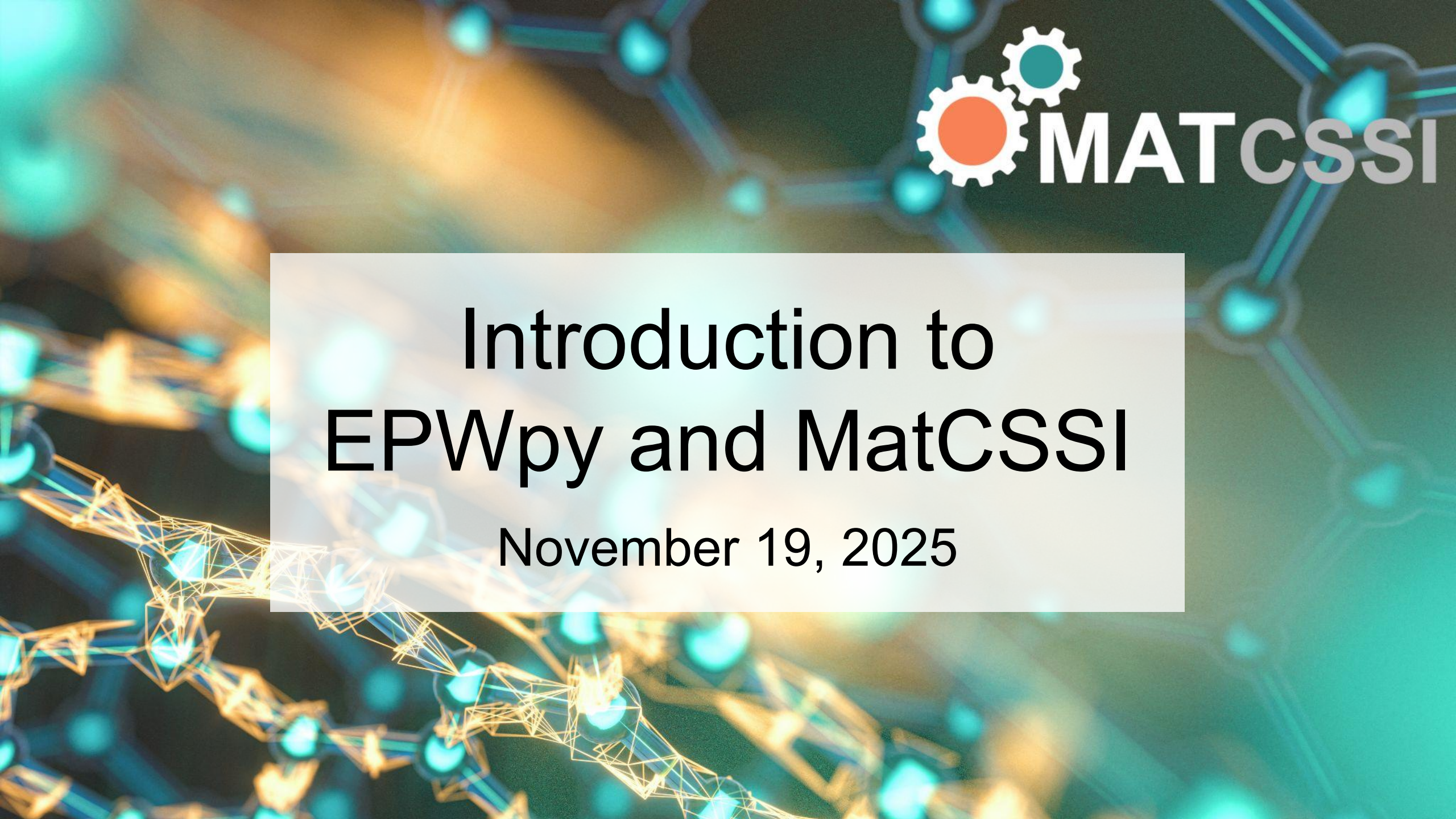


Introduction to EPWpy and MatCSSI

November 19, 2025

Transport & polarons with EPWpy

Jon Lafuente-Bartolome

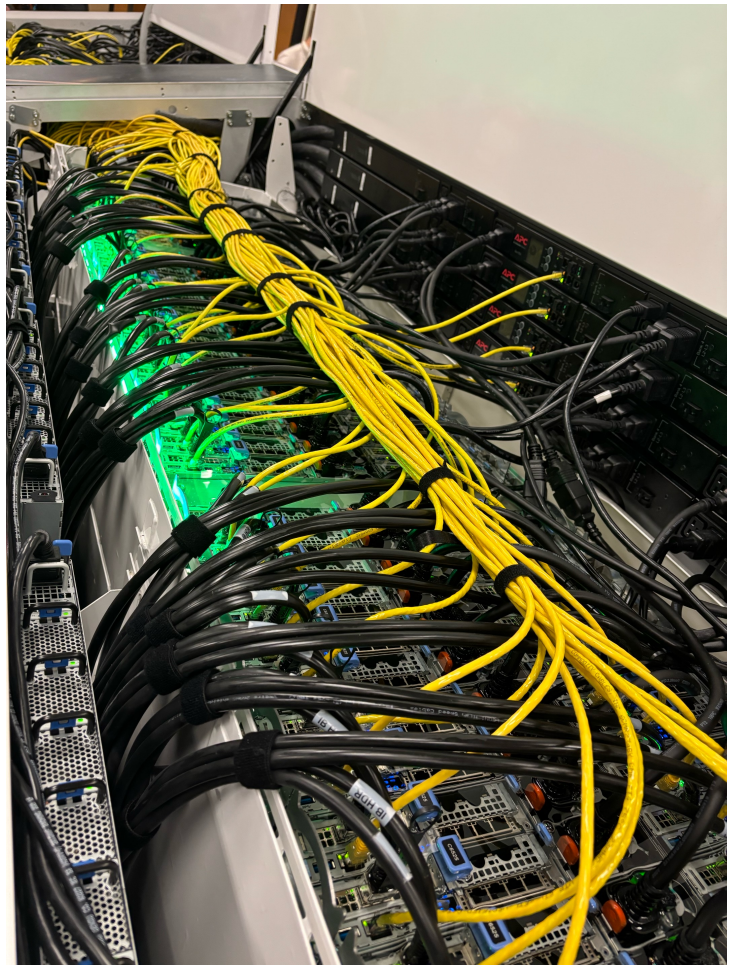
Department of Physics
University of the Basque Country EHU

This initiative is supported by the Office of Advanced Cyberinfrastructure and the Condensed Matter and Materials Theory division of the National Science Foundation under the CSSI Frameworks program, Award #2513830

Lecture summary

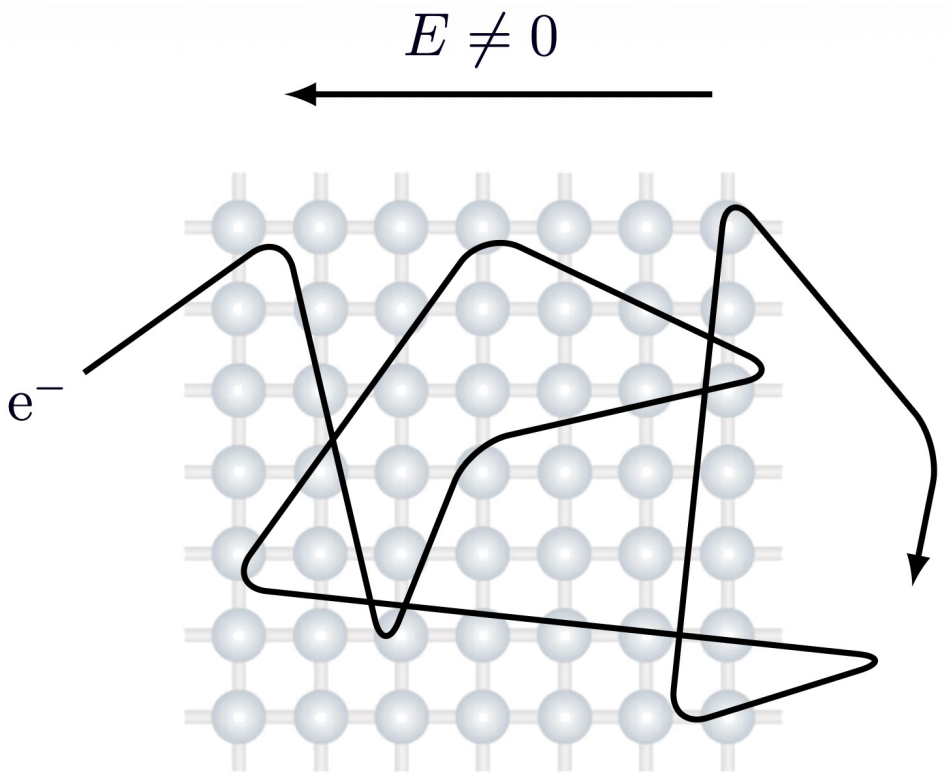
- Introduction
- Boltzmann theory of transport
  - Theory & implementation
  - EPWpy workflow
- Self-trapped polarons
  - Theory & implementation
  - EPWpy workflow
- Conclusions

Introduction

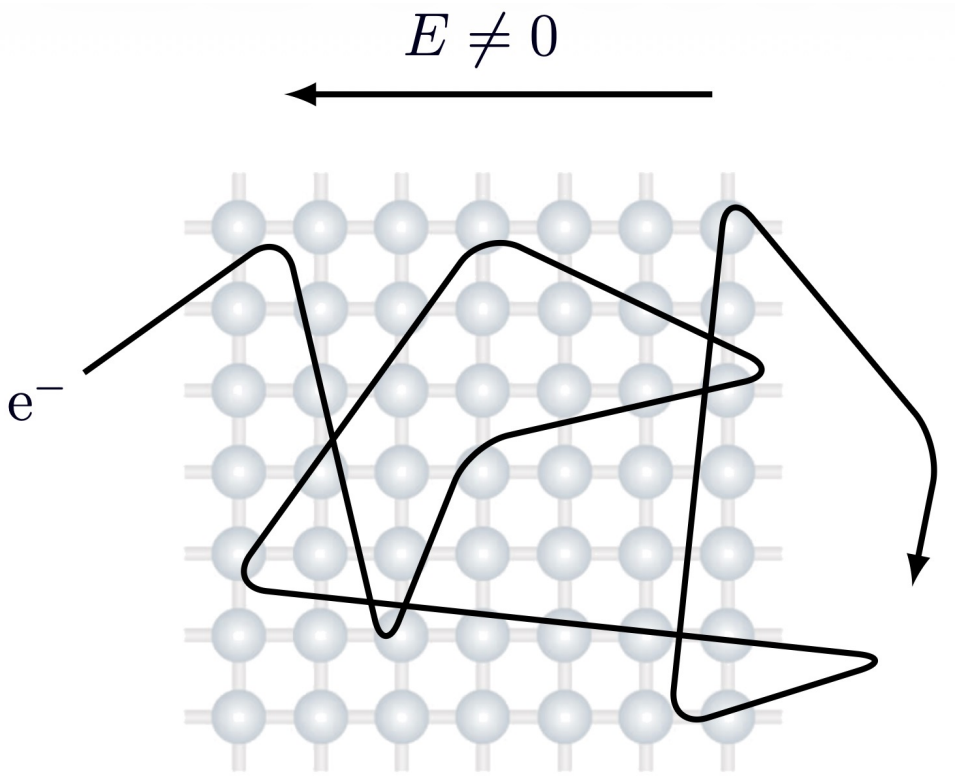


Liquid immersion subsystem by GRC in the Frontera supercomputer at TACC

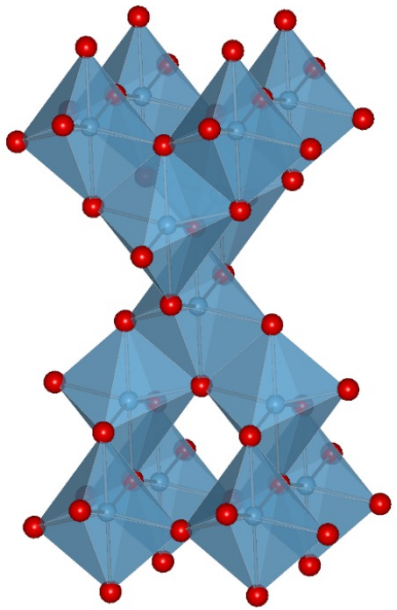
Phonon-limited carrier transport

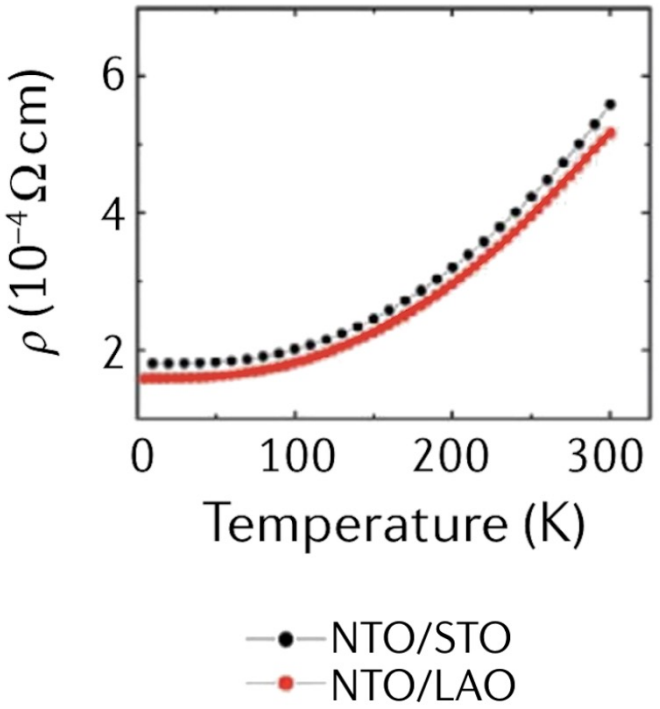


Phonon-limited carrier transport



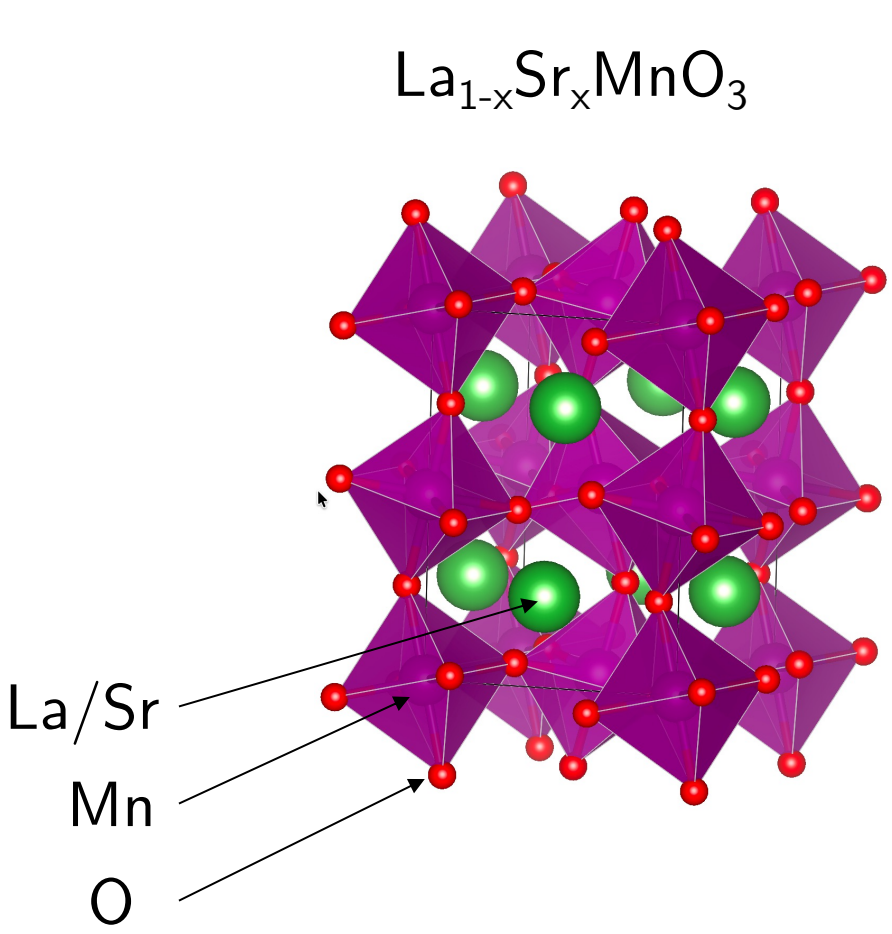
Anatase TiO_2

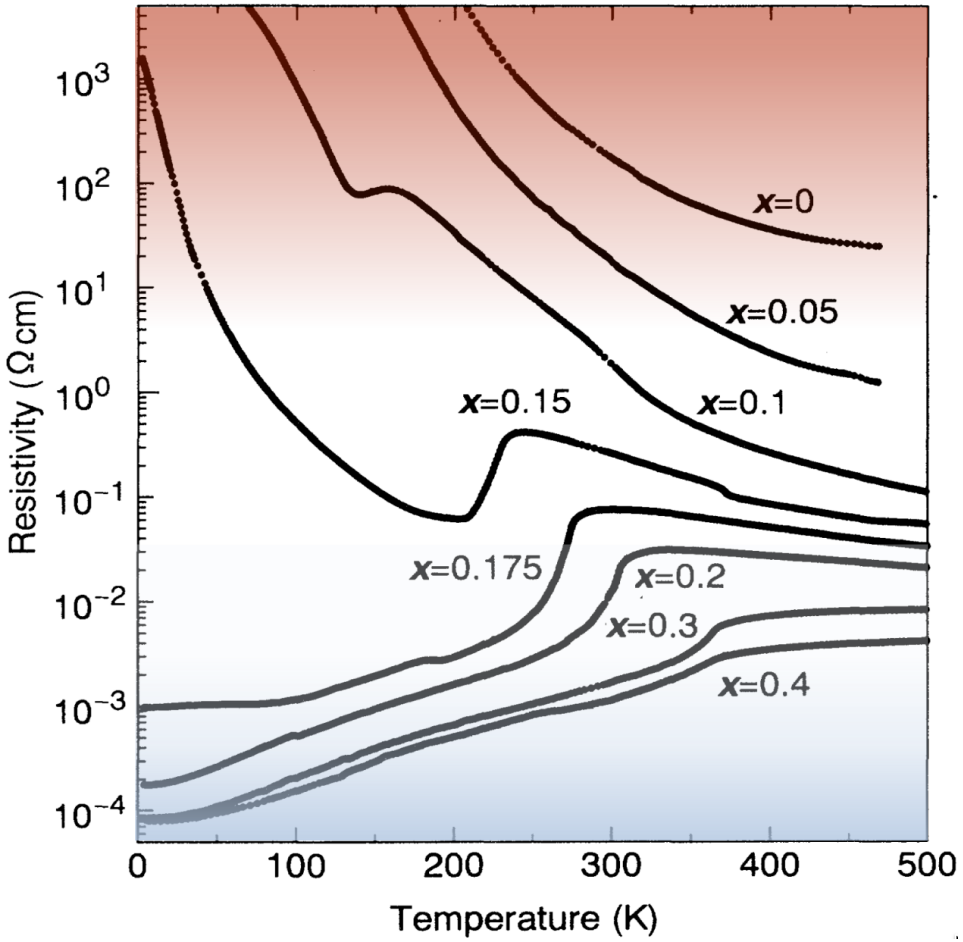




Resistivity data from Zhang et al., J. Appl. Phys. 102, 013701 (2007)

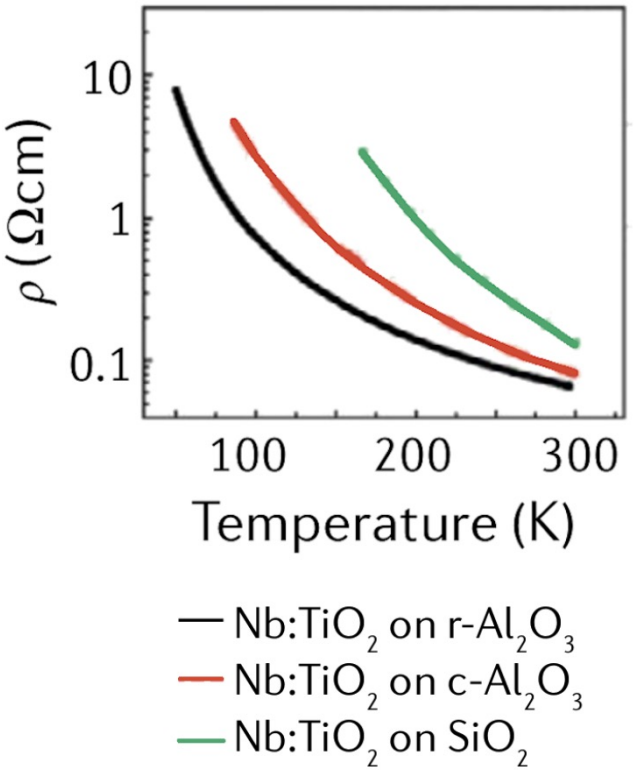
Phonon-limited carrier transport



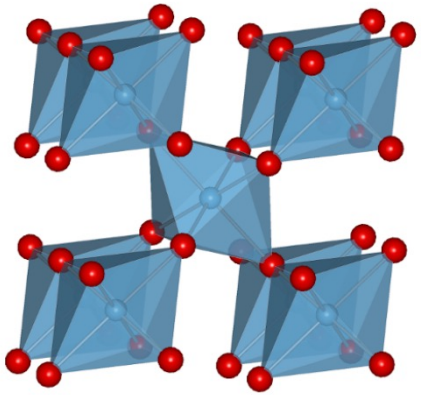


Resistivity data from Urushibara et al., Phys. Rev. B 51, 14103 (1995)

