# Electron-phonon coupling and polarons

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exciting NEWS

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# Outline

- Introduction
- Electron-phonon coupling and polarons: ARPES spectra of doped oxides
  - Theory and experiment: anatase $TiO_2$
  - Experiment and theory: EuO
- Polaron self-trapping: an *ab initio* theory, without supercells
  - Large and small polarons in LiF and $Li_2O_2$

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- Polaron self-trapping: an *ab initio* theory, without supercells
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Feliciano Giustino
Fabio Caruso
Philip King
Jonathon Riley
Weng Hong Sio
Samuel Poncé

# Electron-phonon coupling

Electron-phonon coupling Hamiltonian:

$$\hat{H} = \hat{H}_{\mathrm{e}} + \hat{H}_{\mathrm{p}} + \hat{H}_{\mathrm{ep}} + \ldots$$

$$\hat{H}_{\mathrm{e}} = \sum_{n\mathbf{k}} \varepsilon_{n\mathbf{k}} \hat{c}^{\dagger}_{n\mathbf{k}} \hat{c}_{n\mathbf{k}} \qquad \hat{H}_{\mathrm{p}} = \sum_{\mathbf{q}\nu} \hbar\omega_{\mathbf{q}\nu} \left( \hat{a}^{\dagger}_{\mathbf{q}\nu} \hat{a}_{\mathbf{q}\nu} + 1/2 \right)$$

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$$\hat{H}_{\mathrm{ep}} = \sum_{mn,\mathbf{k}\mathbf{k}'} \langle \psi_{m\mathbf{k}'} | \, \Delta V_{\mathrm{KS}} \, | \psi_{n\mathbf{k}} \rangle \, \hat{c}^{\dagger}_{m\mathbf{k}'} \hat{c}_{n\mathbf{k}}$$

$$= \frac{1}{\sqrt{N_{\mathrm{p}}}} \sum_{mn\nu,\,\mathbf{k}\mathbf{q}} g_{mn\nu}(\mathbf{k},\mathbf{q}) \, \hat{c}^{\dagger}_{m\mathbf{k}+\mathbf{q}} \hat{c}_{n\mathbf{k}} \left( \hat{a}_{\mathbf{q}\nu} + \hat{a}^{\dagger}_{-\mathbf{q}\nu} \right)$$

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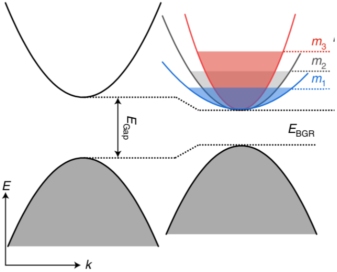
Electron-phonon matrix element:

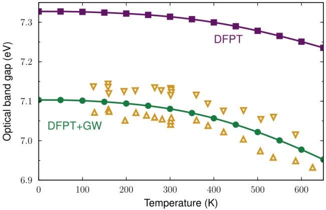
$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \, \partial_{\mathbf{q}\nu} V_{\mathrm{KS}} \, | \psi_{n\mathbf{k}} \rangle$$

# Effects of electron-phonon coupling

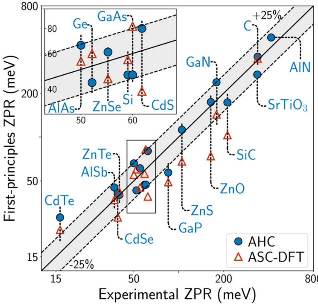
- Temperature dependence of band structures
- Electron/hole effective mass renormalization




Guzelturk *et al.*, Nat. Mater. (2021).




Antonius *et al.*, PRL 112, 215501 (2014).

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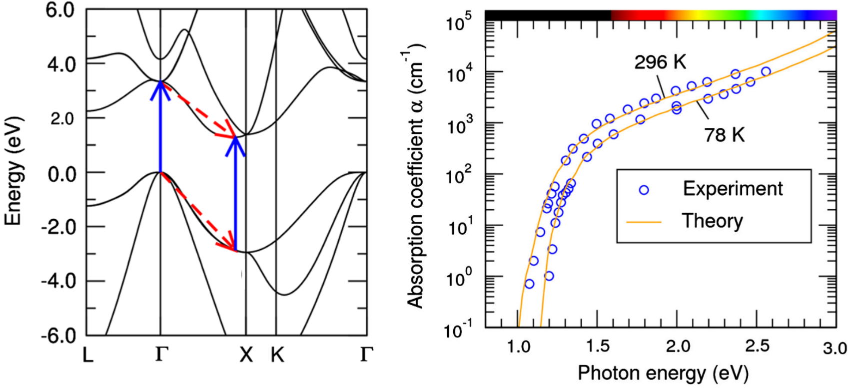
Miglio *et al.*, npj Comp. Mat. 6, 167 (2020).

# Effects of electron-phonon coupling

- Phonon-assisted optical absorption

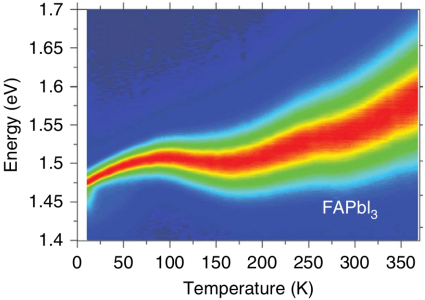



Noffsinger *et al.*, PRL 108, 167402 (2012).

- Phonon-mediated superconductivity

# Effects of electron-phonon coupling

- Temperature-dependent photoluminescence




Wright *et al.*, Nat. Commun. 7, 11755 (2016).

# Effects of electron-phonon coupling

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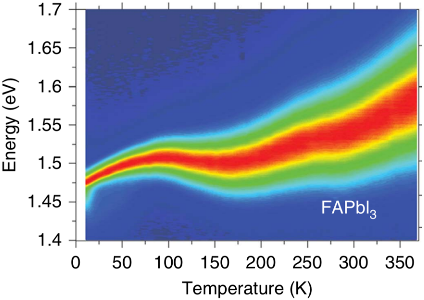
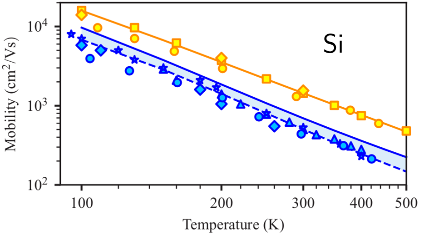
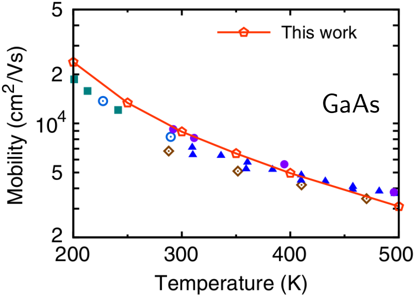



Wright *et al.*, Nat. Commun. 7, 11755 (2016).

- Carrier mobilities

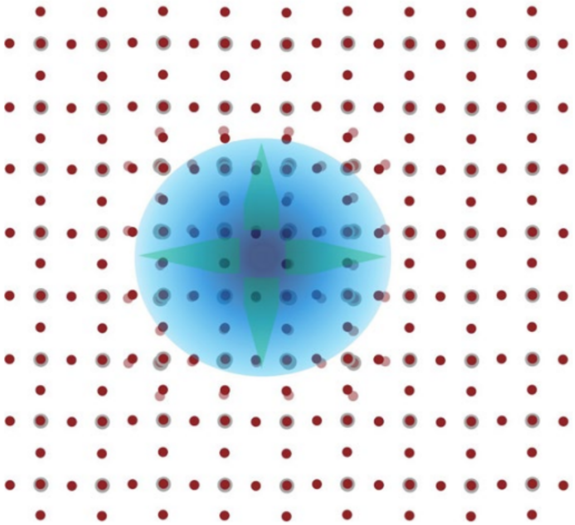



Poncé, Margine and Giustino, PRB 97, 121201 (2018).

