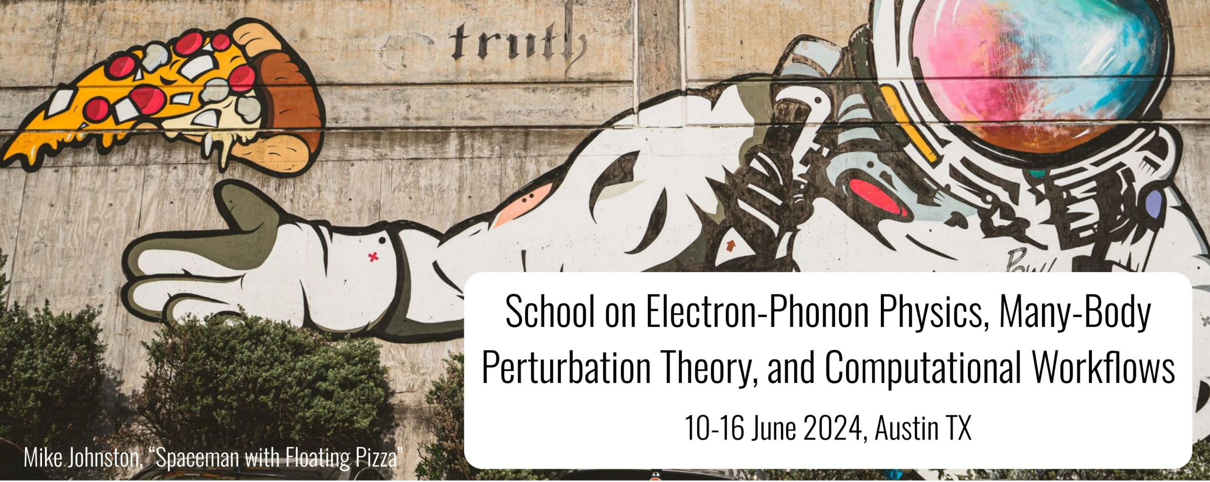

Mike Johnston, "Spaceman with Floating Pizza"

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

10-16 June 2024, Austin TX

U.S. DEPARTMENT OF ENERGY

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ODEN

Lecture Fri.4

Excitonic Polarons with EPW and BerkeleyGW

Zhenbang Dai

Oden Institute for Computational Engineering and Sciences

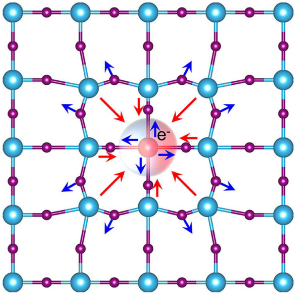
The University of Texas at Austin

Outline

- Theory of excitonic polarons
- Workflow with EPW and BerkeleyGW
- Examples on real materials

Charged polarons vs excitonic polarons

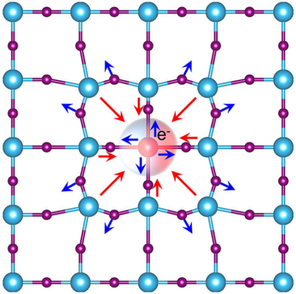
Charged polarons



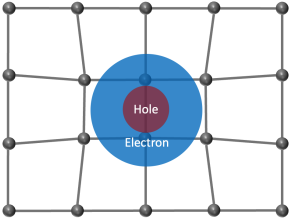
Figures from Natanzon et al, Isr. J. Chem 60, 768 (2020) and Luo et al, Nature 563, 541 (2018)

Charged polarons vs excitonic polarons

Charged polarons



Excitonic polarons



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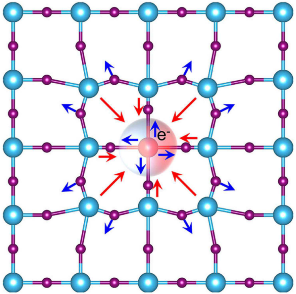

