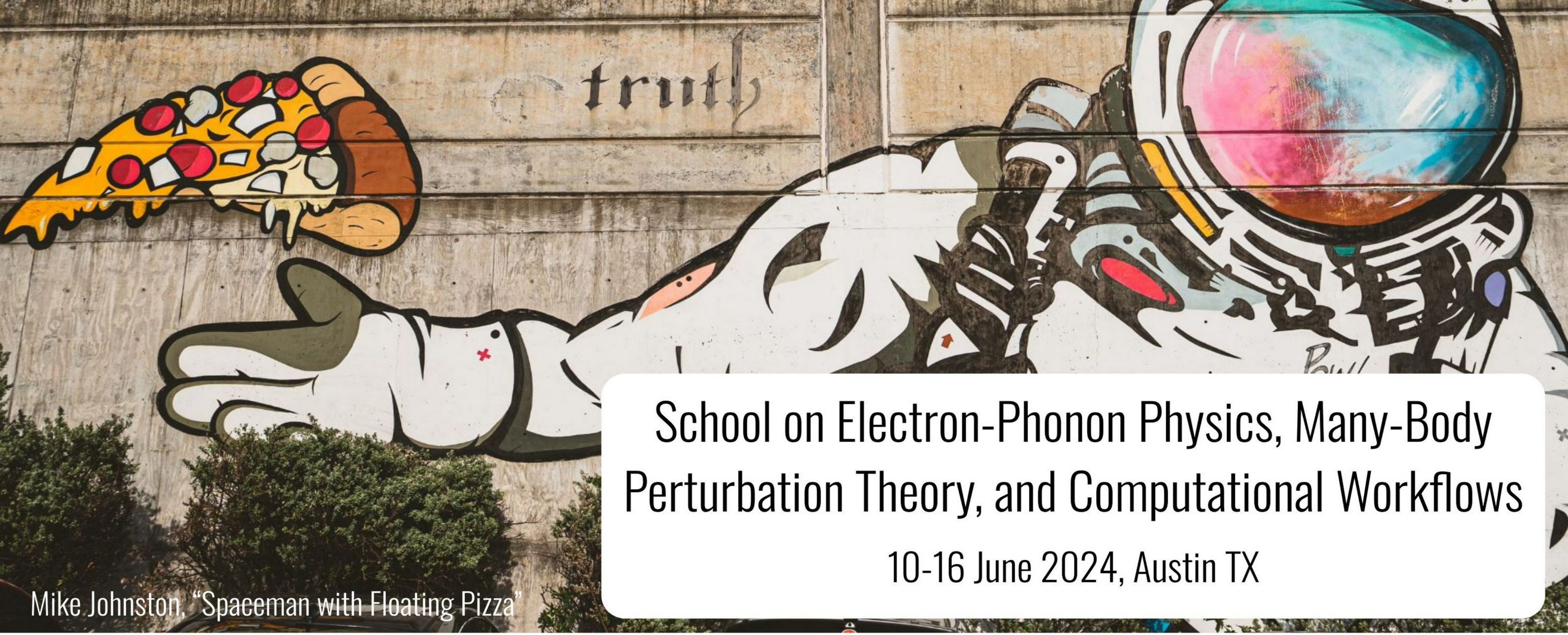


Mike Johnston, “Spaceman with Floating Pizza”

School on Electron-Phonon Physics, Many-Body Perturbation Theory, and Computational Workflows