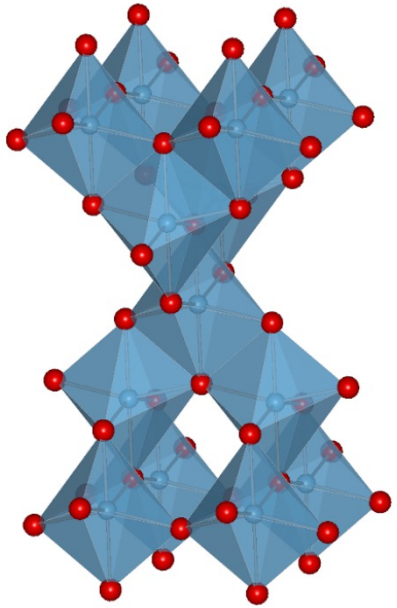
Temperature-activated mobility

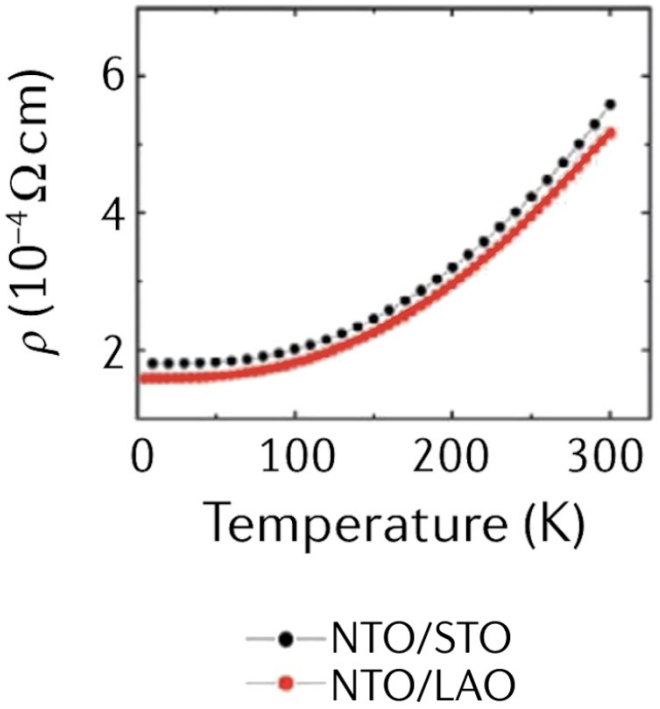


Rutile TiO_2



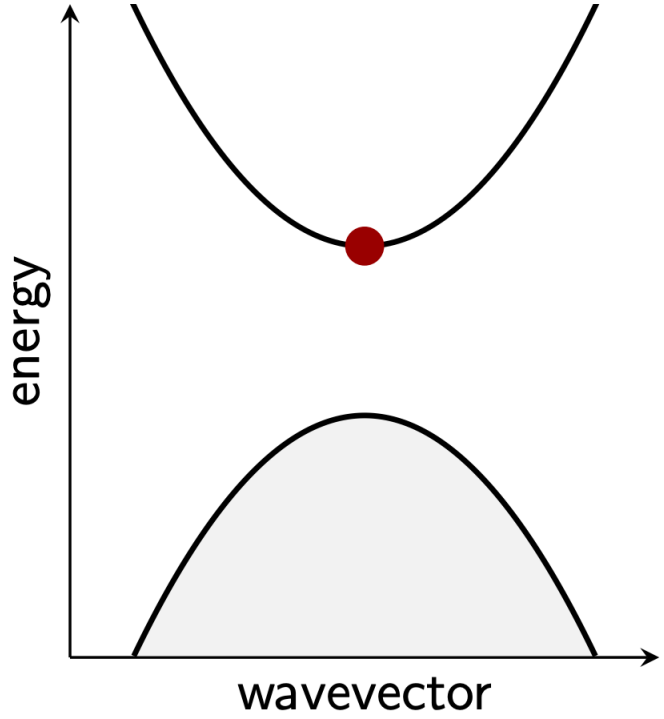
Anatase TiO_2

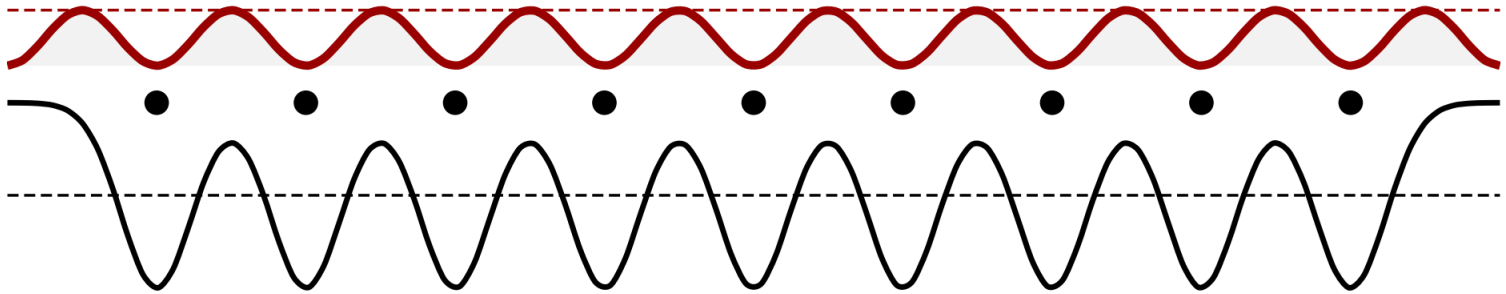




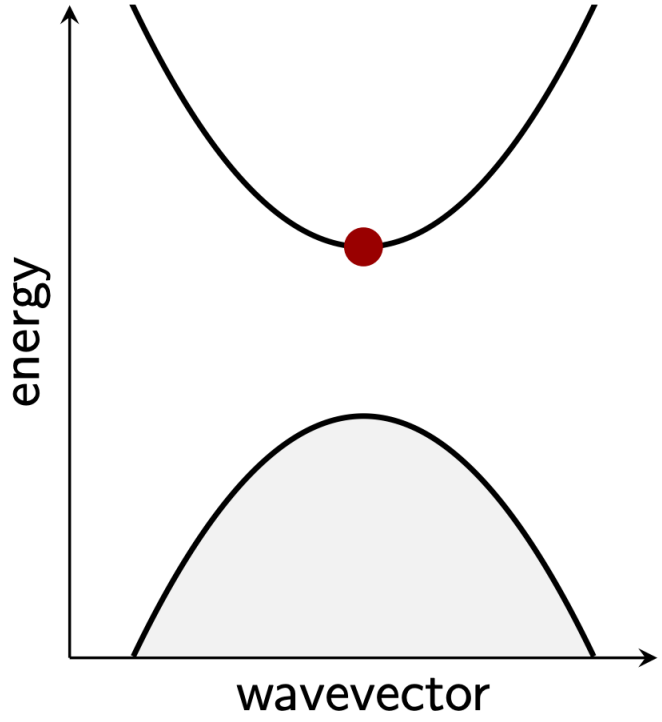
Resistivity data from Zhang et al., J. Appl. Phys. 102, 013701 (2007)

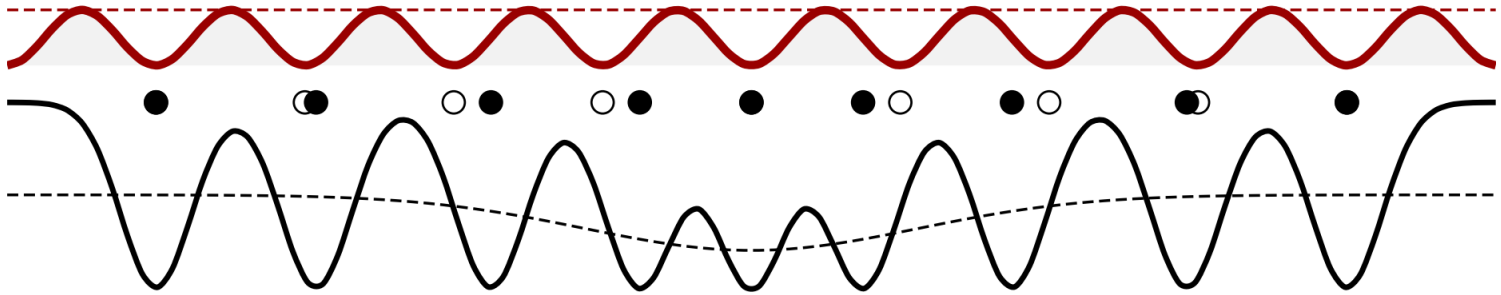
Electron self-trapping



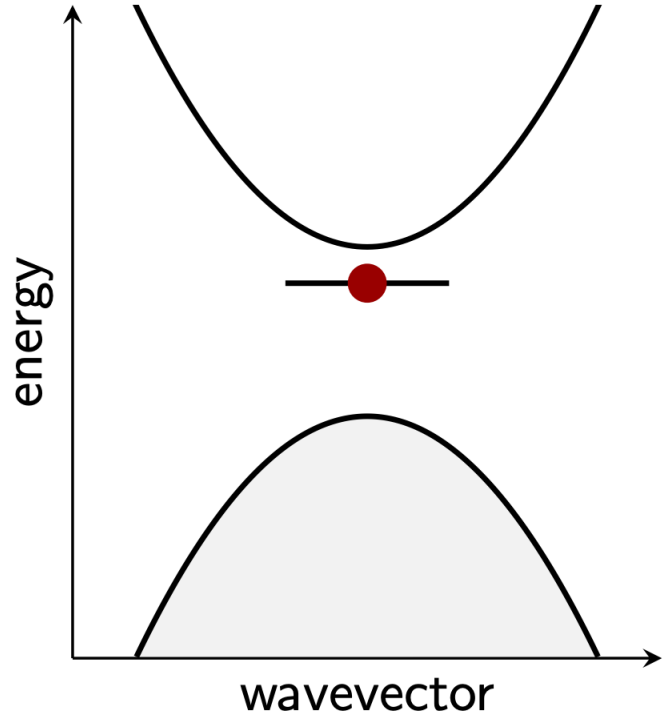


Electron self-trapping

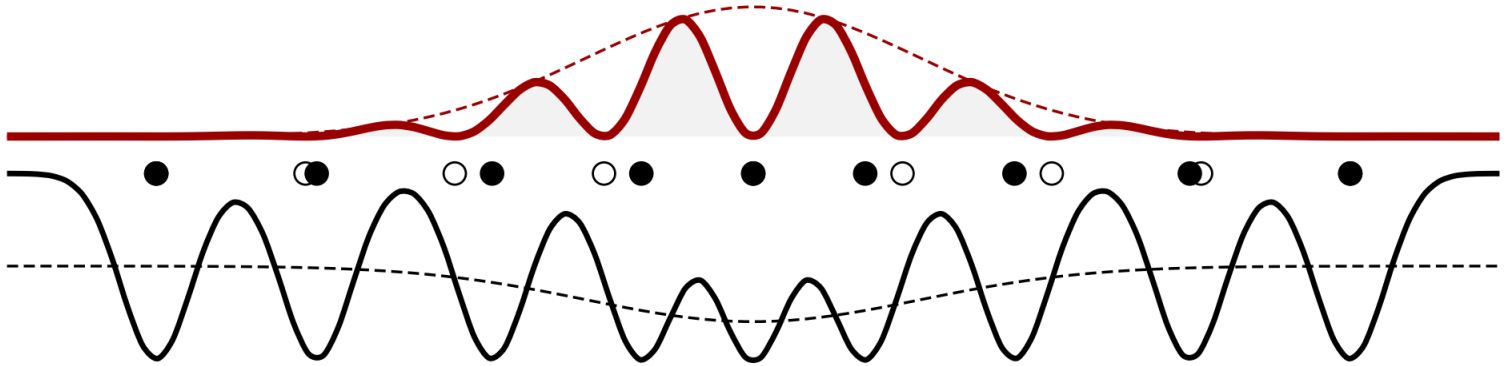




Electron self-trapping



Electron **localized** by lattice distortion



Polaron-hopping transport

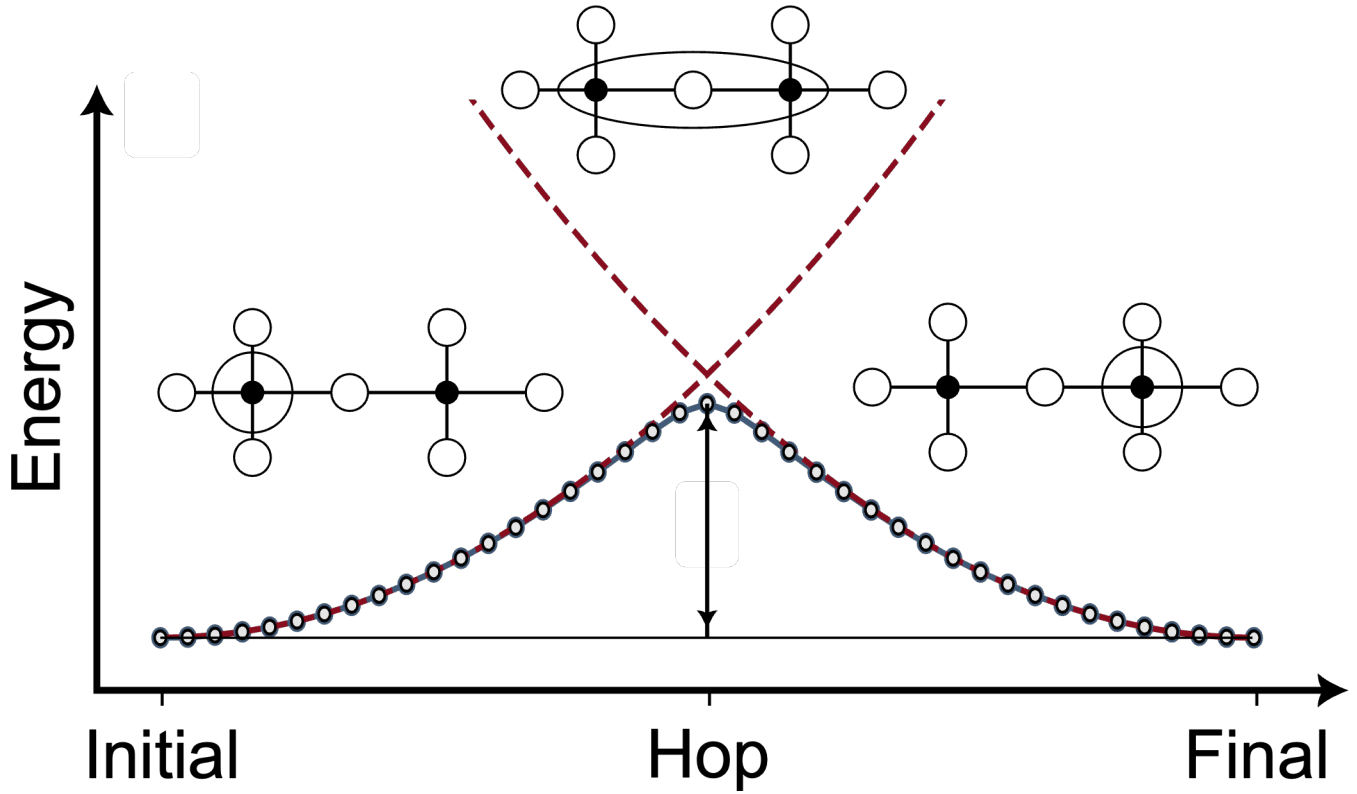


Figure adapted from Deskins and Dupuis, Phys. Rev. B 75, 195212 (2007)

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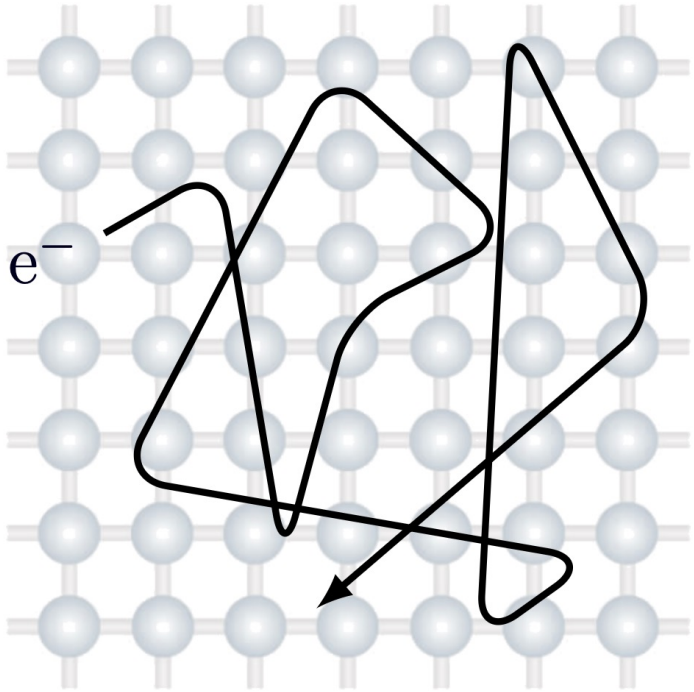
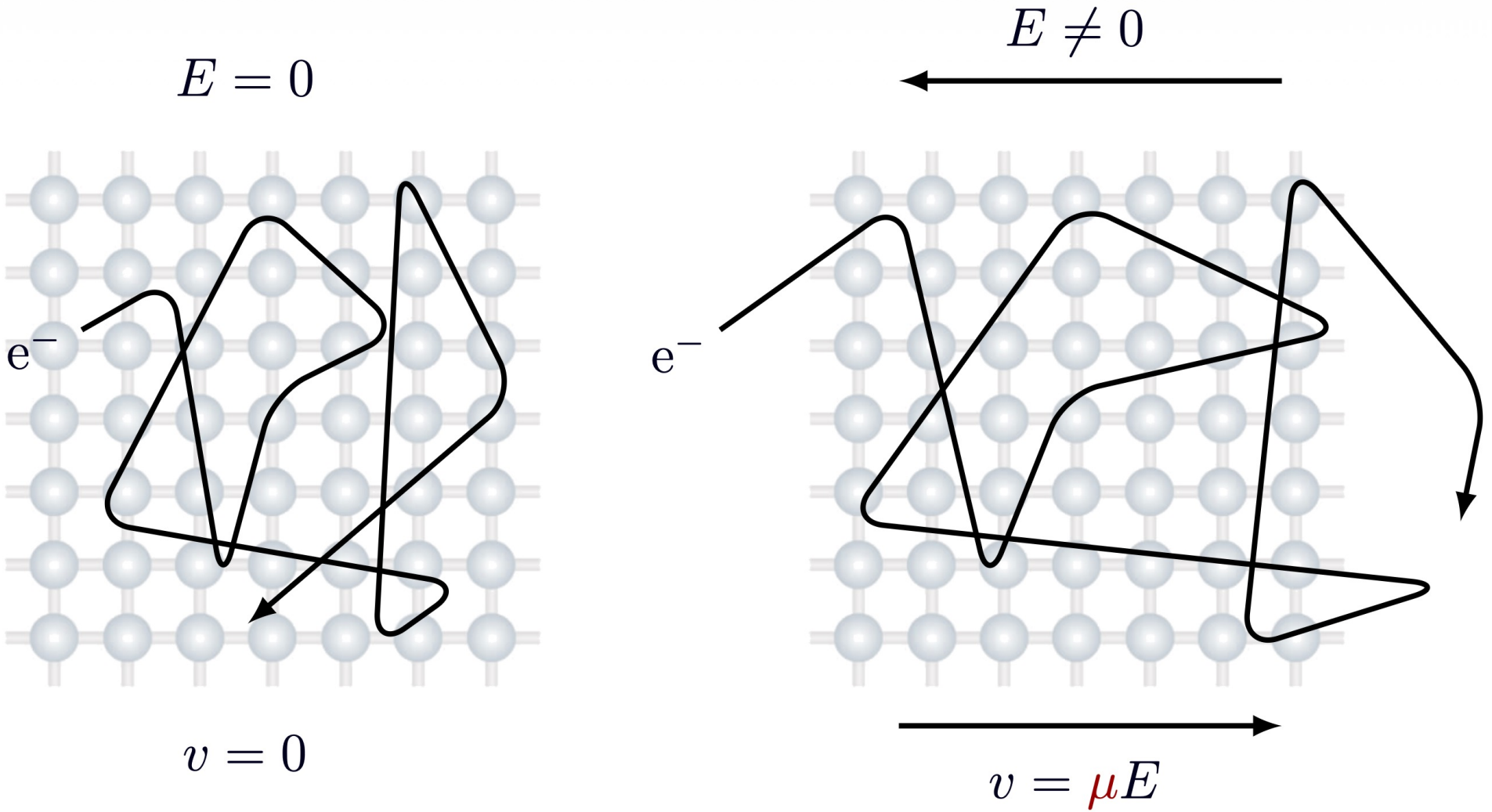
Notion of carrier mobility

$E = 0$

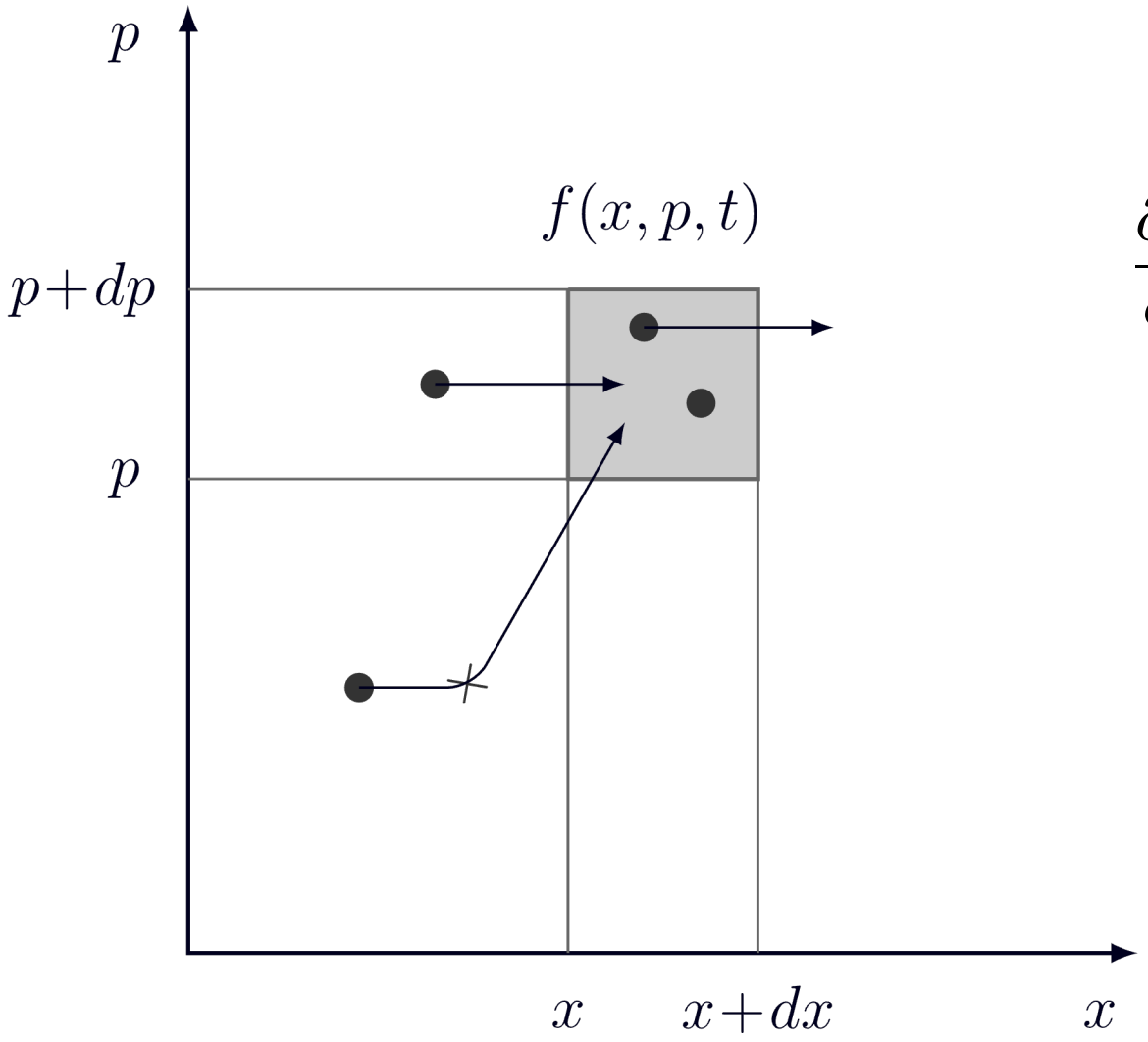


$v = 0$

Notion of carrier mobility



Boltzmann transport equation



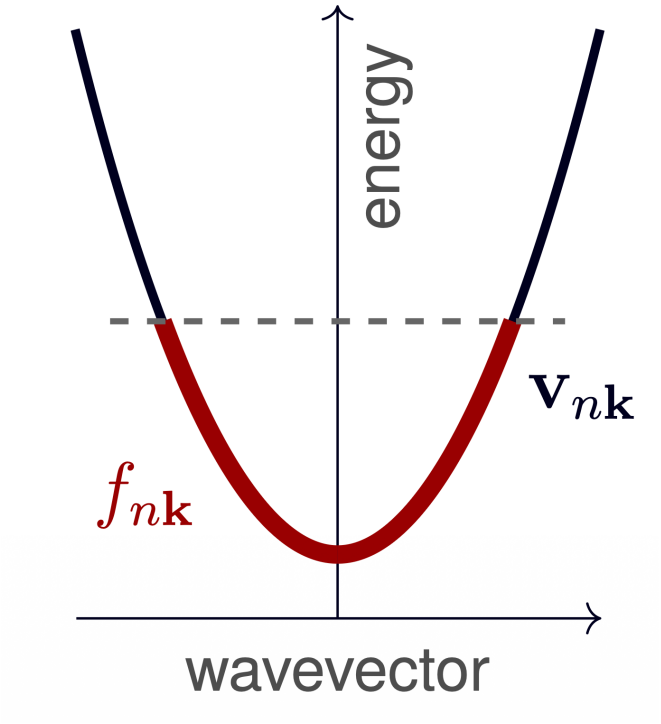
$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial f}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{dt} = \Gamma_{\text{in}} - \Gamma_{\text{out}}$$

$$\mathbf{F} = q\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

Steady-state & homogeneous:

$$q\frac{\partial f}{\partial \mathbf{p}} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) = \Gamma_{\text{in}} - \Gamma_{\text{out}}$$

