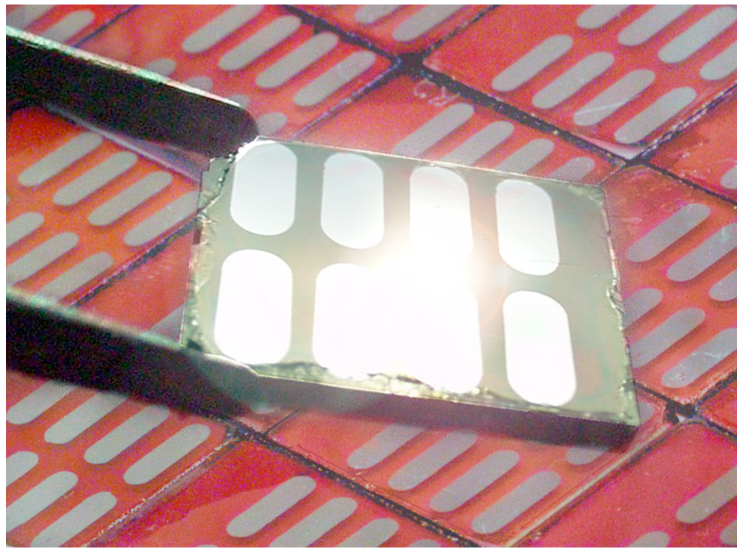
Ultrafast Dynamics of Excited Electrons in Materials for Energy Applications



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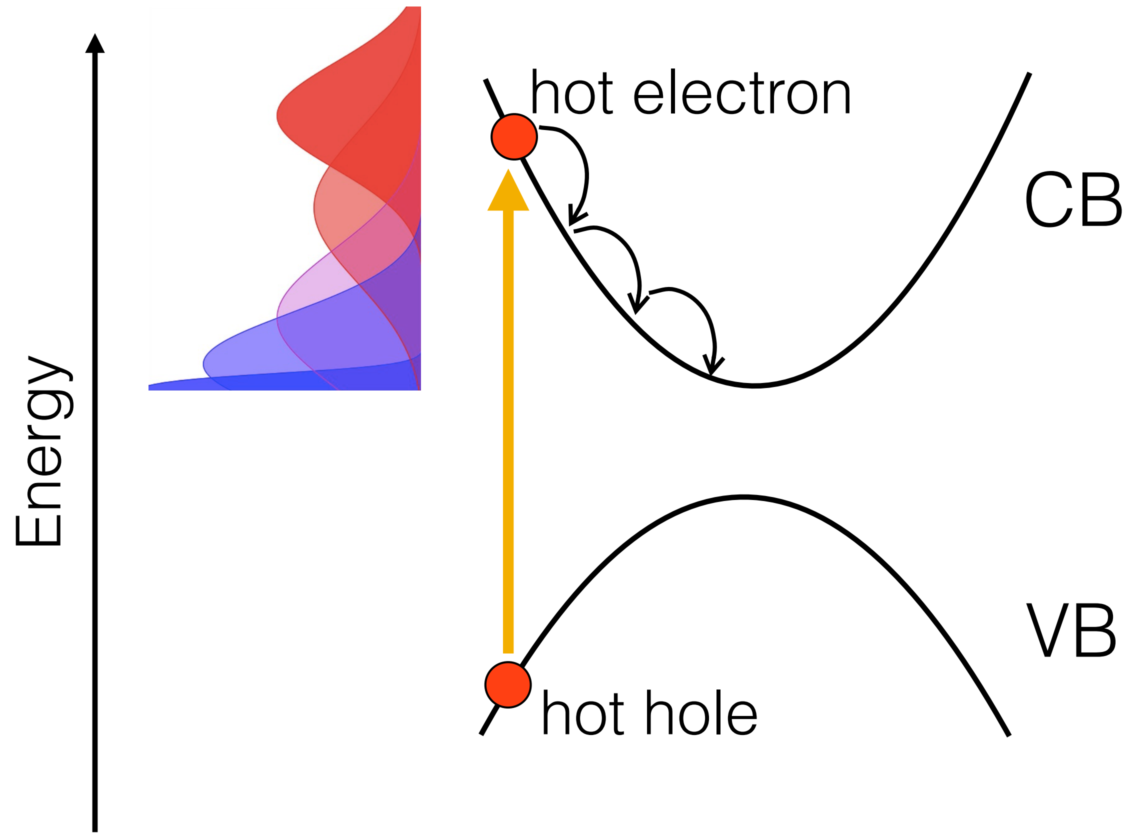
Ultrafast Dynamics of Excited Carriers

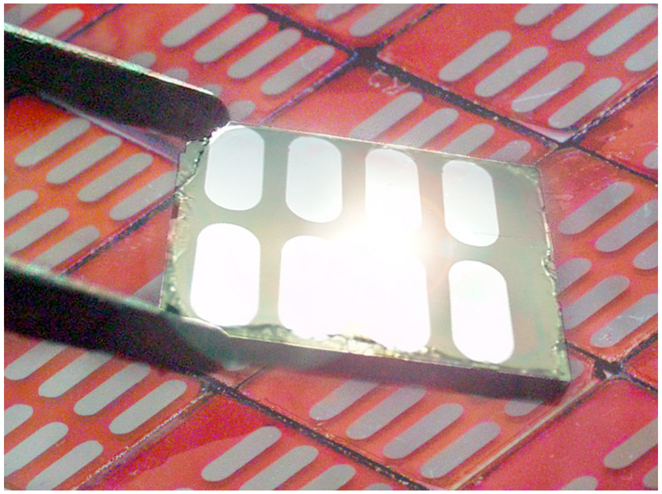


Understand hot carriers in materials:

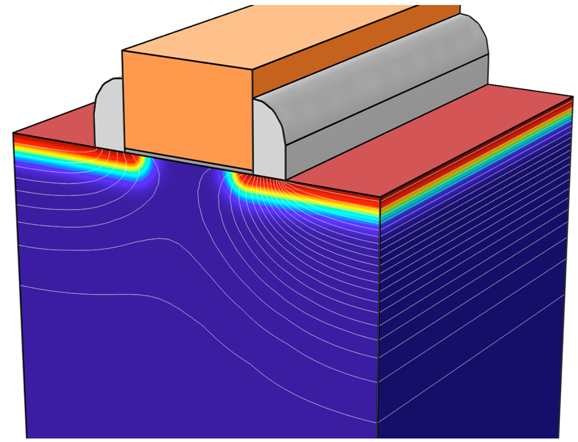
- Energy distribution vs. time
- Timescale (10–100 fs) for energy loss
- Transport and mean free paths

Hot Carriers in Science and Technology

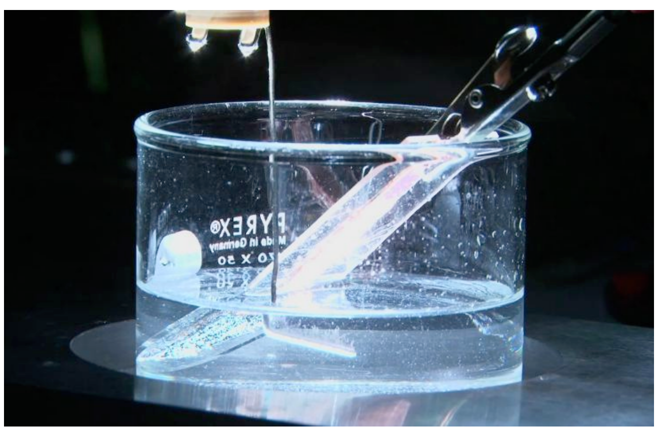
Solar Cells



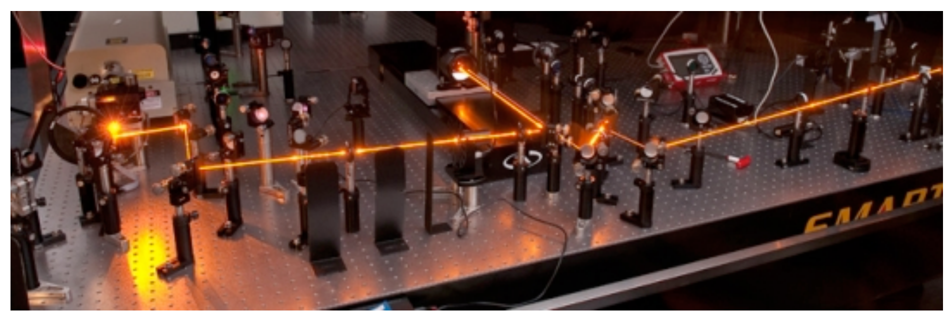
Electronics



Photocatalysis



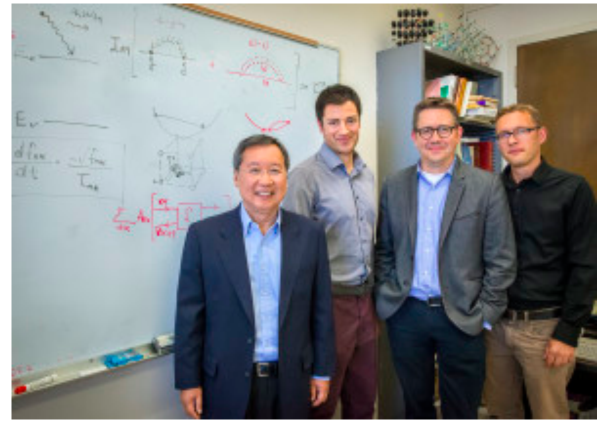
Ultrafast spectroscopy



Hot Carriers from First Principles

First Ab Initio Method for Characterizing Hot Carriers Could Hold the Key to Future Solar Cell Efficiencies