10-16 June 2024, Austin TX

U.S. DEPARTMENT OF ENERGY

NSF

TACC
TEXAS ADVANCED COMPUTING CENTER

ODEN

Intro to Tutorial Fri.5

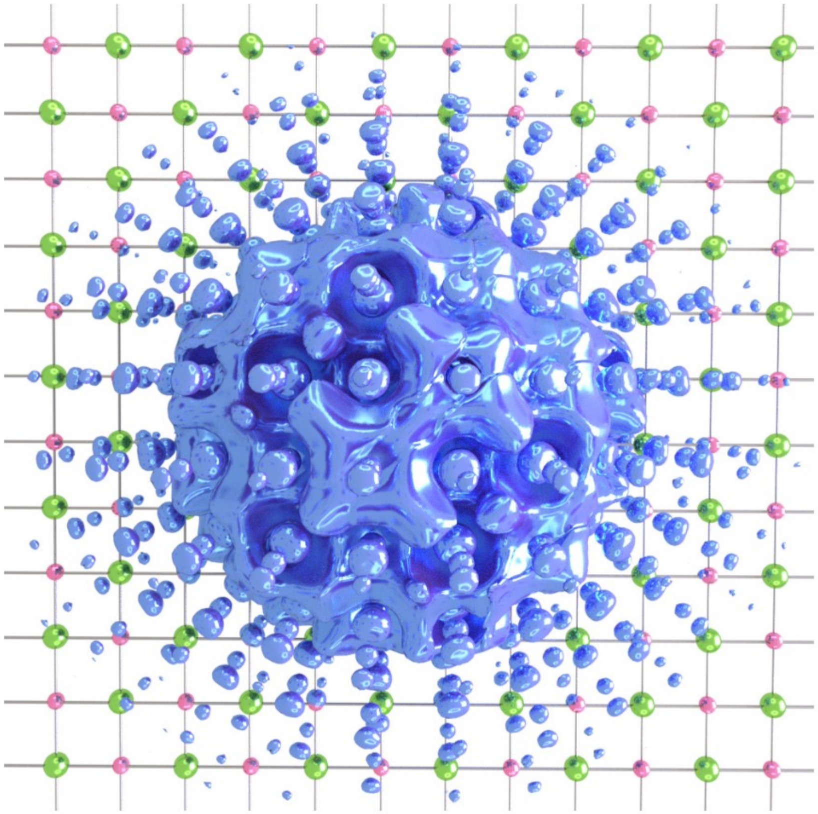
Self-trapped polarons in EPW

Jon Lafuente-Bartolome

Department of Physics

University of the Basque Country UPV/EHU

Goal



Thu.2 Giustino

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

Recap: *ab initio* theory of polarons

Formation energy of a polaron in a BvK supercell (without self-interaction):

$$E_{\mathrm{f}} = \int d\mathbf{r}\, \psi^* \hat{H}_{\mathrm{KS}} \psi + \int d\mathbf{r} |\psi|^2 \frac{\partial V_{\mathrm{KS}}}{\partial \tau_\kappa} u_\kappa + \frac{1}{2} u_\kappa C_{\kappa\kappa'} u_\kappa$$

Sio et al., PRB 99, 235139 (2019)

Recap: *ab initio* theory of polarons

Formation energy of a polaron in a BvK supercell (without self-interaction):

$$E_{\rm f} = \int d\mathbf{r}\, \psi^* \hat{H}_{\rm KS}\psi + \int d\mathbf{r}|\psi|^2 \frac{\partial V_{\rm KS}}{\partial \tau_\kappa} u_\kappa + \frac{1}{2} u_\kappa C_{\kappa\kappa'} u_\kappa$$

Variational minimization:

$$\downarrow$$

$$\begin{cases} \hat{H}_{\rm KS}\psi + \psi \frac{\partial V_{\rm KS}}{\partial \tau_\kappa} u_\kappa = \varepsilon\psi \\ u_\kappa = -(C_{\kappa\kappa'})^{-1} \int d\mathbf{r} \frac{\partial V_{\rm KS}}{\partial \tau} |\psi|^2 \end{cases}$$

Sio et al., PRB 99, 235139 (2019)

Formation energy of a polaron in a BvK supercell (without self-interaction):

$$E_{\mathrm{f}} = \int d\mathbf{r}\, \psi^* \hat{H}_{\mathrm{KS}}\psi + \int d\mathbf{r}|\psi|^2 \frac{\partial V_{\mathrm{KS}}}{\partial \tau_\kappa} u_\kappa + \frac{1}{2} u_\kappa C_{\kappa\kappa'} u_\kappa$$

Variational minimization: $\downarrow$

$$\begin{cases} \hat{H}_{\mathrm{KS}}\psi + \psi \frac{\partial V_{\mathrm{KS}}}{\partial \tau_\kappa} u_\kappa = \varepsilon\psi \\ u_\kappa = -(C_{\kappa\kappa'})^{-1} \int d\mathbf{r} \frac{\partial V_{\mathrm{KS}}}{\partial \tau} |\psi|^2 \end{cases}$$

Expansion in phonons and KS states: $\downarrow$

$$\begin{cases} \frac{2}{N_p} \sum_{\mathbf{q}m\nu} B_{\mathbf{q}\nu} g^*_{mn\nu}(\mathbf{k},\mathbf{q}) A_{n\mathbf{k}+\mathbf{q}} = (\varepsilon_{n\mathbf{k}} - \varepsilon) A_{n\mathbf{k}} \\ B_{\mathbf{q}\nu} = \frac{1}{N_p} \sum_{mn\mathbf{k}} A_{m\mathbf{k}+\mathbf{q}} \frac{g_{mn\nu}(\mathbf{k},\mathbf{q})}{\hbar\omega_{\mathbf{q}\nu}} A_{n\mathbf{k}} \end{cases}$$

Sio et al., PRB 99, 235139 (2019)

$$\begin{cases} \frac{2}{N_p}\sum_{\mathbf{q}m\nu} B_{\mathbf{q}\nu} g^*_{mn\nu}(\mathbf{k},\mathbf{q}) A_{n\mathbf{k}+\mathbf{q}} = (\varepsilon_{n\mathbf{k}} - \varepsilon) A_{n\mathbf{k}} \\ B_{\mathbf{q}\nu} = \frac{1}{N_p}\sum_{mn\mathbf{k}} A_{m\mathbf{k}+\mathbf{q}} \frac{g_{mn\nu}(\mathbf{k},\mathbf{q})}{\hbar\omega_{\mathbf{q}\nu}} A_{n\mathbf{k}} \end{cases}$$

$$\downarrow$$

Ab initio theory of polarons in practice

$$\begin{cases} \frac{2}{N_p} \sum_{\mathbf{q}m\nu} B_{\mathbf{q}\nu} g^*_{mn\nu}(\mathbf{k},\mathbf{q}) A_{n\mathbf{k}+\mathbf{q}} = (\varepsilon_{n\mathbf{k}} - \varepsilon) A_{n\mathbf{k}} \\ B_{\mathbf{q}\nu} = \frac{1}{N_p} \sum_{mn\mathbf{k}} A_{m\mathbf{k}+\mathbf{q}} \frac{g_{mn\nu}(\mathbf{k},\mathbf{q})}{\hbar\omega_{\mathbf{q}\nu}} A_{n\mathbf{k}} \end{cases}$$

$$\downarrow$$

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

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

Generalized eigenvalue problem (Davidson diagonalization)