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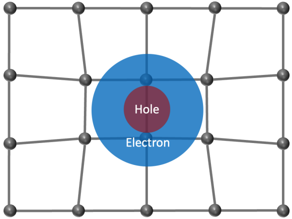
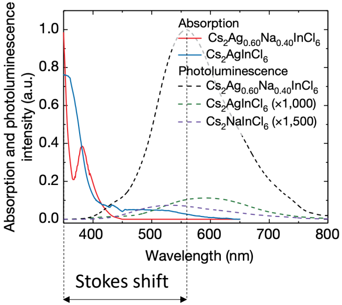


Stoks shift

$Cs_2InAgCl_6$



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Previous works

High-level quantum
chemistry methods

CCSD(T): $|\Psi\rangle = e^T |\Phi\rangle$

CASSCF: $|\Psi\rangle = \sum C_i |\Phi_i\rangle$

Van Ginhoven et al.
J. Chem. Phys. 118, 6582 (2003)

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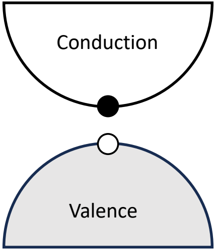
Δscf method: no electron-hole correlation



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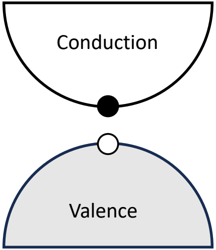

Luo et al.
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Excited state force evaluated from the Bethe-Salpeter equation.

$$\partial_\tau E_S = \partial_\tau E_0 + \partial_\tau \Omega_S$$

Ismail-Beigi and Louie
Phys. Rev. Lett. 95, 156401 (2005)

Charged polarons

Trivial polaron wave-function $\psi(\boldsymbol{r})$ and atomic displacements $\Delta\tau$

↓

Compute DFT total energy $E_{\rm tot} = \langle\psi|\,\hat{H}_{\rm DFT}(\Delta\tau)\,|\psi\rangle$

↓

Minimize $E_{\rm tot}$ with respect to $\psi(\boldsymbol{r})$ and $\Delta\tau$

Underlying ideas

Charged polarons

Trivial polaron wave-function $\psi(\boldsymbol{r})$ and atomic displacements $\Delta\tau$

↓

Compute DFT total energy $E_{\mathrm{tot}} = \langle\psi|\, \hat{H}_{\mathrm{DFT}}(\Delta\tau)\, |\psi\rangle$

↓

Minimize E_{tot} with respect to $\psi(\boldsymbol{r})$ and $\Delta\tau$

Excitonic polarons

Trivial polaron wave-function $\Psi(\boldsymbol{r}_e, \boldsymbol{r}_h)$ and atomic displacements $\Delta\tau$

↓

Compute excited-state total energy $E_{\mathrm{tot}} = E_{\mathrm{tot}}(\Delta\tau)$

↓

Minimize E_{tot} with respect to $\Psi(\boldsymbol{r}_e, \boldsymbol{r}_h)$ and $\Delta\tau$

Excited-state total energy

Two parts in the excited-state total energy

$$E_{\text{tot}} = E_{\text{DFT}} + E_{\text{excitation}}$$

Excited-state total energy

Two parts in the excited-state total energy

$$E_{\text{tot}} = E_{\text{DFT}} + E_{\text{excitation}}$$

$E_{\text{excitation}}$ is accurately captured by the BSE eigenvalues.

$$\hat{H}_{\text{BSE}} \left| s\boldsymbol{Q} \right\rangle = E_{s\boldsymbol{Q}} \left| s\boldsymbol{Q} \right\rangle$$

Excited-state total energy

$$E_{\mathrm{tot}}[\Psi, \Delta\tau] = E_0 + \langle\Psi|\, \hat{H}_{\mathrm{BSE}}[\Delta\tau]\, |\Psi\rangle + \frac{1}{2}\Delta\tau \cdot C \cdot \Delta\tau$$

Excited-state total energy

$$E_{\mathrm{tot}}[\Psi, \Delta\tau] = E_0 + \langle\Psi| \hat{H}_{\mathrm{BSE}}[\Delta\tau] |\Psi\rangle + \frac{1}{2}\Delta\tau \cdot C \cdot \Delta\tau$$

Expand $\hat{H}_{\mathrm{BSE}}(\Delta\tau)$ up to linear order

$$\hat{H}_{\mathrm{BSE}}[\Delta\tau] \approx \hat{H}_{\mathrm{BSE}}[\Delta\tau = 0] + \frac{\partial \hat{H}_{\mathrm{BSE}}}{\partial \tau}\Delta\tau$$