Science Shorts Lynn Yarris (mailto:lcyarris@lbl.gov) • **JULY 17, 2014**



(http://newscenter.lbl.gov/wp-content/uploads/sites/2/2014/07/Steve-Louie-and-Jeff-Neaton.jpg)

Work with Steve Louie and Jeff Neaton (UC Berkeley)

1) Computational approach

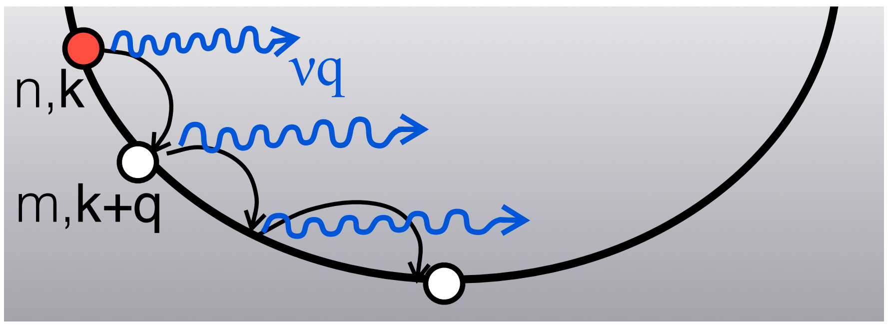
2) Hot carriers in Silicon and GaAs

3) Hot carriers from surface plasmons in Au and Ag

Hot Carrier Scattering

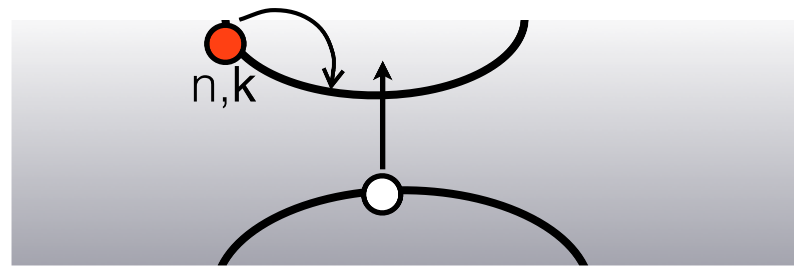
Two ultrafast (<1ps) mechanisms for hot carriers to lose energy

Electron – phonon scattering



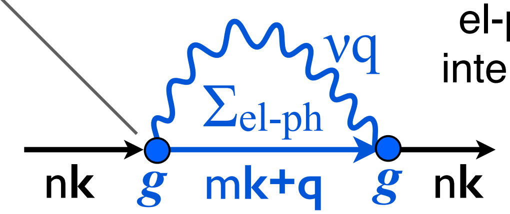
Electron – electron scattering

"Impact ionization" & Auger processes



Use perturbation theory

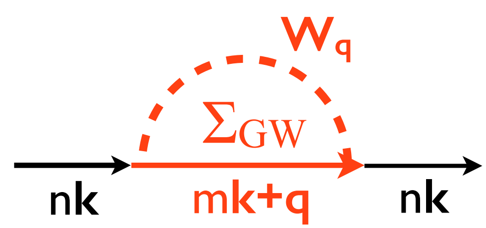
$\boldsymbol{g} \sim \langle mk+q |\, \nabla V_{KS} \cdot \varepsilon_{\nu q} \,| nk \rangle$



el-ph matrix elements
interpolate on fine grids

$(\tau_{\mathbf{nk}}^{-1})_{\text{el-ph}} \sim \mathrm{Im}(\ \Sigma_{\text{nk}}\ )_{\text{el-ph}} = \mathrm{Im}\ g^2 GD$

Quantum Espresso + EPW code



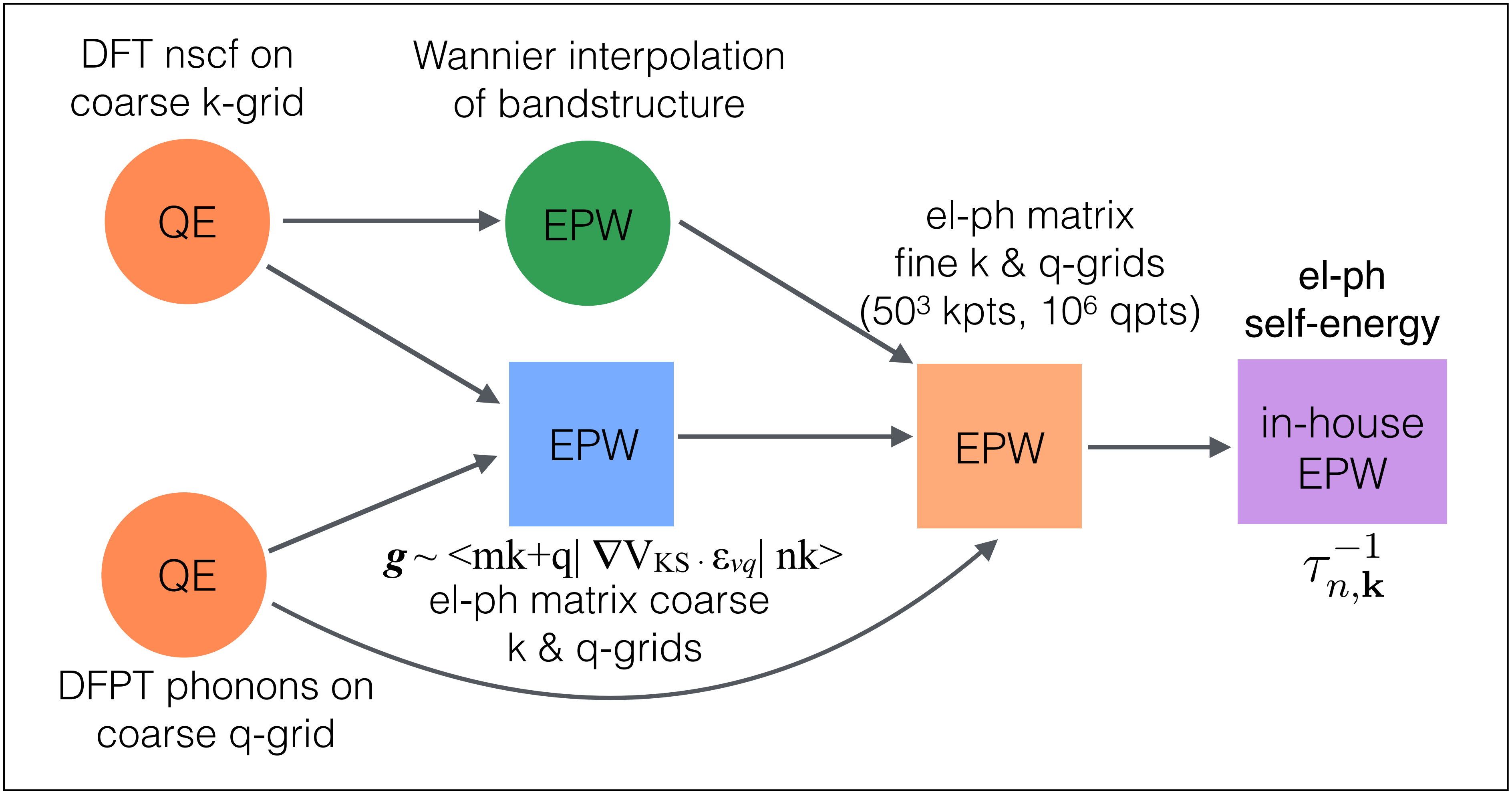
$(\tau_{\mathbf{nk}}^{-1}) \sim \mathrm{Im}(\ \Sigma_{\text{nk}}\ )_{\text{el-el}} = \mathrm{Im} G \cdot (\varepsilon_{RPA}^{-1}\ V)$

