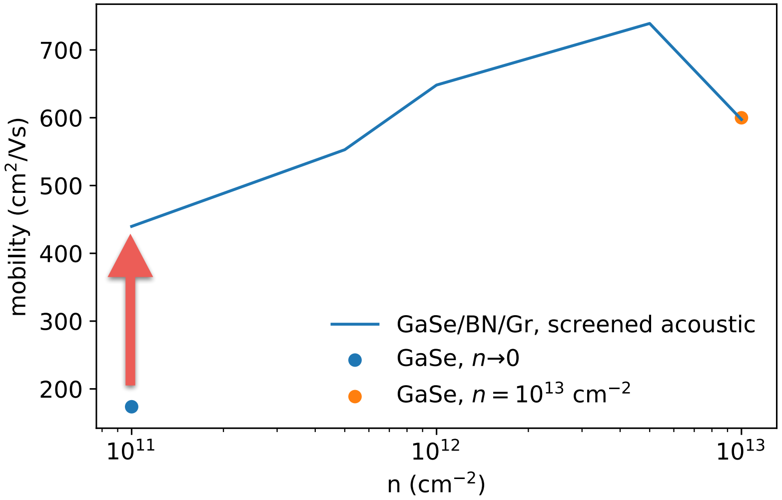
Real device will be encapsulated

Coupling screened remotely with BN (a bit)

Idea: screen remotely with graphene / BN

High mobility also at low doping

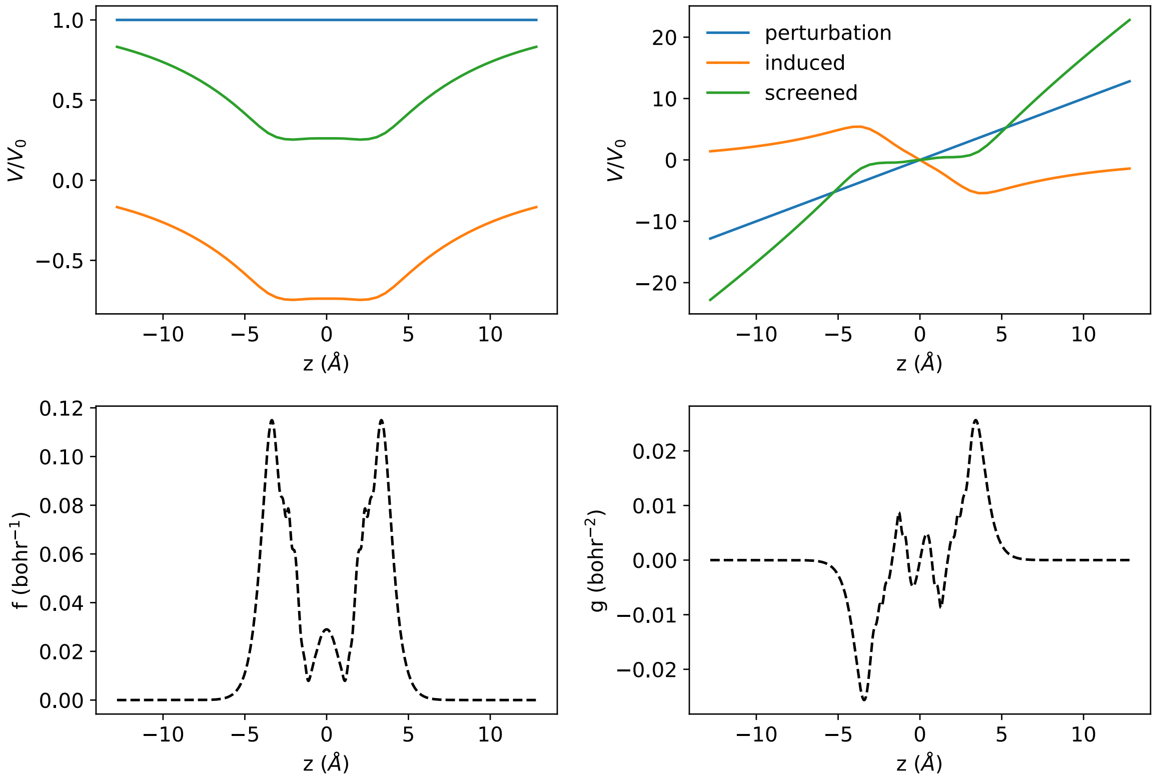
→ **New model for heterostructure response**



Sohier Gibertini Verstraete PRMater 5 024004 (2021)

Coupled heterostructure equations

$$\delta n^k(q,z) = \int \chi^k(q,z,z')\left[V_{\mathrm{ext}}(q,z') + \sum_{m\neq k} v^m_{\mathrm{ind}}(q,z')\right] dz'$$