Zhou and Bernardi, PRB 94, 201201 (2016).

# Polarons



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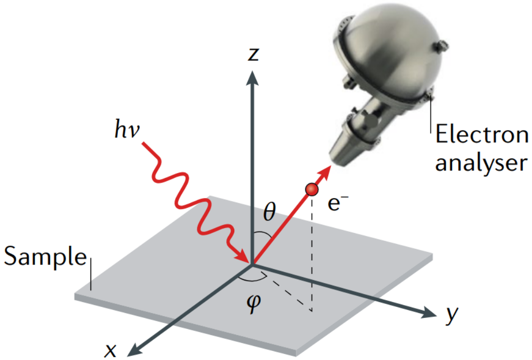
# ARPES experiments

Angle-resolved photoemission spectroscopy




Yang *et al.*, Nat. Mater. 3, 341 (2018).

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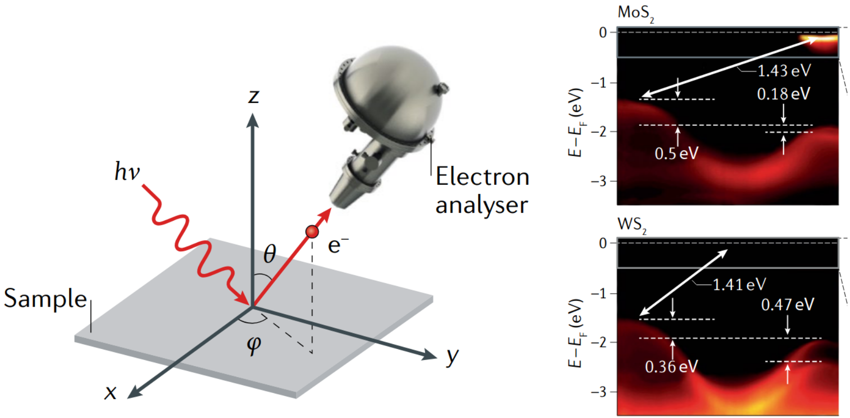


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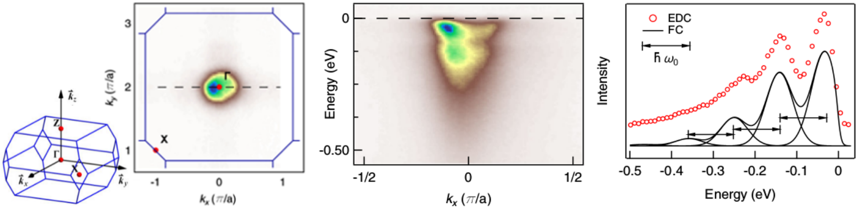
# Polarons in ARPES

Anatase $TiO_2$:




Moser *et al.*, PRL 110, 196403 (2013)

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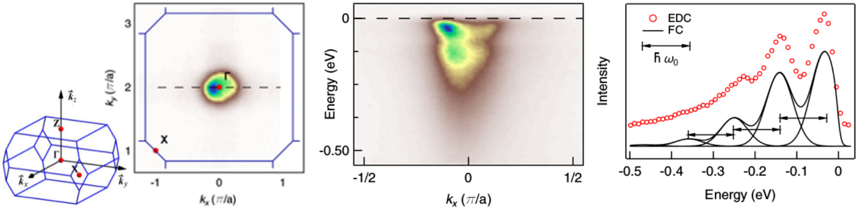


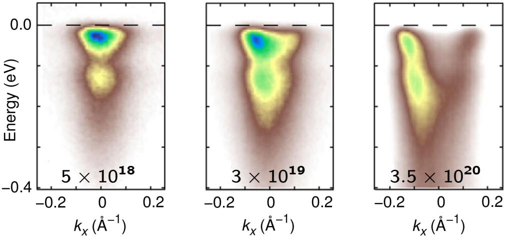


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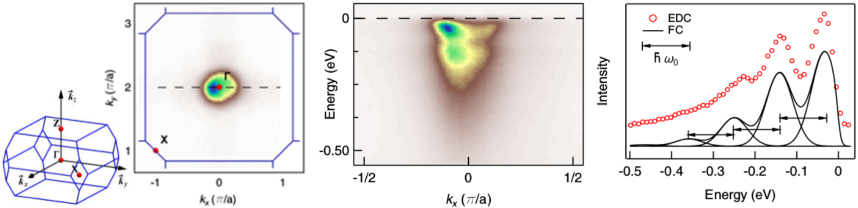
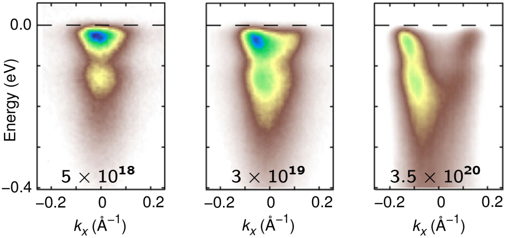


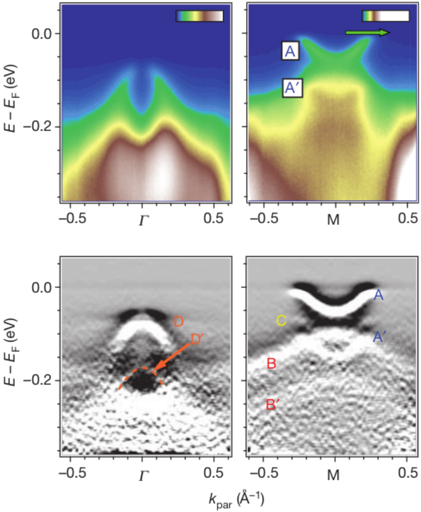




Moser *et al.*, PRL 110, 196403 (2013)

...and Ma *et al.*, Nano Lett. 21, 430 (2021).

# Polarons in ARPES

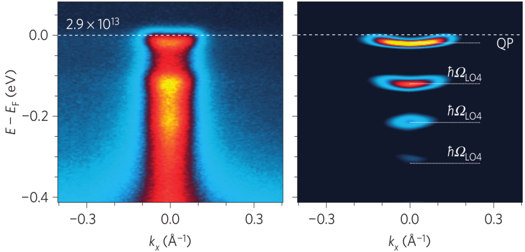
$FeSe/SrTiO_3$:




J. J. Lee *et al.*, Nature 515, 245 (2014).

# Polarons in ARPES

2DEL at the $SrTiO_3(001)$ surface:




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

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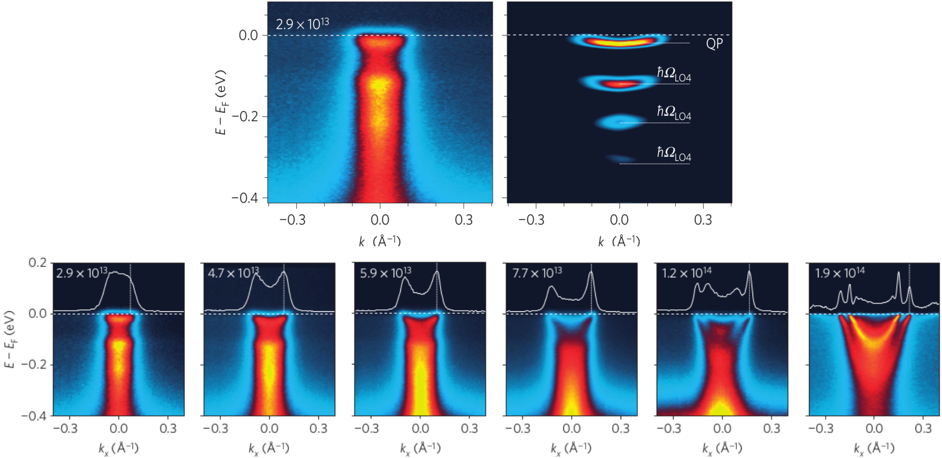


Wang *et al.*, Nat. Mater. 15, 835 (2016).

