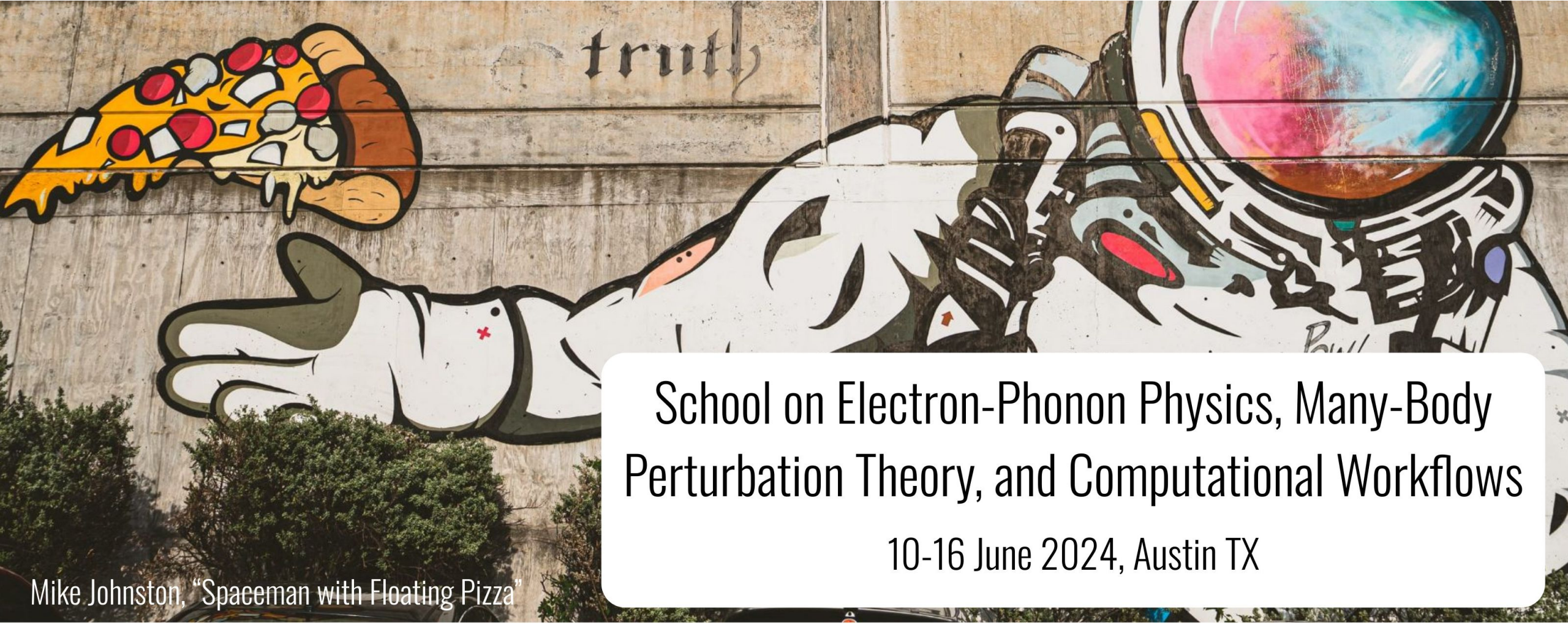

Mike Johnston, “Spaceman with Floating Pizza”

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

10-16 June 2024, Austin TX

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Tutorial Thur.3

Phonon-assisted optical processes

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Phonon-assisted optical absorption

Imaginary dielectric function:

$$\mathrm{Im}[\epsilon(\omega)] = 2\frac{4\pi e^2}{\Omega}\frac{1}{\omega^2}\sum_{mn\nu,\beta=\pm1}\int\frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}}\int\frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}\left|\mathbf{e}\cdot[\mathbf{S}_{1,mn\nu}(\mathbf{k},\mathbf{q})+\mathbf{S}_{2,mn\nu\beta}(\mathbf{k},\mathbf{q})]\right|^2 \times P_{mn\nu\beta}(\mathbf{k},\mathbf{q})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega+\beta\hbar\omega_{\mathbf{q}\nu}),$$

v = velocity matrix elements
g = electron-phonon coupling
e = light polarization

Two paths:

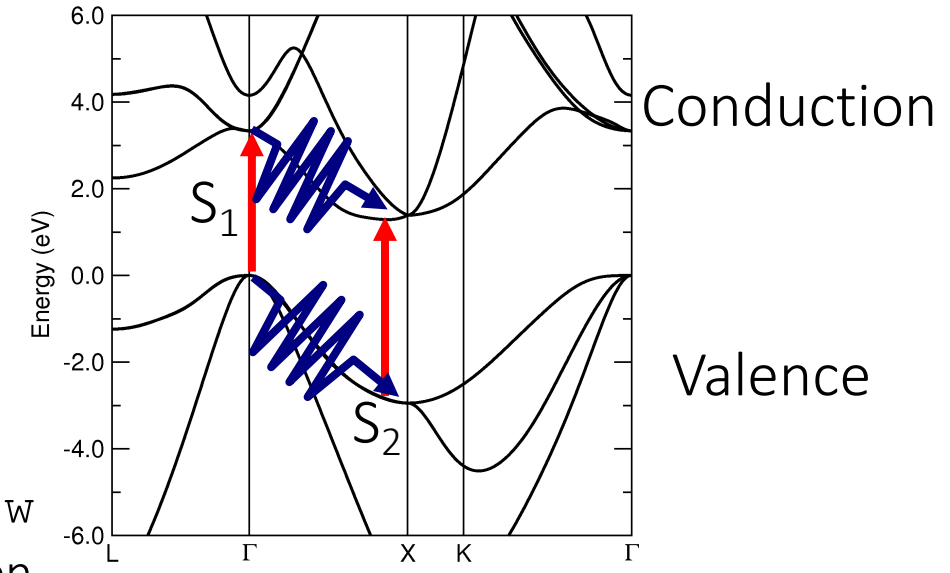
$$\mathbf{S}_{1,mn\nu}(\mathbf{k},\mathbf{q}) = \sum_j \frac{g_{mj\nu}(\mathbf{k},\mathbf{q})\mathbf{v}_{jn}(\mathbf{k})}{\varepsilon_{j\mathbf{k}}-\varepsilon_{n\mathbf{k}}-\hbar\omega+i\eta},$$

$$\mathbf{S}_{2,mn\nu\beta}(\mathbf{k},\mathbf{q}) = \sum_j \frac{\mathbf{v}_{mj}(\mathbf{k}+\mathbf{q})g_{jn\nu}(\mathbf{k},\mathbf{q})}{\varepsilon_{j\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\beta\hbar\omega_{\mathbf{q}\nu}+i\eta},$$

Occupations:

$$P_{mn\nu\beta}(\mathbf{k},\mathbf{q}) = \left(n_{\mathbf{q}\nu}+\frac{1+\beta}{2}\right)f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}}) - \left(n_{\mathbf{q}\nu}+\frac{1-\beta}{2}\right)(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}$$

β: Phonon absorption or emission



- Approximate delta function by Gaussian or Lorenzian. `degaussw` is the broadening parameter. Set it equal to the desired resolution (~0.1 eV) and converge with respect to the k/q grids.
- If you want to apply corrections to the eigenvalues (e.g., GW), need to set flag `eig_read = .true.` and provide file *.eig

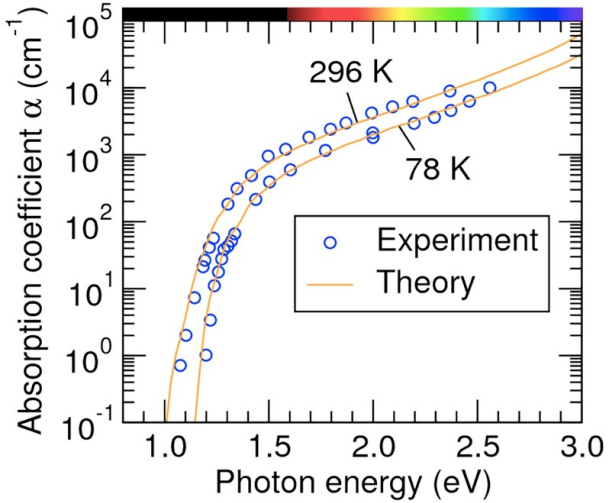
Main keywords for phonon-assisted optics