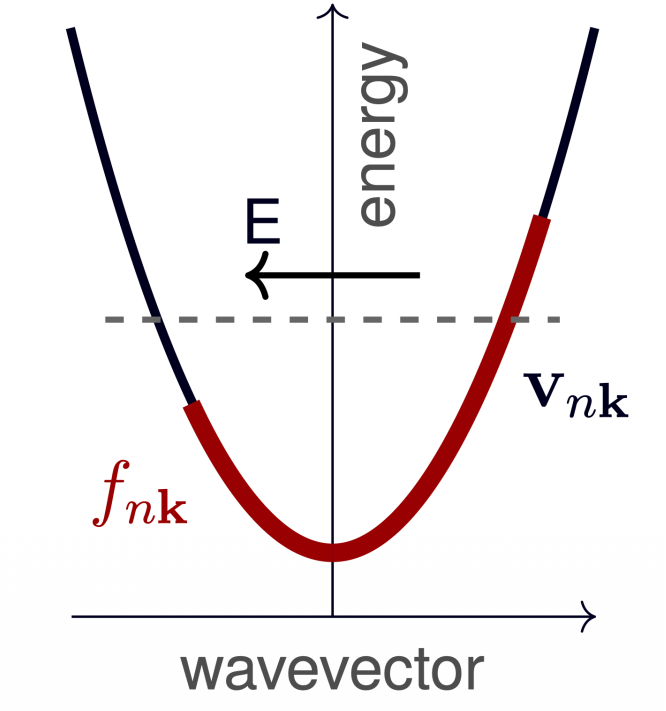
Carrier mobility from first principles



$$\mu_{\alpha\beta} = -\frac{1}{ne}\frac{\partial J_\alpha}{\partial E_\beta}$$

$$\mathbf{J} = -\frac{e}{\Omega}\frac{1}{N_\mathbf{k}}\sum_{n\mathbf{k}} f_{n\mathbf{k}}\mathbf{v}_{n\mathbf{k}}$$

Carrier mobility from first principles



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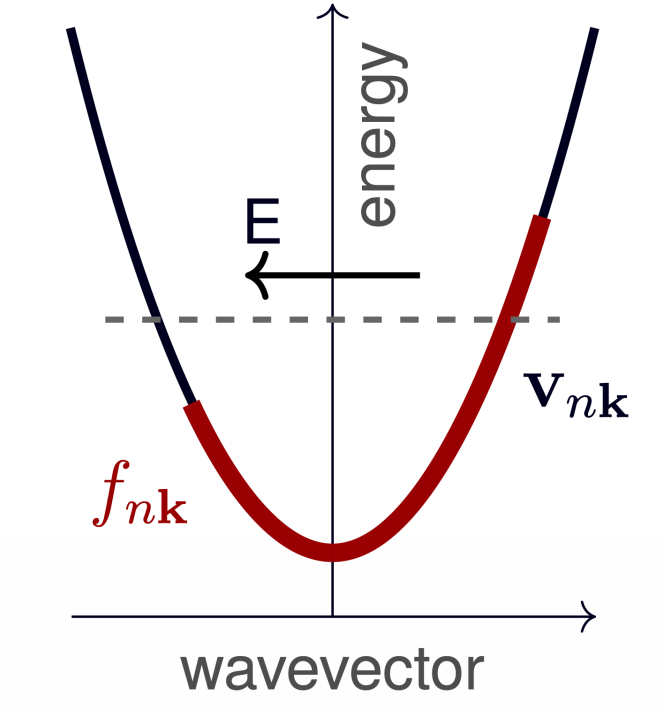
$$f_{n\mathbf{k}}(\mathbf{E}) = f^0_{n\mathbf{k}} + \mathbf{E}\cdot\left.\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0} + \dots$$

Carrier mobility from first principles



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$$\mu_{\alpha\beta} = -\frac{1}{N_e}\sum_{n\mathbf{k}} v_{n\mathbf{k},\alpha}\left.\frac{\partial f_{n\mathbf{k}}}{\partial E_\beta}\right|_{\mathbf{E}=0}$$

Ab initio Boltzmann transport equation

$$
\begin{aligned}
(-e)\,\mathbf{E}\cdot\frac{1}{\hbar}\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{k}} = & \frac{2\pi}{\hbar}\sum_{m\nu}\int\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \\
& \times\{(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\,\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})(1+n_{\mathbf{q}\nu}) \\
& +(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\,\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu} \\
& -f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\,\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})1+n_{\mathbf{q}\nu}) \\
& -f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\,\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu}\}
\end{aligned}
$$

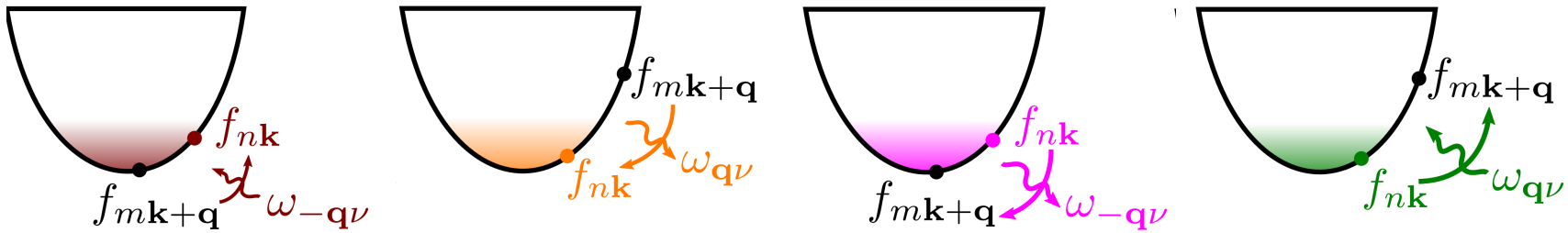

Figure from Poncé et al., Rep. Prog. Phys. 83, 036501 (2020)

Ab initio Boltzmann transport equation

$$\left.\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0} = e\left.\frac{\partial f^0}{\partial \varepsilon}\right|_{\varepsilon_{n\mathbf{k}}} \mathbf{v}_{n\mathbf{k}}\tau^0_{n\mathbf{k}} + \frac{2\pi\tau^0_{n\mathbf{k}}}{\hbar}\sum_{m\nu}\int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \times \Big[(1-f^0_{n\mathbf{k}}+n^0_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega_{\mathbf{q}\nu}) + (f^0_{n\mathbf{k}}+n^0_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_{\mathbf{q}\nu})\Big] \left.\frac{\partial f_{m\mathbf{k}+\mathbf{q}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0}$$

Ab initio Boltzmann transport equation

$$\left.\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0} = e\left.\frac{\partial f^0}{\partial \varepsilon}\right|_{\varepsilon_{n\mathbf{k}}} \mathbf{v}_{n\mathbf{k}}\tau^0_{n\mathbf{k}}$$

RTA: Relaxation time approximation

$$+ \frac{2\pi\tau^0_{n\mathbf{k}}}{\hbar}\sum_{m\nu}\int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2$$

$$\times\Big[(1-f^0_{n\mathbf{k}}+n^0_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega_{\mathbf{q}\nu})$$

$$+(f^0_{n\mathbf{k}}+n^0_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_{\mathbf{q}\nu})\Big]\left.\frac{\partial f_{m\mathbf{k}+\mathbf{q}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0}$$

Ab initio Boltzmann transport equation

$$\left.\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0} = e\left.\frac{\partial f^0}{\partial \varepsilon}\right|_{\varepsilon_{n\mathbf{k}}} \mathbf{v}_{n\mathbf{k}}\tau^0_{n\mathbf{k}}$$

RTA: Relaxation time approximation

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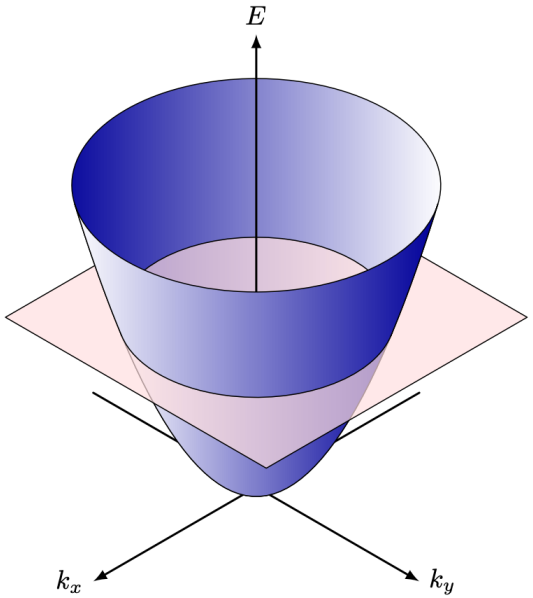
$$\times\left[(1-f^0_{n\mathbf{k}}+n^0_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega_{\mathbf{q}\nu})\right.$$

$$\left.+(f^0_{n\mathbf{k}}+n^0_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_{\mathbf{q}\nu})\right]\left.\frac{\partial f_{m\mathbf{k}+\mathbf{q}}}{\partial \mathbf{E}}\right|_{\mathbf{E}=0}$$

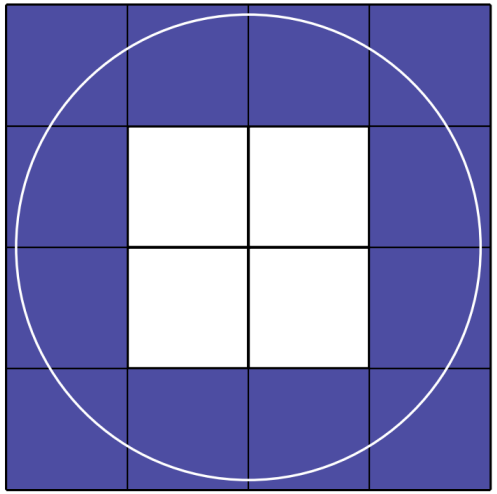
$$\mu_{\alpha\beta} = -\frac{1}{N_e}\sum_{n\mathbf{k}} v_{n\mathbf{k},\alpha}\left.\frac{\partial f_{n\mathbf{k}}}{\partial E_\beta}\right|_{\mathbf{E}=0}$$

The challenge of Brillouin zone sampling

$$\frac{1}{\tau_{n\mathbf{k}}} = \frac{2\pi}{\hbar}\sum_{m\nu}\int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \times \Big[(1-f_{m\mathbf{k}+\mathbf{q}}+n_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_{\mathbf{q}\nu}) + (f_{m\mathbf{k}+\mathbf{q}}+n_{\mathbf{q}\nu})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega_{\mathbf{q}\nu})\Big]$$