# The spectral function

The ARPES photocurrent measures the electron **spectral function**.

$$I(\mathbf{k},\omega) \simeq f(\omega)\, A(\mathbf{k},\omega) \;\longrightarrow\; A(\mathbf{k},\omega) = \pi^{-1}|\mathrm{Im}\, G(\mathbf{k},\omega)|$$

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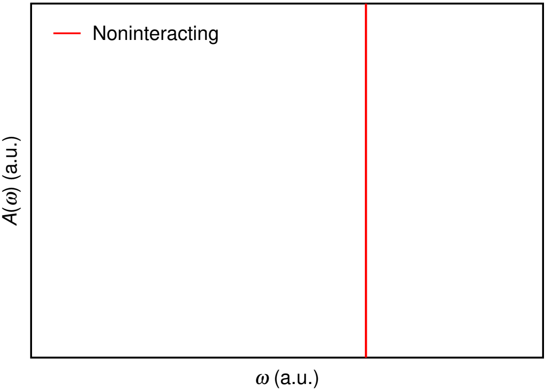

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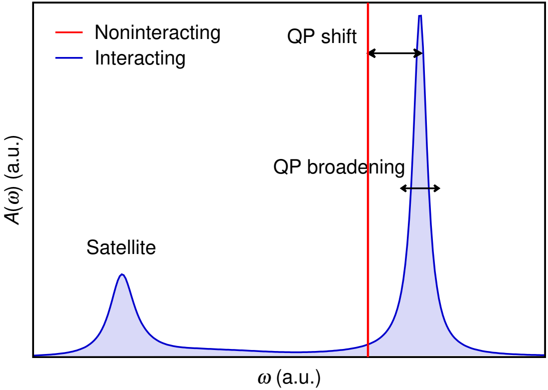
Many-body effects included in the electron **self-energy** $\Sigma(\mathbf{k},\omega)$.



# Self-energy

**Electron-phonon** self-energy (Fan-Migdal) $\Sigma_{n\mathbf{k}}(\omega)$:

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

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**Phonons:** $\omega_{\mathbf{q}\nu}$;

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

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$\downarrow$

Include nonadiabatic effects:

$g^{\text{NA}}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\text{e-ph}}_{mn\nu}(\mathbf{k},\mathbf{q}) / \epsilon(\mathbf{q}, \omega_{\mathbf{q}\nu} + i/\tau_{n\mathbf{k}})$

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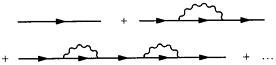
Giustino, Cohen and Louie, PRB 76, 165108 (2007);
Verdi and Giustino, PRL 115, 176401 (2015);
Poncé, Margine, Verdi and Giustino, CPC 209, 116 (2016);
Caruso and Giustino, PRB 94, 115208 (2016).

# Calculating the spectral function

- **Migdal** approximation (one-shot):

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



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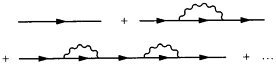
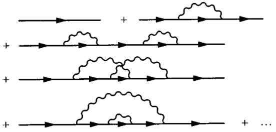


- **Cumulant** expansion (second-order):

$$A(\mathbf{k},\omega) = \frac{1}{\pi}\sum_n \mathrm{Im}\int dt\, e^{i\omega t}\, i\theta(t) e^{-i\varepsilon_{n\mathbf{k}}t}\, e^{C_{n\mathbf{k}}(t)}$$

$$C_{n\mathbf{k}}(t) = -\frac{1}{\pi}\int d\omega\, \mathrm{Im}\Sigma_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}} + \omega)\, \frac{e^{-i\omega t} + i\omega t - 1}{\omega^2}$$



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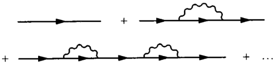

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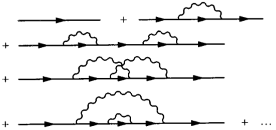
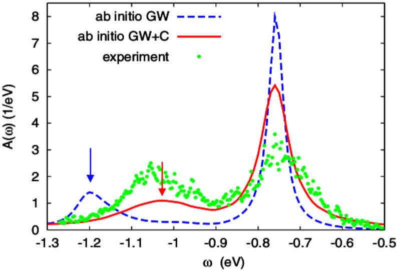
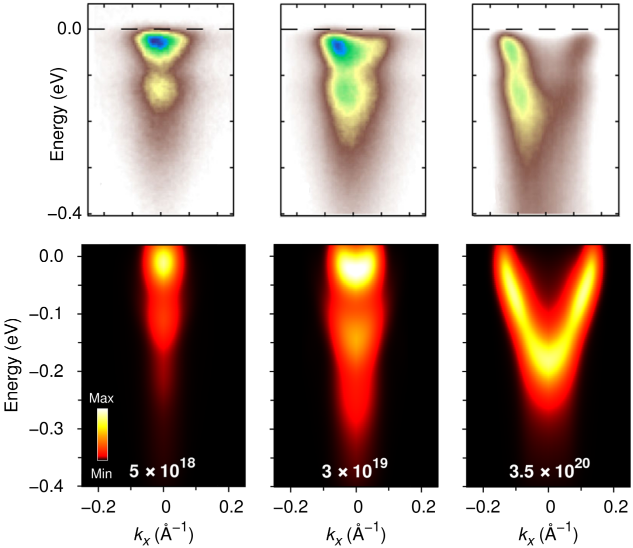





Hedin, Phys. Scr. 21, 477 (1980);
Aryasetiawan *et al.*, PRL 77, 2268 (1996);
Guzzo *et al.*, PRL 107, 166401 (2011);
Lischner, PRL 110, 146801 (2013);
Kas *et al.*, PRB 90, 085112 (2014);
Caruso *et al.*, PRL 114, 146404 (2015);
Zhou *et al.*, JCP 143, 184109 (2015);
Gumhalter *et al.*, PRB 94, 035103 (2016);
Nery *et al.*, PRB 97, 115145 (2018); [...]

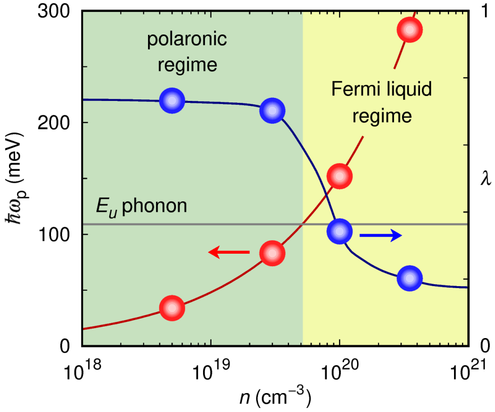
# Polarons in doped anatase $TiO_2$




Moser *et al.*, PRL 110, 196403 (2013).