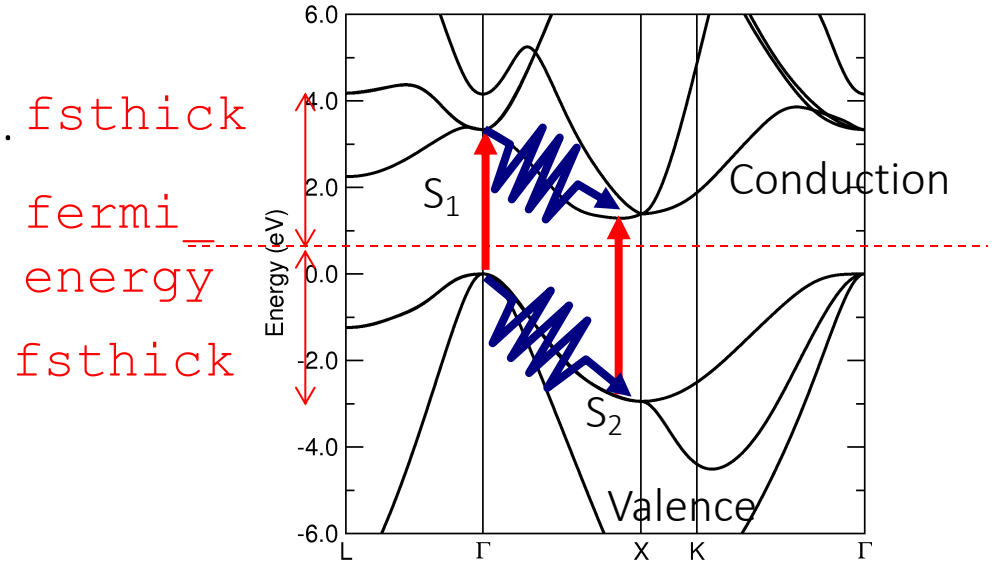
(Restart an epw calculation after you have evaluated the *.epmatwp file)

`lindabs = .true.` : enables phonon-assisted optics
`mp_mesh_k = .true.` : the initial k point is limited to the irreducible wedge. However:

- If you use the irreducible wedge the code does not apply symmetries to the resulting optical spectra. For a cubic crystal like Si, you have to manually average the resulting spectra for the three directions $\alpha = (\alpha_x + \alpha_y + \alpha_z)/3$
- Alternatively, you can set the variable to .false. and use the full grid, but the calculation is much slower and not recommended.

`omegamin`, `omegamax`, `omegastep`: defines the grid of photon energies
`fermi_energy` and `fsthick`: limits the sum only over states that lie within the truncation window. Window needs to be wider than `omega_max` + highest phonon frequency + ~5*`degaussw`





Practical tips

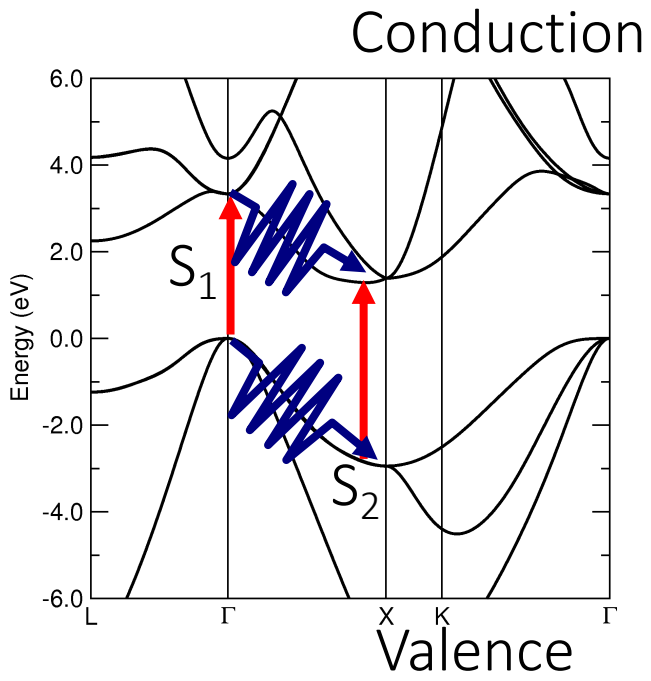
- You need to include as many Wannier functions as you need to reproduce the band structure for all states that contribute to phonon-assisted absorption, not just the band extrema.

- The k-grid and q-grid that you need to converge for a given energy resolution (`degaussw`) can be estimated from the density of states.

