2022 Summer School on Electron-Phonon Physics from First Principles

Austin Texas

NSF

U.S. DEPARTMENT OF ENERGY

TACC
TEXAS ADVANCED COMPUTING CENTER

ODEN

Lecture Thu.1

Introduction to polarons

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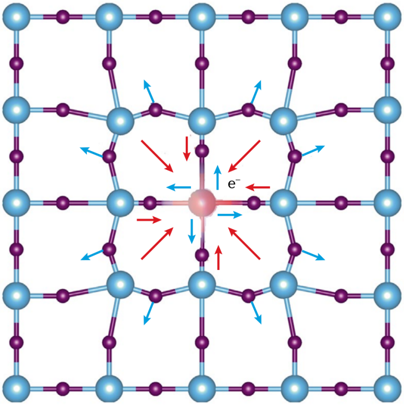
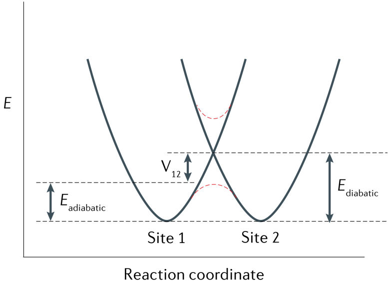
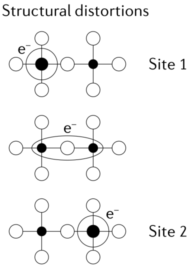
The University of Texas at Austin

- Introduction to the polaron concept
- Polaron satellites in photoemission spectra
- DFT calculations of polarons
- Landau-Pekar theory
- *Ab initio* polaron equations

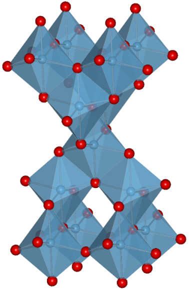




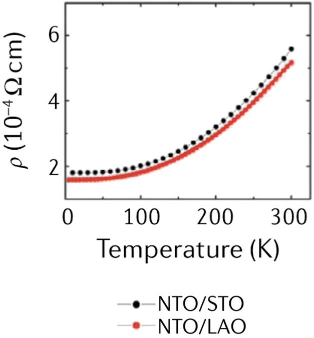


Figures from Franchini et al, Nat. Rev. Mater. 2021, 10.1038/s41578-021-00289-w

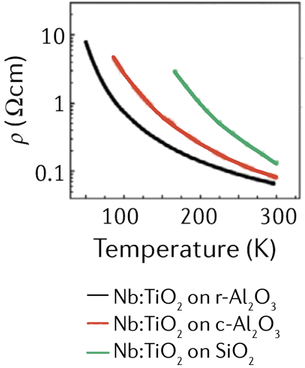
Transport signatures of polarons

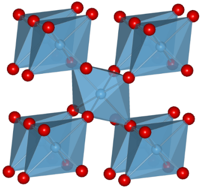


Anatase TiO_2



Rutile TiO_2





Diffusive

Activated

Hall mobility data from Zhang et al, J. Appl. Phys. 102, 013701 (2007);
see discussion in Franchini et al, Nat. Rev. Mater. 2021, 10.1038/s41578-021-00289-w

Angle-resolved photoelectron spectroscopy (ARPES)

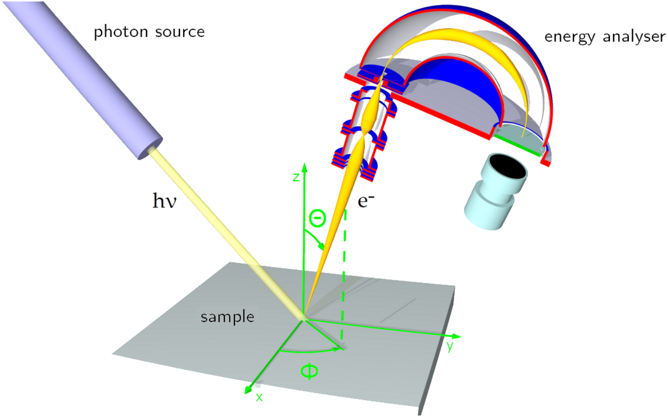


Figure from commons.wikimedia.org/wiki/File:ARPESgeneral.png

Polaron satellites (aka phonon sidebands)

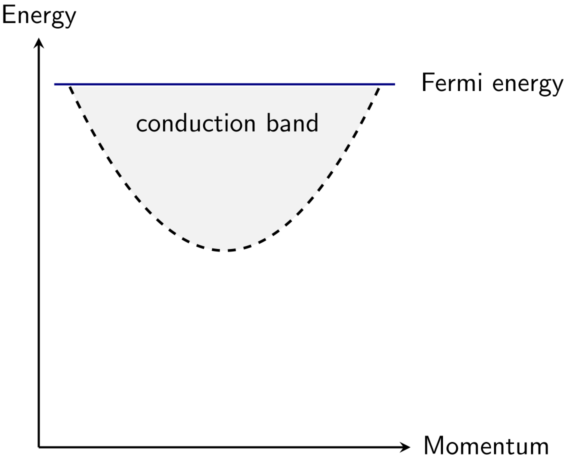


Figure adapted from Kandolf et al, Phys. Rev. B 105, 085148 (2022)

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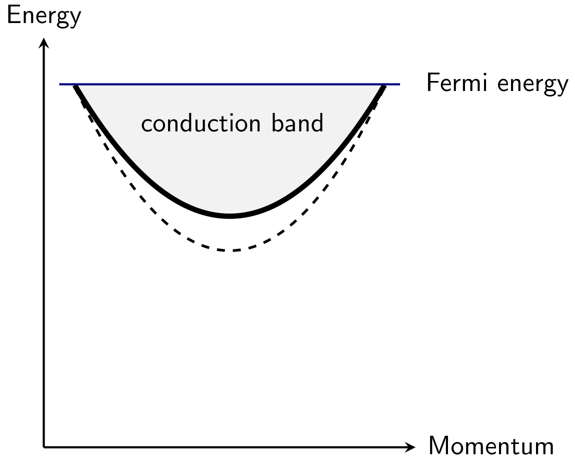