Verdi, Caruso and Giustino, Nat. Commun. 8, 15769 (2017).

# From polarons to Fermi liquid




Mass renormalization:

$$m^* = m_\mathrm{b}\,(1+\lambda)$$

$$\lambda = -\partial \mathrm{Re}\Sigma/\partial\omega|_{\varepsilon_\mathrm{F}}$$

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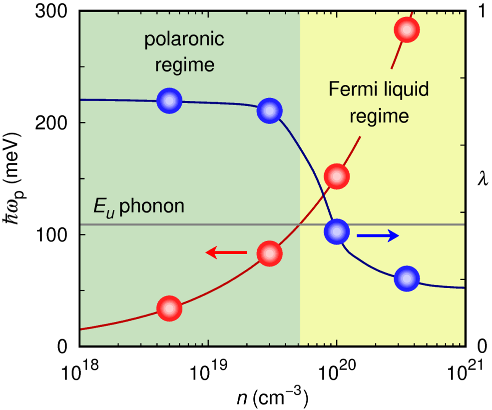


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Plasma energy:

$$\omega_P = \left( \frac{4\pi n e^2}{\epsilon_\infty m_b} \right)^{1/2}$$

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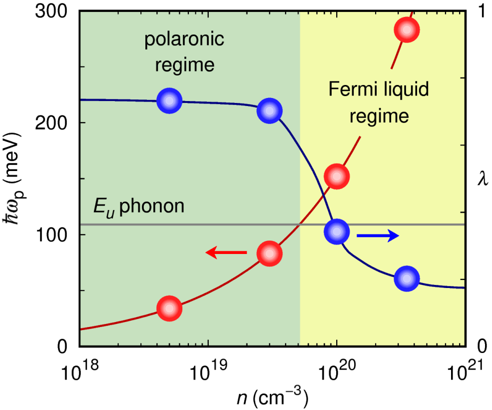


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When $\omega_P \gg \omega_{LO}$, polar coupling is suppressed.

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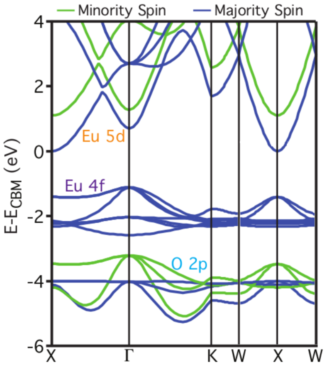
# EuO: a doped FM semiconductor

Spin-polarized electron gas at the conduction-band bottom at X:




DFT+$U$ calculations.

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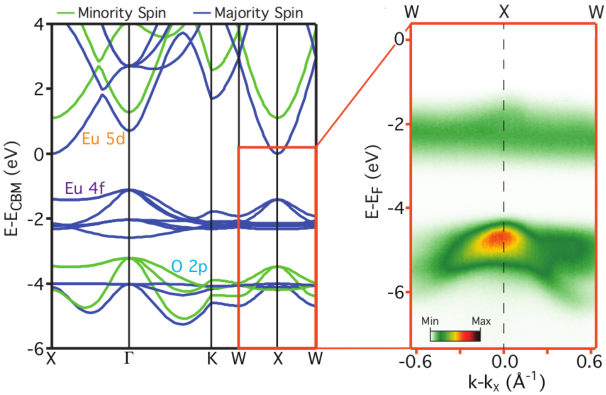


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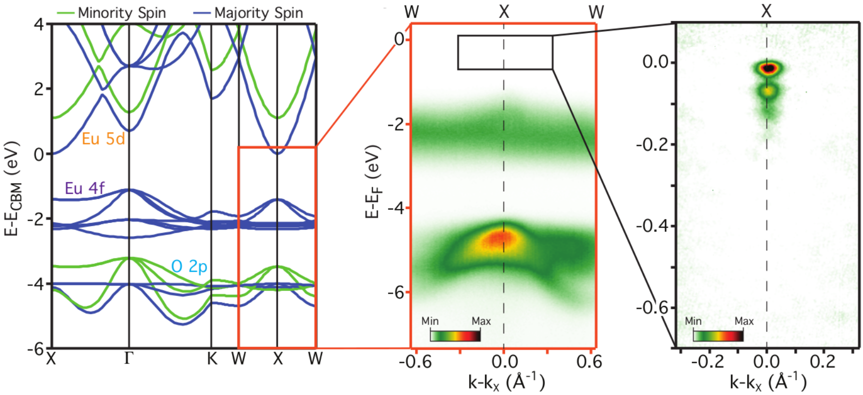


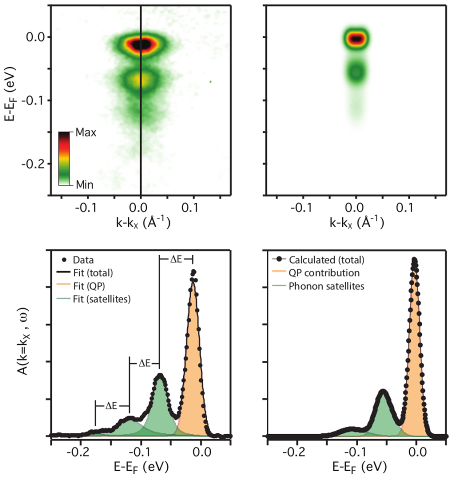

DFT+$U$ calculations. ARPES measurements.

Riley *et al.*, Nat. Commun. 9, 2305 (2018).

# Polarons in EuO

Fröhlich polarons:

$n = 9.3 \times 10^{17}$ cm$^{-3}$



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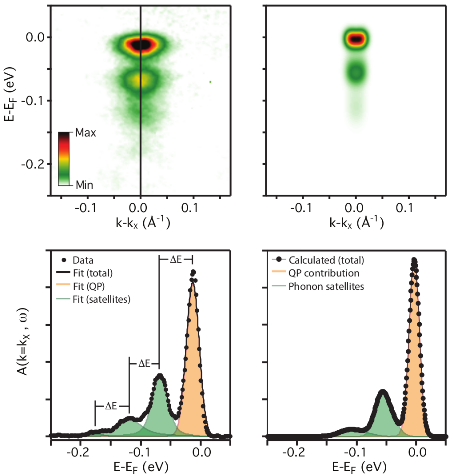
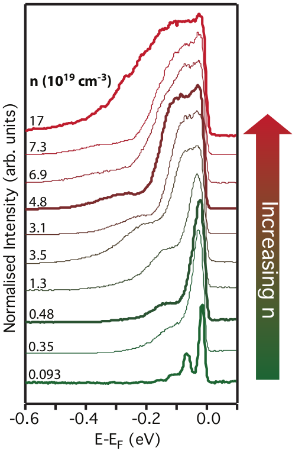



Satellites blue-shift relative to QP peak with increasing doping:



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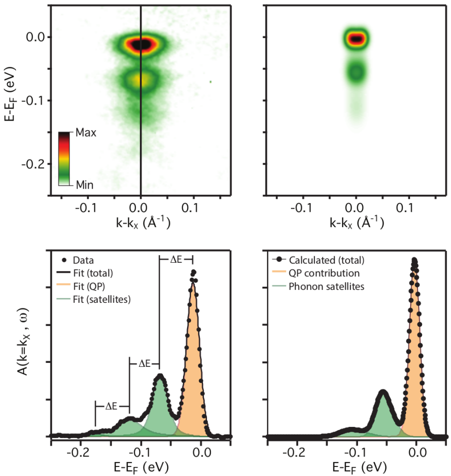


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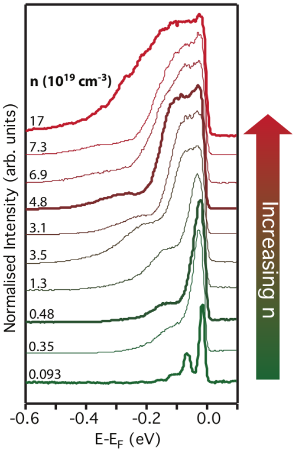


$\longrightarrow$ Coupling to **carrier plasmons**?