Quantum Espresso + Berkeley GW

Relaxation time of carrier in state *n*,k

$$(\tau_{\text{nk}})^{-1} = \mathrm{Im}(\ \Sigma_{\mathbf{nk}}\ )_{\text{el-ph}} + \mathrm{Im}(\ \Sigma_{\mathbf{nk}}\ )_{\text{el-el}}$$

Workflow for Electron-Phonon Calculation



el-ph matrix elements
5-dim array

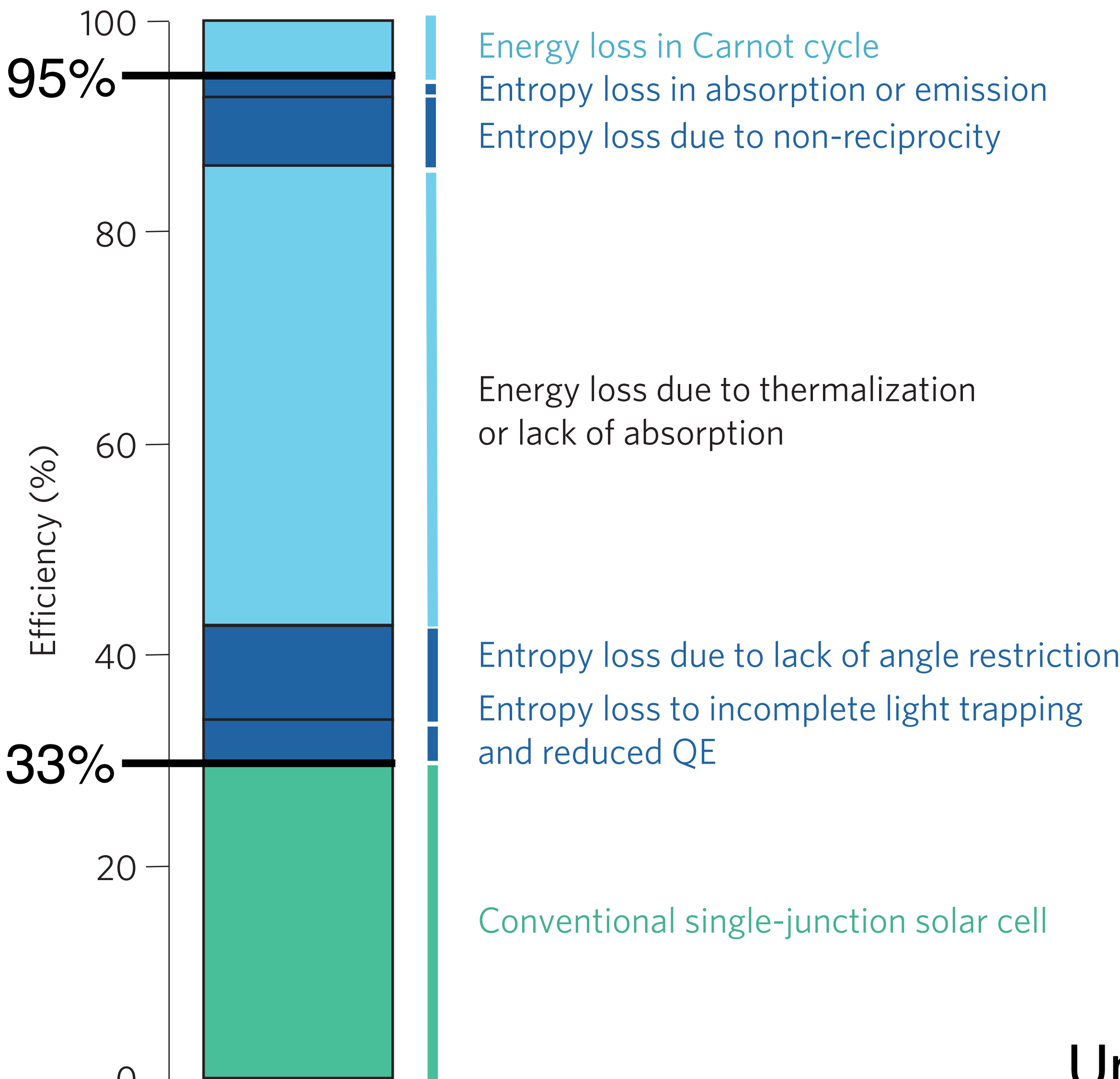
$$\tau_{n\mathbf{k}}^{-1} = \frac{2\pi}{\hbar}\frac{1}{N_{\mathbf{q}}}\sum_{m,\nu,\mathbf{q}} |g_{nm\mathbf{k}}^{\nu\mathbf{q}}|^2 [(N_{\nu\mathbf{q}}+1-f_{m,\mathbf{k+q}})\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m,\mathbf{k+q}}-\hbar\omega_{\nu\mathbf{q}})+(N_{\nu\mathbf{q}}+f_{m,\mathbf{k+q}})\delta(\epsilon_{n\mathbf{k}}-\epsilon_{m,\mathbf{k+q}}+\hbar\omega_{\nu,\mathbf{q}})]$$