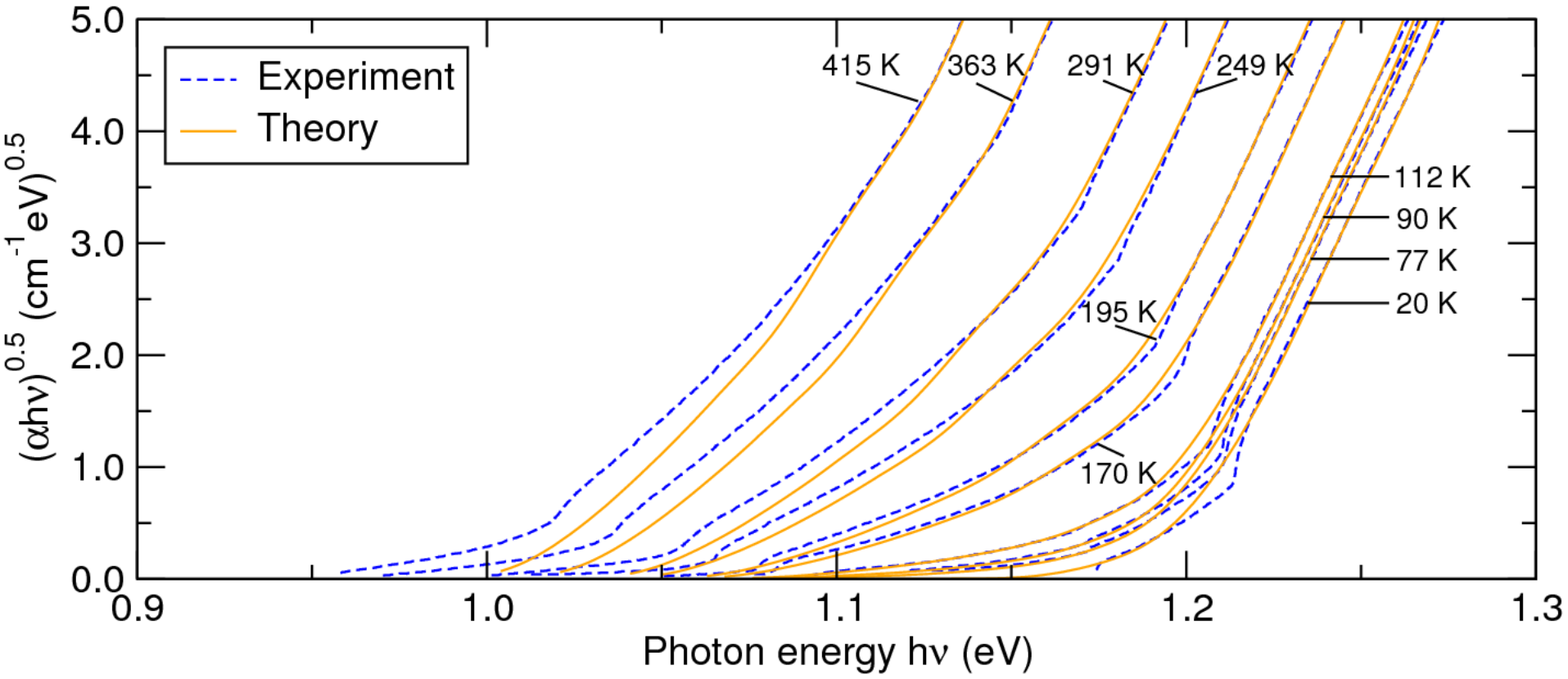
- The calculated spectra should not depend strongly on the imaginary denominator broadening parameter. If they do, that is a sign of a divergence, caused by an intermediate state getting close in energy to the initial and final states. This typically happens for photon energies near the direct band gap, where direct absorption dominates.

$$\mathbf{S}_{1,mn\nu}(\mathbf{k},\mathbf{q}) = \sum_j \frac{g_{mj\nu}(\mathbf{k},\mathbf{q})\mathbf{v}_{jn}(\mathbf{k})}{\varepsilon_{j\mathbf{k}} - \varepsilon_{n\mathbf{k}} - \hbar\omega + i\eta},$$

$$\mathbf{S}_{2,mn\nu\beta}(\mathbf{k},\mathbf{q}) = \sum_j \frac{\mathbf{v}_{mj}(\mathbf{k}+\mathbf{q})g_{jn\nu}(\mathbf{k},\mathbf{q})}{\varepsilon_{j\mathbf{k}+\mathbf{q}} - \varepsilon_{n\mathbf{k}} + \beta\hbar\omega_{\mathbf{q}\nu} + i\eta},$$