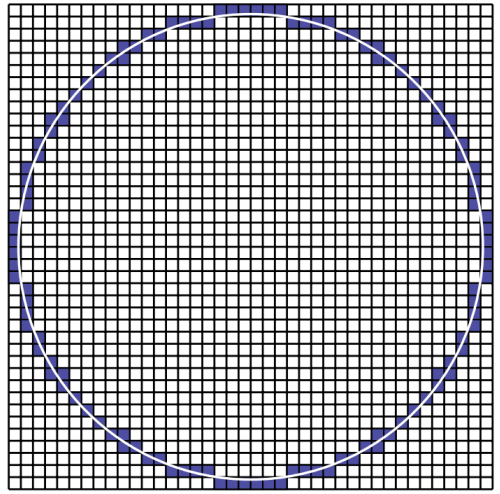


4 x 4 grid



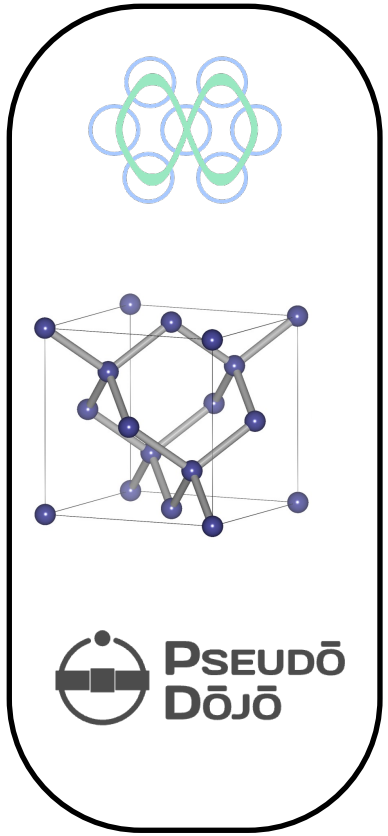
Coarse BZ sampling

40 x 40 grid

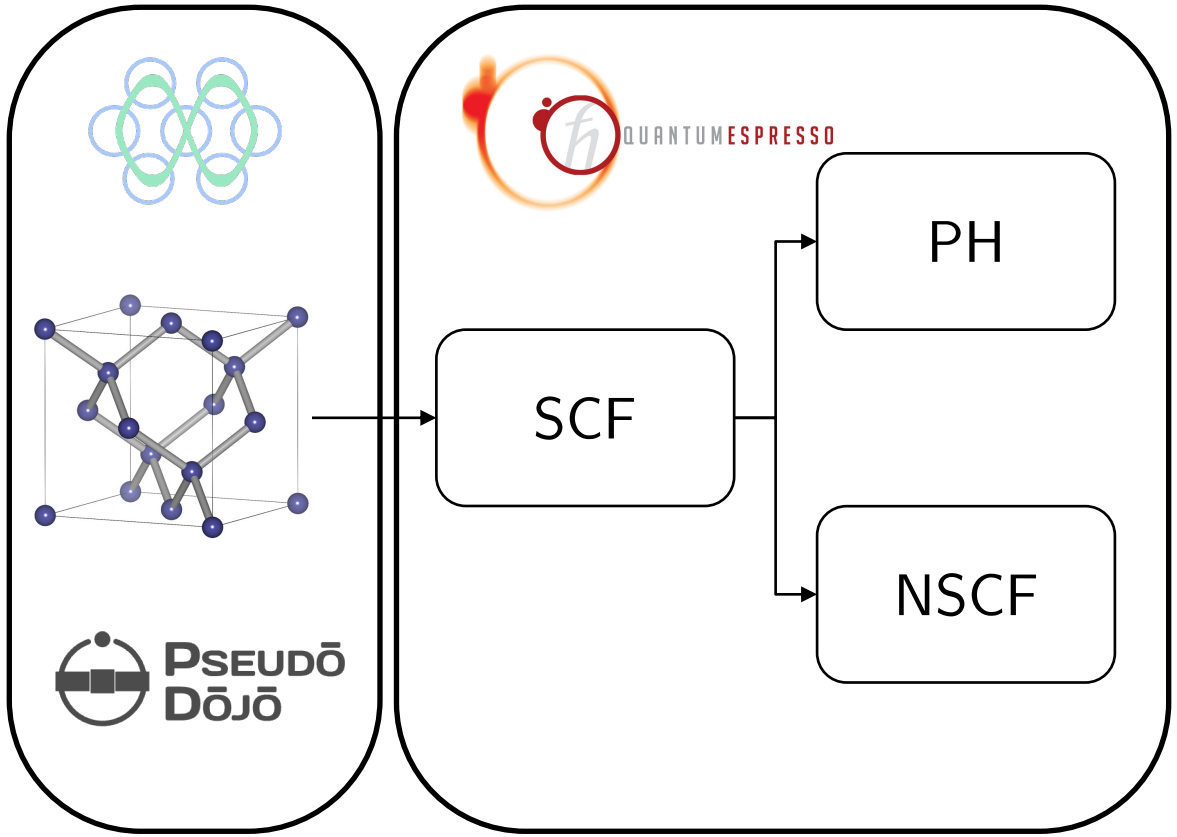


Fine BZ sampling

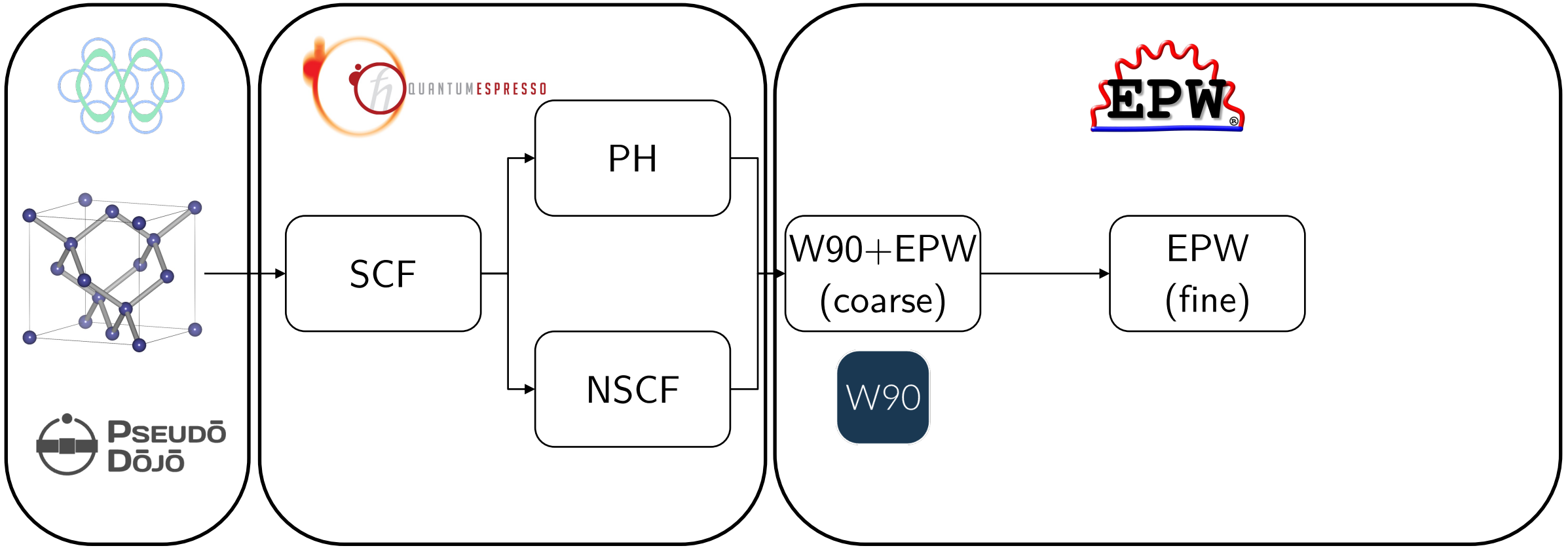
Workflow



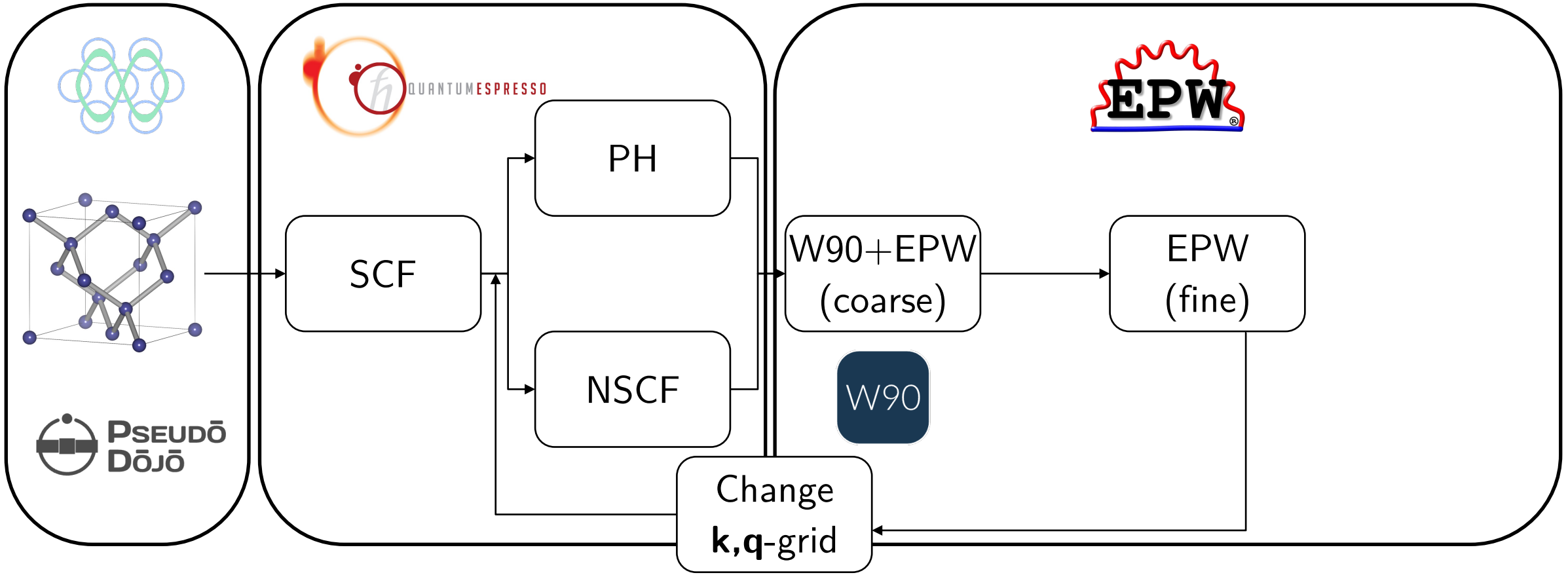
Workflow



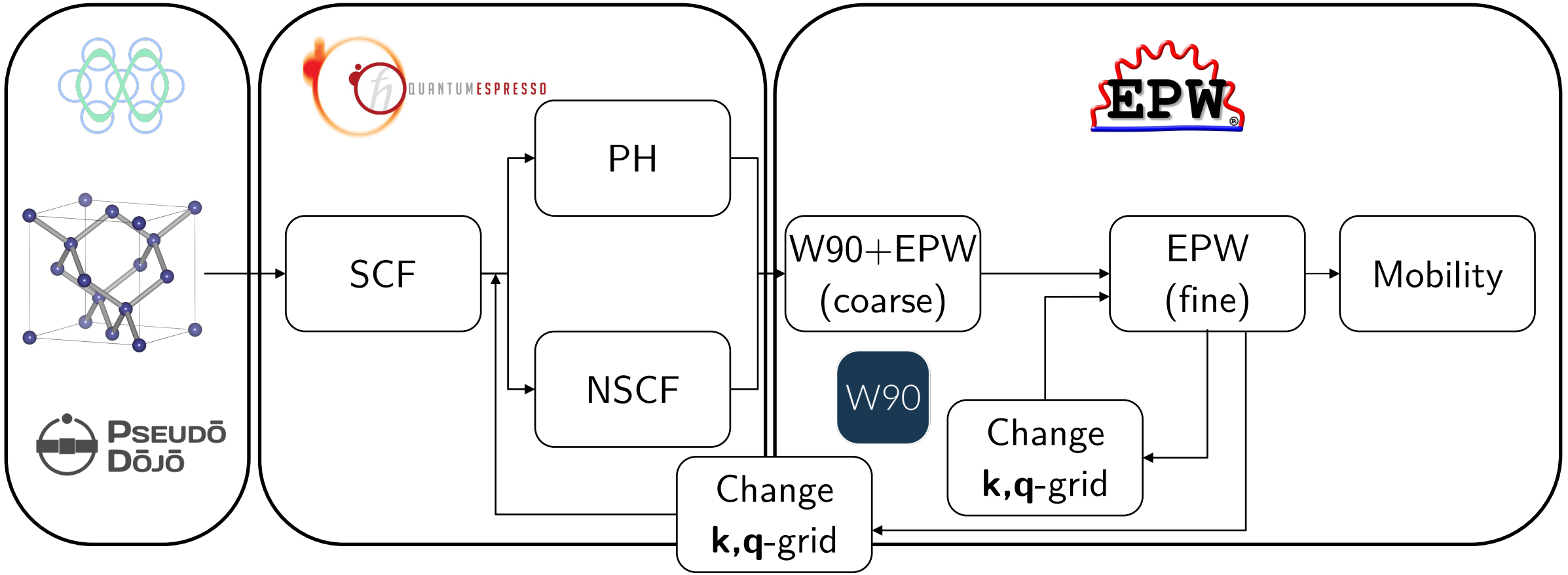
Workflow


QUANTUMESPRESSO
PH
SCF
NSCF
EPW
W90+EPW
(coarse)
EPW
(fine)
W90
PSEUDŌ
DŌJŌ

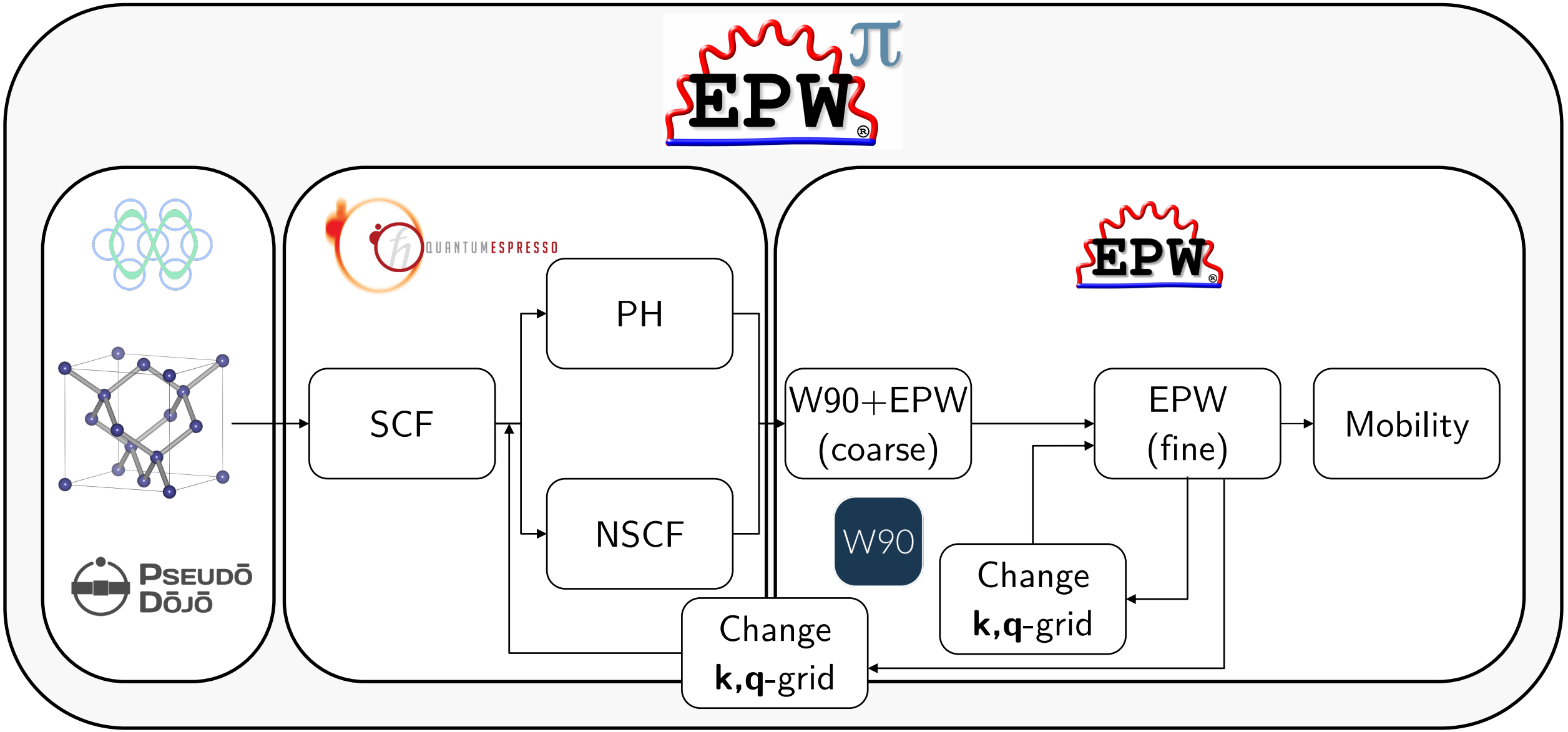
Workflow


QUANTUMESPRESSO
EPW
PSEUDŌ DŌJŌ
SCF
PH
NSCF
W90+EPW (coarse)
EPW (fine)
W90
Change **k**,**q**-grid

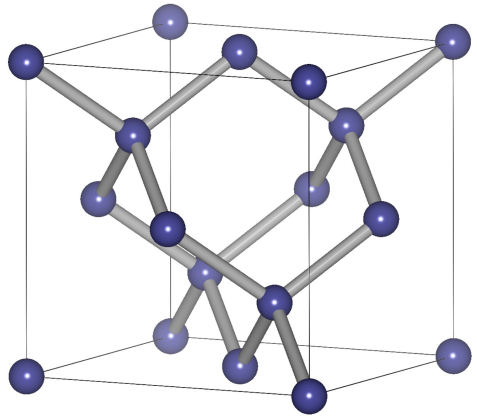
Workflow

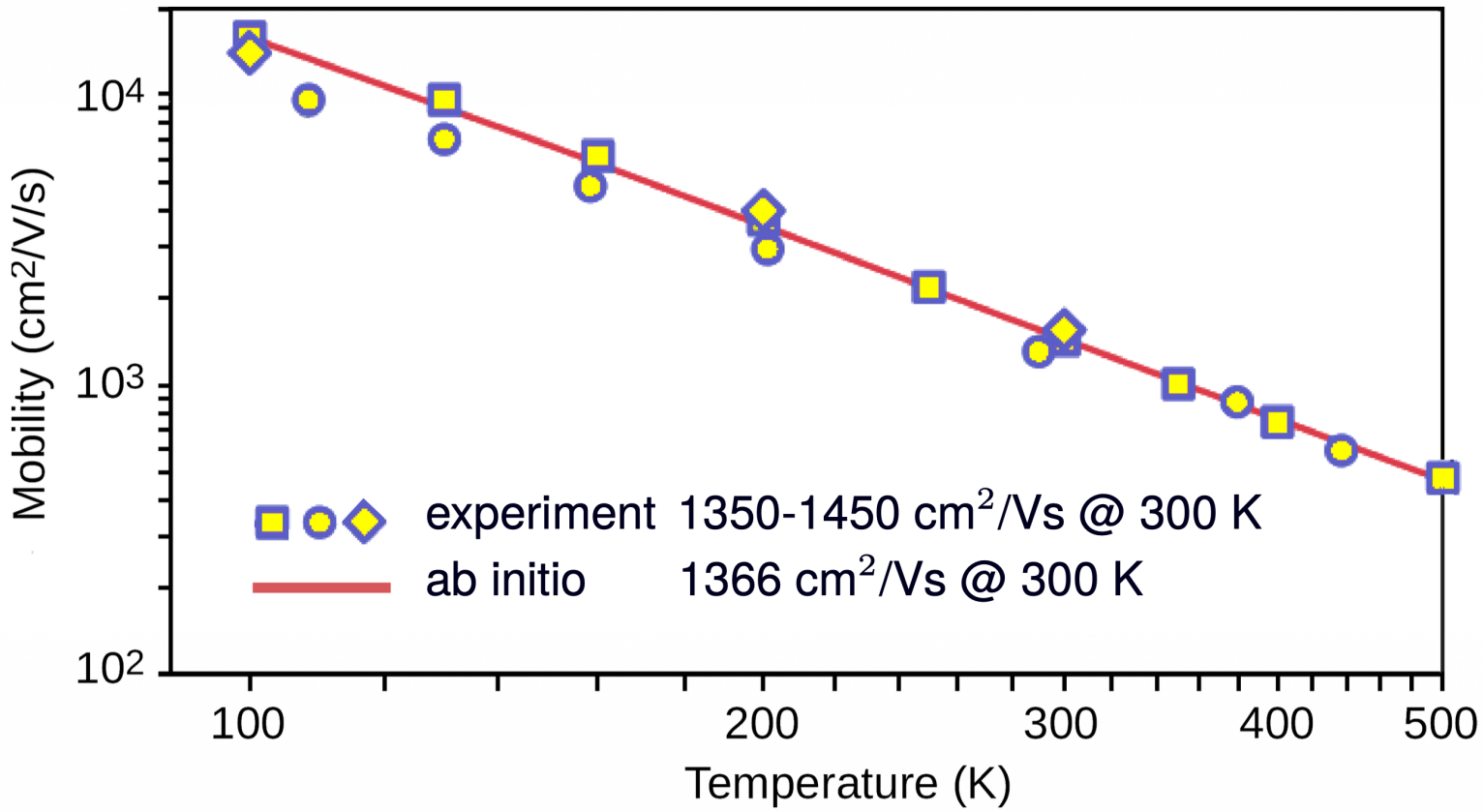

QUANTUMESPRESSO
EPW
PSEUDŌ DŌJŌ
SCF
PH
NSCF
W90+EPW (coarse)
W90
EPW (fine)
Mobility
Change k,q-grid
Change k,q-grid

Workflow


EPW
QUANTUMESPRESSO
PSEUDŌ DŌJŌ
SCF
PH
NSCF
Change k,q-grid
EPW
W90+EPW (coarse)
W90
Change k,q-grid
EPW (fine)
Mobility

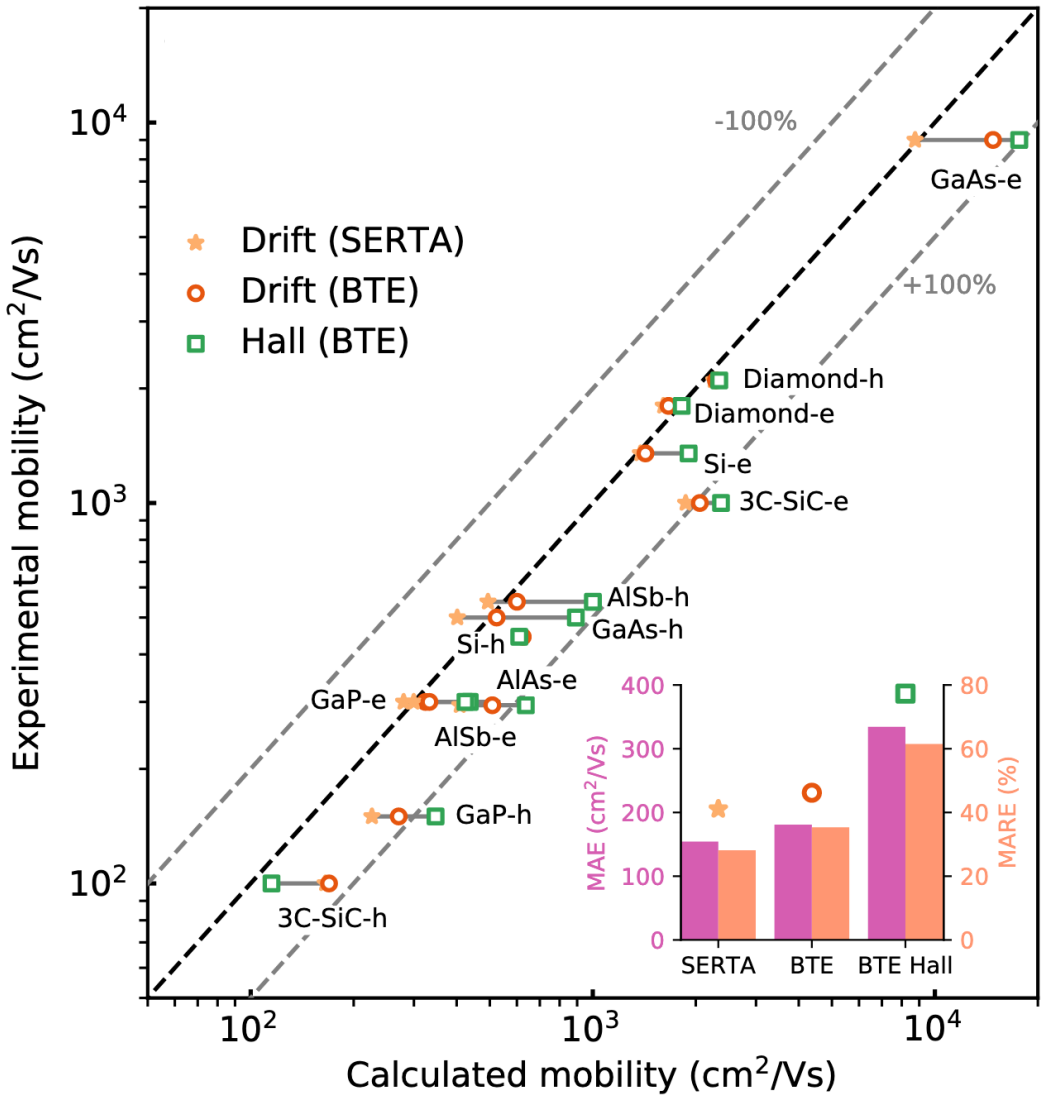
Example: Theory vs. experiment comparison in silicon





Poncé, Margine, Giustino, Phys. Rev. B 97, 121201 (2018)

Example: Theory vs. experiment comparison



Poncé et al., Phys. Rev. Research 3, 043022 (2021)

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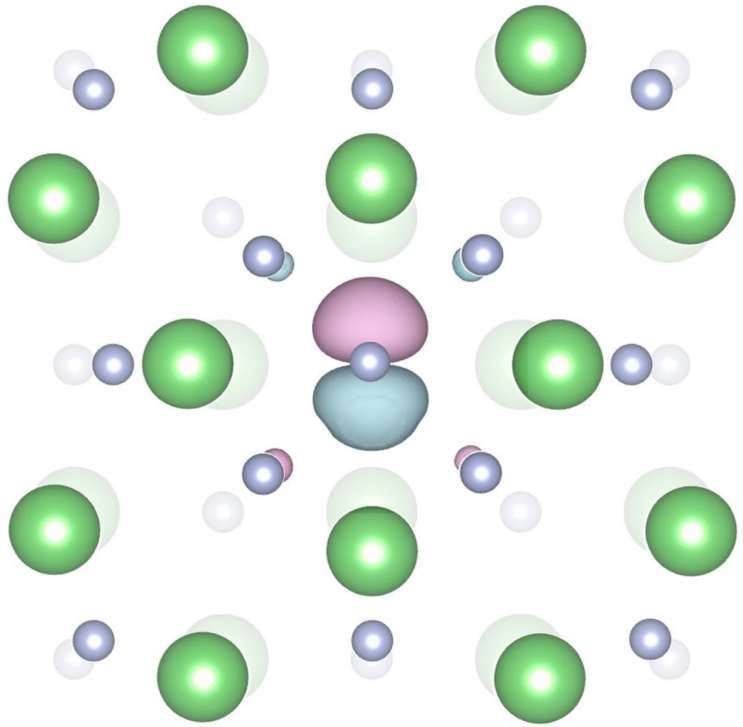
- Conclusions

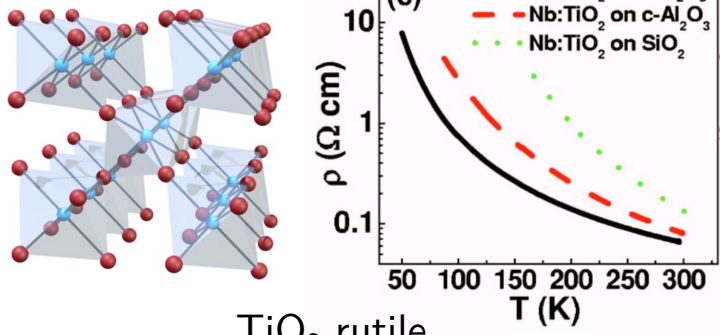
Self-trapped polarons



Landau, Phys. Z. Soviet. 3, 664 (1933); S. Pekar, Zh. Eksp. Teor. Fiz. 16, 335 (1946)
Sadigh et al., Phys. Rev. B 92, 075202 (2015); Falletta et al., Phys. Rev. Lett. 129, 126401 (2021);
Sio et al., Phys. Rev. Lett. 122, 246403 (2019); Vasilchenko et al., Phys. Rev. B 112, 014314 (2025);
Luo et al., Nat. Phys. 21, 1275 (2025); Lafuente-Bartolome et al., Phys. Rev. Lett. 129, 076402 (2022)
Franchini et al., Nat. Rev. Mater. 6, 560 (2021)

Experimental fingerprints of polarons

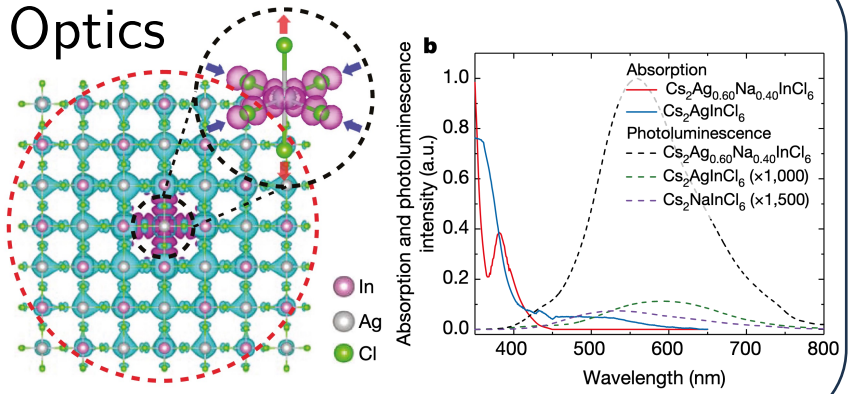
Transport



TiO_2 rutile

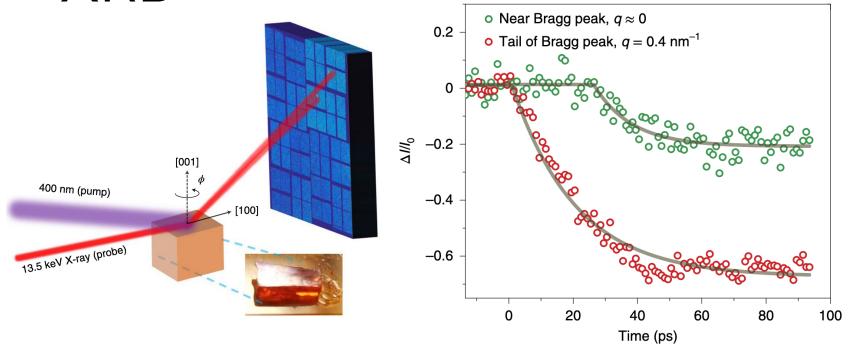
Zhang et al., J. Appl. Phys. 102, 013701 (2007)