random q-grid
"Monte Carlo" integration

Lorentzian 10 meV
broadening

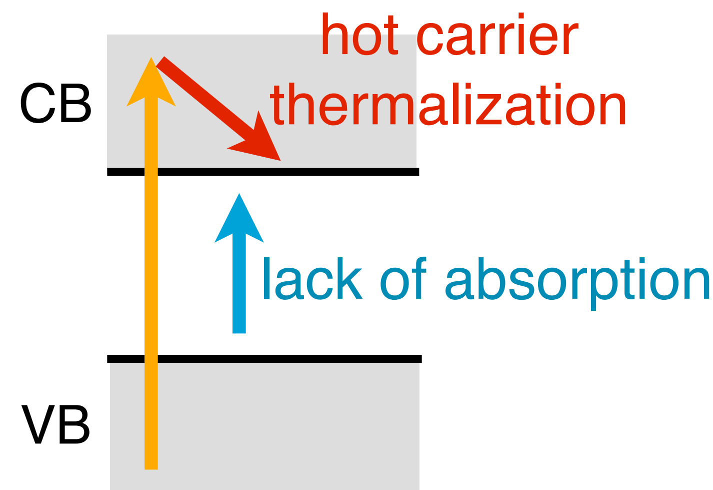
Thermalization Loss in Solar Cells

Shockley-Queisser efficiency limit for a single-junction solar cell: ~33%



H. Atwater, A. Polman, Nat. Mater. 11, 174 (2012)

Two main losses in PV



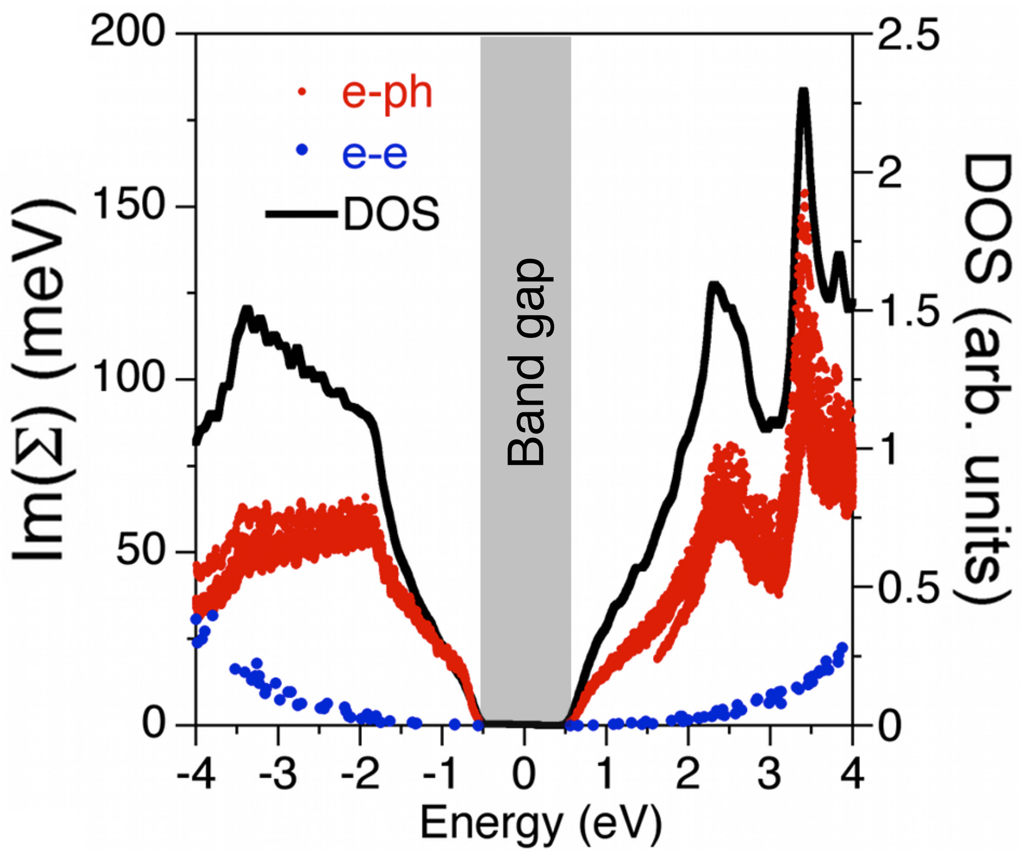
Silicon

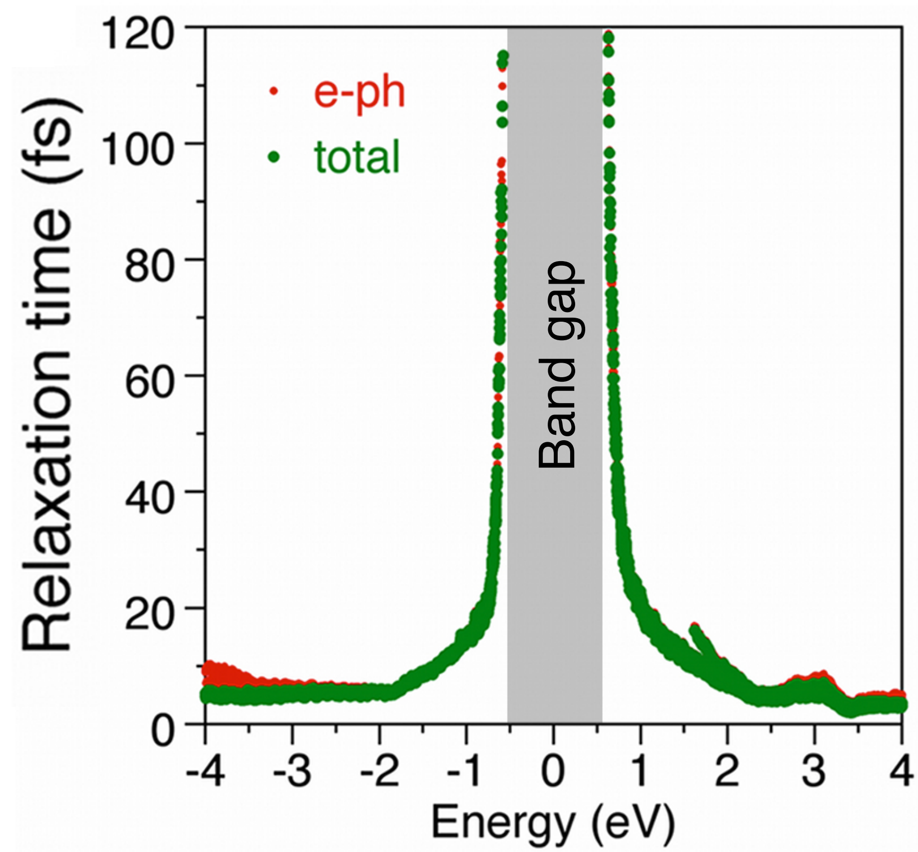
Absorption loss ~20%

Thermalization loss ~25%

Understand ultrafast (sub-ps) loss of solar energy from first principles

Hot Carrier Relaxation Times in Silicon





El-ph scattering dominates thermalization

El-ph scattering rate ~ electronic DOS

Fast relaxation away from band edge: ~10 fs

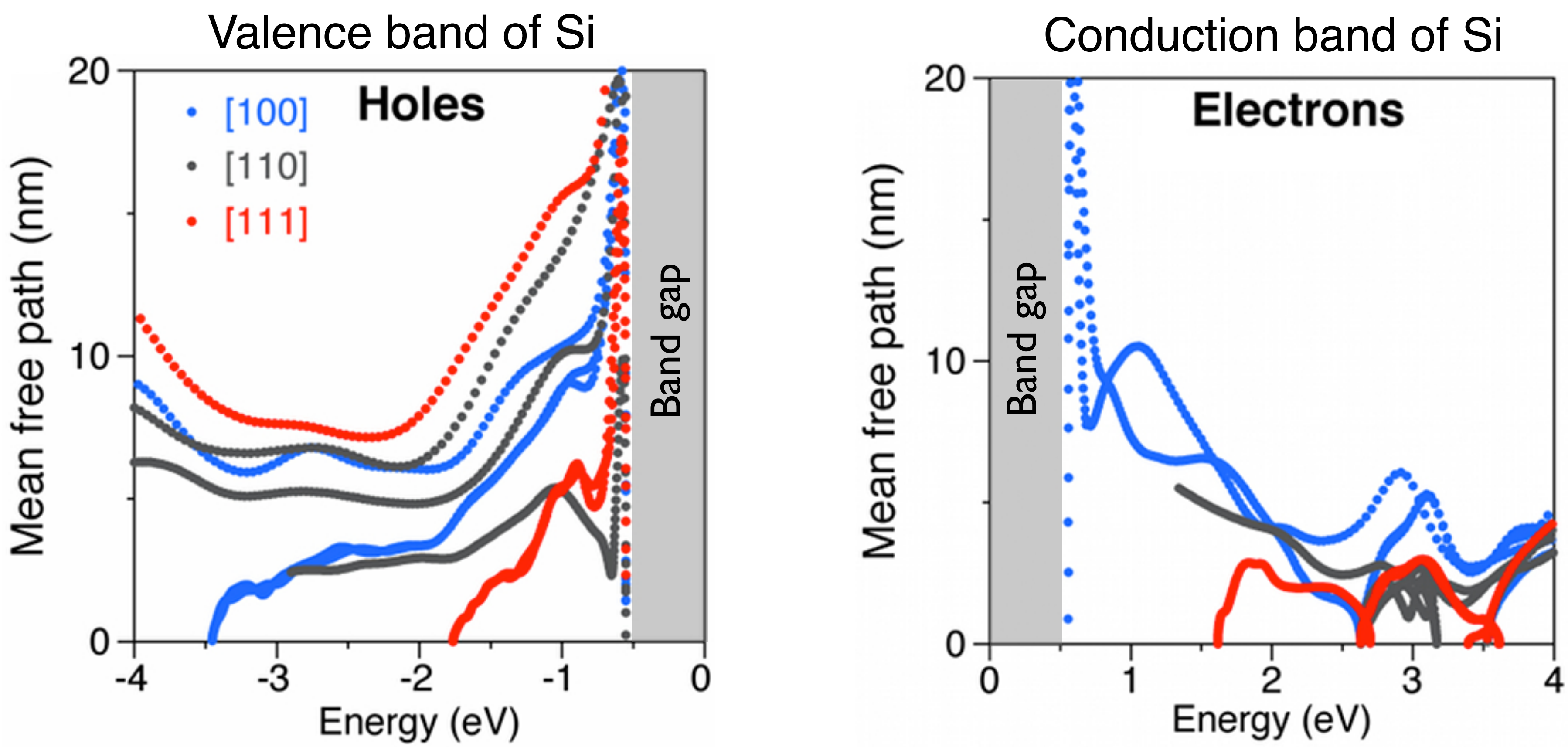
Slower relaxation near the band edge: >100 fs