Excitonic polaron equations

$$\left(\hat{H}_{\mathrm{BSE}}[\Delta\tau = 0] + \frac{\partial \hat{H}_{\mathrm{BSE}}}{\partial \tau}\Delta\tau\right)|\Psi\rangle = \varepsilon\,|\Psi\rangle$$

Excitonic polaron equations

$$\left(\hat{H}_{\mathrm{BSE}}[\Delta\tau = 0] + \frac{\partial \hat{H}_{\mathrm{BSE}}}{\partial \tau}\Delta\tau\right)|\Psi\rangle = \varepsilon\,|\Psi\rangle$$

$$\Delta\tau = -C^{-1}\left\langle \Psi \left| \frac{\partial \hat{H}_{\mathrm{BSE}}}{\partial \tau} \right| \Psi \right\rangle$$

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Avoid supercells

$$\Psi(\boldsymbol{r}_e, \boldsymbol{r}_h) = \frac{1}{\sqrt{N_p}} \sum_{s\boldsymbol{Q}} A_{s\boldsymbol{Q}} \Omega_{s\boldsymbol{Q}}(\boldsymbol{r}_e, \boldsymbol{r}_h)$$

Excitonic polaron equations

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Avoid supercells

$$\Psi(\boldsymbol{r}_e, \boldsymbol{r}_h) = \frac{1}{\sqrt{N_p}} \sum_{s\boldsymbol{Q}} A_{s\boldsymbol{Q}} \Omega_{s\boldsymbol{Q}}(\boldsymbol{r}_e, \boldsymbol{r}_h)$$

Tamm-Dancoff approximation

$$\Omega_{s\boldsymbol{Q}}(\boldsymbol{r}_e, \boldsymbol{r}_h) = \sum_{vc\boldsymbol{k}} a^{s\boldsymbol{Q}}_{vc\boldsymbol{k}} \psi^*_{v\boldsymbol{k}}(\boldsymbol{r}_h)\psi_{c\boldsymbol{k}+\boldsymbol{Q}}(\boldsymbol{r}_e)$$

Excitonic polaron equations–reciprocal space

$$E_{\boldsymbol{Q}} A_{\boldsymbol{Q}} - \frac{2}{N_p} \sum_{\boldsymbol{Q}'} B_{\boldsymbol{Q}-\boldsymbol{Q}'} \mathcal{G}(\boldsymbol{Q}', \boldsymbol{Q} - \boldsymbol{Q}') A_{\boldsymbol{Q}'} = \varepsilon A_{\boldsymbol{Q}}$$

$$B_{\boldsymbol{Q}} = \frac{1}{N_p \hbar \omega_{\boldsymbol{Q}}} \sum_{\boldsymbol{Q}'} A^*_{\boldsymbol{Q}'} A_{\boldsymbol{Q}+\boldsymbol{Q}'} \mathcal{G}^*(\boldsymbol{Q}', \boldsymbol{Q})$$

$$E_{\boldsymbol{Q}} A_{\boldsymbol{Q}} - \frac{2}{N_p} \sum_{\boldsymbol{Q}'} B_{\boldsymbol{Q}-\boldsymbol{Q}'} \mathcal{G}(\boldsymbol{Q}', \boldsymbol{Q}-\boldsymbol{Q}') A_{\boldsymbol{Q}'} = \varepsilon A_{\boldsymbol{Q}}$$

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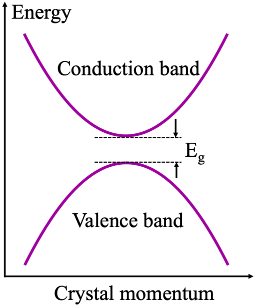
Exciton-phonon coupling matrix element