Optics



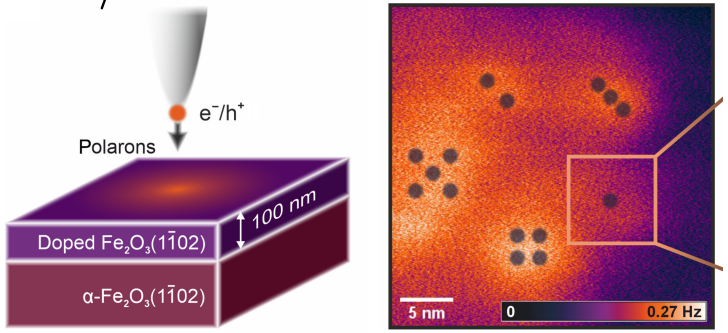
Luo et al., Nature 563, 541–545 (2018)

XRD



Guzelturk et al., Nat. Mater. 20, 618–623 (2021)

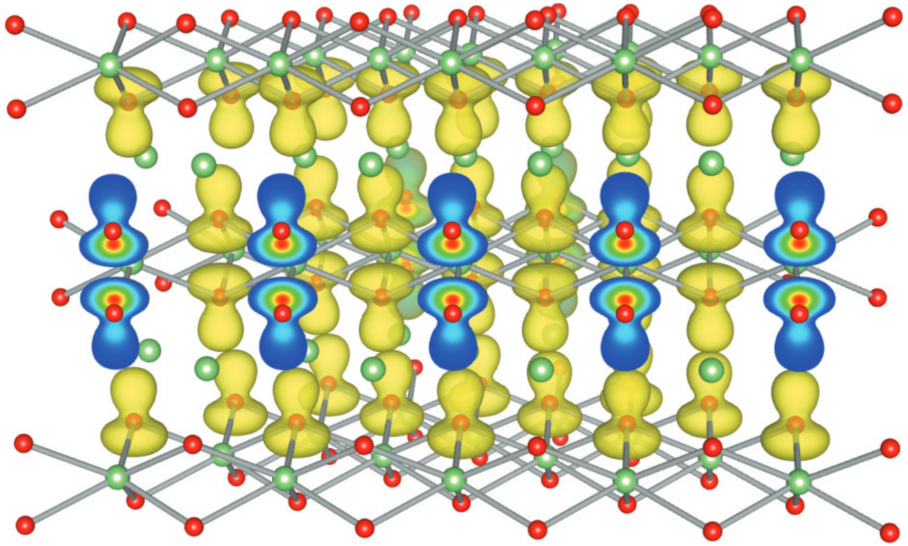
STM/AFM

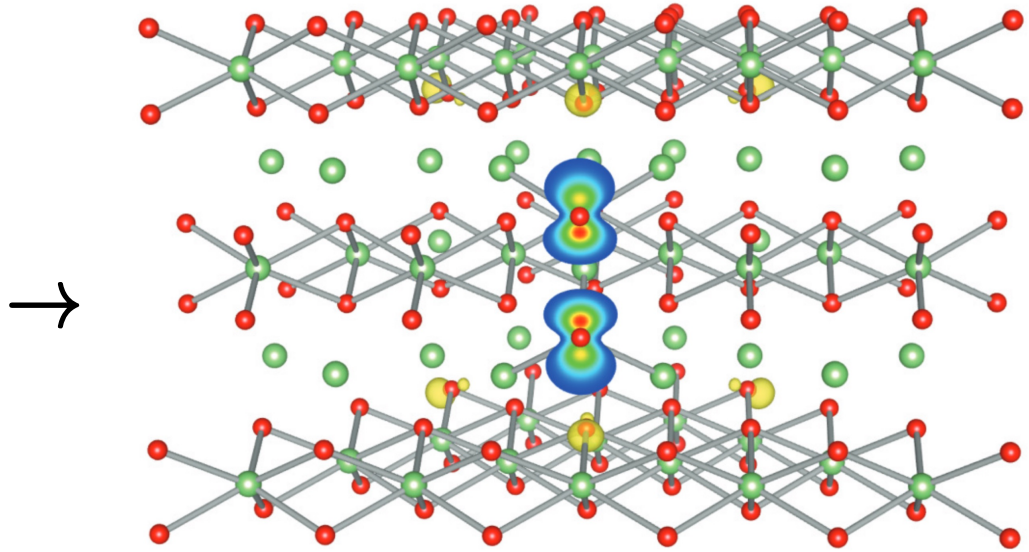


Redondo et al. Sci. Adv.10, eadp7833 (2024)

DFT calculations of polarons

Extra electron added to Li_2O_2





After ionic relaxation

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

DFT calculations of polarons

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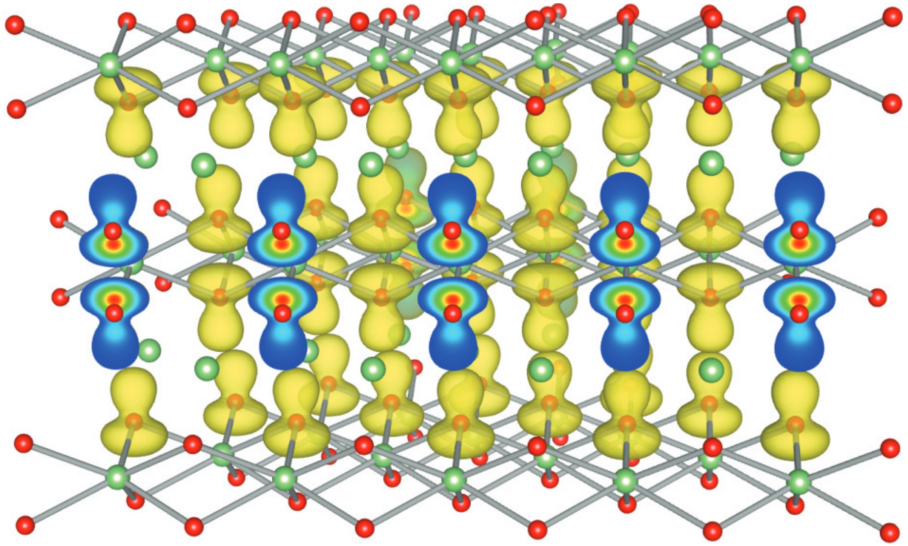

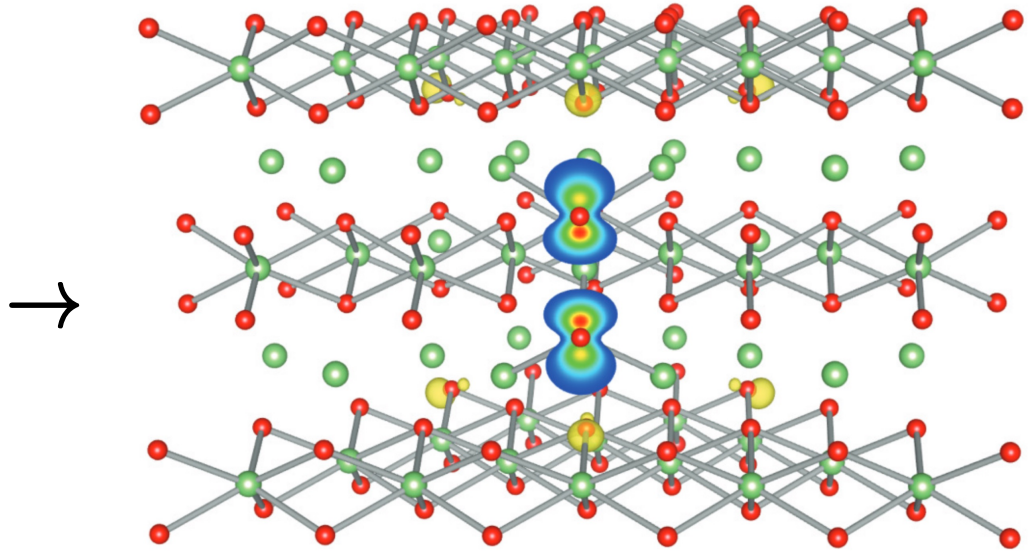

After ionic relaxation

Challenges:

- Self-interaction; sensitivity to the XC functional
- Polaron/supercell size

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

DFT calculations of polarons

Total energy in DFT:

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

DFT calculations of polarons

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Add one electron:
$$\begin{cases} n(\mathbf{r}) \longrightarrow n(\mathbf{r}) + |\psi(\mathbf{r})|^2 \\ \\ \boldsymbol{\tau}_\kappa \longrightarrow \boldsymbol{\tau}_\kappa + \mathbf{u}_\kappa \end{cases}$$

DFT calculations of polarons

Total energy in DFT (N+1 electrons):

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

DFT calculations of polarons

Total energy in DFT (N+1 electrons):

Self-interaction terms (to be removed)

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Expand to lowest order in displacements

Ab initio polaron equations (in real space)

Formation energy:

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

Derivation in Sio et al, Phys. Rev. B 99, 235139 (2019)

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Variational minimization with respect to ψ and $\mathbf{u}_\kappa$
& normalization of ψ:

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

Derivation in Sio et al, Phys. Rev. B 99, 235139 (2019)

Ab initio polaron equations (in reciprocal space)

Expand wave function and displacements in Bloch states:

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

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

Derivation in Sio et al, Phys. Rev. B 99, 235139 (2019)

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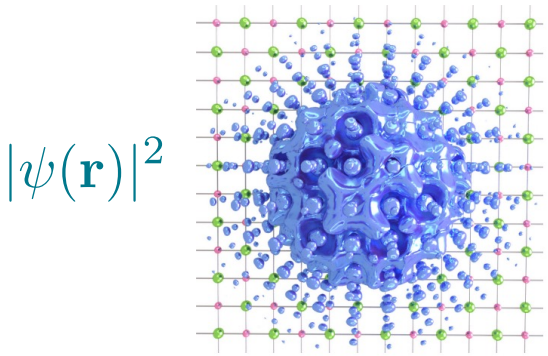
***Ab initio* polaron equations:** $\downarrow$

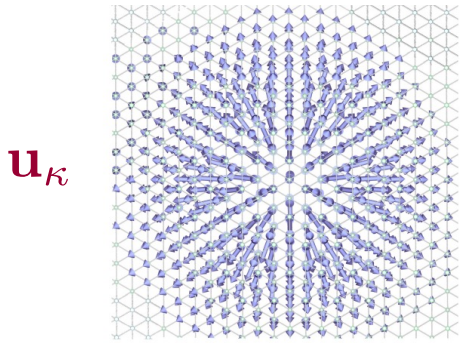
$$\frac{2}{N_p} \sum_{\mathbf{q}m\nu} B_{\mathbf{q}\nu} g^*_{mn\nu}(\mathbf{k},\mathbf{q}) A_{m\mathbf{k}+\mathbf{q}} = (\varepsilon_{n\mathbf{k}} - \varepsilon)\, A_{n\mathbf{k}}$$

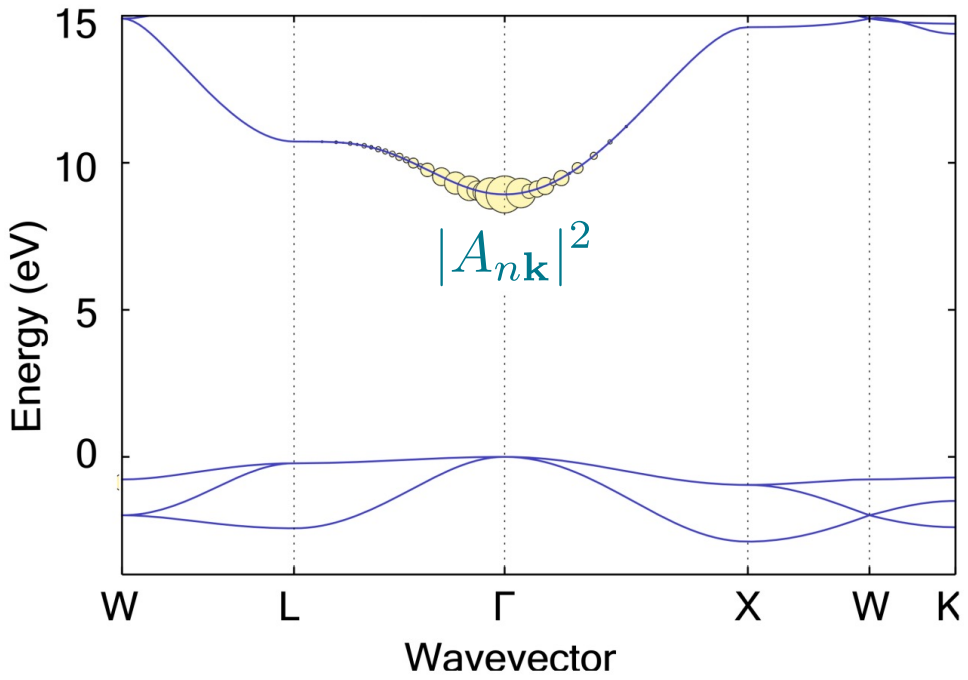
$$B_{\mathbf{q}\nu} = \frac{1}{N_p} \sum_{mn\mathbf{k}} A^*_{m\mathbf{k}+\mathbf{q}} \frac{g_{mn\nu}(\mathbf{k},\mathbf{q})}{\hbar\omega_{\mathbf{q}\nu}} A_{n\mathbf{k}}$$

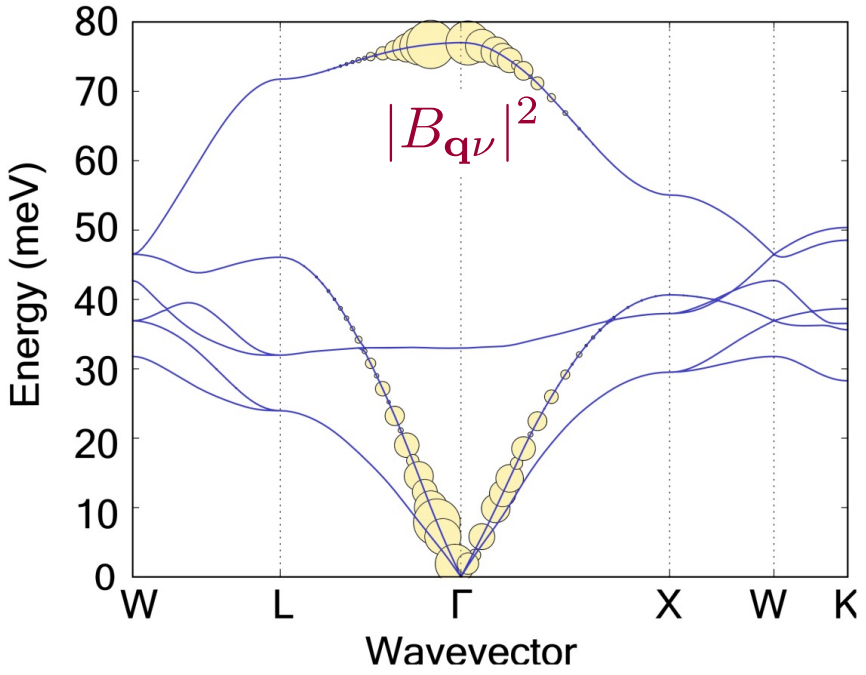
Derivation in Sio et al, Phys. Rev. B 99, 235139 (2019)

Example: Electron polaron in LiF









Figures from Sio et al, Phys. Rev. B 99, 235139 (2019)

Formation energy

$$\Delta E_{\mathrm{f}} = \frac{1}{N_p} \sum_{n\mathbf{k}} |A_{n\mathbf{k}}|^2 \left(\varepsilon_{n\mathbf{k}} - \varepsilon_{\mathrm{CBM}}\right) - \frac{1}{N_p} \sum_{\mathbf{q}\nu} |B_{\mathbf{q}\nu}|^2 \hbar\omega_{\mathbf{q}\nu}$$

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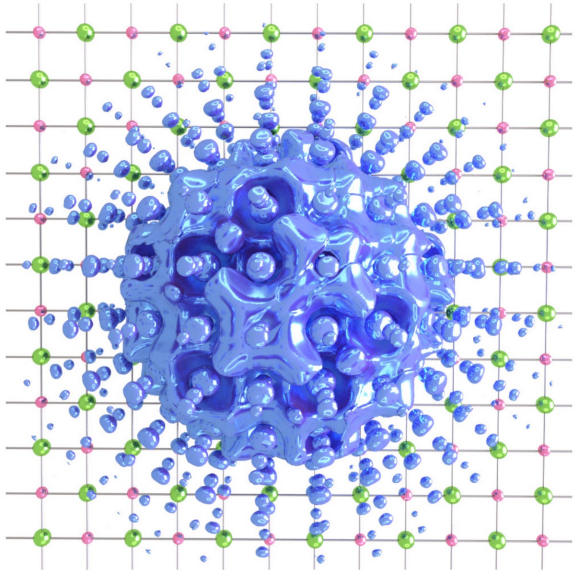
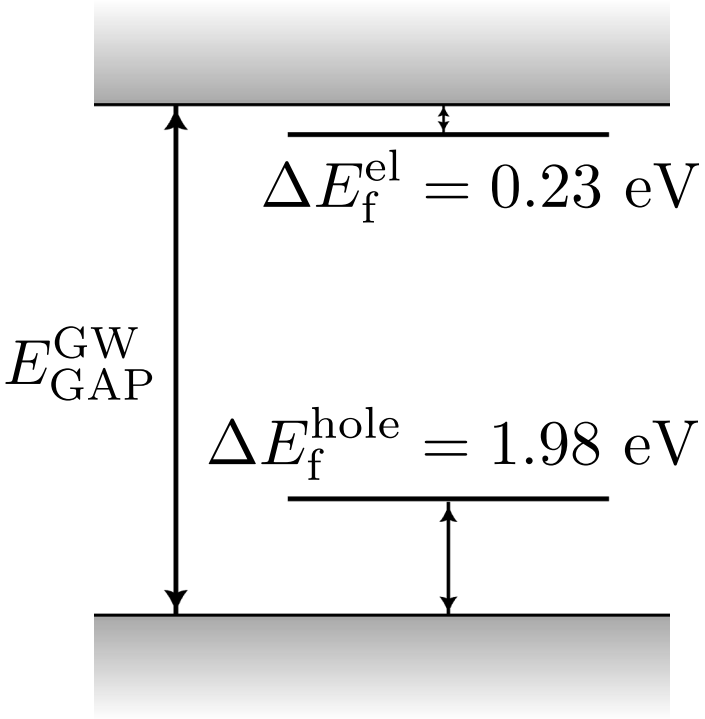
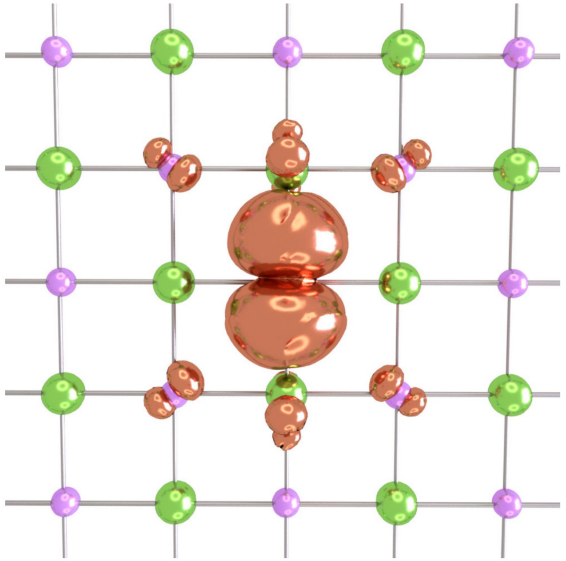
Electron polaron





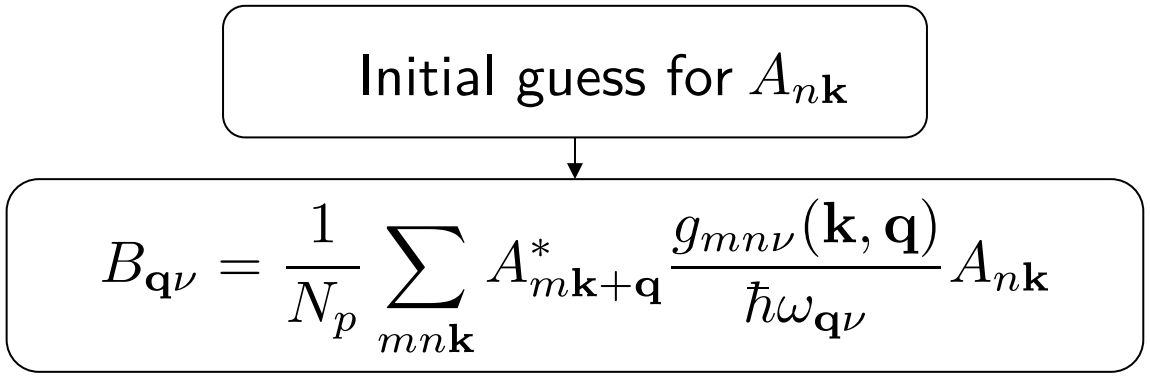
Hole polaron



Polaron calculations in practice: the self-consistent loop

Initial guess for $A_{n\mathbf{k}}$

Polaron calculations in practice: the self-consistent loop



Polaron calculations in practice: the self-consistent loop

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

$$H_{n\mathbf{k},n'\mathbf{k}'} = \delta_{n\mathbf{k},n'\mathbf{k}'}\varepsilon_{n\mathbf{k}} - \frac{2}{N_p} \sum_{\nu} B^*_{\mathbf{k}-\mathbf{k}',\nu} g_{nn'\nu}(\mathbf{k}', \mathbf{k}-\mathbf{k}')$$