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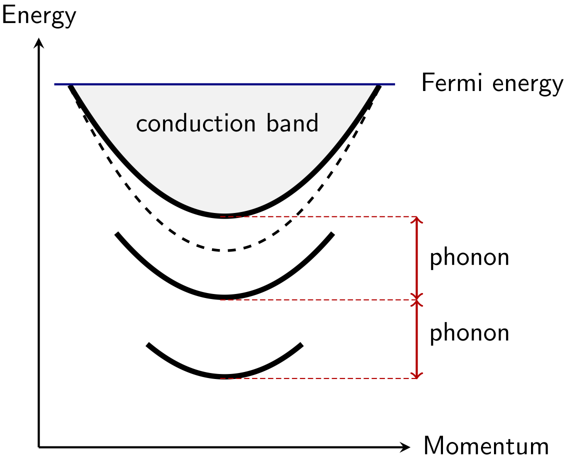

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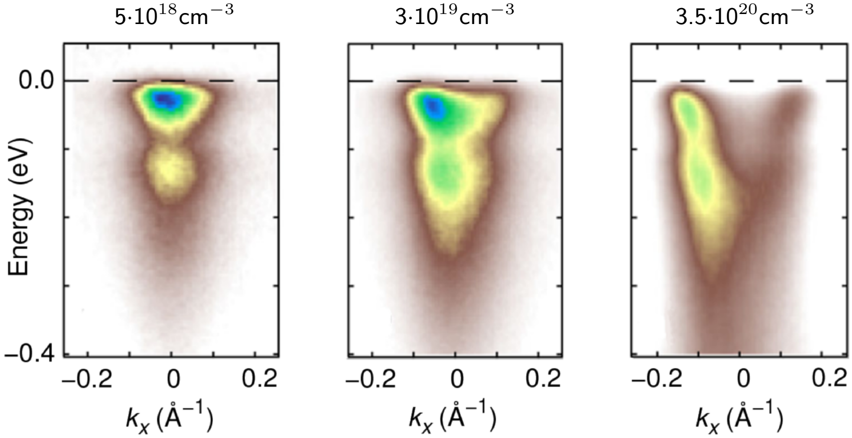


Figure from Moser et al, Phys. Rev. Lett. 110, 196403 (2013)

Polaron satellites in EuO

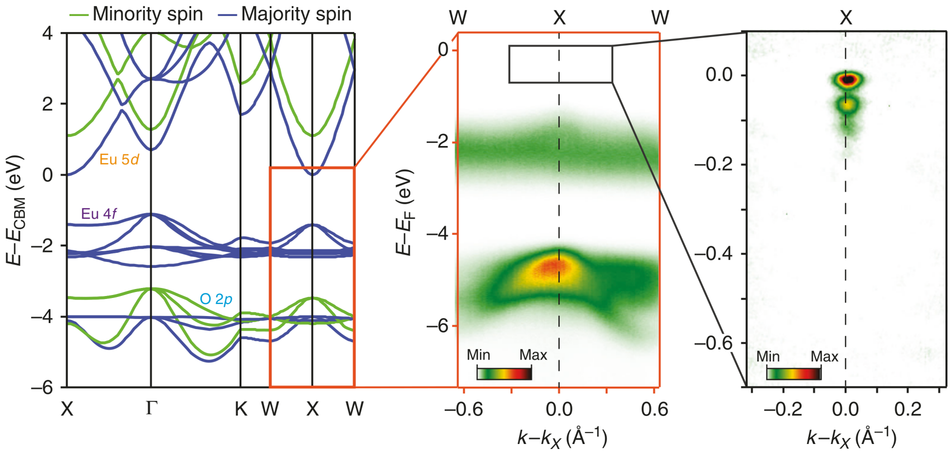


Figure from Riley et al, Nat. Commun. 9, 2305 (2018)

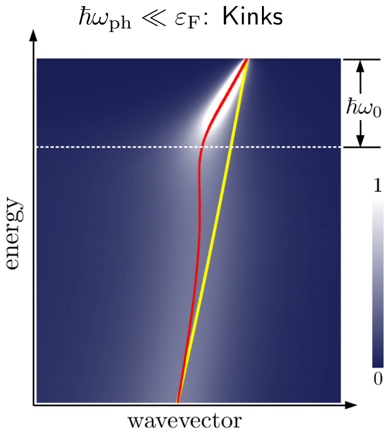


Figure from FG, Rev. Mod. Phys. 89, 015003 (2017)

Kinks vs. satellites in ARPES

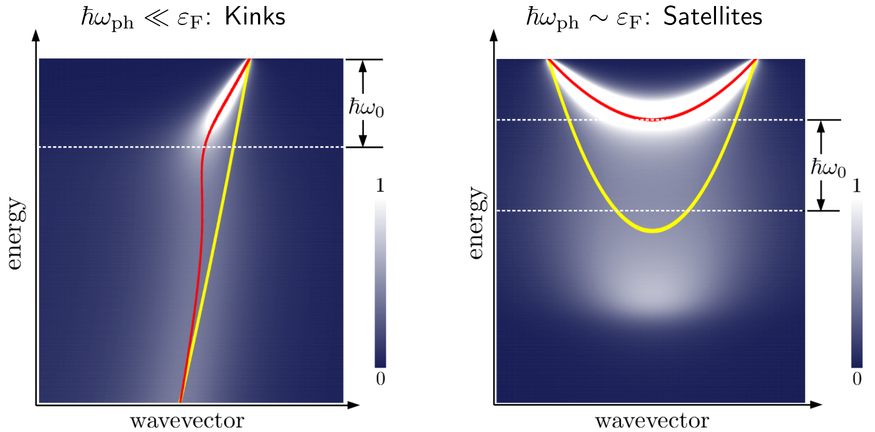


Figure from FG, Rev. Mod. Phys. 89, 015003 (2017)