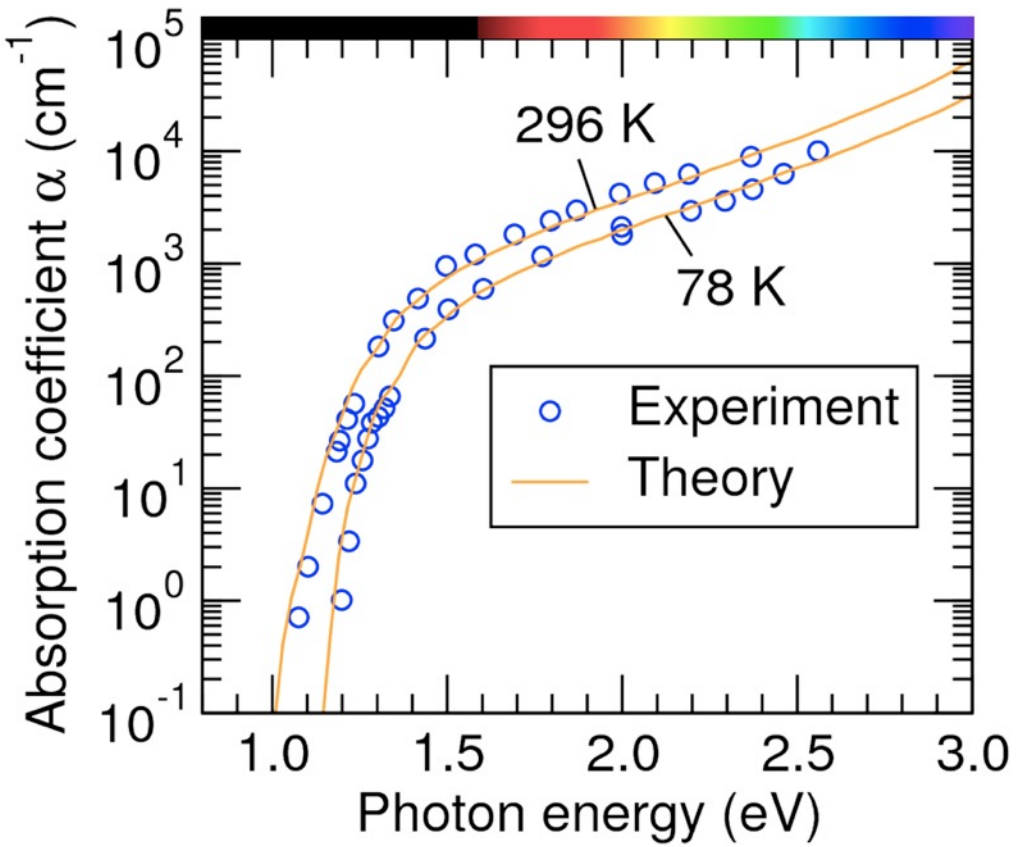
Indirect absorption edge for silicon



Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)