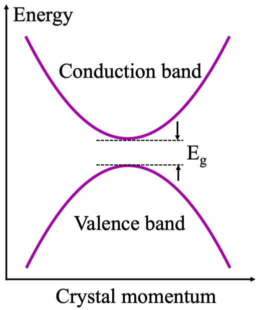
$$\mathcal{G}_{ss'\nu}(\mathbf{Q},\mathbf{q}) = \sum_{vc\mathbf{k}} a^{s\mathbf{Q}+\mathbf{q}*}_{vc\mathbf{k}} \left[\sum_{c'} g_{cc'\nu}(\mathbf{k}+\mathbf{Q},\mathbf{q}) a^{s'\mathbf{Q}}_{vc'\mathbf{k}} - \sum_{v'} g_{v'v\nu}(\mathbf{k},\mathbf{q}) a^{s'\mathbf{Q}}_{v'c\mathbf{k}+\mathbf{q}} \right]$$

Wannier excitons

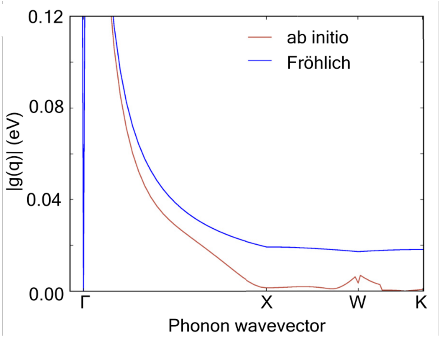


Excitonic polarons in a model system

Wannier excitons

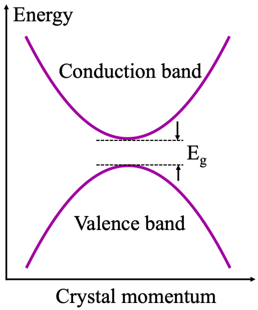


Fröhlich e-ph coupling



Excitonic polarons in a model system

Wannier excitons



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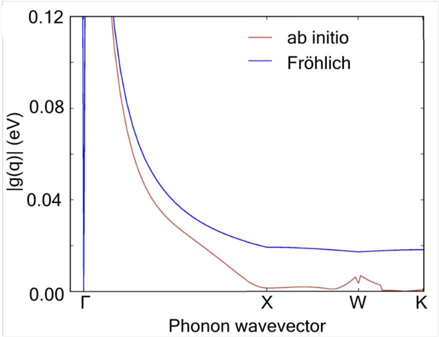
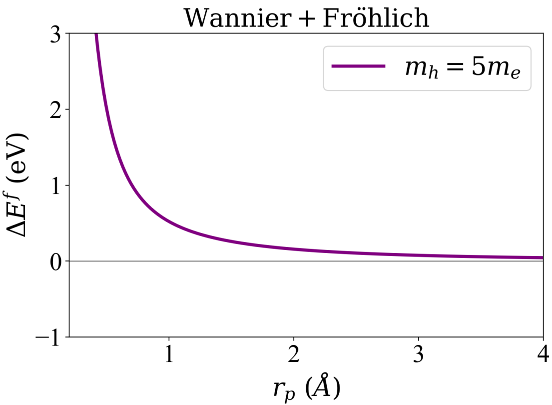


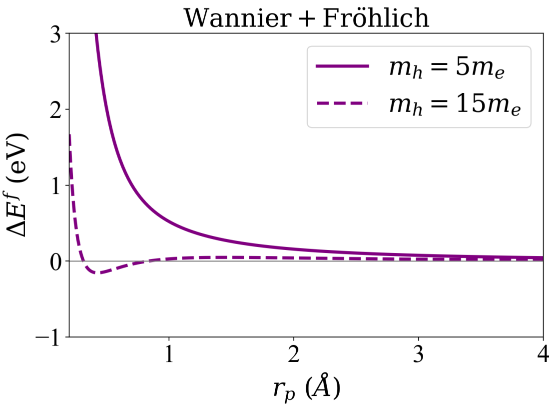
Hydrogenic ansatz

$$A_{\boldsymbol{Q}} = 8\sqrt{\frac{\pi r_p^3}{\Omega}} \frac{1}{(r_p^2|Q|^2 + 1)^2}$$