# Self-energy

**Electron-phonon** self-energy (Fan-Migdal) $\Sigma_{n\mathbf{k}}(\omega)$:

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

**Phonons:** $\omega_{\mathbf{q}\nu}$;

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

$$\downarrow$$

Include nonadiabatic effects:

$$g^{\text{NA}}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\text{e-ph}}_{mn\nu}(\mathbf{k},\mathbf{q}) / \epsilon(\mathbf{q}, \omega_{\mathbf{q}\nu} + i/\tau_{n\mathbf{k}})$$

EPW®

Giustino, Cohen and Louie, PRB 76, 165108 (2007);
Verdi and Giustino, PRL 115, 176401 (2015);
Poncé, Margine, Verdi and Giustino, CPC 209, 116 (2016);
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$\downarrow$

Include nonadiabatic effects:

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**Plasmons:** $\omega_{\mathbf{q}\nu} \to \omega_{\text{P}}(\mathbf{q})$;

$$g^{\text{eP}}_{mn}(\mathbf{k},\mathbf{q}) = \left[ \frac{\Omega}{4\pi e^2} \frac{\partial \epsilon(\mathbf{q},\omega)}{\partial \omega} \bigg|_{\omega_\mathbf{P}} \right]^{-1/2} \frac{1}{|\mathbf{q}|} \times \langle \psi_{m\mathbf{k}+\mathbf{q}} | \, e^{i\mathbf{q}\cdot\mathbf{r}} \, | \psi_{n\mathbf{k}} \rangle$$

EPW®

Giustino, Cohen and Louie, PRB 76, 165108 (2007);
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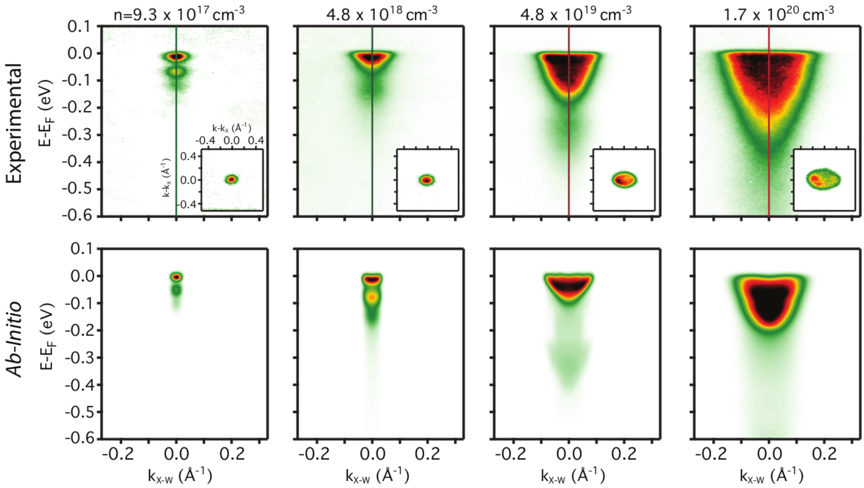
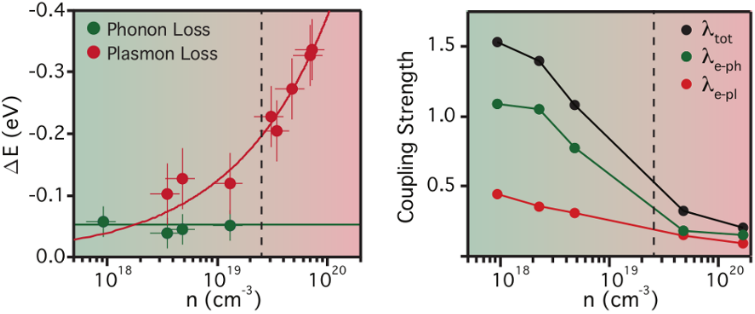
Poncé, Margine, Verdi and Giustino, CPC 209, 116 (2016);
Caruso and Giustino, PRB 94, 115208 (2016).

# Doping evolution of polarons




Spectral function calculated with $\Sigma_{n\mathbf{k}}(\omega) = \Sigma^{\text{e-LO}}_{n\mathbf{k}}(\omega) + \Sigma^{\text{eP}}_{n\mathbf{k}}(\omega)$.

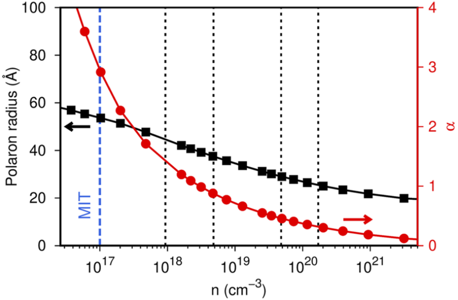
# Doping evolution of boson coupling

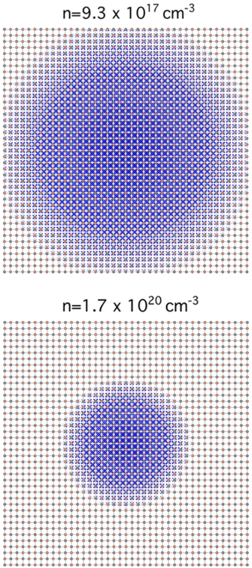



- Resolve a phonon satellite and a plasmon satellite peak.
- Track the coupling strength $\lambda$ as function of doping.

Riley *et al.*, Nat. Commun. 9, 2305 (2018).

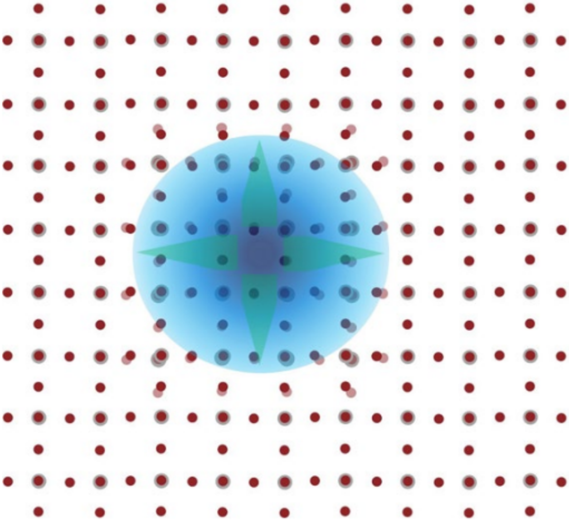
# Plasmonic polaron structure




Plasmonic polaron radius $r_\mathrm{p} \simeq (3/0.44\alpha)^{1/2}\,(2m\,\omega_\mathrm{P})^{-1/2}$ *decreases* with the coupling constant $\alpha$.