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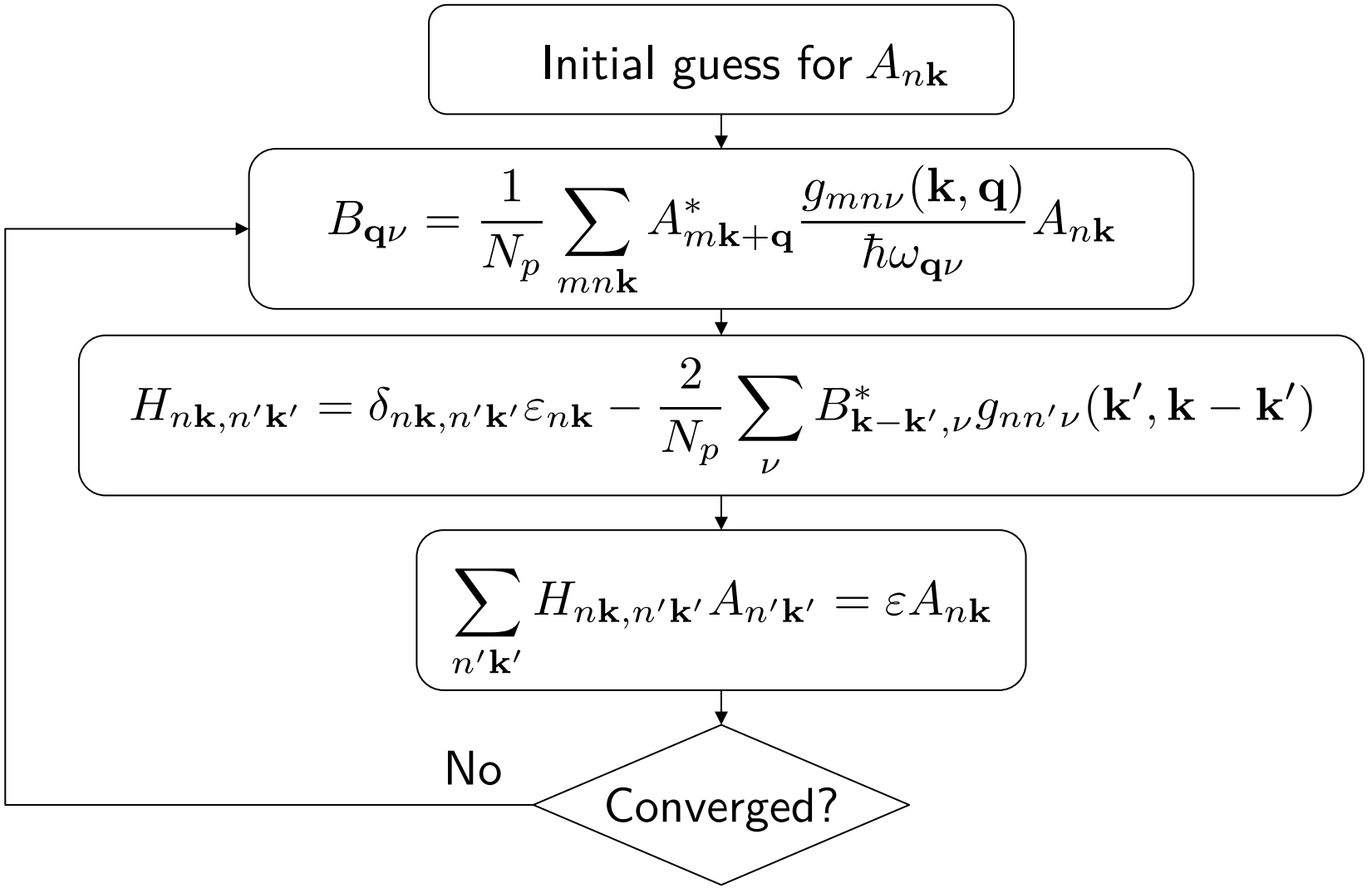
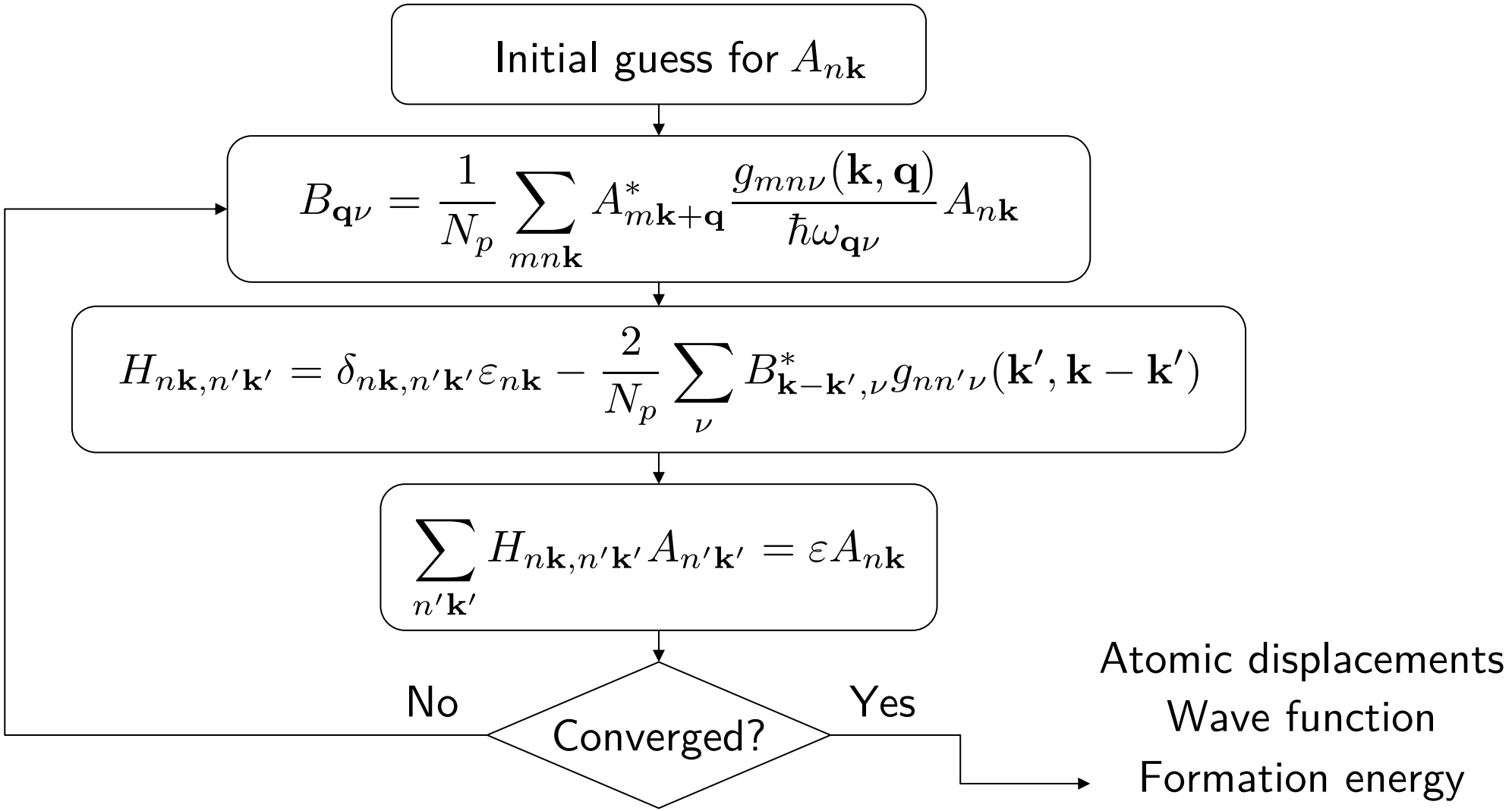
$$\sum_{n'\mathbf{k}'} H_{n\mathbf{k},n'\mathbf{k}'} A_{n'\mathbf{k}'} = \varepsilon A_{n\mathbf{k}}$$

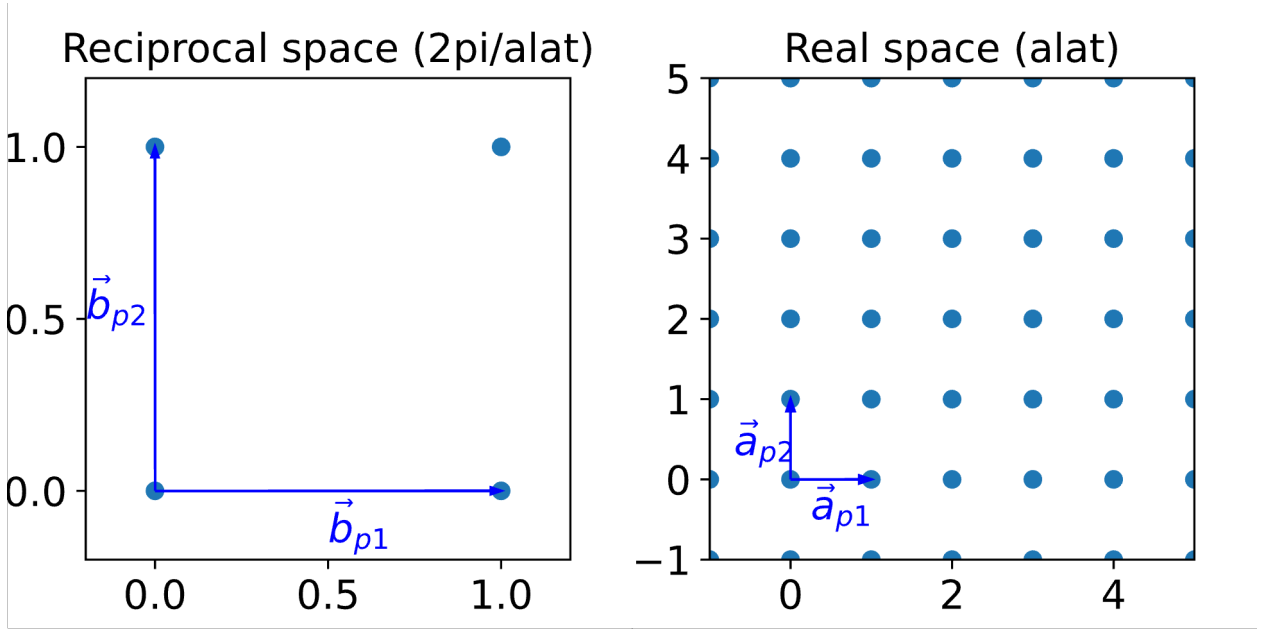
Polaron calculations in practice: the self-consistent loop



Polaron calculations in practice: the self-consistent loop



Periodicity



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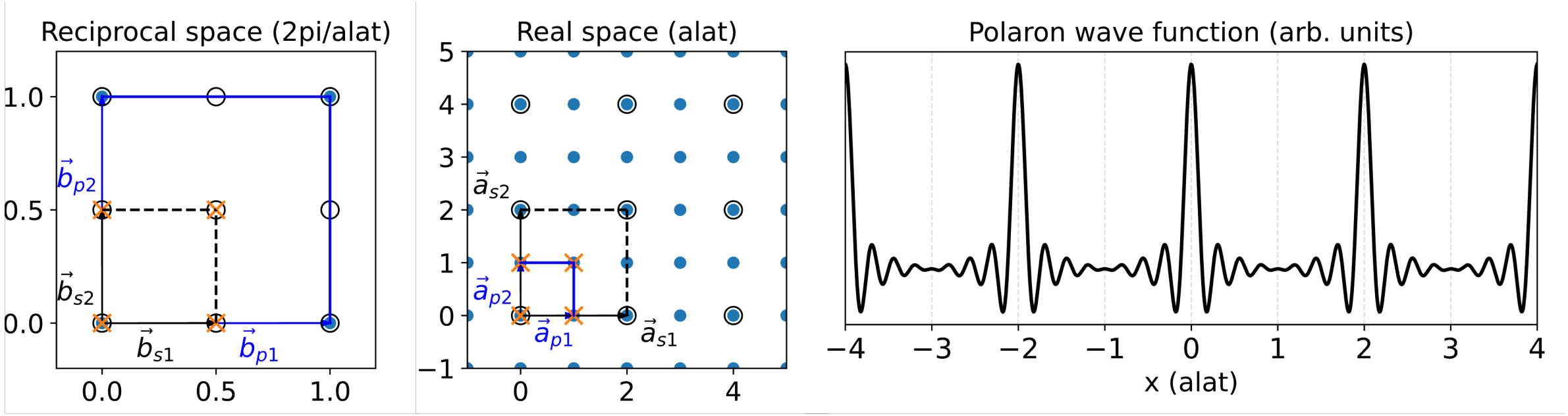

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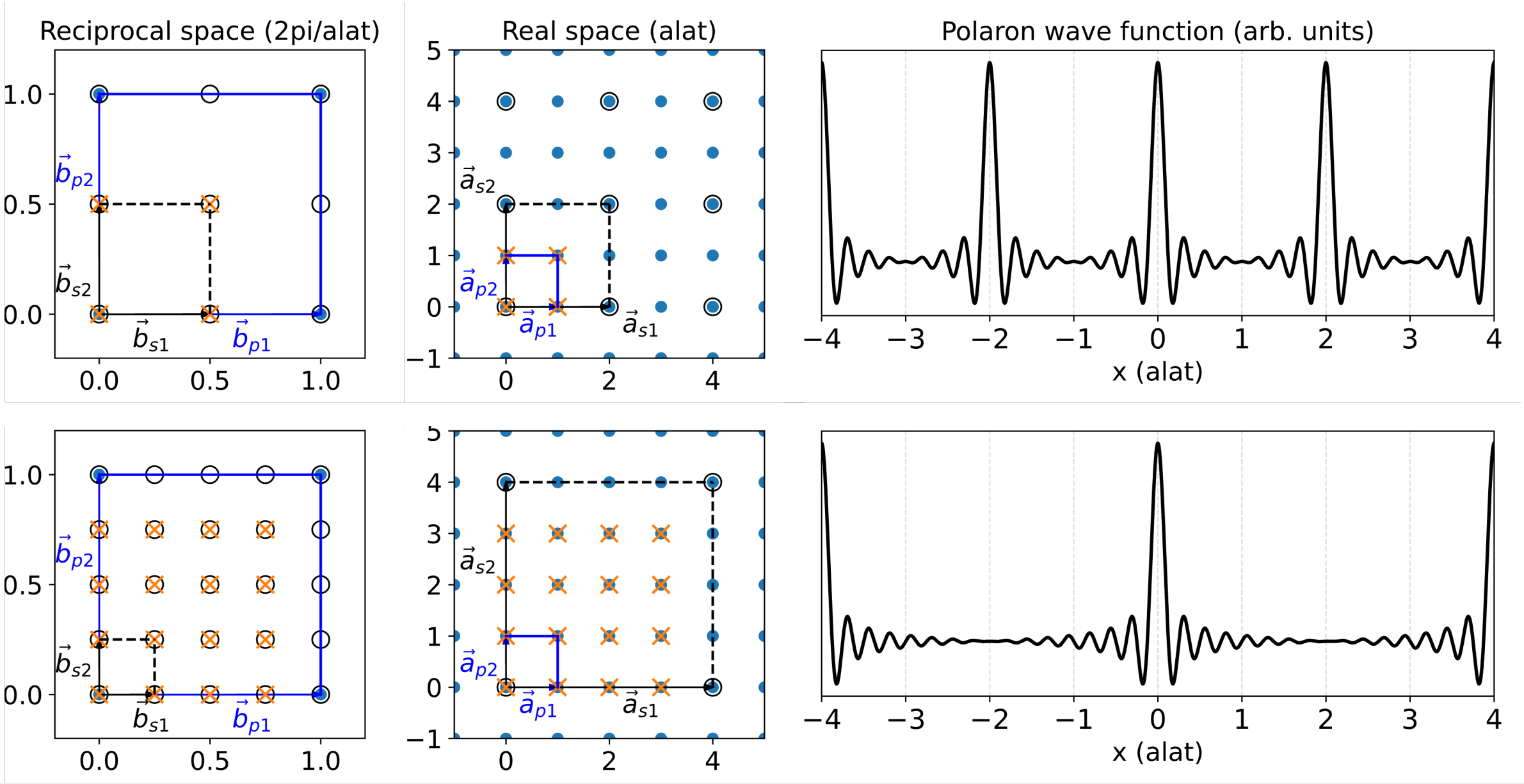

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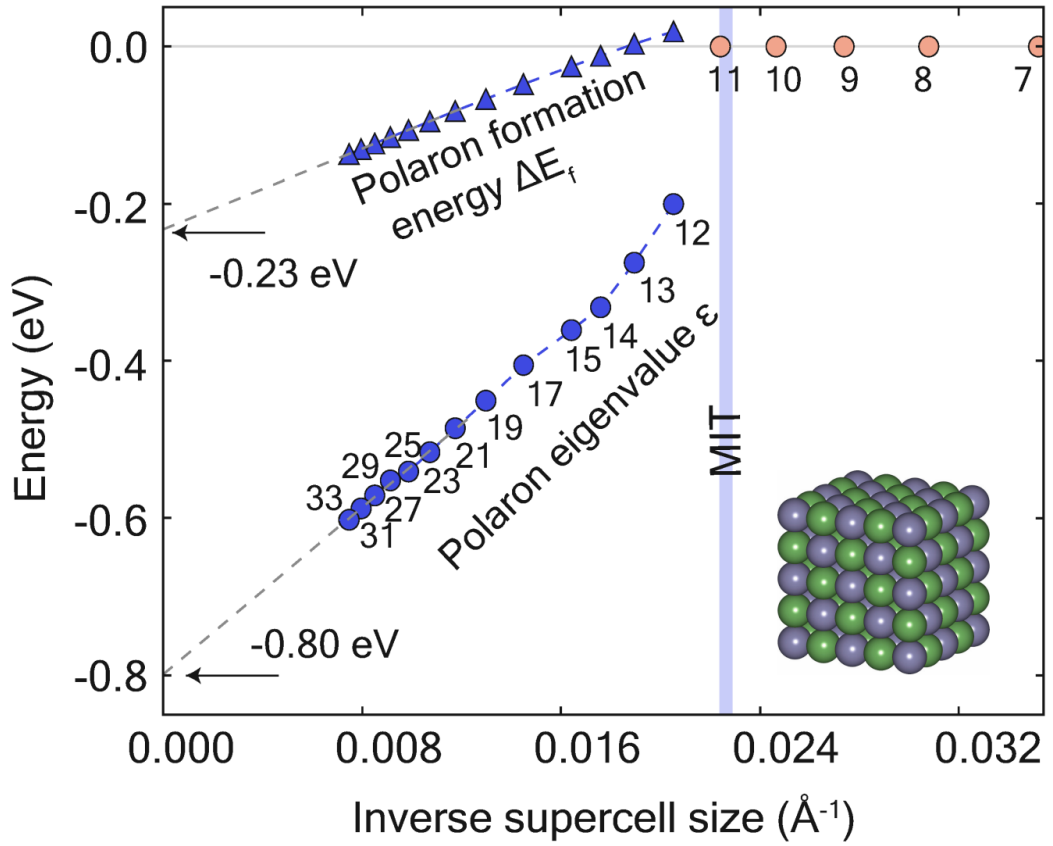
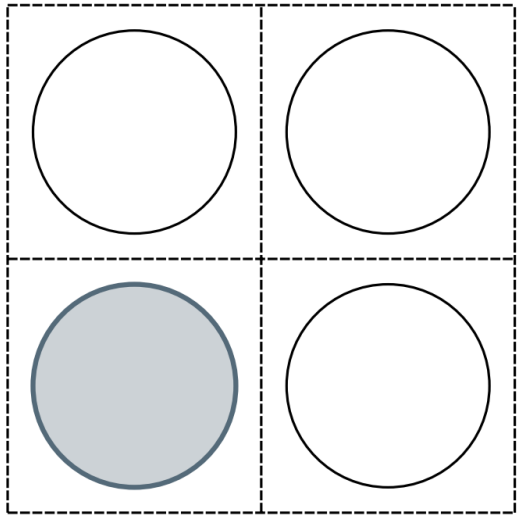
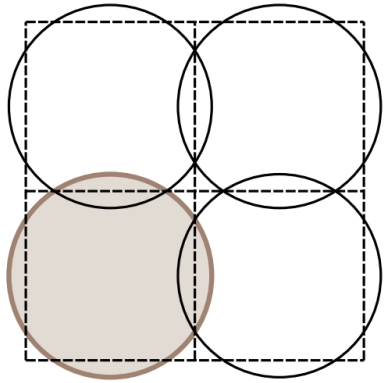




Low density



High density

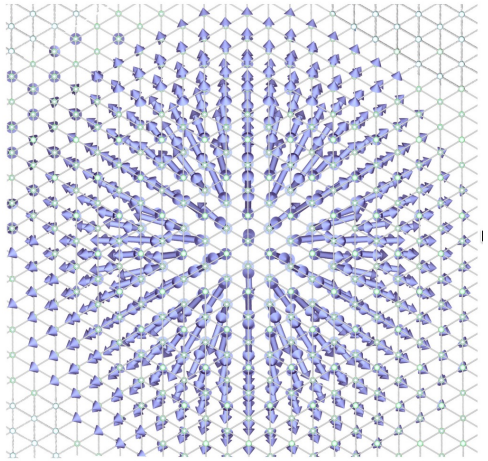
Figure from Sio et al, Phys. Rev. B 99, 235139 (2019)

Post-processing and visualization (real space)

Atomic displacements:

$$u_{\kappa\alpha p} = -\frac{2}{N_p} \sum_{\mathbf{q}\nu} B^*_{\mathbf{q}\nu} \left(\frac{\hbar}{2M_\kappa \omega_{\mathbf{q}\nu}} \right)^{1/2} e_{\kappa\alpha,\nu}(\mathbf{q})\, e^{i\mathbf{q}\cdot\mathbf{R}_p}$$

Convergence: $\mathrm{MAX}\left[|\mathbf{u}^i_{\kappa p} - \mathbf{u}^{i-1}_{\kappa p}|\right] < \mathbf{u}^{\mathrm{thr}}$ `conv_thr`



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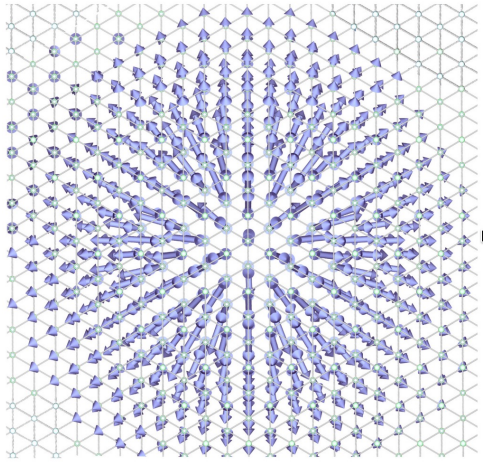
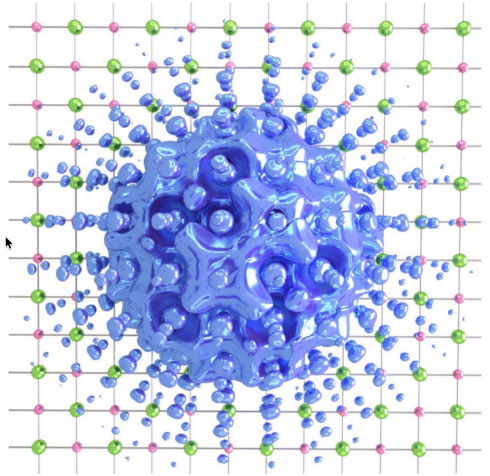


Polaron wave function:

Transform coefs. to Wannier space: $A_m(\mathbf{R}_p) = \frac{1}{N_p} \sum_{n\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_p} U^\dagger_{mn\mathbf{k}}\, A_{n\mathbf{k}}$

$\psi(\mathbf{r})$ in terms of Wannier functions: $\psi(\mathbf{r}) = \sum_{mp} A_m(\mathbf{R}_p)\, w_m(\mathbf{r} - \mathbf{R}_p)$



Post-processing and visualization (reciprocal space)

Polaron calculations on a **reciprocal-space grid**:

$\{B_{\mathbf{q}\nu}\}$

$\{A_{n\mathbf{k}}\}$

Post-processing and visualization (reciprocal space)

Polaron calculations on a **reciprocal-space grid**:

Transformation to **real space grid**:

$$\{B_{\mathbf{q}\nu}\} \longrightarrow \{\mathbf{u}_{\kappa p}\}$$

$$\{A_{n\mathbf{k}}\} \longrightarrow \{A_m(\mathbf{R}_p)\}$$

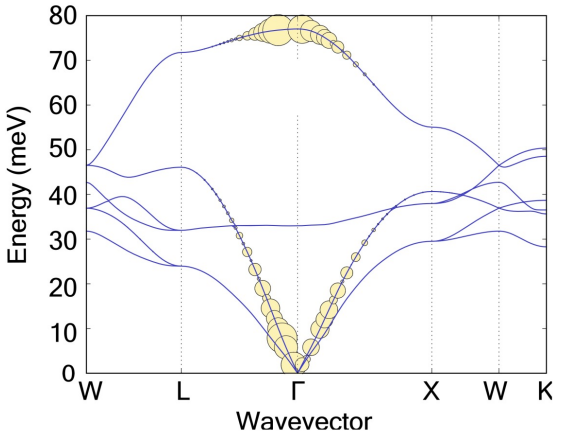
Post-processing and visualization (reciprocal space)

Polaron calculations on a **reciprocal-space grid**:

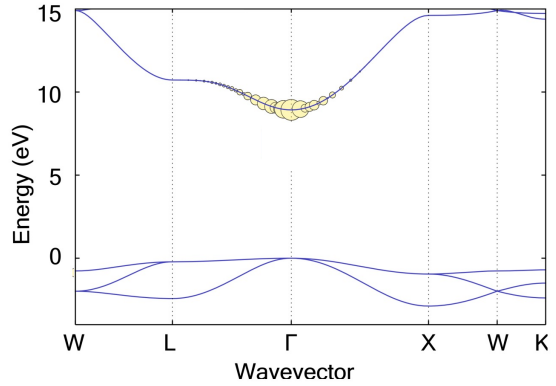
Transformation to **real space grid**:

Interpolate to a **reciprocal-space path**:

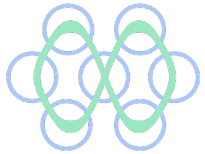
$$\{B_{\mathbf{q}\nu}\} \longrightarrow \{\mathbf{u}_{\kappa p}\} \longrightarrow$$

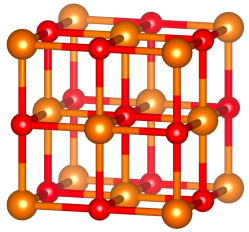


$$\{A_{n\mathbf{k}}\} \longrightarrow \{A_m(\mathbf{R}_p)\} \longrightarrow$$



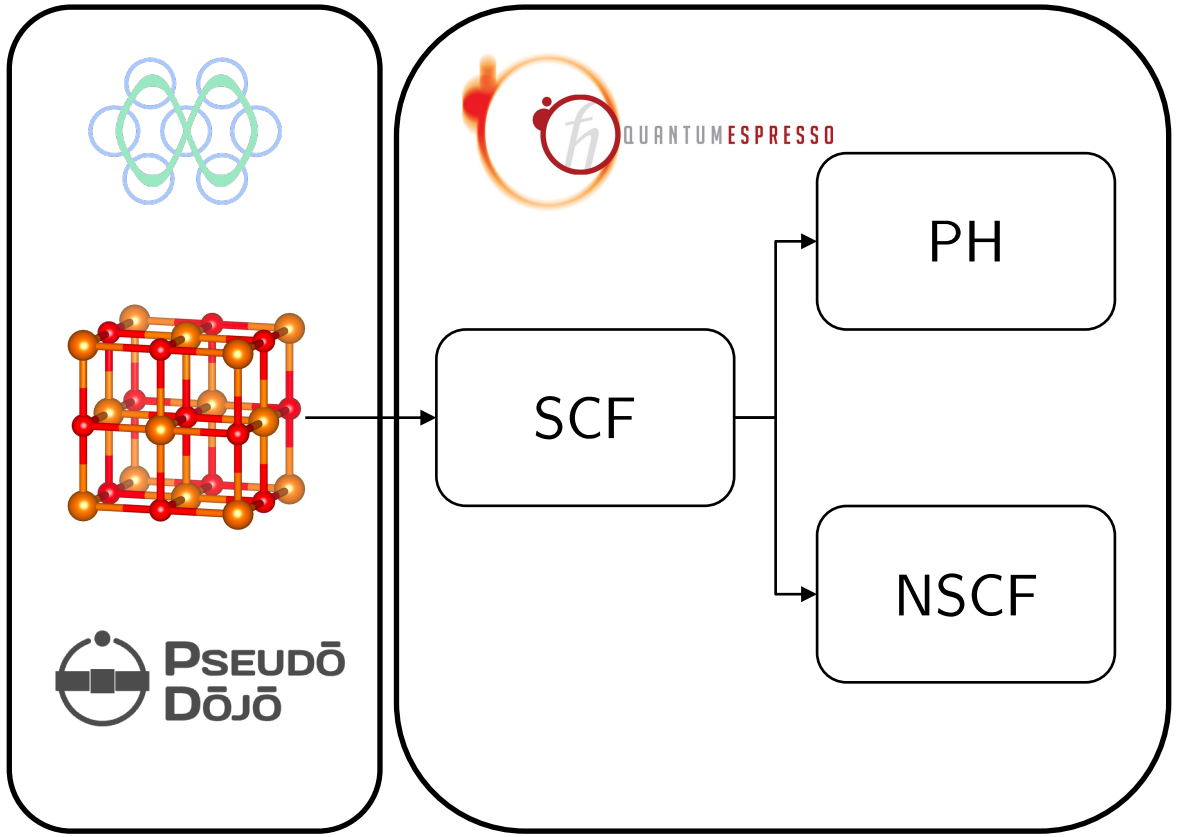
Workflow



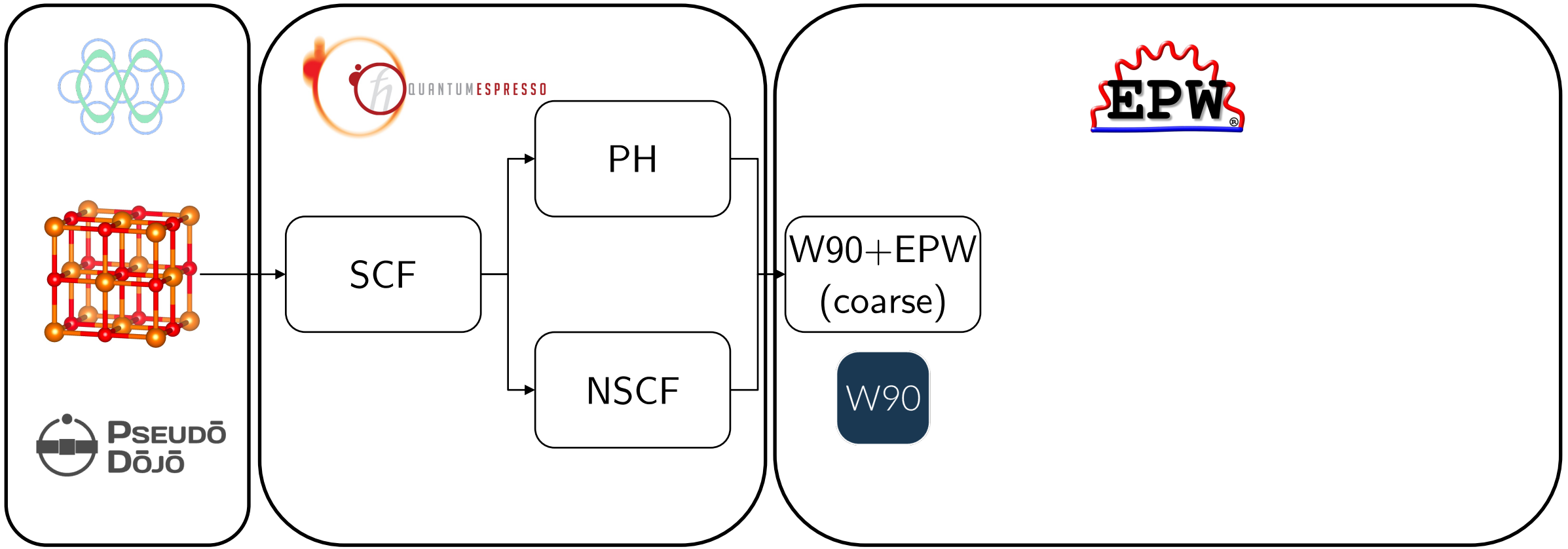


PSEUDŌ DŌJŌ

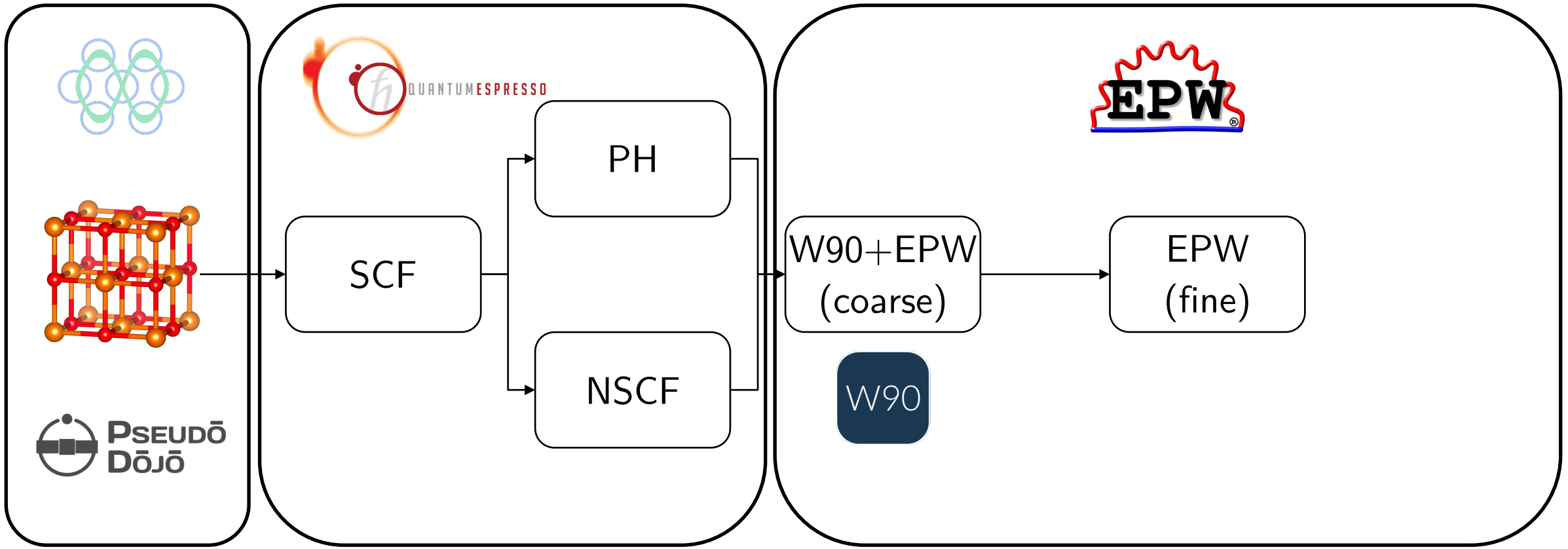
Workflow



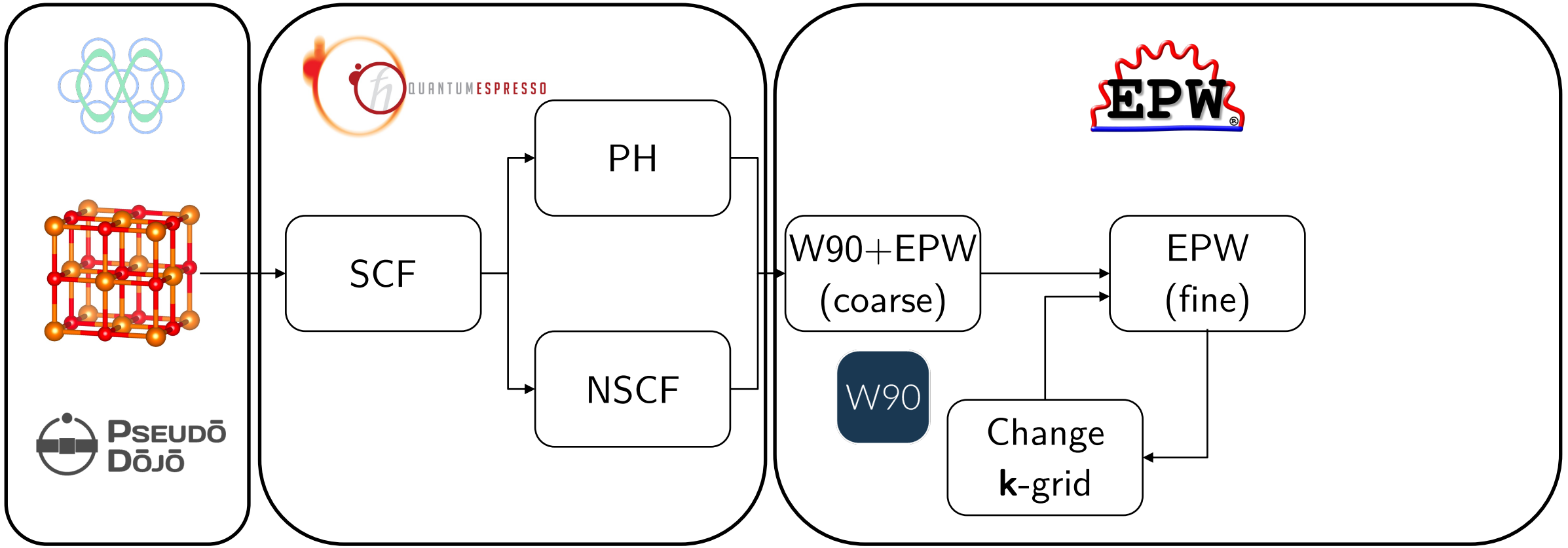
Workflow


QUANTUMESPRESSO
PH
SCF
NSCF
W90+EPW
(coarse)
W90
EPW
PSEUDŌ
DŌJŌ

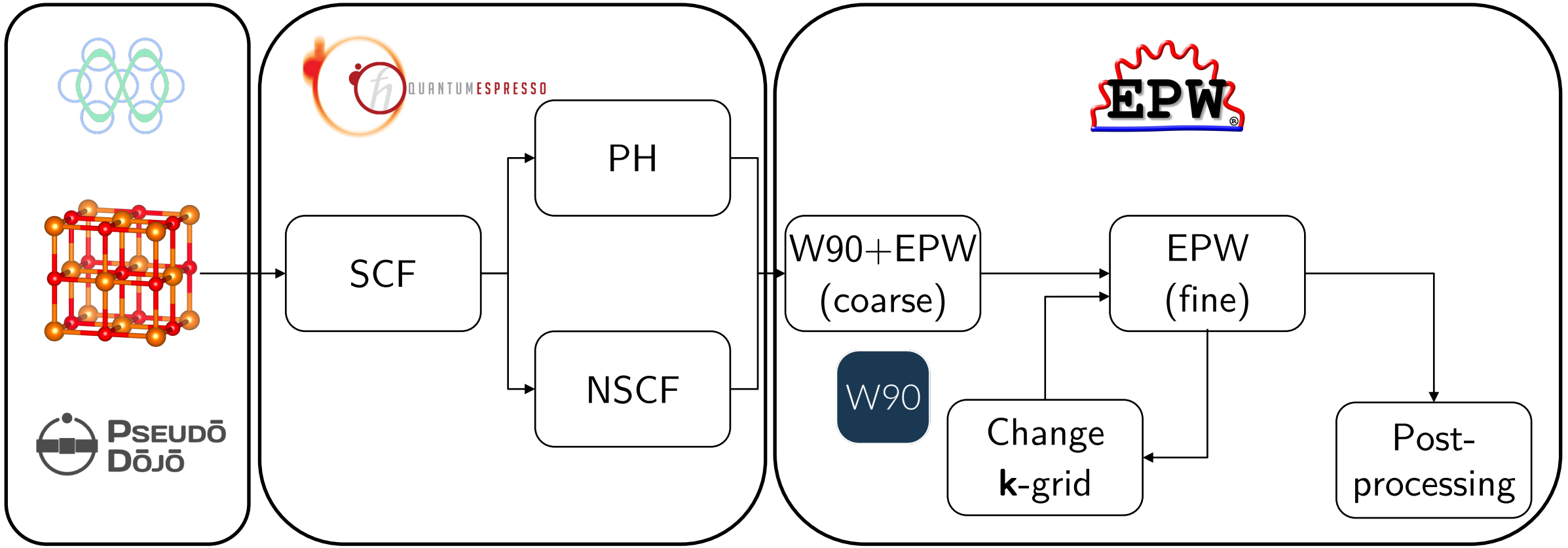
Workflow


QUANTUMESPRESSO
EPW
PSEUDŌ DŌJŌ
SCF
PH
NSCF
W90+EPW (coarse)
W90
EPW (fine)

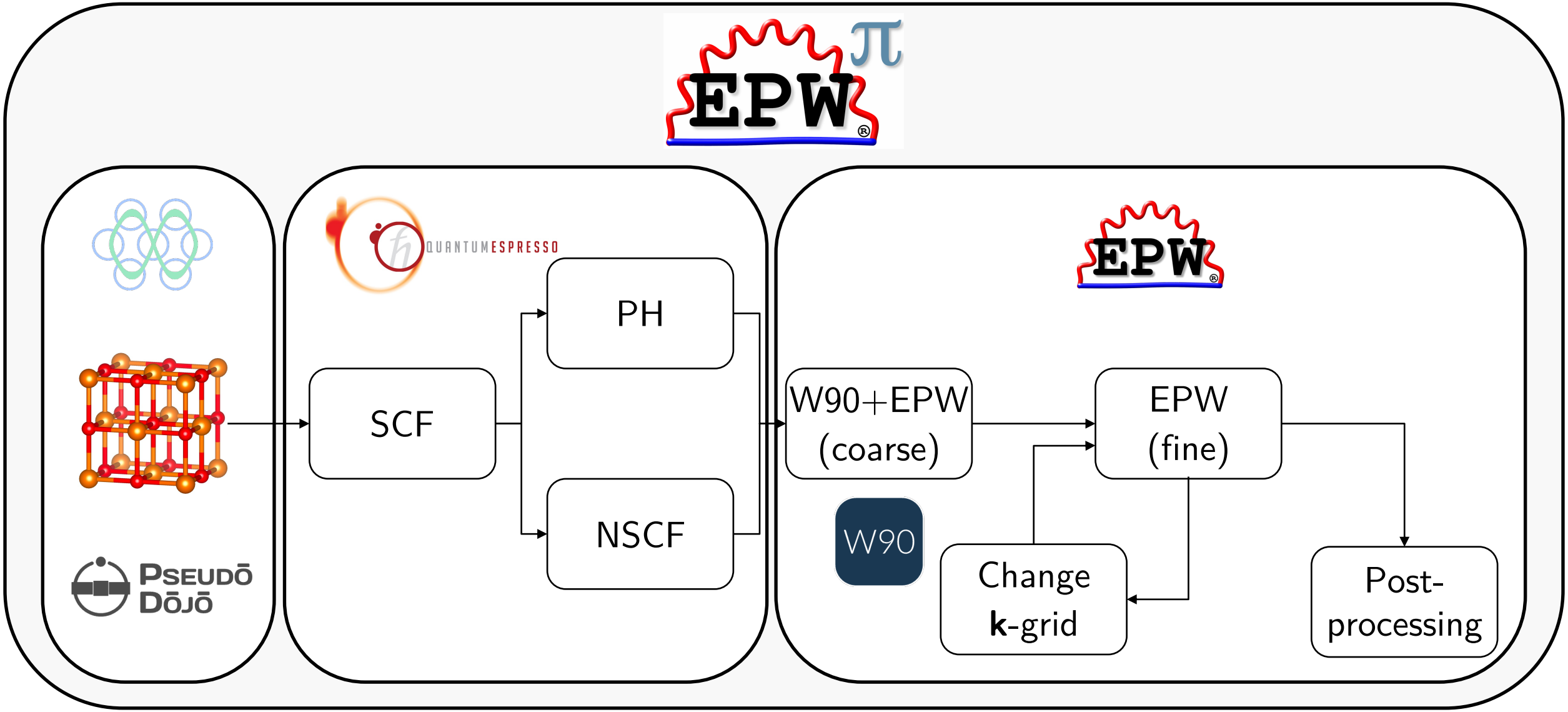
Workflow


QUANTUMESPRESSO
PSEUDŌ DŌJŌ
SCF
PH
NSCF
EPW
W90+EPW (coarse)
W90
Change **k**-grid
EPW (fine)

Workflow

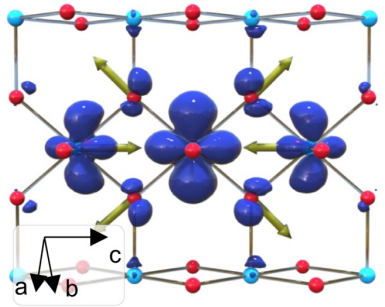

QUANTUMESPRESSO
EPW
PSEUDŌ DŌJŌ
SCF
PH
NSCF
W90+EPW (coarse)
W90
EPW (fine)
Change **k**-grid
Post-processing