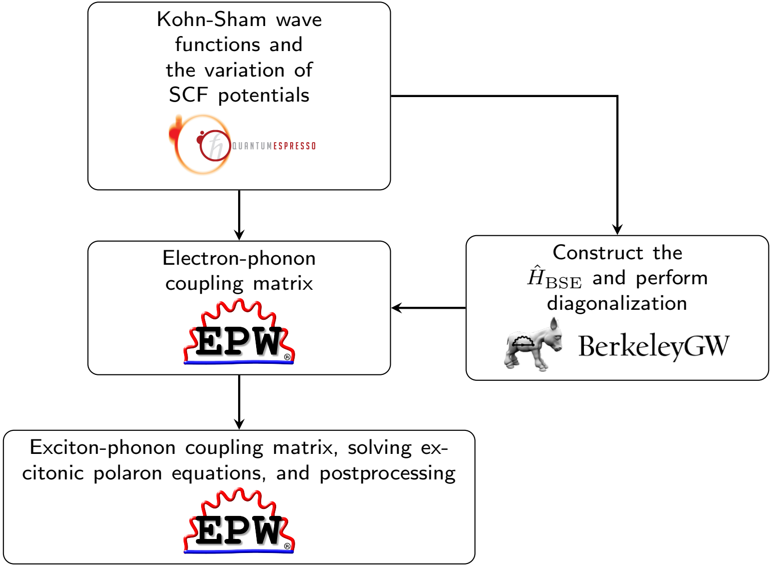
Excitonic polarons in a model system



Excitonic polarons in a model system



Workflow


Kohn-Sham wave functions and the variation of SCF potentials
QUANTUMESPRESSO
Electron-phonon coupling matrix
EPW
Construct the $\hat{H}_{\mathrm{BSE}}$ and perform diagonalization
BerkeleyGW
Exciton-phonon coupling matrix, solving excitonic polaron equations, and postprocessing
EPW

EPW step

Step 1: Construct the exciton-phonon coupling matrix.

```
--
epw1.in
&inputepw
epwread        = .false.
exciton        = .true.
explrn         = .false.
negnv          = 4
nbndv          = 3
nbndc          = 7
```

EPW step

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&inputepw
epwread         = .false.
exciton         = .true.
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negnv           = 4
nbndv           = 3
nbndc           = 7
```

Step 2: Build the excitonic polaron equations and solve them iteratively.

```
--
epw2.in
&inputepw
epwread         = .true.
exciton         = .true.
explrn          = .true.
negnv           = 4
nbndv           = 3
nbndc           = 7
init_plrn       = 5
niter_plrn      = 500
```

EPW step

Step 1: Construct the exciton-phonon coupling matrix.