Polaron self-consistent loop

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

`init_plrn = 1`

Polaron self-consistent loop

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

`init_plrn = 1`

↓

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

Polaron self-consistent loop

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

`init_plrn = 1`

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

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

Polaron self-consistent loop

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

`init_plrn = 1`

↓

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

↓

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

↓

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

`ethrdg_polaron`

Polaron self-consistent loop

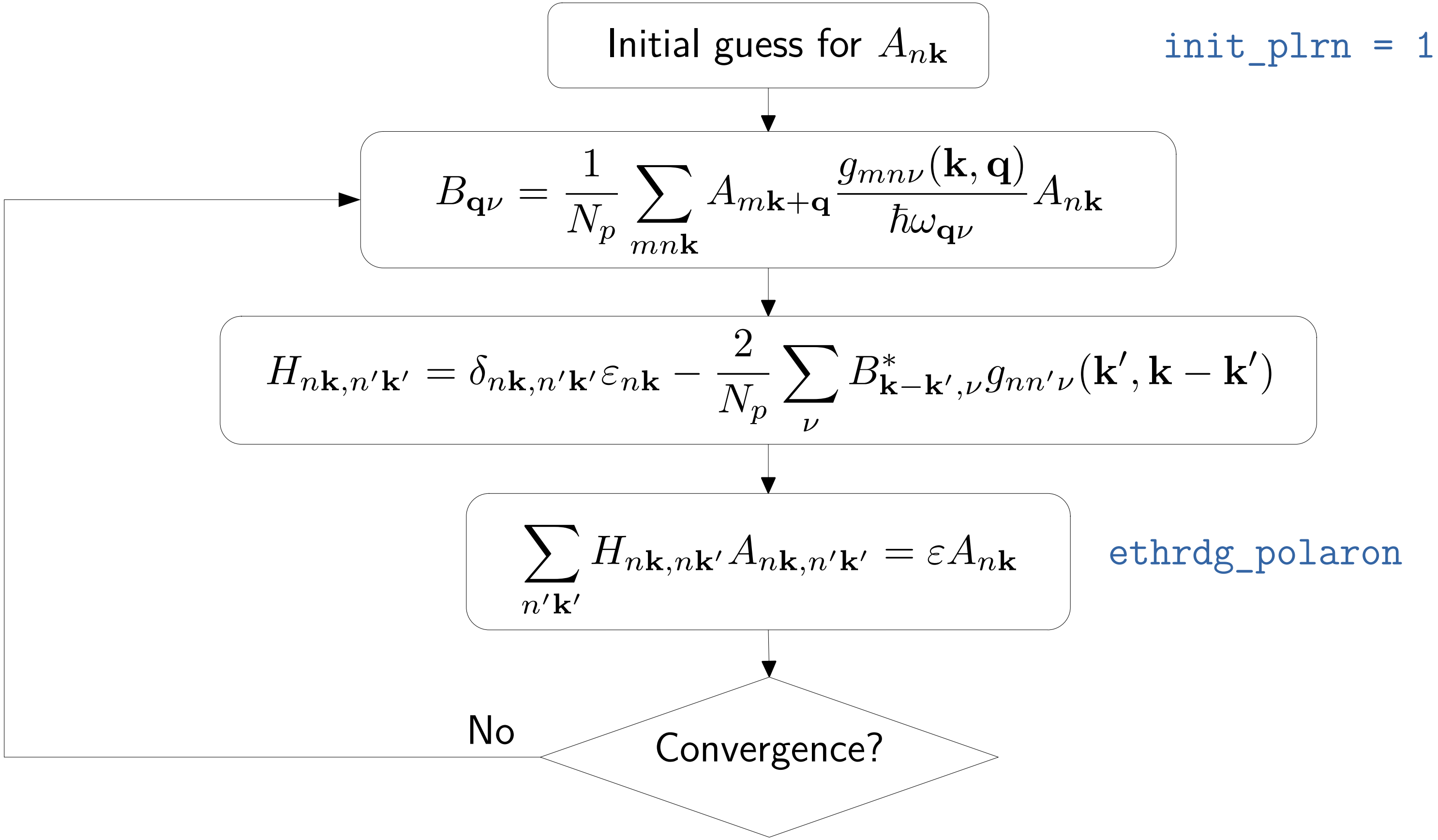
Initial guess for $A_{n\mathbf{k}}$ `init_plrn = 1`