Workflow

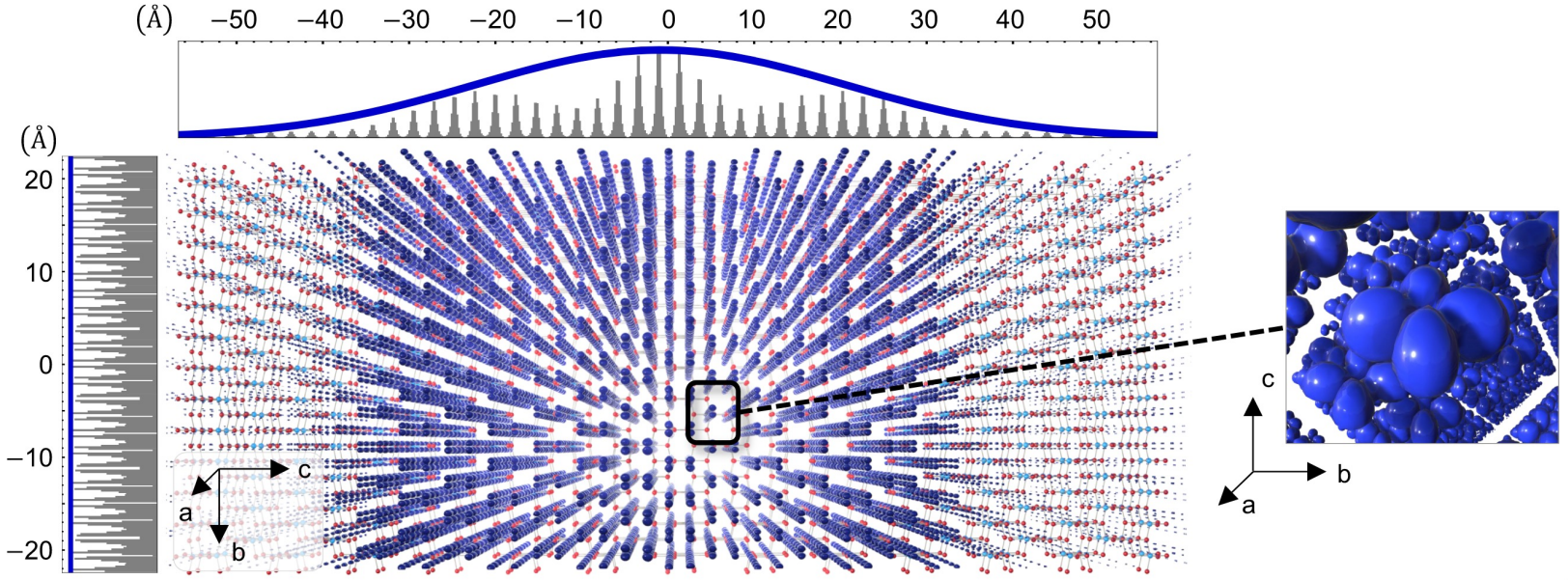

EPW
QUANTUMESPRESSO
PSEUDŌ DŌJŌ
SCF
PH
NSCF
W90+EPW (coarse)
W90
Change k-grid
EPW (fine)
Post-processing

Example: Electron polarons in TiO_2

Small electron polarons in **rutile** TiO_2:



Large electron polarons in **anatase** TiO_2:



Dai and Giustino, PNAS 121, e2414203121 (2024)

Polaron energy landscape

$$\Delta\tilde{E}_{\mathrm{f}} = \varepsilon - \varepsilon_{\mathrm{CBM}} + \frac{1}{N_p}\sum_{\mathbf{q}\nu} |B_{\mathbf{q}\nu}|^2 \hbar\omega_{\mathbf{q}\nu}$$

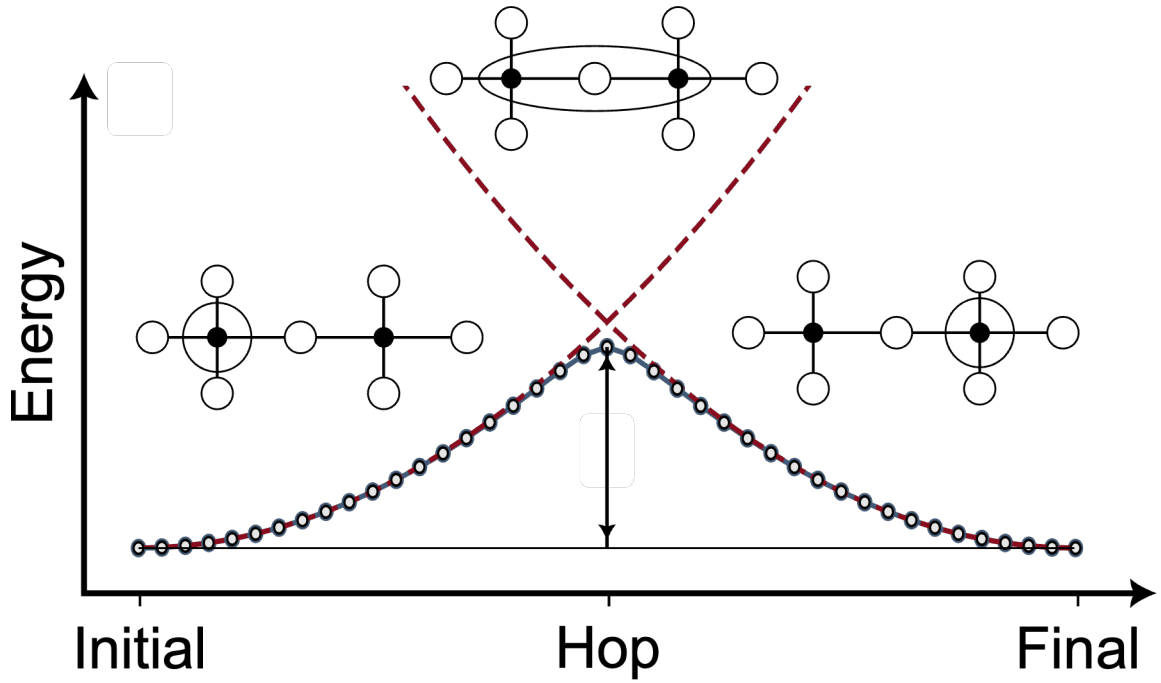


Figure adapted from Deskins and Dupuis, Phys. Rev. B 75, 195212 (2007)

Polaron energy landscape in practice

Input displacement configuration $\{\mathbf{u}_{\kappa p}\}$

```
init_plrn = 6
```

Polaron energy landscape in practice

Input displacement configuration $\{\mathbf{u}_{\kappa p}\}$

```
init_plrn = 6
```

$$B^*_{\mathbf{q}\nu} = \sum_{\kappa\alpha p} \left(\frac{M_\kappa \omega_{\mathbf{q}\nu}}{2\hbar} \right)^{1/2} e^*_{\kappa\alpha p,\nu}(\mathbf{q})\, e^{-i\mathbf{q}\cdot\mathbf{R}_p}\, u_{\kappa\alpha p}$$

Polaron energy landscape in practice

Input displacement configuration $\{\mathbf{u}_{\kappa p}\}$

```
init_plrn = 6
```

$$B^*_{\mathbf{q}\nu} = \sum_{\kappa\alpha p} \left(\frac{M_\kappa \omega_{\mathbf{q}\nu}}{2\hbar} \right)^{1/2} e^*_{\kappa\alpha p,\nu}(\mathbf{q})\, e^{-i\mathbf{q}\cdot\mathbf{R}_p}\, u_{\kappa\alpha p}$$

$$H_{n\mathbf{k},n'\mathbf{k}'} = \delta_{n\mathbf{k},n'\mathbf{k}'}\varepsilon_{n\mathbf{k}} - \frac{2}{N_p}\sum_\nu B^*_{\mathbf{k}-\mathbf{k}',\nu} g_{nn'\nu}(\mathbf{k}', \mathbf{k}-\mathbf{k}')$$

$$\sum_{n'\mathbf{k}'} H_{n\mathbf{k},n'\mathbf{k}'} A_{n'\mathbf{k}'} = \varepsilon A_{n\mathbf{k}}$$

Polaron energy landscape in practice

Input displacement configuration $\{\mathbf{u}_{\kappa p}\}$

`init_plrn = 6`

$$B^*_{\mathbf{q}\nu} = \sum_{\kappa\alpha p} \left(\frac{M_\kappa \omega_{\mathbf{q}\nu}}{2\hbar}\right)^{1/2} e^*_{\kappa\alpha p,\nu}(\mathbf{q})\, e^{-i\mathbf{q}\cdot\mathbf{R}_p}\, u_{\kappa\alpha p}$$

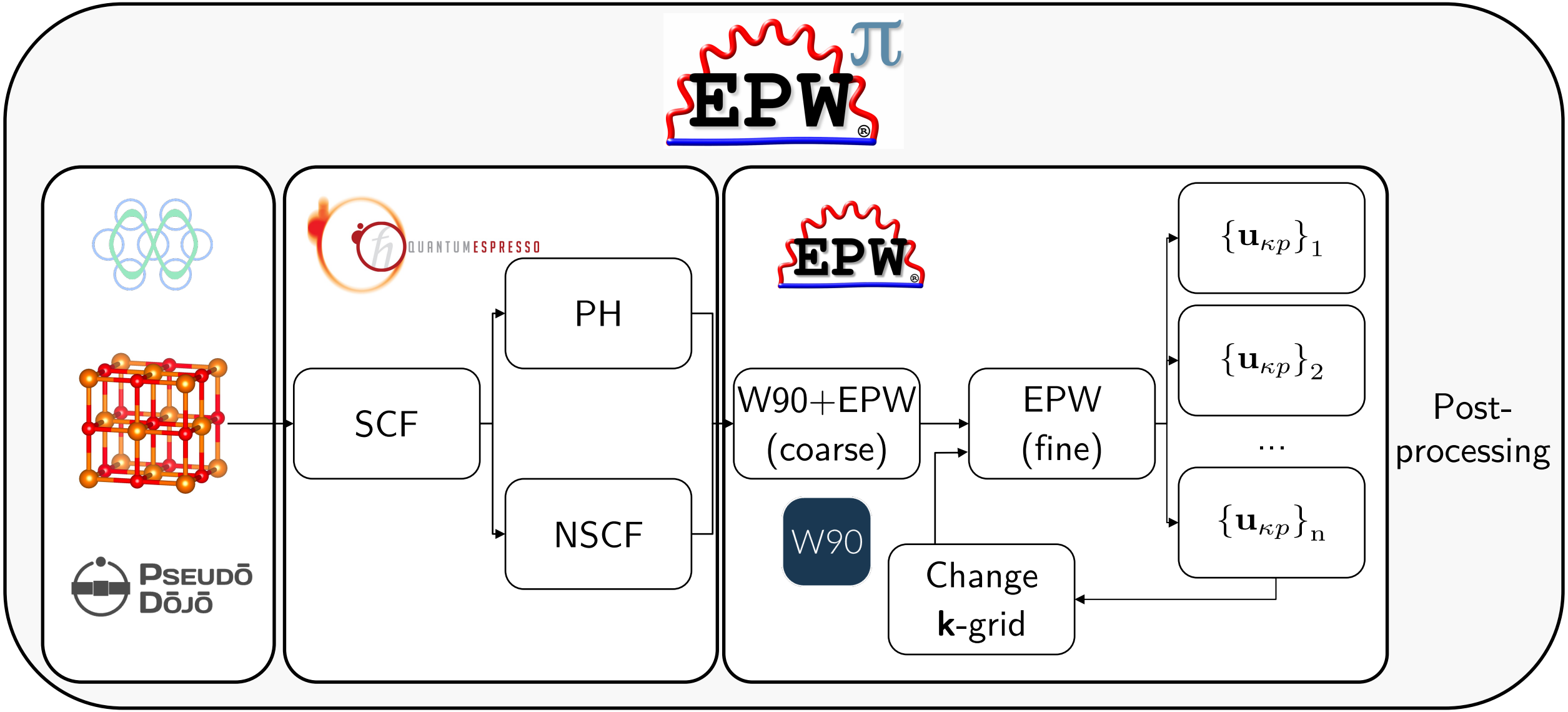
$$H_{n\mathbf{k},n'\mathbf{k}'} = \delta_{n\mathbf{k},n'\mathbf{k}'}\varepsilon_{n\mathbf{k}} - \frac{2}{N_p}\sum_\nu B^*_{\mathbf{k}-\mathbf{k}',\nu} g_{nn'\nu}(\mathbf{k}', \mathbf{k}-\mathbf{k}')$$

$$\sum_{n'\mathbf{k}'} H_{n\mathbf{k},n'\mathbf{k}'} A_{n'\mathbf{k}'} = \varepsilon A_{n\mathbf{k}}$$

$$\Delta\tilde{E}_\mathrm{f} = \varepsilon - \varepsilon_\mathrm{CBM} + \frac{1}{N_p}\sum_{\mathbf{q}\nu} |B_{\mathbf{q}\nu}|^2 \hbar\omega_{\mathbf{q}\nu}$$

`niter_plrn = 1`

Polaron energy landscape workflow



Example: Electron polarons in $Cs_2AgBiBr_6$

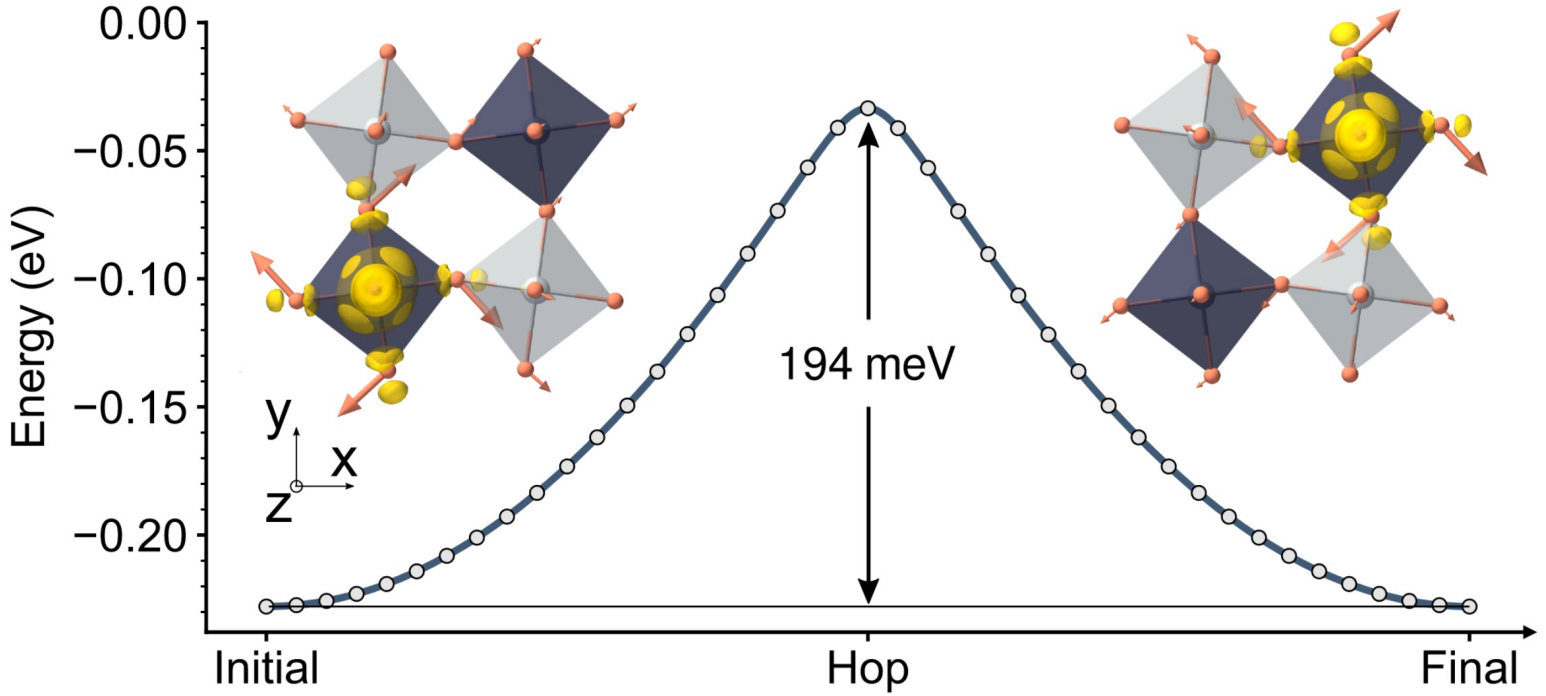
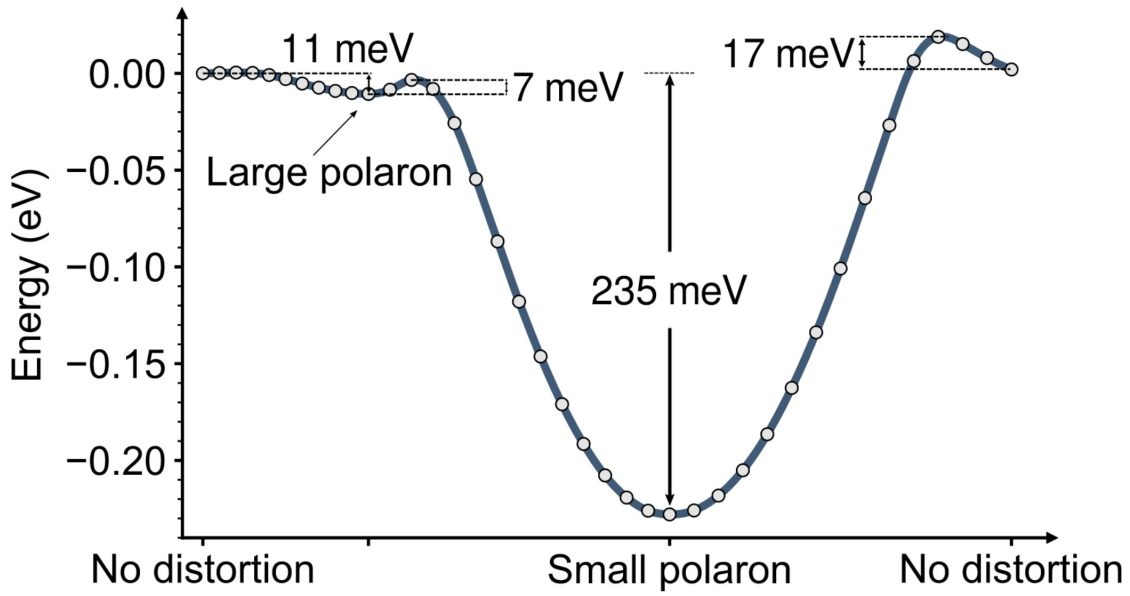


Figure from Lafuente-Bartolome et al, PNAS 121, e2318151121 (2024)

Example: Electron polarons in $Cs_2AgBiBr_6$

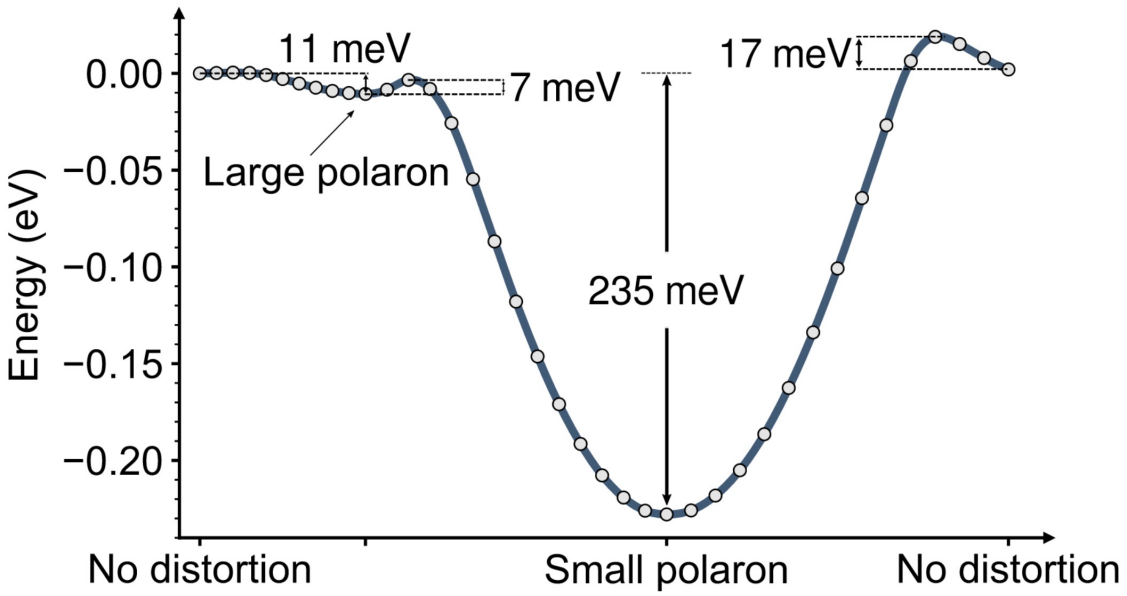
Multiple polaron solutions



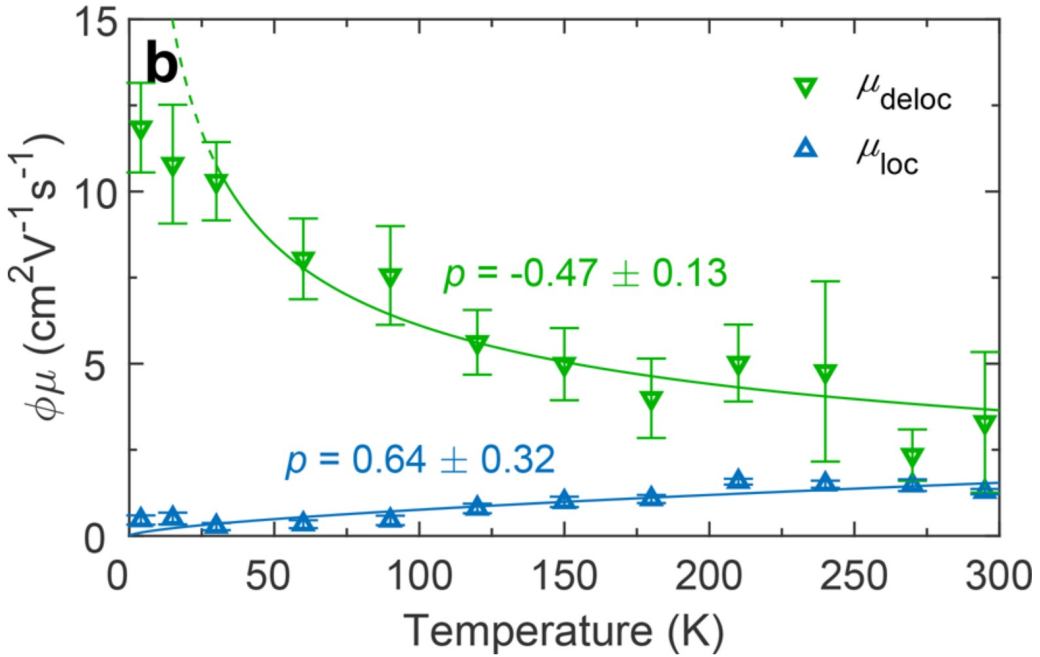
Lafuente-Bartolome et al, PNAS 121, e2318151121 (2024)

Example: Electron polarons in $Cs_2AgBiBr_6$

Multiple polaron solutions



Lafuente-Bartolome et al, PNAS 121, e2318151121 (2024)



Wright et al., J. Phys. Chem. Lett. 12, 3352 (2021)

Summary

- Transport & polaron calculations require dense reciprocal-space grids, and complex workflows with multiple calculation steps.
- Practical calculations can be streamlined with EPWpy.
- *Ab initio* Boltzmann transport equations allow predictive calculations for band-like carrier mobilities.
- *Ab initio* polaron equations enable systematic study of polarons in materials.
- Predictive calculations of polaron-hopping transport are in early development.