Calculated vs. measured spectral function: EuO

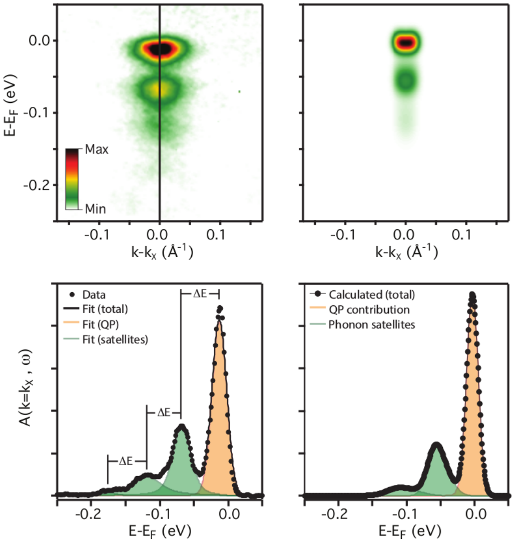
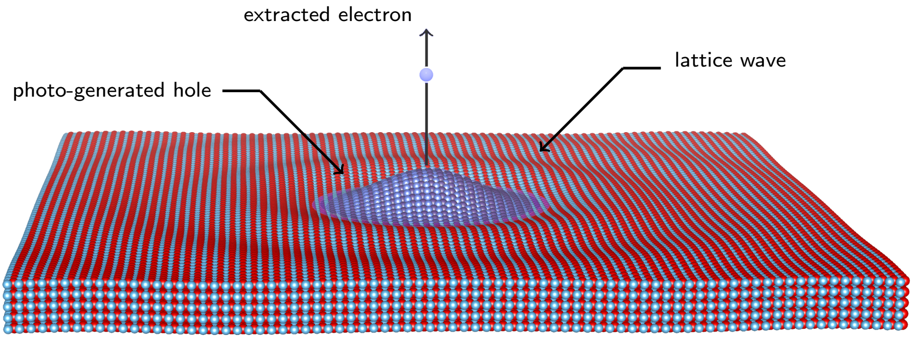


Figure from Riley et al,
Nat. Commun. 9, 2305 (2018)

Meaning of satellite bands



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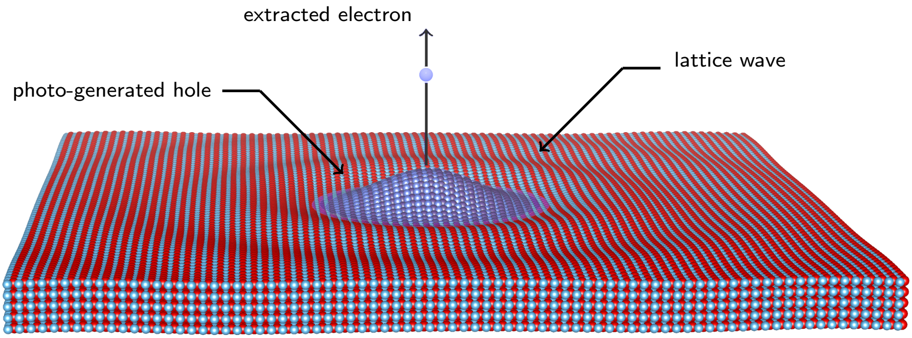
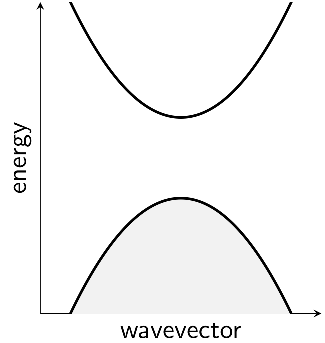
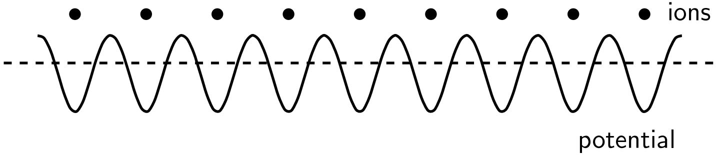


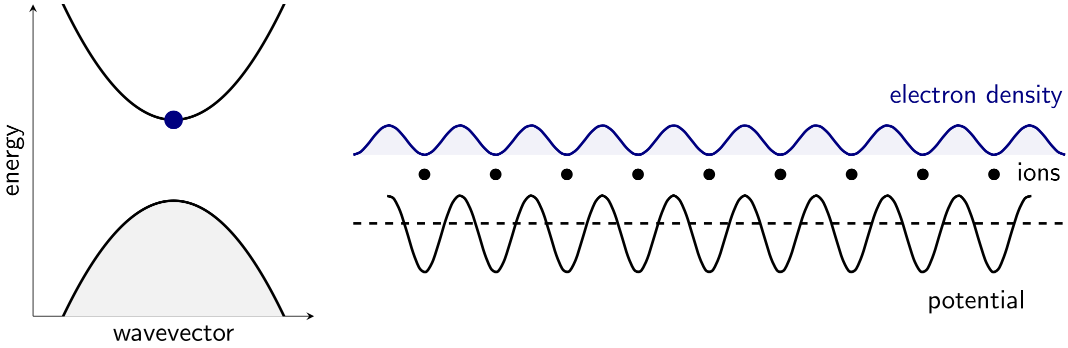
- Satellites are shake-up excitations
- The polaron is the quasiparticle peak

Intuitive notion of electron localization





Intuitive notion of electron localization



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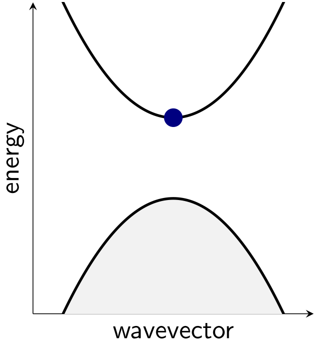
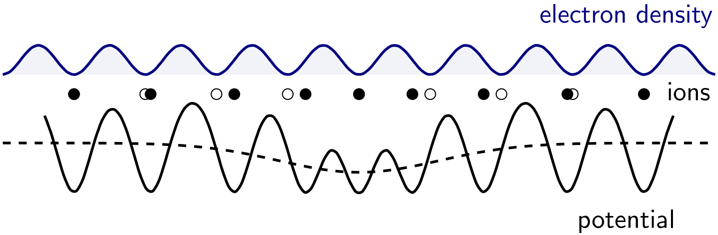
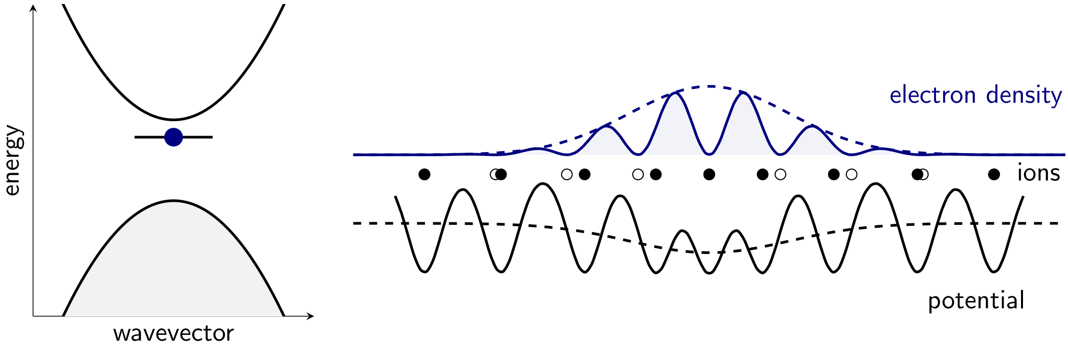