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

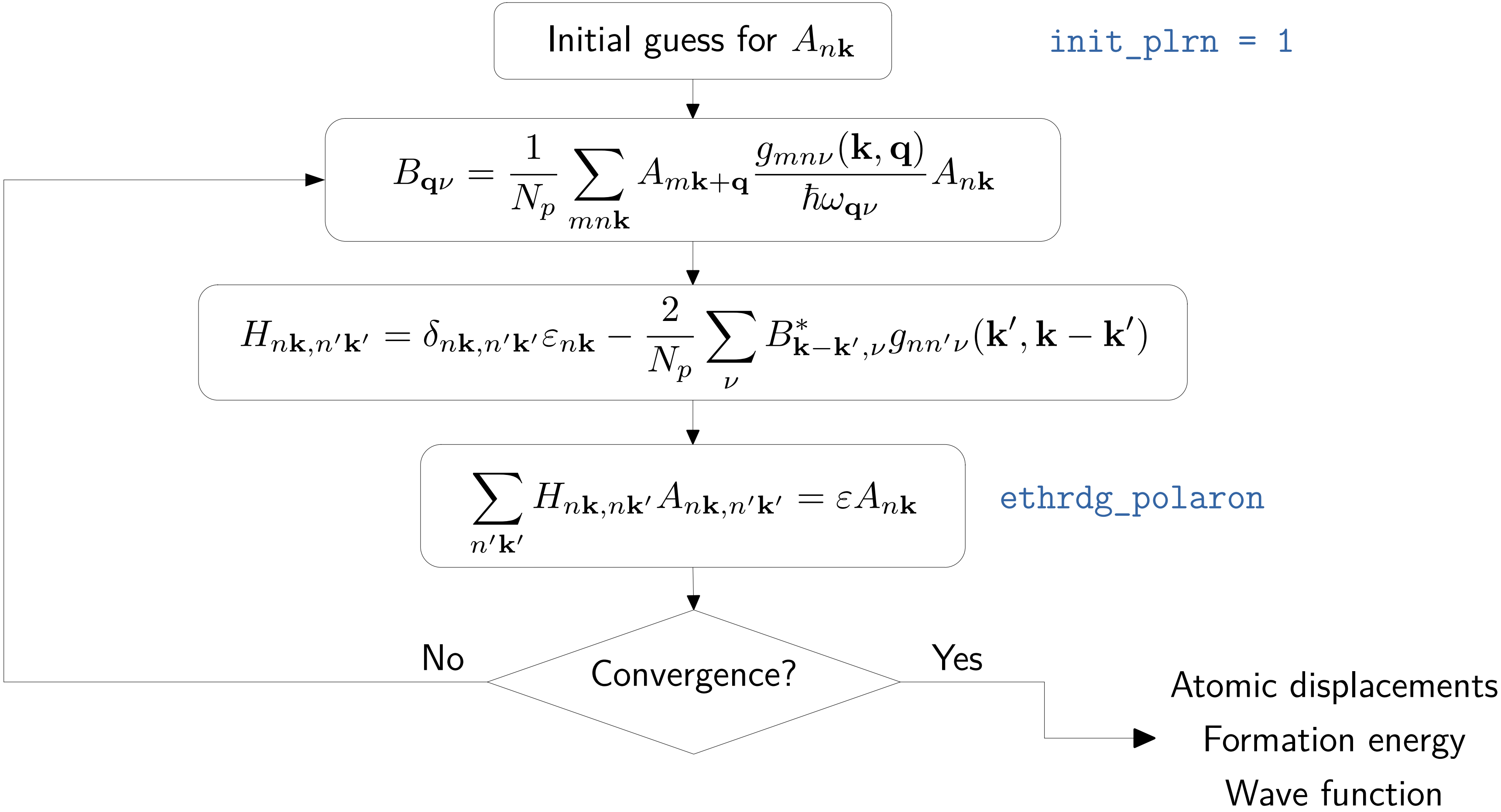
$$H_{n\mathbf{k},n'\mathbf{k}'} = \delta_{n\mathbf{k},n'\mathbf{k}'}\varepsilon_{n\mathbf{k}} - \frac{2}{N_p} \sum_{\nu} B^{*}_{\mathbf{k}-\mathbf{k}',\nu} g_{nn'\nu}(\mathbf{k}',\mathbf{k}-\mathbf{k}')$$

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

Convergence?


Initial guess for $A_{n\mathbf{k}}$
init_plrn = 1
$B_{\mathbf{q}\nu} = \frac{1}{N_p} \sum_{mn\mathbf{k}} A_{m\mathbf{k}+\mathbf{q}} \frac{g_{mn\nu}(\mathbf{k},\mathbf{q})}{\hbar\omega_{\mathbf{q}\nu}} A_{n\mathbf{k}}$
$H_{n\mathbf{k},n'\mathbf{k}'} = \delta_{n\mathbf{k},n'\mathbf{k}'}\varepsilon_{n\mathbf{k}} - \frac{2}{N_p} \sum_{\nu} B^{*}_{\mathbf{k}-\mathbf{k}',\nu} g_{nn'\nu}(\mathbf{k}',\mathbf{k}-\mathbf{k}')$
$\sum_{n'\mathbf{k}'} H_{n\mathbf{k},n\mathbf{k}'} A_{n\mathbf{k},n'\mathbf{k}'} = \varepsilon A_{n\mathbf{k}}$
ethrdg_polaron
No
Convergence?