```
--
epw1.in
&inputepw
epwread        = .false.
exciton        = .true.
explrn         = .false.
negnv          = 4
nbndv          = 3
nbndc          = 7
```

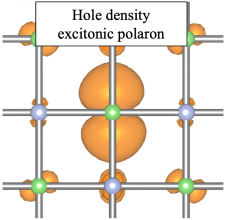
Step 2: Build the excitonic polaron equations and solve them iteratively.

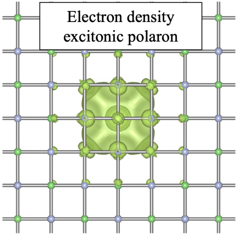
```
--
epw2.in
&inputepw
epwread        = .true.
exciton        = .true.
explrn         = .true.
negnv          = 4
nbndv          = 3
nbndc          = 7
init_plrn      = 5
niter_plrn     = 500
```

Step 3: Calculate electron and hole charge densities and atomic displacements.

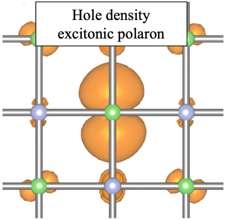
```
--
epw3.in
&inputepw
epwread        = .true.
exciton        = .true.
explrn         = .true.
negnv          = 4
nbndv          = 3
nbndc          = 7
plot_explrn_e = .false.
plot_explrn_h = .true.
```

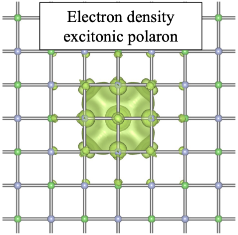
Example: LiF–Wavefunctions

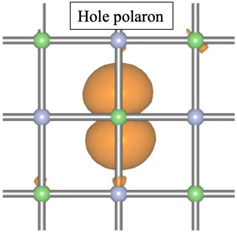


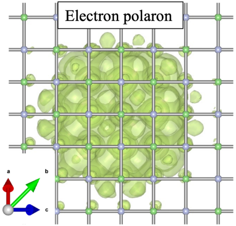


Example: LiF–Wavefunctions

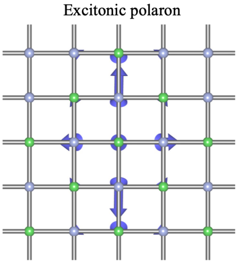


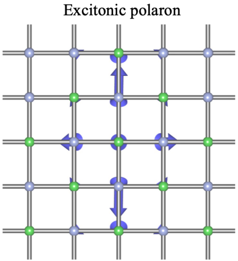


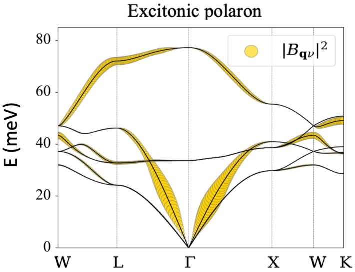




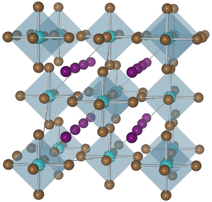
Example: LiF–Atomic Displacements



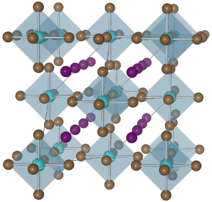

Excitonic polaron

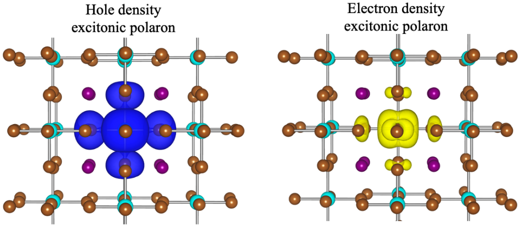

Excitonic polaron
$|B_{\mathbf{q}\nu}|^2$
E (meV)
80
60
40
20
0
W
L
Γ
X
W
K

Example: Cs_2ZrBr_6



Example: Cs_2ZrBr_6





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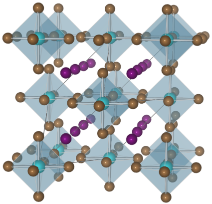

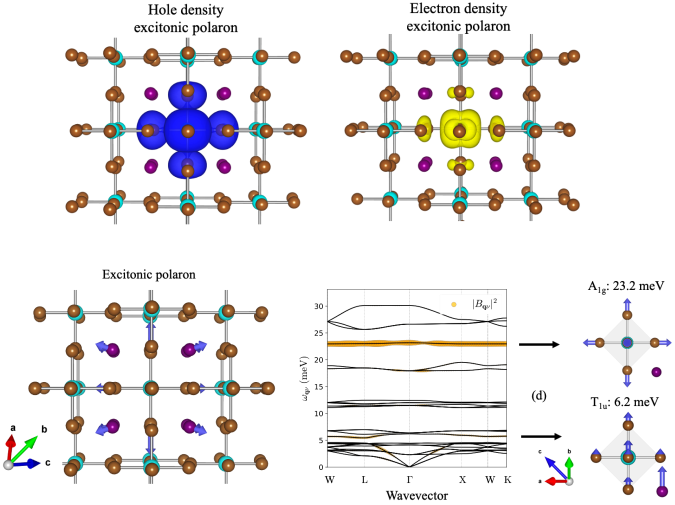

Summary

- We developed an *ab initio* theory of excitonic polarons that do not need supercells.
- The theory can be implemented by combining EPW and BerkeleyGW.
- The theory can give the formation energy, charge densities, lattice distortions, and phonon contributions all at once.

References

- W. H. Sio, C. Verdi, S. Poncé, and F. Giustino, Physical Review B, 99, 235139 (2019). [link]
- Z. Dai, C. Lian, J. Lafuente-Bartolome, and F. Giustino, Physical Review Letters, 132, 036902 (2024). [link]
- Z. Dai, C. Lian, J. Lafuente-Bartolome, and F. Giustino, Physical Review B, 109, 045202 (2024). [link]