Intuitive notion of electron localization



Polarons in DFT calculations

Electron aded to Li_2O_2 ground state

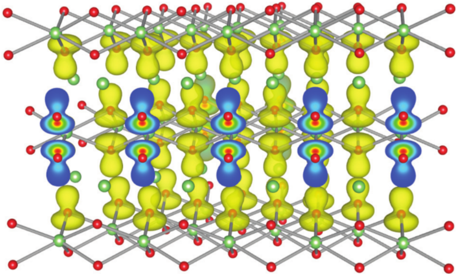
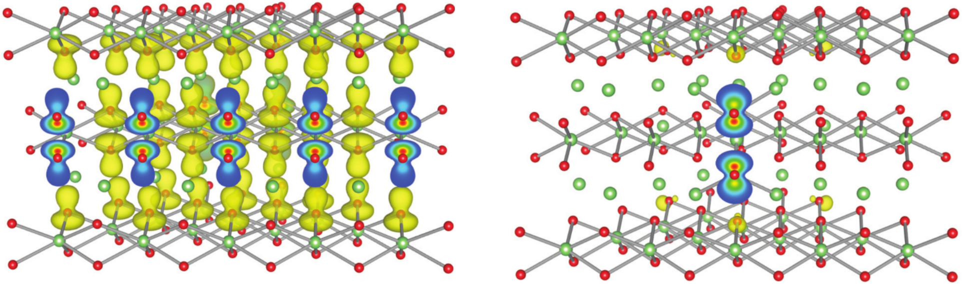


Figure from Feng et al, Phys. Rev. B 88, 184302 (2013)

Polarons in DFT calculations

Electron aded to Li_2O_2 ground state

Self-localization after ionic relaxation



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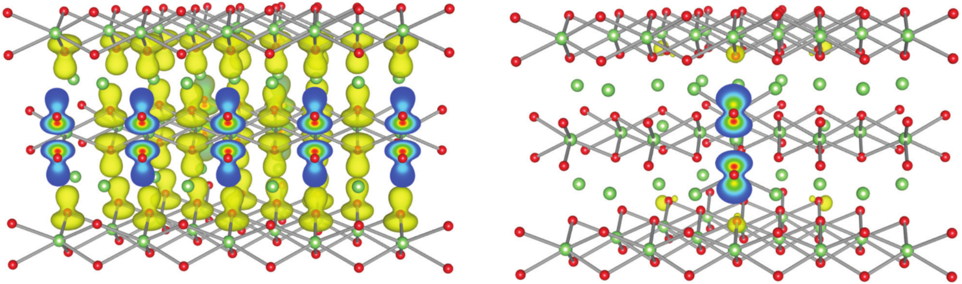
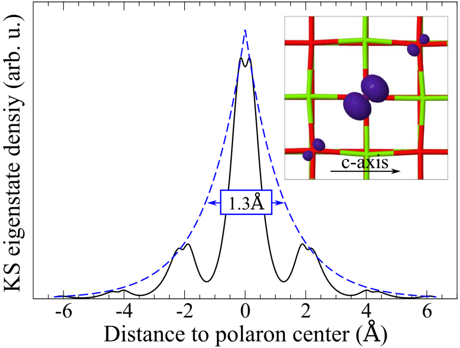


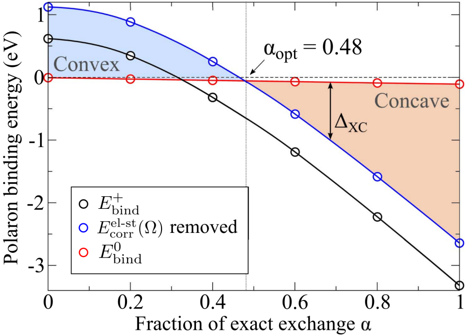
- Formation energy and size sensitive to the XC functional
- Only very small polarons accessible

Figure from Feng et al, Phys. Rev. B 88, 184302 (2013)

Koopman's based correction schemes

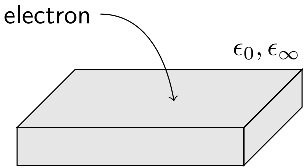
Small hole polaron in MgO by hybrid functionals





Figures from Kokott et al, New J. Phys. 20 (2018)

Ground state of the polaron in the Landau-Pekar model



Pekar, Zh. Eksp. Teor. Fiz. 16, 341 (1946); Landau and Pekar, Zh. Eksp. Teor. Fiz. 18, 419 (1948)

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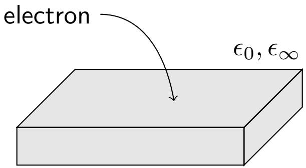

$$E = \frac{\hbar^2}{2m^*}\int d\mathbf{r}\, |\nabla\psi|^2 + \frac{1}{2}\int d\mathbf{r}\; \mathbf{E}\cdot\mathbf{D}$$

Pekar, Zh. Eksp. Teor. Fiz. 16, 341 (1946); Landau and Pekar, Zh. Eksp. Teor. Fiz. 18, 419 (1948)

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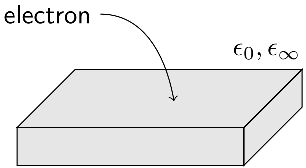

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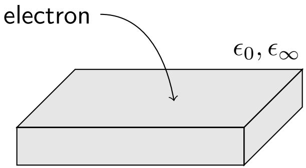

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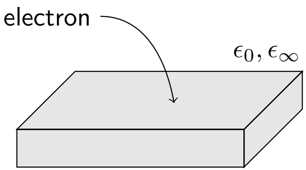

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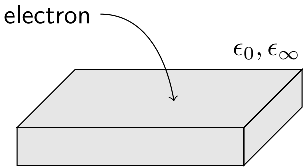