# Self-trapped polarons from first principles?



Guzelturk *et al.*, Nat. Mater. (2021).

# The Landau-Pekar model

- Single electron added to a polar insulator
- Continuum electrostatic model

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$$E_{\mathrm{LP}}[\psi] = \frac{1}{2m^*}\int d\mathbf{r}\,|\nabla\psi(\mathbf{r})|^2 - \frac{e^2}{2}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\int d\mathbf{r}\,d\mathbf{r}'\,\frac{|\psi(\mathbf{r})|^2|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}.$$

Devreese and Alexandrov, Rep. Prog. Phys. 72, 066501 (2009).

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$$\left[-\frac{\nabla^2}{2m^*} - e^2\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\int d\mathbf{r}'\,\frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\right]\psi(\mathbf{r}) = \varepsilon\,\psi(\mathbf{r})$$

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- Trial wavefunction $\psi(\mathbf{r}) = (\pi r_{\rm p}^3)^{-1/2}\exp(-|\mathbf{r}|/r_{\rm p})$

$$E_{\rm LP}(r_{\rm p}) = \frac{1}{2m^* r_{\rm p}^2} - \frac{5}{16}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\frac{e^2}{r_{\rm p}}$$

Devreese and Alexandrov, Rep. Prog. Phys. 72, 066501 (2009).

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- Self-trapped polaron energy

$$E_{\mathrm{LP}} = -\frac{50}{512}\,\alpha^2\,\hbar\omega_{\mathrm{LO}}$$

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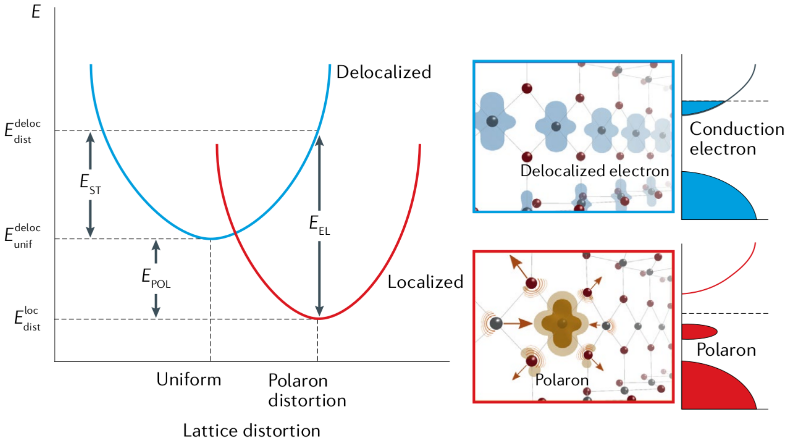
# Polarons in density-functional theory




Franchini, Reticcioli, Setvin and Diebold, Nat. Rev. Mater. (2021).

# Polarons in density-functional (perturbation) theory

Total energy in density-functional theory (**DFT**):

$$
\begin{aligned}
E[\{\psi_{v\mathbf{k}}\},\{\boldsymbol{\tau}_{\kappa p}\}] = & -2\sum_{v\mathbf{k}}\int d\mathbf{r}\,\psi^*_{v\mathbf{k}}\frac{\nabla^2}{2}\psi_{v\mathbf{k}} \\
& + \frac{e^2}{2}\sum_{\mathbf{T}}\int d\mathbf{r}d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'-\mathbf{T}|} + E_{xc}[n^{\uparrow},n^{\downarrow}] \\
& - e\sum_{\kappa p\mathbf{T}}\int d\mathbf{r}\frac{Z_\kappa n(\mathbf{r})}{|\mathbf{r}-\boldsymbol{\tau}_{\kappa p}-\mathbf{T}|} + \frac{e^2}{2}\sum_{\substack{\kappa p\mathbf{T}\\ \kappa' p'}}\frac{Z_\kappa Z_{\kappa'}}{|\boldsymbol{\tau}_{\kappa p}-\boldsymbol{\tau}_{\kappa' p'}-\mathbf{T}|}
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Total energy of an **added electron** (lowest order):

$$E_{\mathrm{p}}[\psi,\{\Delta\boldsymbol{\tau}_{\kappa p}\}] = \int d\mathbf{r}\,\psi^*(\mathbf{r})\left[\hat{H}_{\mathrm{KS}} + \sum_{\kappa\alpha p}\frac{\partial V_{\mathrm{KS}}}{\partial\tau_{\kappa\alpha p}}\Delta\tau_{\kappa\alpha p}\right]\psi(\mathbf{r}) + \frac{1}{2}\sum_{\substack{\kappa\alpha p\\ \kappa'\alpha' p'}} C_{\kappa\alpha p,\kappa'\alpha' p'}\Delta\tau_{\kappa\alpha p}\Delta\tau_{\kappa'\alpha' p'}$$

# Polarons in density-functional (perturbation) theory

**Minimize** the polaron functional with respect to $\psi$, $\Delta\boldsymbol{\tau}_{\kappa p}$:

$$\hat{H}_{\mathrm{KS}}\psi(\mathbf{r}) + \sum_{\kappa\alpha p} \frac{\partial V_{\mathrm{KS}}}{\partial \tau_{\kappa\alpha p}} \Delta\tau_{\kappa\alpha p}\, \psi(\mathbf{r}) = \varepsilon\, \psi(\mathbf{r})$$

$$\Delta\tau_{\kappa\alpha p} = -\sum_{\kappa'\alpha' p'} (C)^{-1}_{\kappa\alpha p, \kappa'\alpha' p'} \int d\mathbf{r}\, \frac{\partial V_{\mathrm{KS}}(\mathbf{r})}{\partial \tau_{\kappa'\alpha' p'}} |\psi(\mathbf{r})|^2$$

Sio, Verdi, Poncé and Giustino, PRL 122, 246403 (2019) and PRB 99, 235139 (2019).

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Now we have the *ab initio* version of the Landau-Pekar **polaron equation**:

$$\left[\hat{H}_{\mathrm{KS}} - \sum_{\substack{\kappa\alpha p \\ \kappa'\alpha' p'}} \frac{\partial V_{\mathrm{KS}}}{\partial \tau_{\kappa\alpha p}} (C)^{-1}_{\kappa\alpha p,\kappa'\alpha' p'} \int d\mathbf{r}'\, \frac{\partial V_{\mathrm{KS}}(\mathbf{r}')}{\partial \tau_{\kappa'\alpha' p'}} |\psi(\mathbf{r}')|^2\right] \psi(\mathbf{r}) = \varepsilon\, \psi(\mathbf{r})$$

Sio, Verdi, Poncé and Giustino, PRL 122, 246403 (2019) and PRB 99, 235139 (2019).