M. Bernardi et al., Phys. Rev. Lett. 112, 257402 (2014)

Mean Free Paths

Distance hot carriers can travel before emitting a phonon

Mean free path: $L_{n,\vec{k}} = v_{n,\vec{k}} \cdot \tau_{n\vec{k}}$



Mean free path ~ 5–10 nm in Si

[100] direction favorable for hot electron extraction

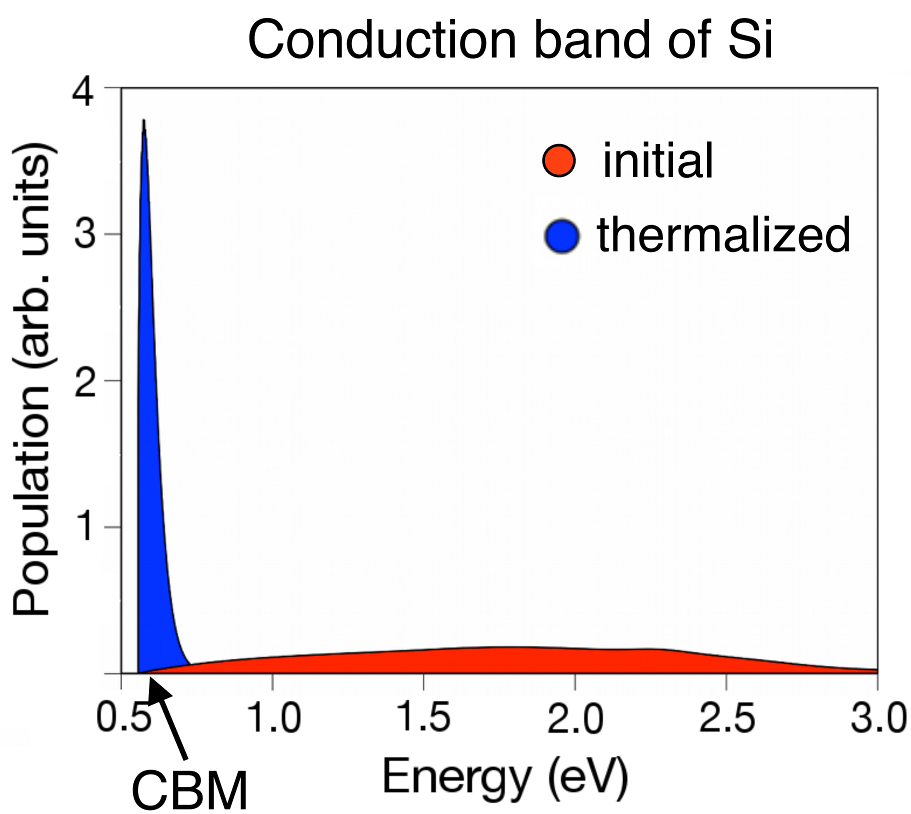
M. Bernardi *et al.*, *Phys. Rev. Lett.* 112, 257402 (2014)

The First Picosecond after Sunlight Absorption in Silicon

Initial population at t=0 under AM1.5 solar illumination

$$f(E,t=0) \propto \int_0^{4\ \mathrm{eV}} d\omega\, \underbrace{D(E-\omega)}_{\text{Electron DOS}} \cdot \underbrace{J_{ph}(\omega)}_{\text{AM1.5 photon flux}} \cdot \underbrace{\alpha(\omega)}_{\text{Experimental absorption}}$$

Thermalized population at t ≈1 ps: Fermi-Dirac at T=300K (~10^{17} cm^{-3} carriers)



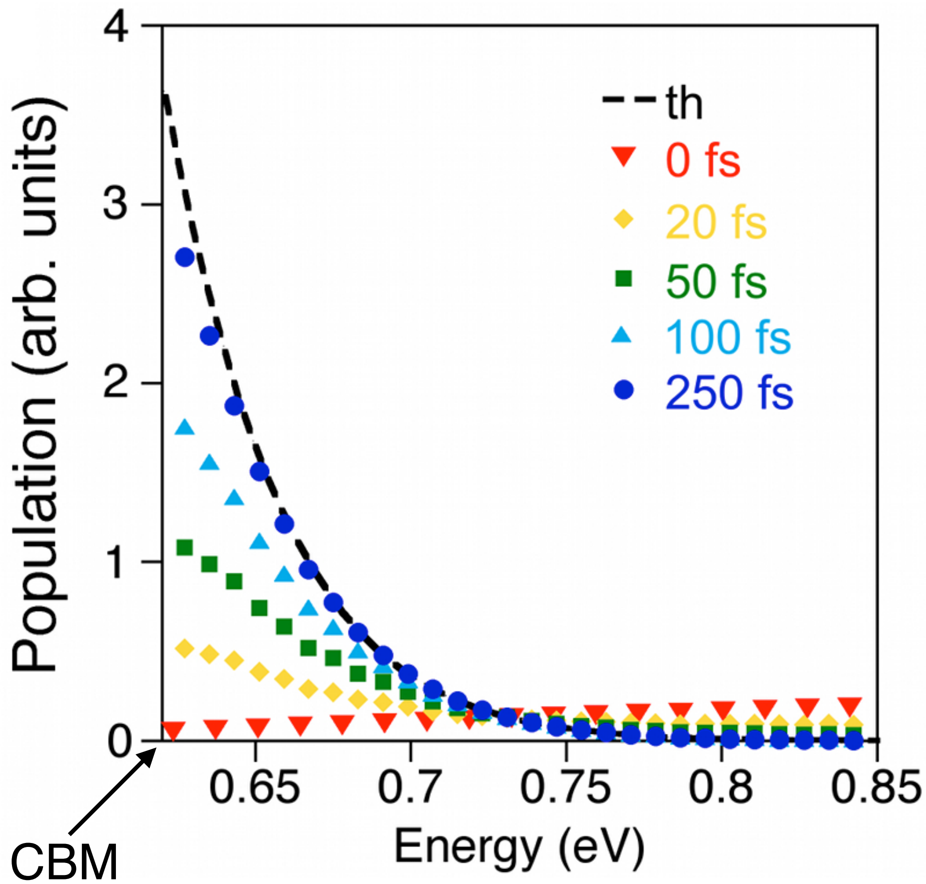
Carrier Dynamics

Boltzmann equation for carrier in state *n*,**k**

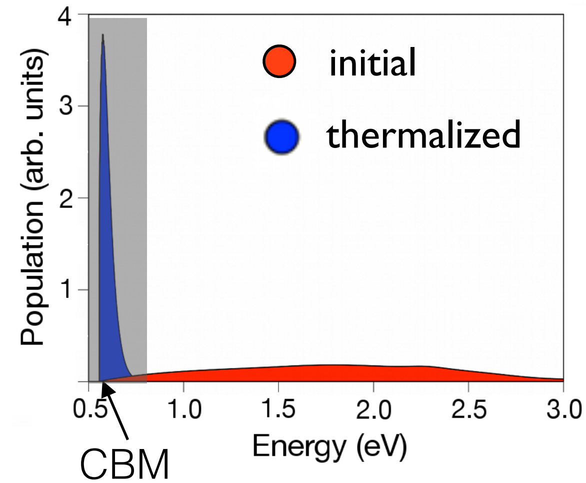
$$\frac{df_{n,\mathbf{k}}(t)}{dt} = -\frac{f_{n,\mathbf{k}}(t) - f_{n,\mathbf{k}}(t_{th})}{\tau_{n,\mathbf{k}}}$$

The First Picosecond after Sunlight Absorption in Silicon

Hot electron thermalization near the conduction band minimum (CBM)



Conduction band of Si



Excellent agreement with pump-probe experiments

Experiment: thermalization in ~250–300 fs near CBM

Model hot carriers and ultrafast spectroscopy

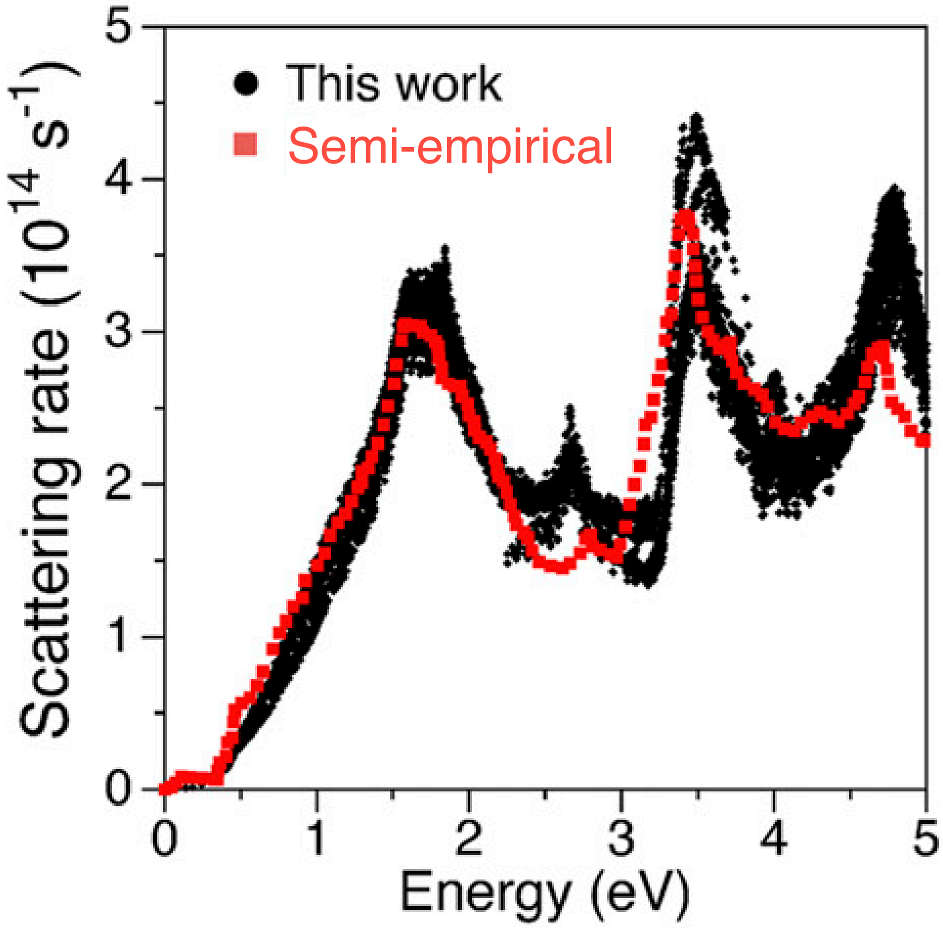
M. Bernardi *et al.*, *Phys. Rev. Lett.* 112, 257402 (2014)