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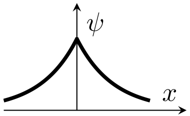
$$-\frac{\hbar^2}{2m^*}\nabla^2\psi(\mathbf{r}) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}\right)\int d\mathbf{r}' \frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\psi(\mathbf{r}) = \varepsilon\,\psi(\mathbf{r})$$

Pekar, Zh. Eksp. Teor. Fiz. 16, 341 (1946); Landau and Pekar, Zh. Eksp. Teor. Fiz. 18, 419 (1948)

Landau-Pekar equation

Simplest trial solution: $\psi(\mathbf{r}) = \exp(-|\mathbf{r}|/r_{\mathrm{p}})$



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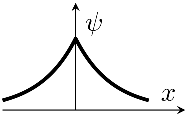
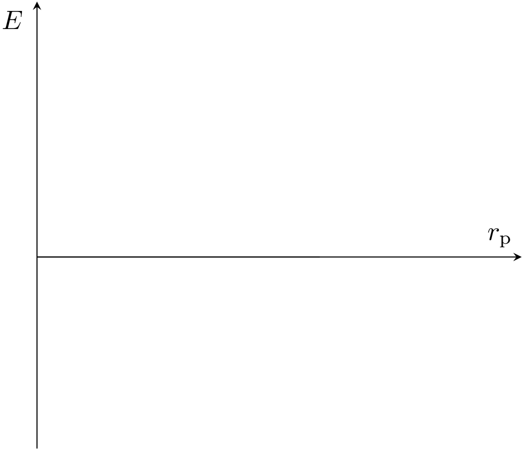


$E =$



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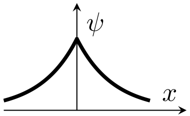
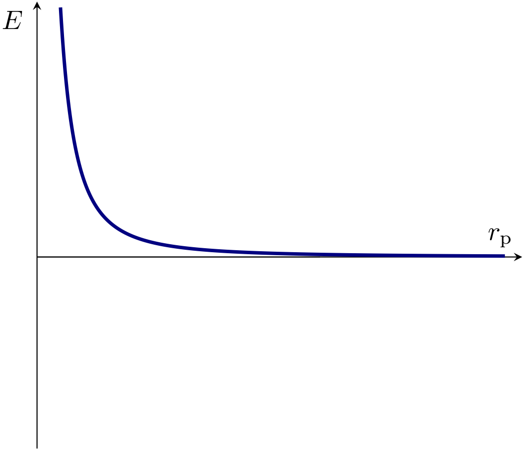


$$E = \frac{\hbar^2}{2m^*}\frac{1}{r_\mathrm{p}^2}$$



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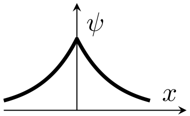
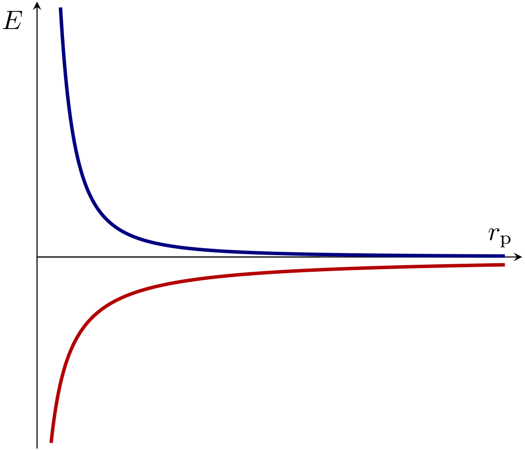


$$E = \frac{\hbar^2}{2m^*}\frac{1}{r_\mathrm{p}^2} - \frac{5}{16}\left(\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}\right)\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_\mathrm{p}}$$



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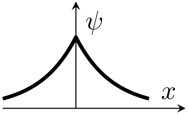

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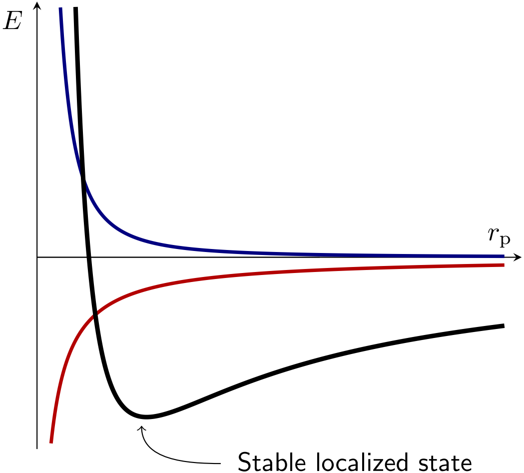
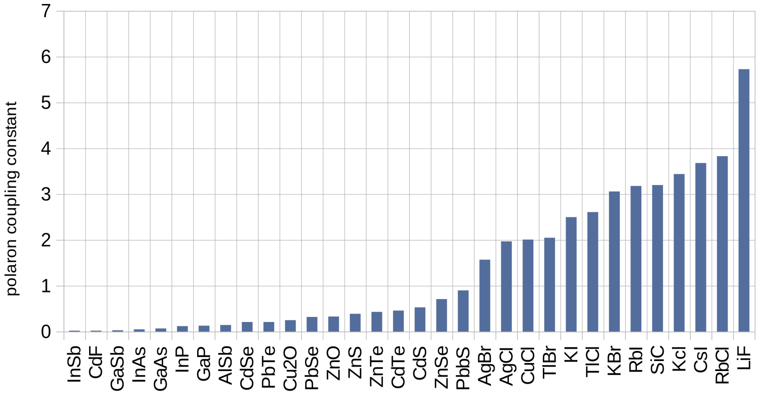


The polaron coupling constant

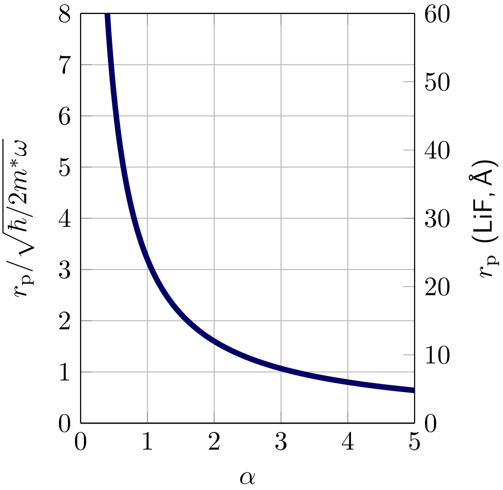
$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{m^*}{2\hbar\omega}}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right) \qquad \lambda \sim \frac{\alpha}{6}$$