Polaron self-consistent loop



Atomic displacements:

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

Convergence: $\mathrm{MAX}\left[\left|\Delta\tau^{i}_{\kappa\alpha p} - \Delta\tau^{i-1}_{\kappa\alpha p}\right|\right] < \Delta\tau^{\mathrm{thr}}$ `conv_thr_plrn`

Atomic displacements and wave function

Atomic displacements:

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

Convergence: $\mathrm{MAX}\left[|\Delta\tau^{i}_{\kappa\alpha p} - \Delta\tau^{i-1}_{\kappa\alpha p}|\right] < \Delta\tau^{\mathrm{thr}}$ `conv_thr_plrn`

Wave function:

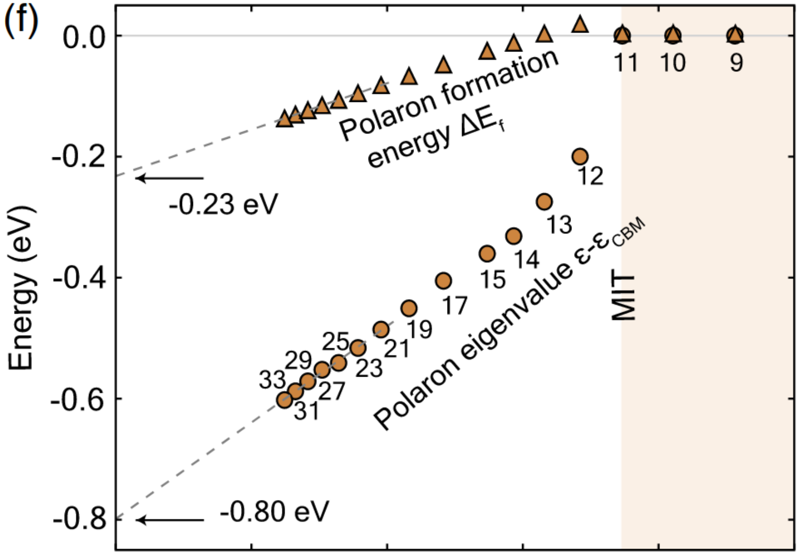
$$\psi(\mathbf{r}) = \sum_{mp} A_m(\mathbf{R}_p) w_m(\mathbf{r}-\mathbf{R}_p)$$

$$A_m(\mathbf{R}_p) = \frac{1}{N_p}\sum_{n\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_p} U^\dagger_{mn\mathbf{k}} A_{n\mathbf{k}}$$

Polaron formation energy

Formation energy:

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

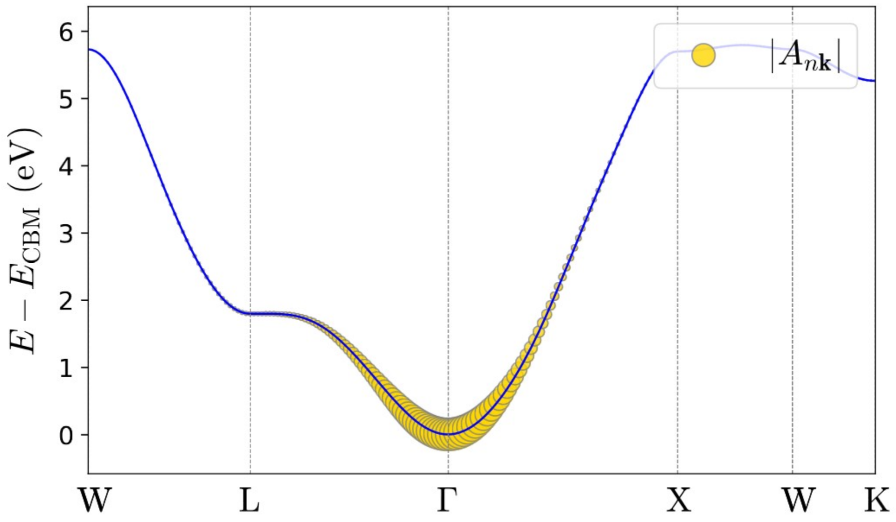


nkf1, nkf2, nkf3
nqf1, nqf2, nqf3

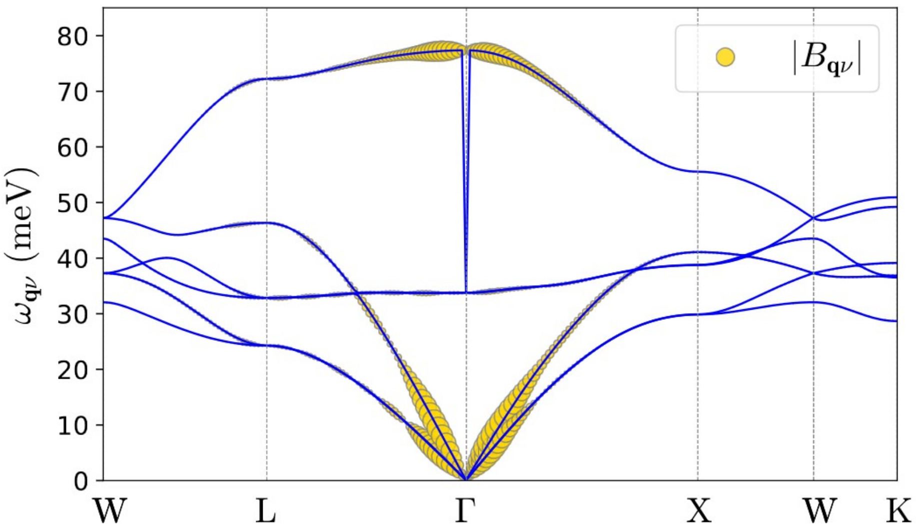
Figure from: Sio et al., PRL 122, 246403 (2019)