Hot Electrons in GaAs

Ab initio phonon and bandstructure calculations

Compute ~50 trillion el-ph matrix elements

No adjustable parameters in the calculation

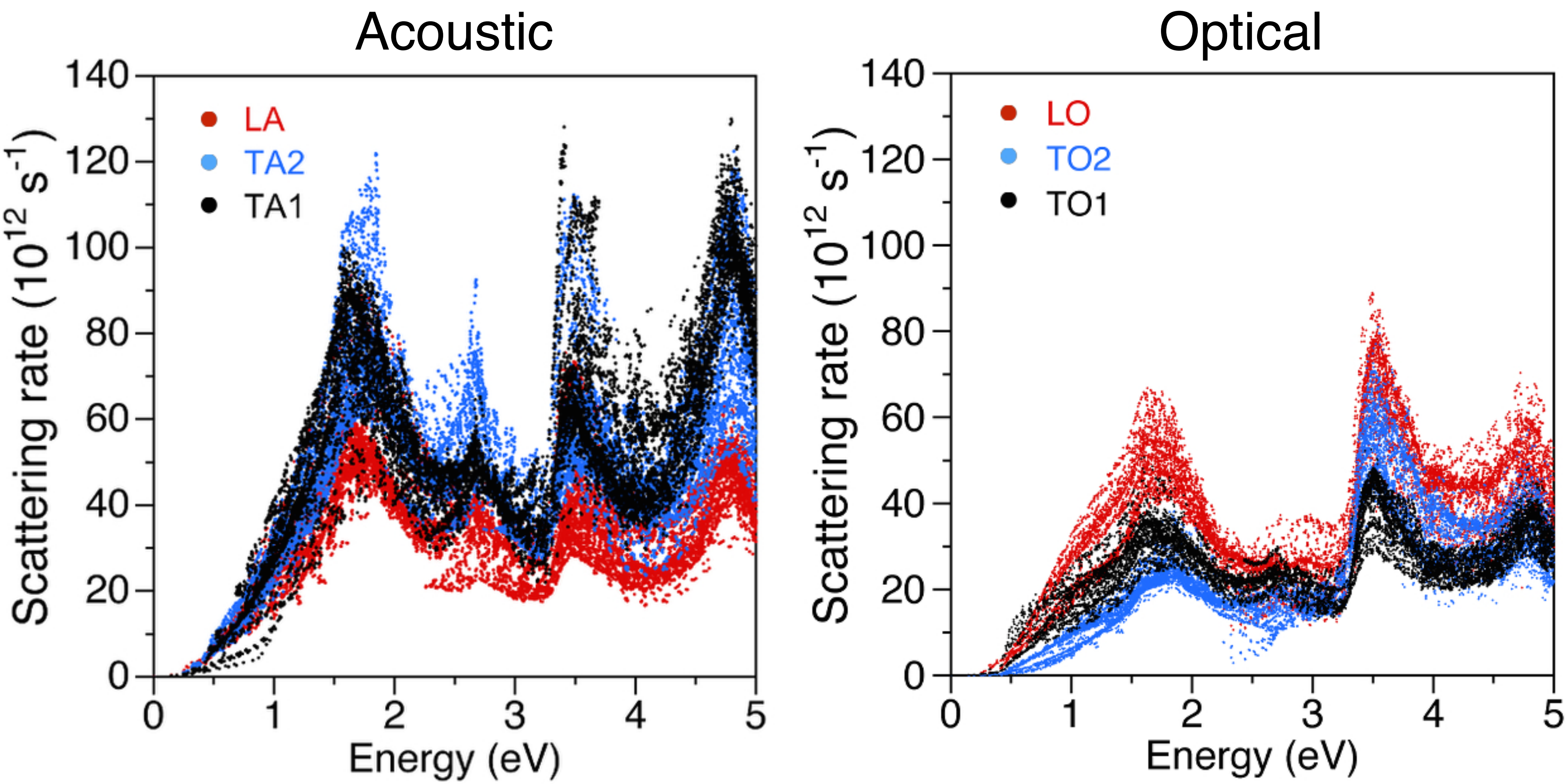


M. Fischetti, et al. Phys. Rev. B 38, 9721 (1988)

Multiple parameters for el-ph coupling (deformation potentials)

M. Bernardi et al., *PNAS* 112, 5291(2015)

GaAs – Mode Contributions



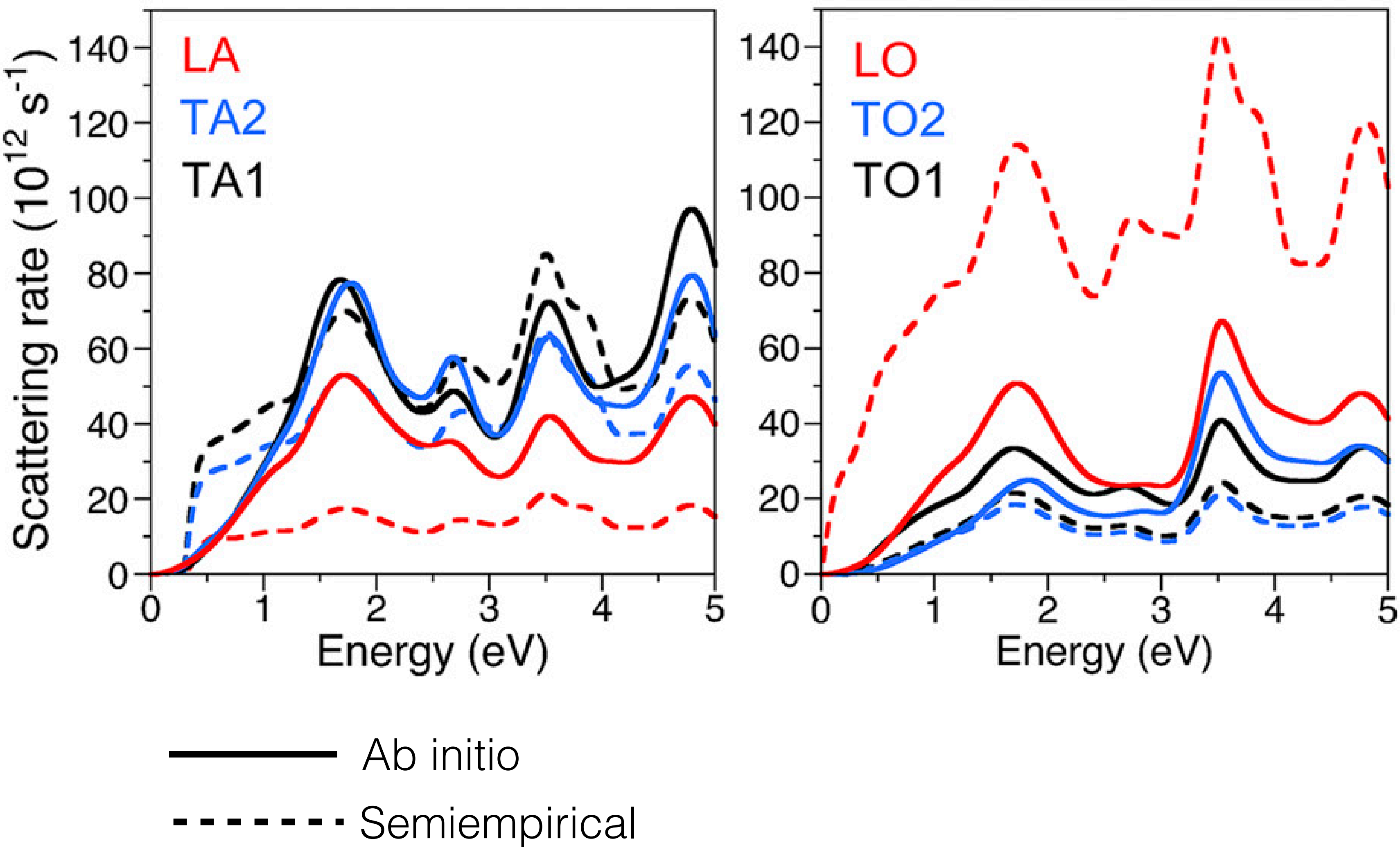
Acoustic modes dominate hot electron scattering (not LO!)