Data from Iadonisi, Riv. Nuovo Cim. 7, 1 (1984)

Size of a polaron in the Landau-Pekar model

Radius: $r_{\mathrm{p}} = \frac{16}{5}\sqrt{\frac{\hbar}{2m^*\omega}}\,\frac{1}{\alpha}$



Total energy in DFT

$$
\begin{aligned}
E &= \sum_{i\in \mathrm{occ}} \int d\mathbf{r} |\nabla \psi_i|^2 + \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n] \\
&+ \sum_{\kappa} \int d\mathbf{r} \, \frac{Z_\kappa n(\mathbf{r})}{|\mathbf{r}-\boldsymbol{\tau}_\kappa|} + \frac{1}{2}\sum_{\kappa\kappa'} \frac{Z_\kappa Z_{\kappa'}}{|\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'}|}
\end{aligned}
$$

Total energy in DFT

$$E = \sum_{i\in\text{occ}} \int d\mathbf{r} |\nabla\psi_i|^2 + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n]$$

$$+ \sum_{\kappa} \int d\mathbf{r} \frac{Z_\kappa n(\mathbf{r})}{|\mathbf{r}-\boldsymbol{\tau}_\kappa|} + \frac{1}{2}\sum_{\kappa\kappa'} \frac{Z_\kappa Z_{\kappa'}}{|\boldsymbol{\tau}_\kappa - \boldsymbol{\tau}_{\kappa'}|}$$

Add one electron

$$n(\mathbf{r}) \to n(\mathbf{r}) + |\psi(\mathbf{r})|^2$$

$$\boldsymbol{\tau}_\kappa \to \boldsymbol{\tau}_\kappa + \mathbf{u}_\kappa$$

Total energy in DFT

$$E =$$

Total energy in DFT

$$E = \sum_{i\in\text{occ}} \int d\mathbf{r} |\nabla \psi_i|^2 + \int d\mathbf{r} |\nabla \psi|^2$$

Total energy in DFT

$$
\begin{aligned}
E &= \sum_{i\in\text{occ}} \int d\mathbf{r} |\nabla \psi_i|^2 + \int d\mathbf{r} |\nabla \psi|^2 \\
&+ \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \frac{\left[n(\mathbf{r}) + |\psi(\mathbf{r})|^2\right]\left[n(\mathbf{r}') + |\psi(\mathbf{r}')|^2\right]}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n + |\psi|^2]
\end{aligned}
$$

$$E = \sum_{i\in\mathrm{occ}} \int d\mathbf{r} |\nabla\psi_i|^2 + \int d\mathbf{r} |\nabla\psi|^2$$

$$+ \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \frac{\left[n(\mathbf{r}) + |\psi(\mathbf{r})|^2\right]\left[n(\mathbf{r}') + |\psi(\mathbf{r}')|^2\right]}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n + |\psi|^2]$$

$$+ \sum_{\kappa} \int d\mathbf{r} \frac{Z_\kappa \left[n(\mathbf{r}) + |\psi(\mathbf{r})|^2\right]}{|\mathbf{r} - (\boldsymbol{\tau}_\kappa + \mathbf{u}_\kappa)\,|} + \frac{1}{2}\sum_{\kappa\kappa'} \frac{Z_\kappa Z_{\kappa'}}{|\,(\boldsymbol{\tau}_\kappa + \mathbf{u}_\kappa) - (\boldsymbol{\tau}_{\kappa'} + \mathbf{u}_{\kappa'})\,|}$$

Formation energy functional of an extra electron, without self-interaction

$$E = \int d\mathbf{r}\, \psi^* \hat{H}_{\mathrm{KS}}\, \psi + \int d\mathbf{r}\, |\psi|^2 \frac{\partial V_{\mathrm{KS}}}{\partial \boldsymbol{\tau}_\kappa} \cdot \mathbf{u}_\kappa + \frac{1}{2} \mathbf{u}_\kappa \cdot \mathbf{C}_{\kappa\kappa'} \cdot \mathbf{u}_{\kappa'}$$

Polarons in density-functional perturbation theory

Formation energy functional of an extra electron, without self-interaction

$$E = \int d\mathbf{r}\, \psi^* \hat{H}_{\mathrm{KS}}\, \psi + \int d\mathbf{r}\, |\psi|^2 \frac{\partial V_{\mathrm{KS}}}{\partial \boldsymbol{\tau}_\kappa} \cdot \mathbf{u}_\kappa + \frac{1}{2} \mathbf{u}_\kappa \cdot \mathbf{C}_{\kappa\kappa'} \cdot \mathbf{u}_{\kappa'}$$

Variational minimization with respect to ψ and $\mathbf{u}_\kappa$

$$\begin{cases} \hat{H}_{\mathrm{KS}}\, \psi + \psi \dfrac{\partial V_{\mathrm{KS}}}{\partial \boldsymbol{\tau}_\kappa} \cdot \mathbf{u}_\kappa = \lambda\, \psi \\ \mathbf{u}_\kappa = -(\mathbf{C})^{-1}_{\kappa\kappa'} \cdot \displaystyle\int d\mathbf{r}\, \frac{\partial V_{\mathrm{KS}}}{\partial \boldsymbol{\tau}_{\kappa'}} |\psi|^2 \end{cases}$$

Polarons in reciprocal space

cf. Tut. Thu.4 Lian & Lafuente

$$\psi(\mathbf{r}) = \frac{1}{N_p} \sum_{n\mathbf{k}} A_{n\mathbf{k}} \, \psi_{n\mathbf{k}}(\mathbf{r})$$

$$\mathbf{u}_\kappa(\mathbf{R}) = -\frac{2}{N_p} \sum_{\mathbf{q}\nu} B^*_{\mathbf{q}\nu} \sqrt{\frac{\hbar}{2M_\kappa \omega_{\mathbf{q}\nu}}} \, e^{i\mathbf{q}\cdot\mathbf{R}} \, \mathbf{e}_{\kappa,\mathbf{q}\nu}$$

cf. Tut. Thu.4 Lian & Lafuente

$$\psi(\mathbf{r}) = \frac{1}{N_p}\sum_{n\mathbf{k}} A_{n\mathbf{k}}\,\psi_{n\mathbf{k}}(\mathbf{r})$$

$$\mathbf{u}_\kappa(\mathbf{R}) = -\frac{2}{N_p}\sum_{\mathbf{q}\nu} B^*_{\mathbf{q}\nu}\sqrt{\frac{\hbar}{2M_\kappa\omega_{\mathbf{q}\nu}}}\, e^{i\mathbf{q}\cdot\mathbf{R}}\,\mathbf{e}_{\kappa,\mathbf{q}\nu}$$