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

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

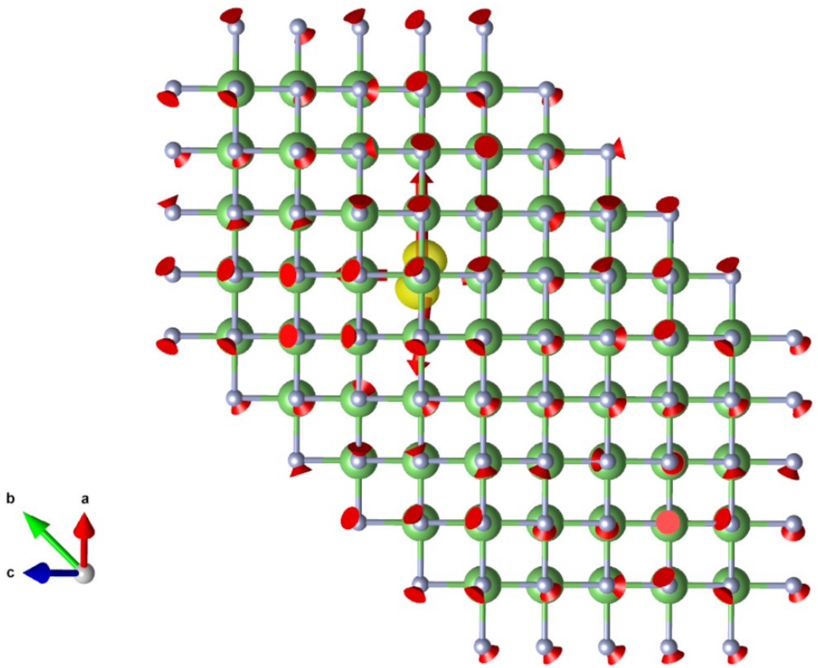


interp_Ank_plrn

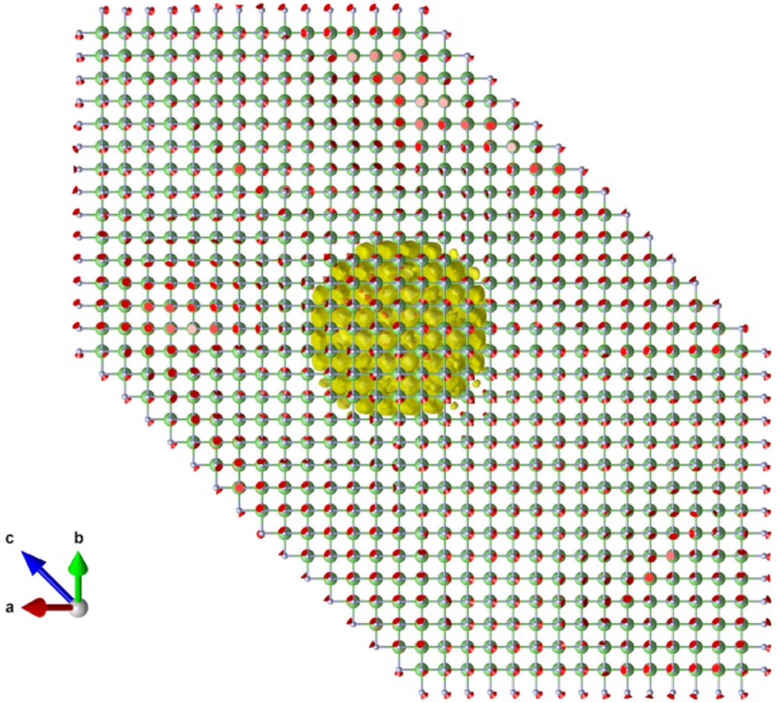


interp_Bqv_plrn

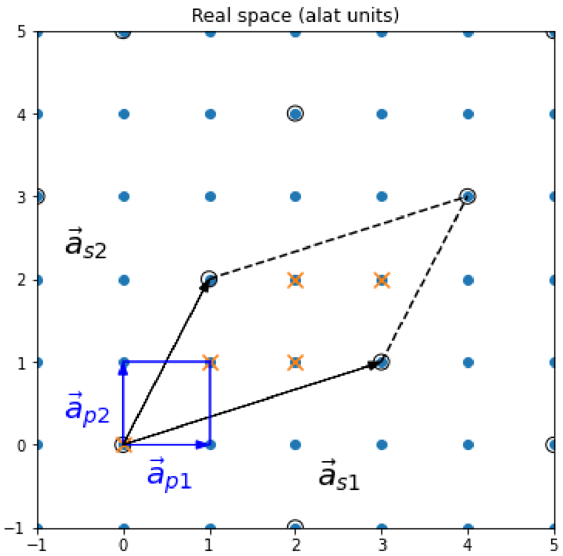
Exercise 1: Hole polaron

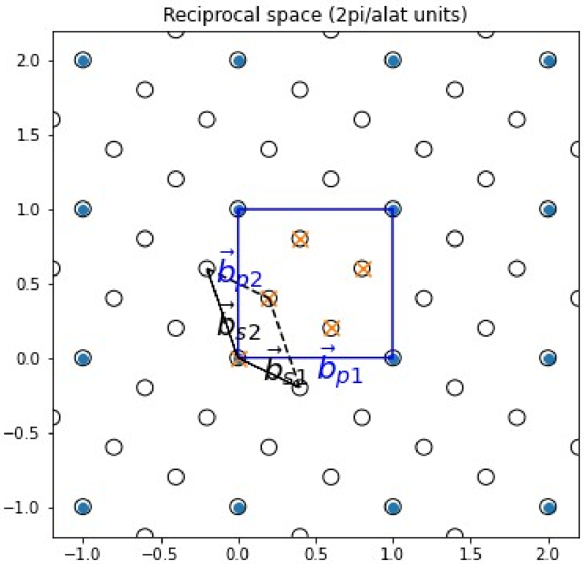


Exercise 2: Electron polaron



$$\begin{pmatrix} \mathbf{a}_{s1} \\ \mathbf{a}_{s2} \\ \mathbf{a}_{s3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} \mathbf{a}_{p1} \\ \mathbf{a}_{p2} \\ \mathbf{a}_{p3} \end{pmatrix} \qquad \begin{pmatrix} \mathbf{b}_{s1} \\ \mathbf{b}_{s2} \\ \mathbf{b}_{s3} \end{pmatrix} = \begin{pmatrix} \bar{S}_{11} & \bar{S}_{12} & \bar{S}_{13} \\ \bar{S}_{21} & \bar{S}_{22} & \bar{S}_{23} \\ \bar{S}_{31} & \bar{S}_{32} & \bar{S}_{33} \end{pmatrix} \begin{pmatrix} \mathbf{b}_{p1} \\ \mathbf{b}_{p2} \\ \mathbf{b}_{p3} \end{pmatrix}$$