# From supercell to reciprocal space

Expand the solutions in terms of Kohn-Sham states and phonon eigenmodes:

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{N_p}} \sum_{n\mathbf{k}} A_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}); \quad \Delta\tau_{\kappa\alpha p} = -\frac{2}{N_p} \sum_{\mathbf{q}\nu} B^*_{\mathbf{q}\nu} \left( \frac{\hbar}{2M_\kappa \omega_{\mathbf{q}\nu}} \right)^{1/2} e_{\kappa\alpha,\mathbf{q}\nu}\, e^{i\mathbf{q}\cdot\mathbf{R}_p}$$

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Self-consistent eigenvalue problem:

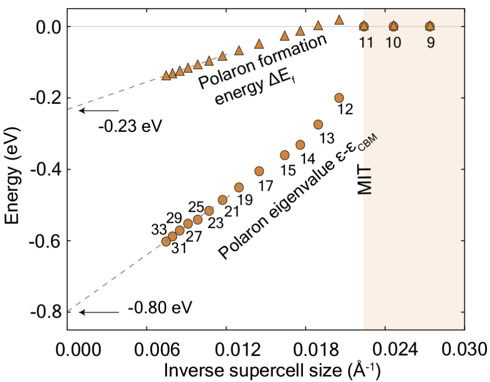
$$\frac{2}{N_p} \sum_{\mathbf{q}m\nu} B_{\mathbf{q}\nu} \, g^*_{mn\nu}(\mathbf{k},\mathbf{q}) \, A_{m\mathbf{k}+\mathbf{q}} = (\varepsilon_{n\mathbf{k}} - \varepsilon) \, A_{n\mathbf{k}},$$

$$B_{\mathbf{q}\nu} = \frac{1}{N_p} \sum_{mn\mathbf{k}} A^*_{m\mathbf{k}+\mathbf{q}} \, \frac{g_{mn\nu}(\mathbf{k},\mathbf{q})}{\hbar\omega_{\mathbf{q}\nu}} \, A_{n\mathbf{k}}$$

Calculate the polaron wave function starting from **standard ingredients of DFT calculations in the unit cell**.

Sio, Verdi, Poncé and Giustino, PRL 122, 246403 (2019) and PRB 99, 235139 (2019).

# Electron polaron in LiF




Polaron formation energy:

$$\Delta E_f = \min E_{\mathrm{p}}[\psi, \{\Delta\tau_{\kappa\alpha\mathbf{p}}\}] - \min E_{\mathrm{p}}[\psi, \{\Delta\tau_{\kappa\alpha\mathbf{p}} = 0\}]$$
$$= \varepsilon - \varepsilon_{\mathrm{CBM}} + \frac{1}{N_{\mathrm{p}}} \sum_{\mathbf{q}\nu} |B^2_{\mathbf{q}\nu}| \hbar\omega_{\mathbf{q}\nu}$$

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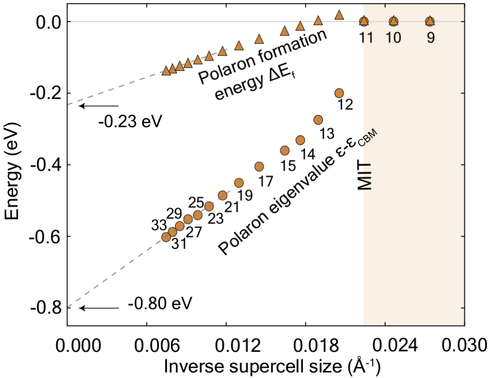


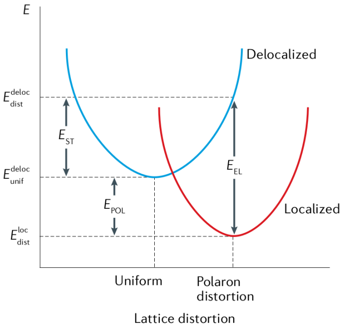


Franchini, Reticcioli, Setvin and Diebold, Nat. Rev. Mater. (2021).

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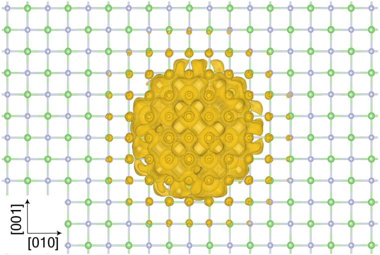


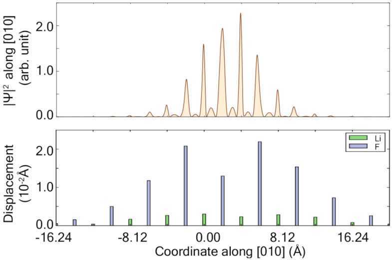

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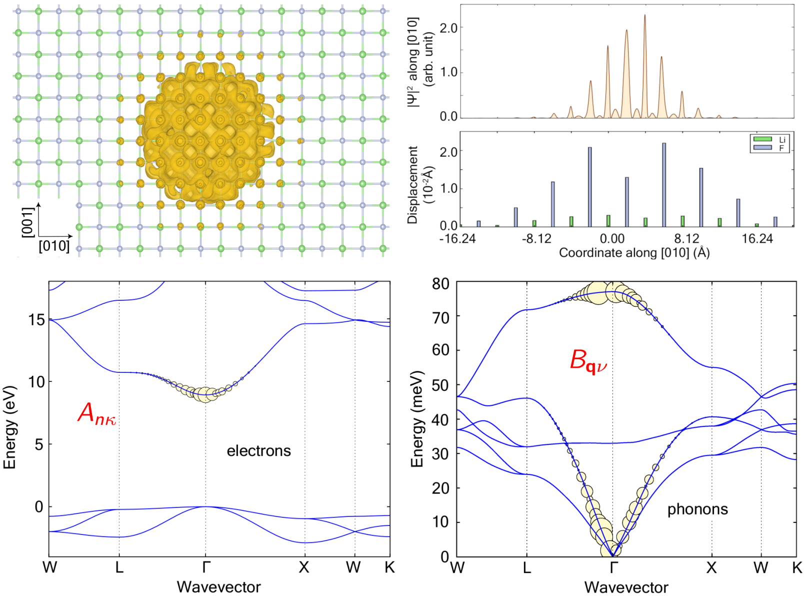
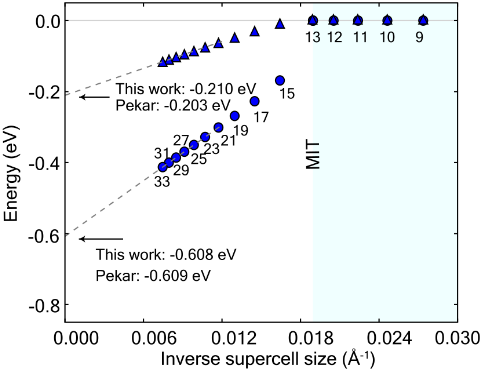


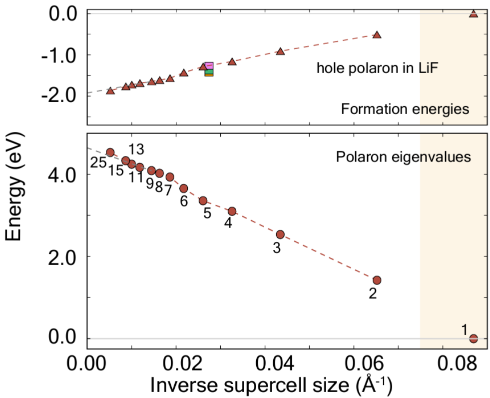
# Validation (i): Landau-Pekar model




Calculations using:

- single parabolic band (DFT effective mass);
- dispersionless LO phonon mode;
- Fröhlich e-ph matrix element.