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

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

Ab initio polaron equations

Electron polaron in LiF

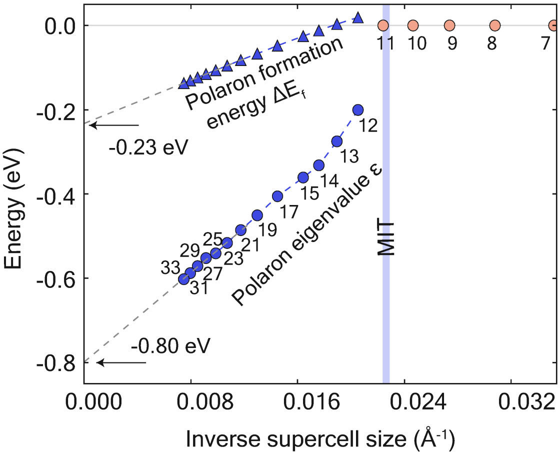
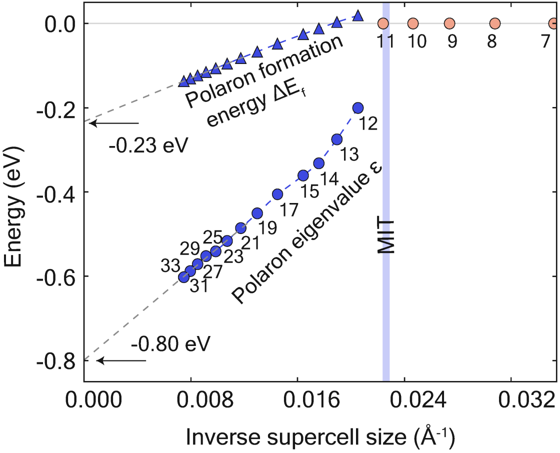


Figure from Sio et al, PRL 122, 246403 (2019)



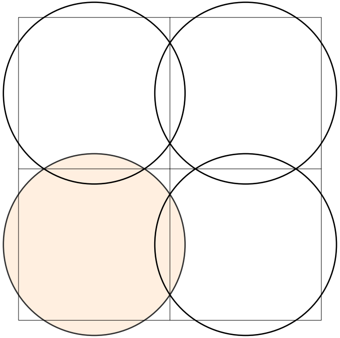


Figure from Sio et al, PRL 122, 246403 (2019)

Electron polaron in LiF

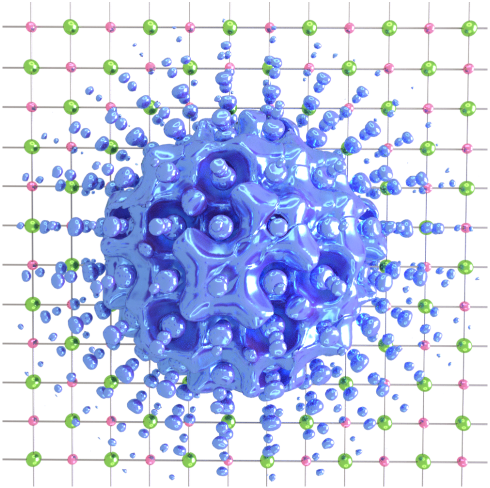
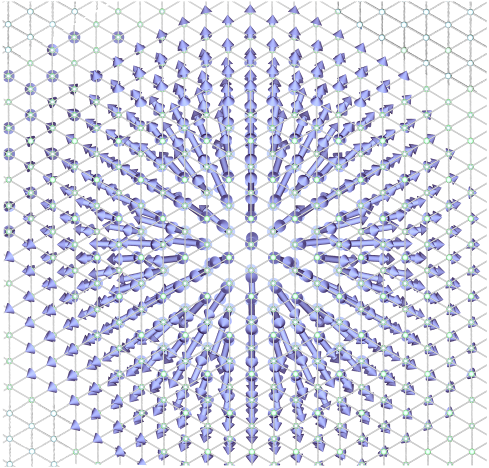


Figure from Sio et al, PRL 122, 246403 (2019)

Electron polaron in LiF



fluorine displacements

Figure from Sio et al, PRL 122, 246403 (2019)

Hole polaron in LiF

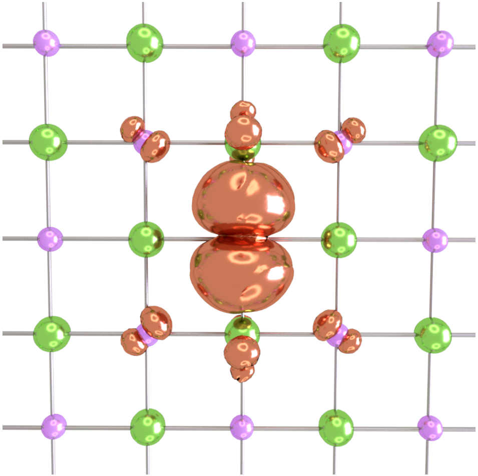
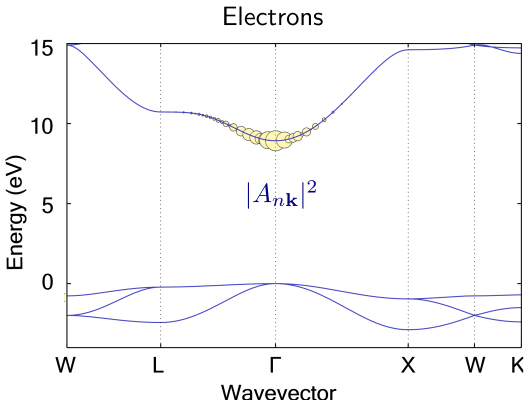
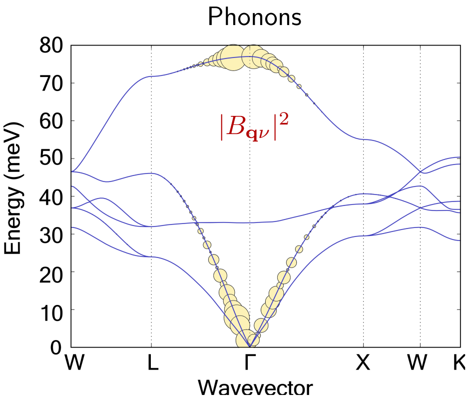
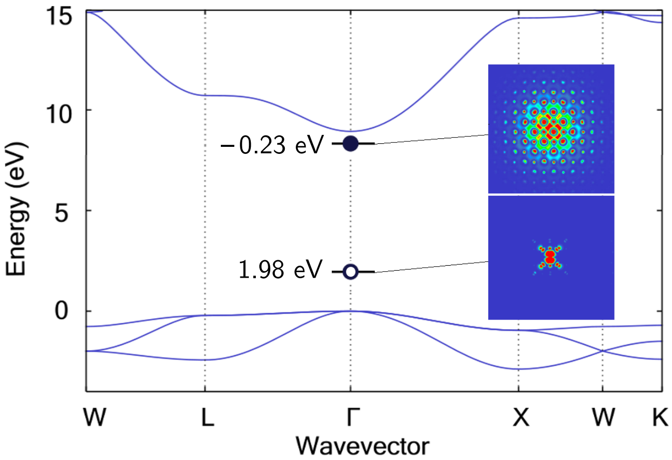