LO strongest among optical modes

M. Bernardi et al., *PNAS* 112, 5291(2015)

GaAs – Mode Contributions Comparison

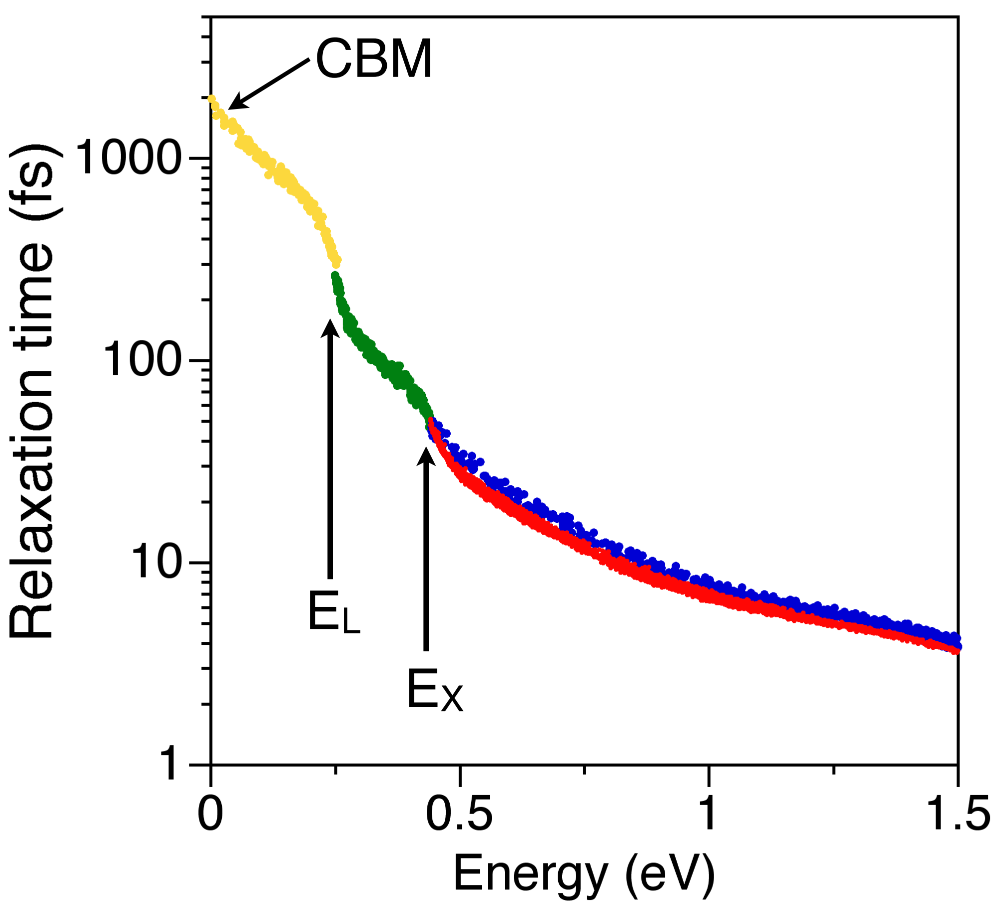
Where did the “old” (semiempirical) calculations go wrong?



M. Bernardi et al., *PNAS* 112, 5291(2015)

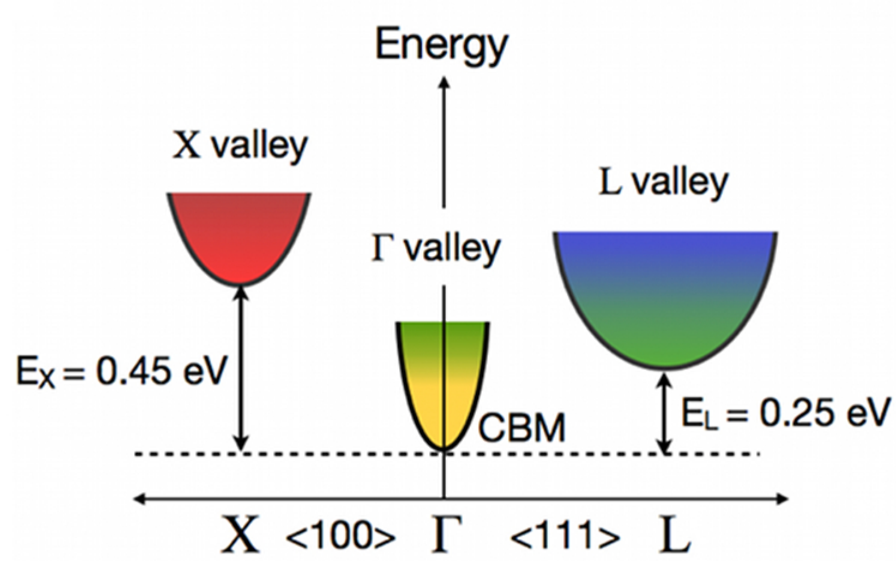
Hot Electron Thermalization in GaAs

Conduction band of GaAs



Experiment: pump with 2 eV light yields three time decay signals: ~40 fs, ~200 fs, 1.5 ps

Young, et al. *Phys. Rev. B* **50**, 2208 (1994)