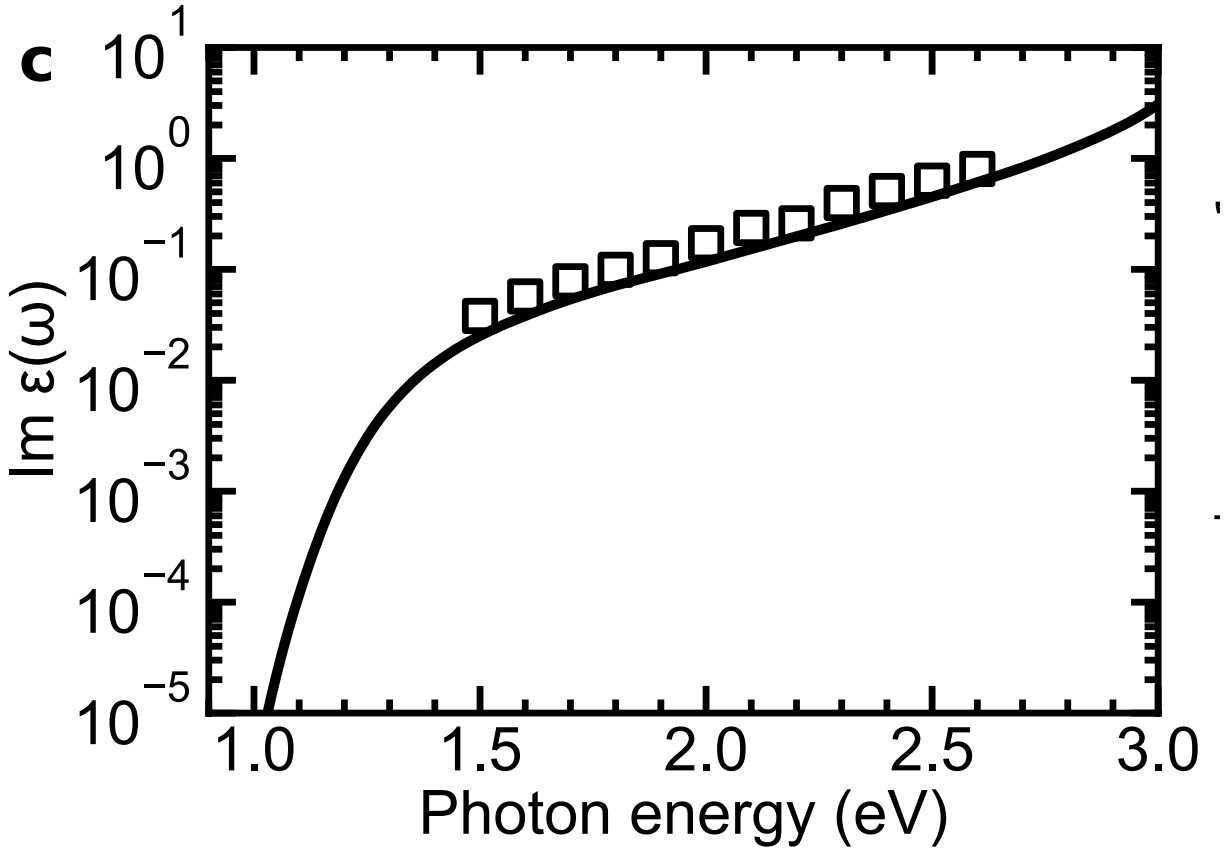
* Shifted the energy of onset by 0.15-0.23 eV to match experimental linear region

Si absorption in the visible



Noffsinger, Kioupakis, Van de Walle, Louie, and Cohen, *Phys. Rev. Lett*. **108**, 167402 (2012)

* Shifted the energy of onset to match experimental trend



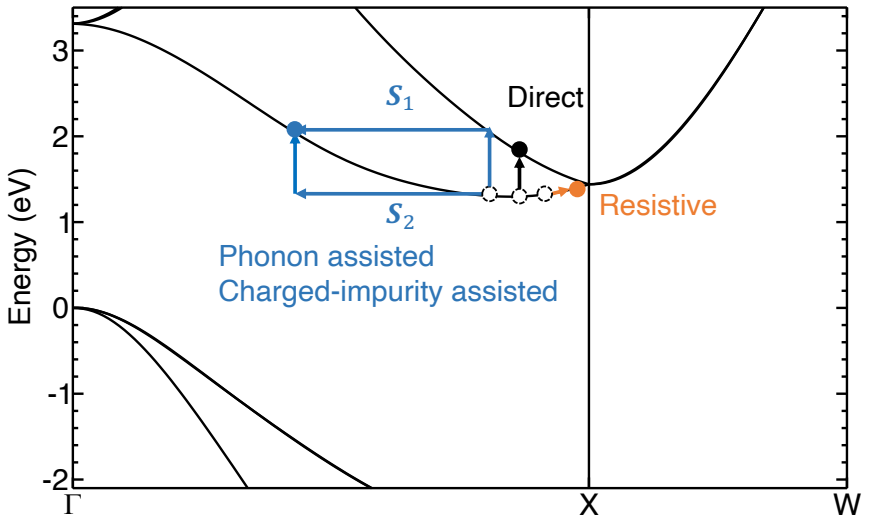
H. Lee et al., npj Comput Mater 9, 156 (2023).085