Figure from Sio et al, PRB 99, 235139 (2019)

Example: Electron polaron in LiF







Shown are formation energies w.r.t. delocalized solutions

Effect of self-interaction: A lesson from the Landau-Pekar model

$$\hat{H}_{\rm LP} = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int d\mathbf{r}'\,\frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

Effect of self-interaction: A lesson from the Landau-Pekar model

DFT-like self-interaction

$$\hat{H}_{\mathrm{LP}} = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\int d\mathbf{r}'\,\frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{e^2}{4\pi\varepsilon_0}\int d\mathbf{r}'\,\frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

Effect of self-interaction: A lesson from the Landau-Pekar model

DFT-like self-interaction

$$\hat{H}_{\mathrm{LP}} = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\int d\mathbf{r}' \frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} + \boxed{\frac{e^2}{4\pi\varepsilon_0}\int d\mathbf{r}' \frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}}$$

$$\hat{H}_{\mathrm{LP}} = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\underbrace{\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} - 1\right)}_{[-1,0)}\int d\mathbf{r}' \frac{|\psi(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}$$

- Hartree self-interaction suppresses localization
- Hybrid functionals partly cancel self-interaction

Take-home messages

- ARPES measurements and many-body calculations provide spectral function of polarons, but no wavefunction
- DFT calculations of polarons suffer from the self-interaction error
- *Ab initio* polaron equations yield self-interaction-free polaron energies and wavefunctions, at the cost of unit-cell calculations

References

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- Devreese et al, Rep. Prog. Phys. 72, 066501 (2009) [link]
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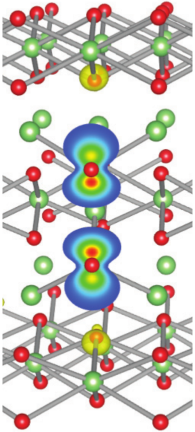
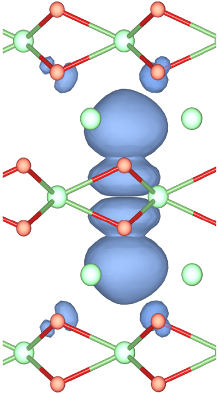
- Lee et al, Phys. Rev. Materials 5, 063805 (2021) [link]

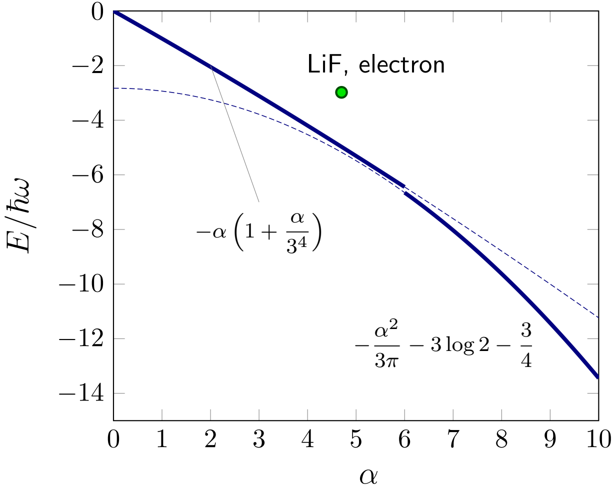




Left figure from Feng et al, PRB 88, 184302 (2013); Right figure from Sio et al, PRL 122, 246403 (2019)

Feynman's polaron

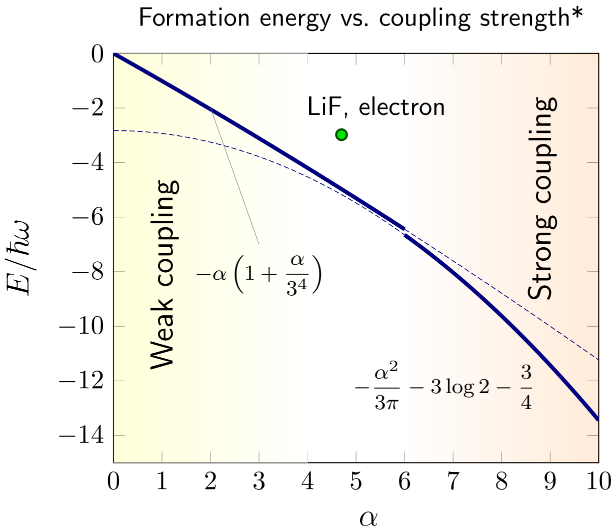
Formation energy vs. coupling strength*



Similar to DMC results by Mishchenko et al, Phys. Rev. B 62, 6317 (2000)

*Valid only for Fröhlich model

From: Feynman and Hibbs, p. 318



Similar to DMC results by Mishchenko et al, Phys. Rev. B 62, 6317 (2000)

*Valid only for Fröhlich model

From: Feynman and Hibbs, p. 318