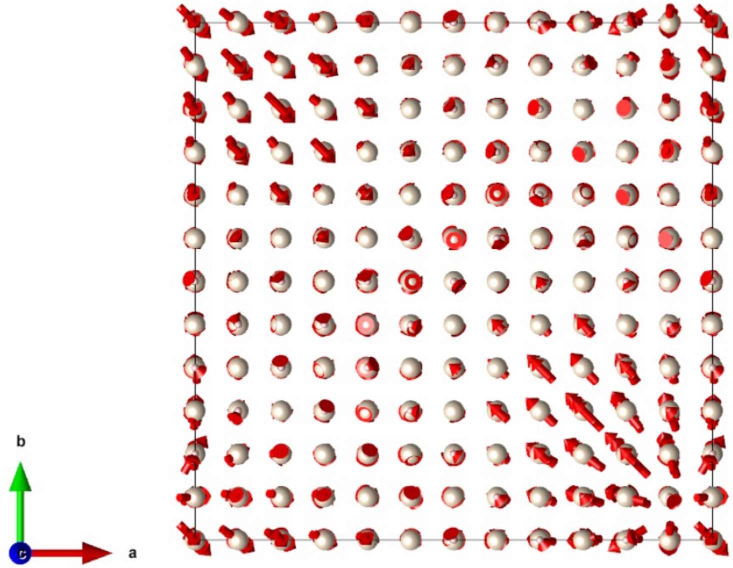


Non-diagonal supercells can be obtained by solving the polaron equations in non-uniform BZ grids!

$$\begin{pmatrix} \mathbf{a}_{s1} \\ \mathbf{a}_{s2} \\ \mathbf{a}_{s3} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{pmatrix} \begin{pmatrix} \mathbf{a}_{p1} \\ \mathbf{a}_{p2} \\ \mathbf{a}_{p3} \end{pmatrix}$$

```
scell_mat_plrn = .true.

scell_mat(1, 1:3) = -6, 6, -6
scell_mat(2, 1:3) = -6, 6,  6
scell_mat(3, 1:3) =  6, 6, -6
```



Exercise 4: Polaron energy landscape

$$E_{\mathrm{f}} = \int d\mathbf{r}\, \psi^* \hat{H}_{\mathrm{KS}} \psi + \int d\mathbf{r} |\psi|^2 \frac{\partial V_{\mathrm{KS}}}{\partial \tau_\kappa} u_\kappa + \frac{1}{2} u_\kappa C_{\kappa\kappa'} u_\kappa$$

Variational minimization w/r wave function **only**:

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

Polaron formation energy for a particular displacement configuration:

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

Exercise 4: Polaron energy landscape

Displacement configuration $\Delta\tau_{\kappa\alpha p}$

`init_plrn = 6`

Exercise 4: Polaron energy landscape

Displacement configuration $\Delta\tau_{\kappa\alpha p}$

```
init_plrn = 6
```

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

Exercise 4: Polaron energy landscape

Displacement configuration $\Delta\tau_{\kappa\alpha p}$

`init_plrn = 6`

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

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

Exercise 4: Polaron energy landscape

Displacement configuration $\Delta\tau_{\kappa\alpha p}$ `init_plrn = 6`

↓

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

↓

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

↓

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

Exercise 4: Polaron energy landscape

Displacement configuration $\Delta\tau_{\kappa\alpha p}$

`init_plrn = 6`

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

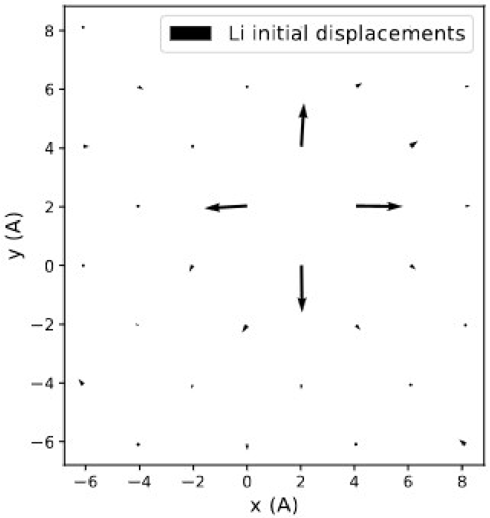
$$H_{n\mathbf{k},n'\mathbf{k}'} = \delta_{n\mathbf{k},n'\mathbf{k}'}\varepsilon_{n\mathbf{k}} - \frac{2}{N_p}\sum_{\nu} B^*_{\mathbf{k}-\mathbf{k}',\nu} g_{nn'\nu}(\mathbf{k}', \mathbf{k}-\mathbf{k}')$$

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

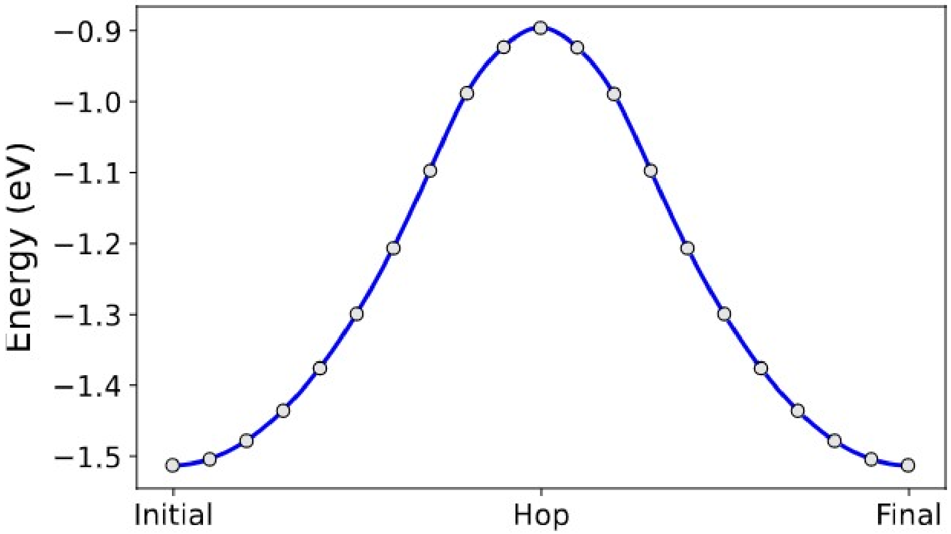
`niter_plrn = 1`

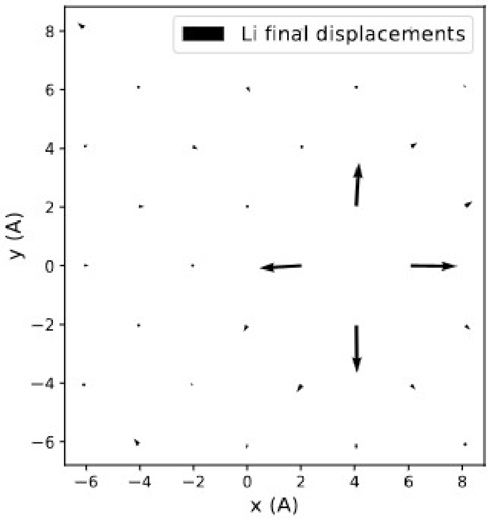
$$\tilde{E}_{\mathrm{f}} = \varepsilon - \varepsilon_{\mathrm{CBM}} + \frac{1}{N_p}\sum_{\mathbf{q}\nu} |B_{\mathbf{q}\nu}|^2 \hbar\omega_{\mathbf{q}\nu}$$

Exercise 4: Polaron energy landscape



Hopping barrier for hole polarons in LiF:





Intro to Tutorial Fri.5

Self-trapped polarons in EPW

Jon Lafuente-Bartolome

Department of Physics
University of the Basque Country UPV/EHU