Phonon-assisted free carrier absorption

Inputs for free-carrier absorption

- `Carrier = .true.`: enable free carriers
- `ncarrier = 1e19`: free-carrier density, positive for free electrons and negative for free holes, in cm^{-3}
- `ii_g,ii_n,ii_lscreen:` charged-impurity-assisted optics
- `sigma_ref:` reference conductivity for resistive contribution
- The k-grid and q-grid for converged free-carrier absorption is typically denser than cross-gap absorption
- The calculated spectra for phonon-assisted and charged-impurity-assisted contribution show dependence on the imaginary broadening
- Numerical approaches to compensate the divergence: ACS Nano, 10.1, 957-966 (2016)

$$\varepsilon_2(\omega) = 2\times\varepsilon_2(\omega)\Big|_{2\eta} - \varepsilon_2(\omega)\Big|_{\eta}$$

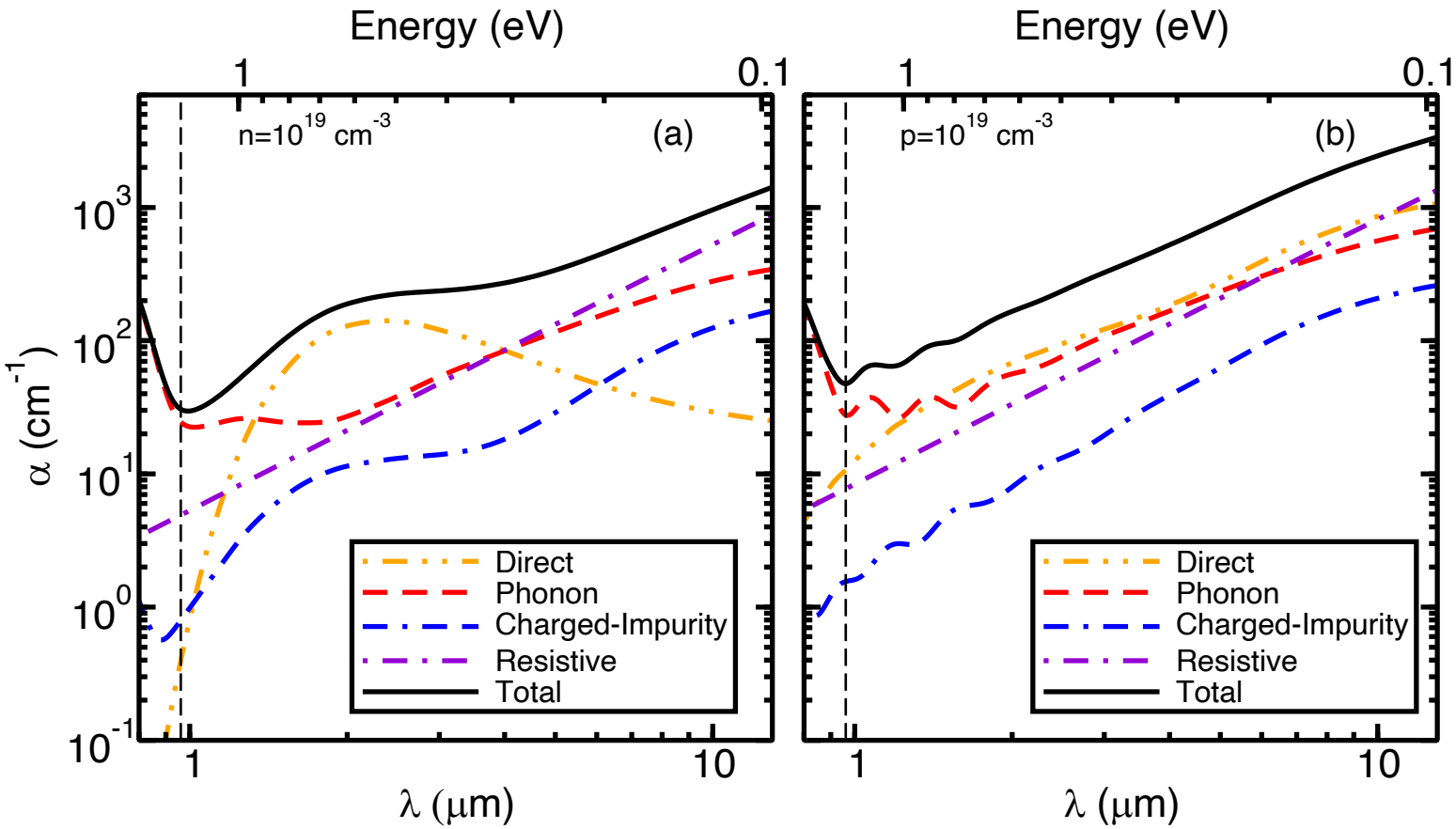


Partially occupied CBM
Partially empty VBM
↓
Sub-gap free-carrier absorption

- Special displacement: Fri. by Marios Zacharias
- Quasi-degenerate perturbation theory: Sat. by Sabyasachi Tiwari