Const / linear perturbation:

$$\begin{aligned}\chi(q,z,z') &= Q(q)f(q,z-z_0)f(q,z'-z_0)\\ &+P(q)g(q,z-z_0)g(q,z'-z_0)\end{aligned}$$

Full pipeline:

1) reference system EPC

2) re-screen Fröhlich interaction in layer

3) BTE mobility with full band structure

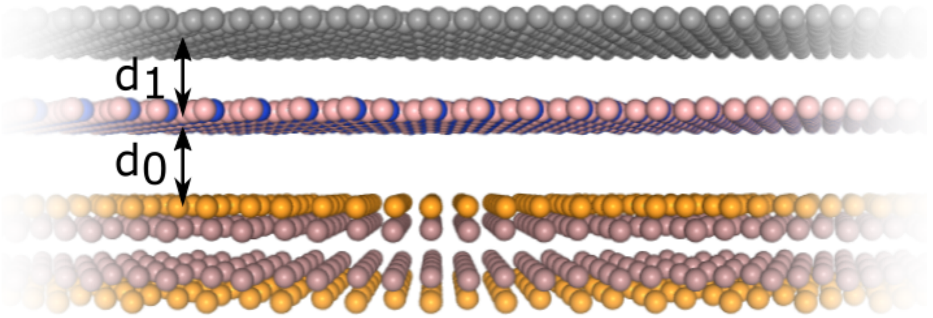
Sohier Gibertini Verstraete PRMater 5 024004 (2021)

2D transport takeaway

Full stack dielectric model

Any layers any doping

Remote screening concept quantified

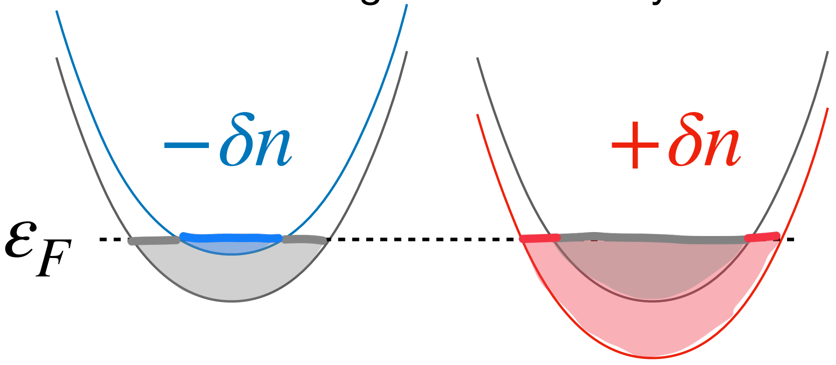


Ongoing work

- other phonons: piezo, acoustic
- multi valley screening and transport

Sohier Physical Review X (2019)
Sohier Melo Zanolli Verstraete in preparation

Screening with two valleys



Acknowledgements

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FLAG-ERA

fnrs LA LIBERTÉ DE CHERCHER

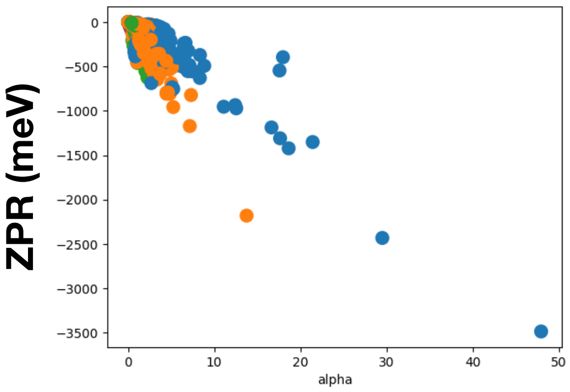
FÉDÉRATION WALLONIE-BRUXELLES

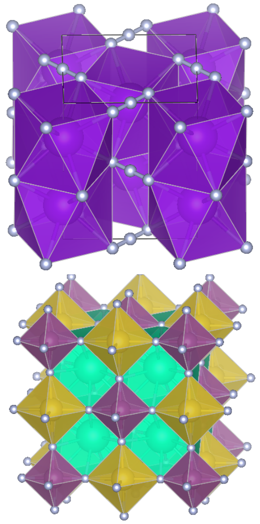
C.E.C.I

PRACE

High throughput Fröhlich

- Clustering by element period/ionicity
- Competing constraints in $\varepsilon_0\ \omega_{LO}\ \varepsilon_\infty\ m^*$
- Valid predictor for order of magnitude
- Highest LO does not dominate





2D dielectric engineering

- Full stack dielectric model
- Screen Frohlich w/ remote graphene
- Re-calculate EPC and transport