# Hole polaron in LiF

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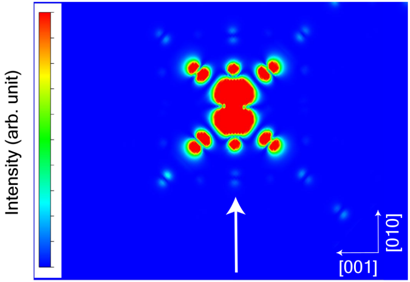


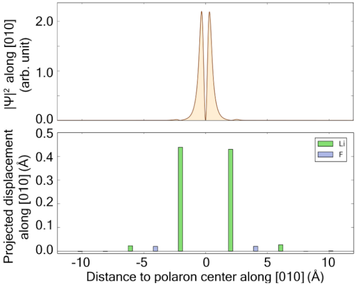

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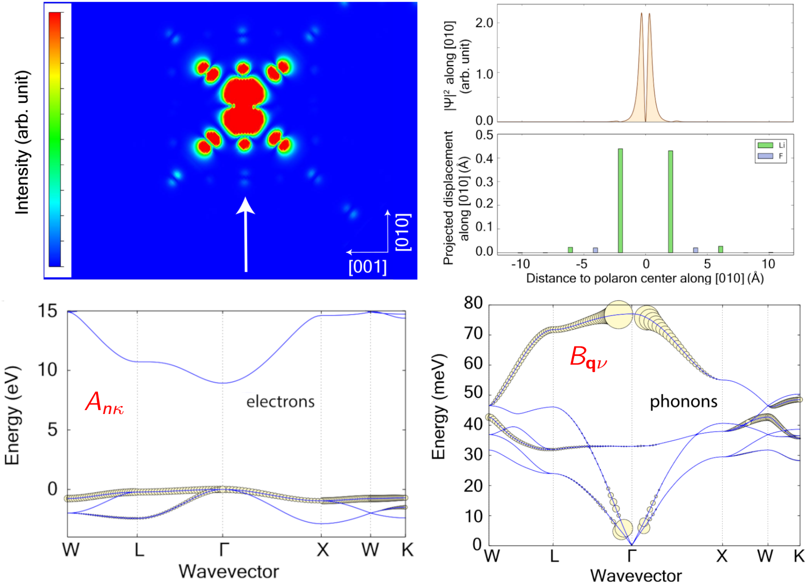
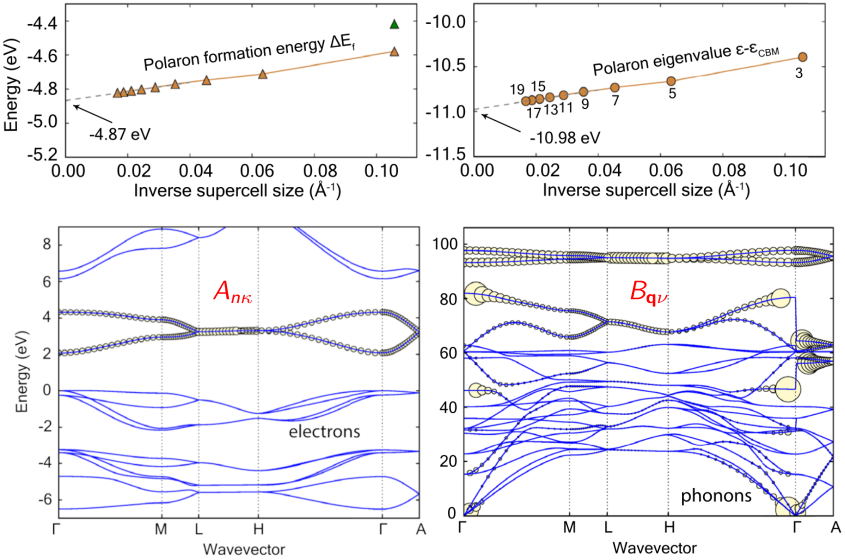
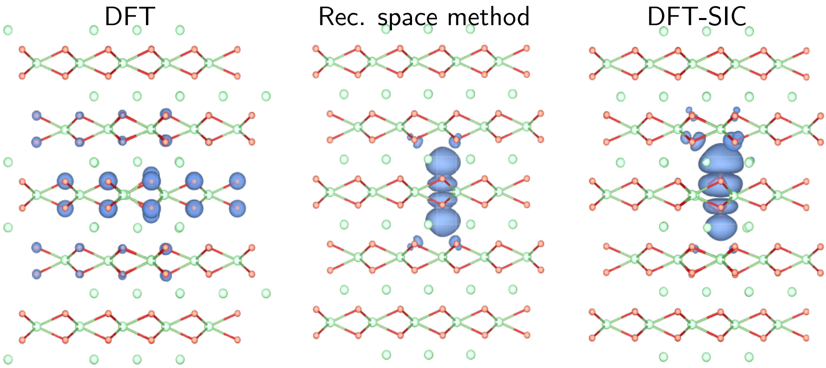


# Electron polaron in $Li_2O_2$

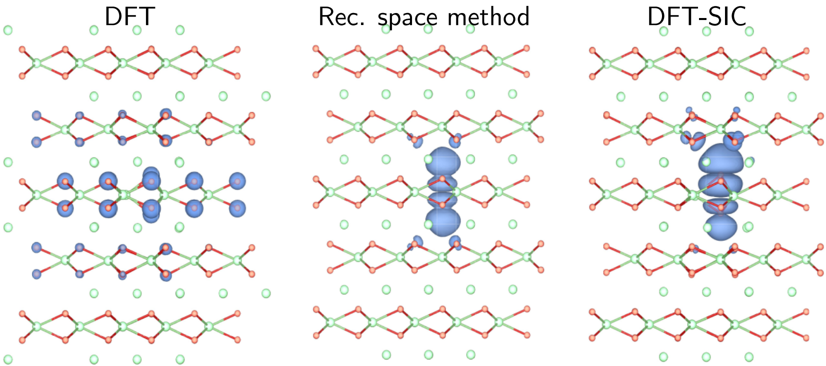


# Validation (ii): DFT calculations




Sio, Verdi, Poncé and Giustino, PRB 99, 235139 (2019).

# Validation (ii): DFT calculations



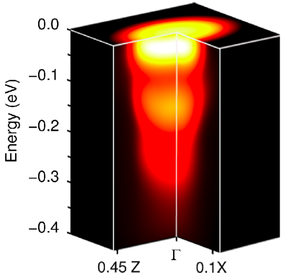

DFT-SIC removes the self-interaction of the polaron:

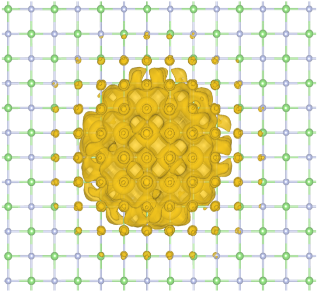
$$E^{\mathrm{SIC}}[n_\uparrow + \Delta n, n_\downarrow] = E[n_\uparrow + \Delta n, n_\downarrow] - E_{\mathrm{H}}[\Delta n - \Delta n_{\mathrm{B}}] - \frac{1}{2}\Big(E_{xc}[n_\uparrow + \Delta n, n_\downarrow] - 2E_{xc}[n_\uparrow, n_\downarrow] + E_{xc}[n_\uparrow - \Delta n, n_\downarrow]\Big)$$

Sio, Verdi, Poncé and Giustino, PRB 99, 235139 (2019).

# Summary

- **ARPES spectra** of doped oxides from first principles using many-body perturbation theory: phonon and plasmon polarons.
  Examples: anatase $TiO_2$, EuO.
- **Polaron self-trapping** in semiconductors and insulators via density-functional perturbation theory approach: wavefunctions and energies of large and small polarons.
  Examples: LiF and $Li_2O_2$.



# Aknowledgments

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| F. Giustino | F. Caruso | W. H. Sio | S. Poncé | P. King | J. Riley |
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# THANK YOU!

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