Silicon free-carrier absorption

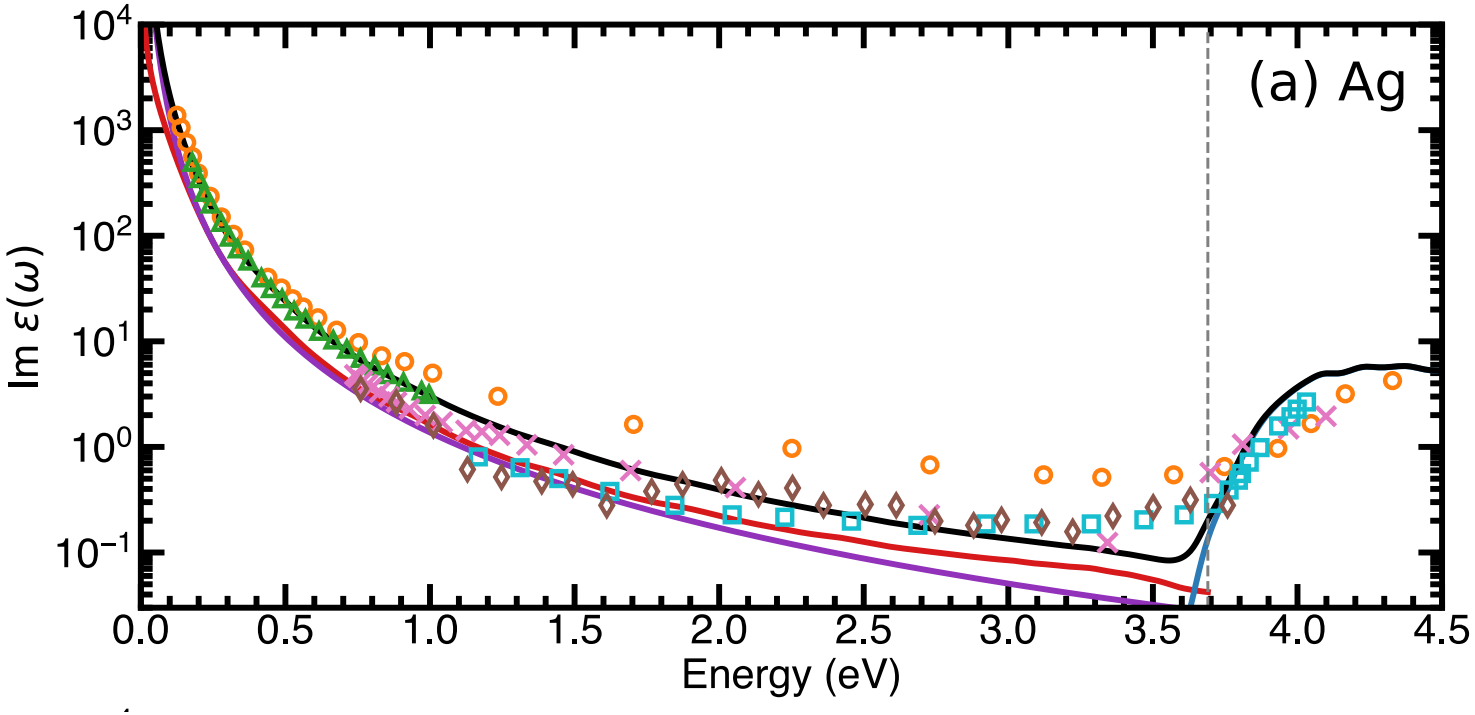
Different free-carrier absorption mechanisms: Direct, charged-impurity-assisted, resistive



Phys. Rev. B 106, 205203

Metallic systems

`assume_metal:` determine Fermi level inside bands



In preparation