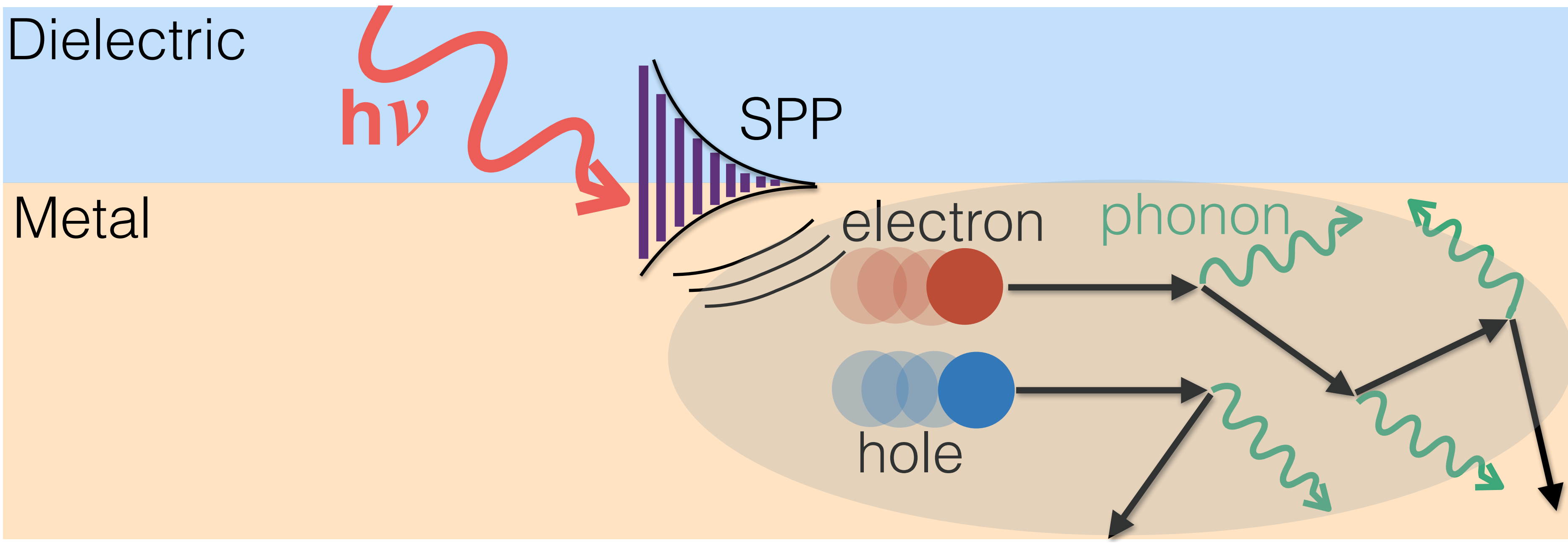
Each valley sampled with 200^3 k-grid

Excellent agreement with pump-probe experiments

Help resolve a long-standing controversy on HCs in GaAs

M. Bernardi et al., *PNAS* 112, 5291(2015)

Surface Plasmon Polariton (SPP)-to-Hot Carrier Conversion in Noble Metals



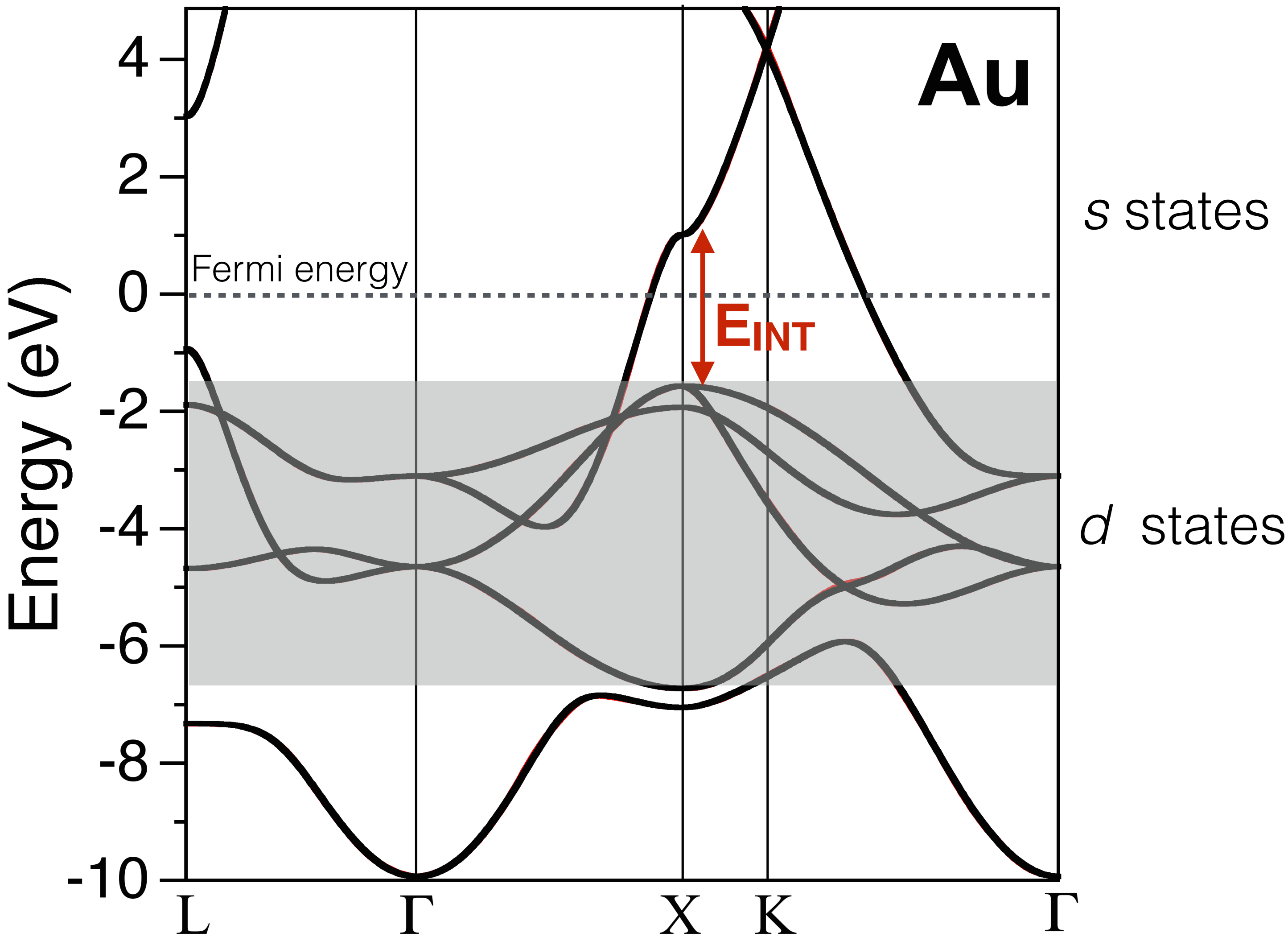
M. Bernardi et al., Nature Communications 6, 7044 (2015)

1) Hot carrier generation and energy distribution in Au & Ag

2) Ultrafast hot carrier transport – mean free path, relaxation time

3) Ideal regime to extract hot carriers

Noble Metals Bandstructure



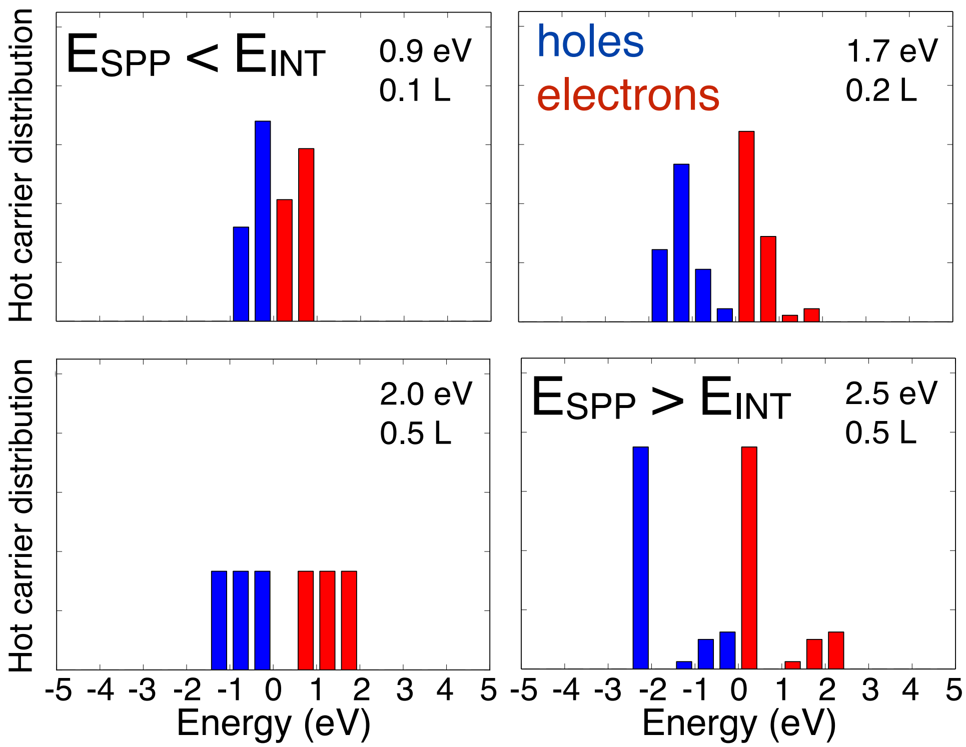
The relative energies of *d* and *s* states are crucial

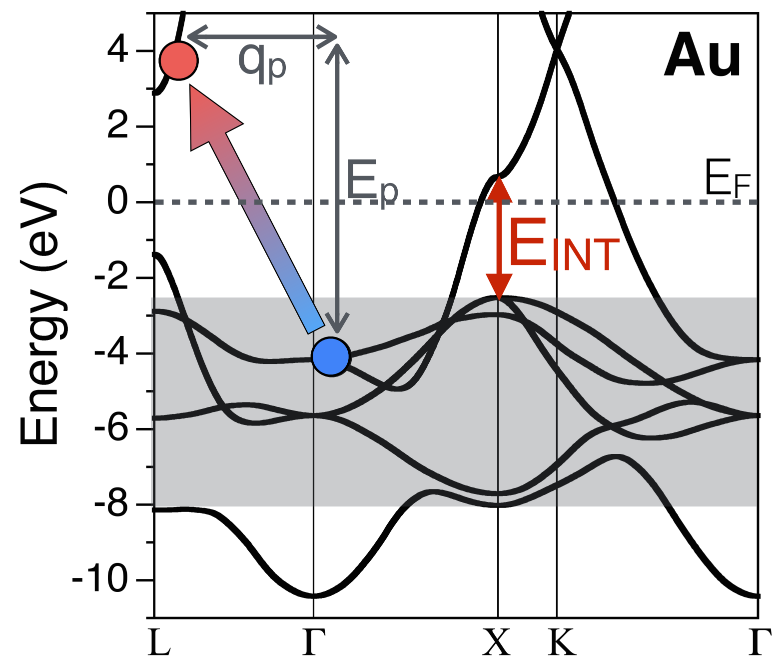
in the generation and transport of hot carriers (need GW)

Hot Carrier Generation

Energy and momentum conserving transitions generate hot carriers with a distribution of energies (in a probabilistic sense)

Hot carrier population distribution (arb. units) vs. Energy

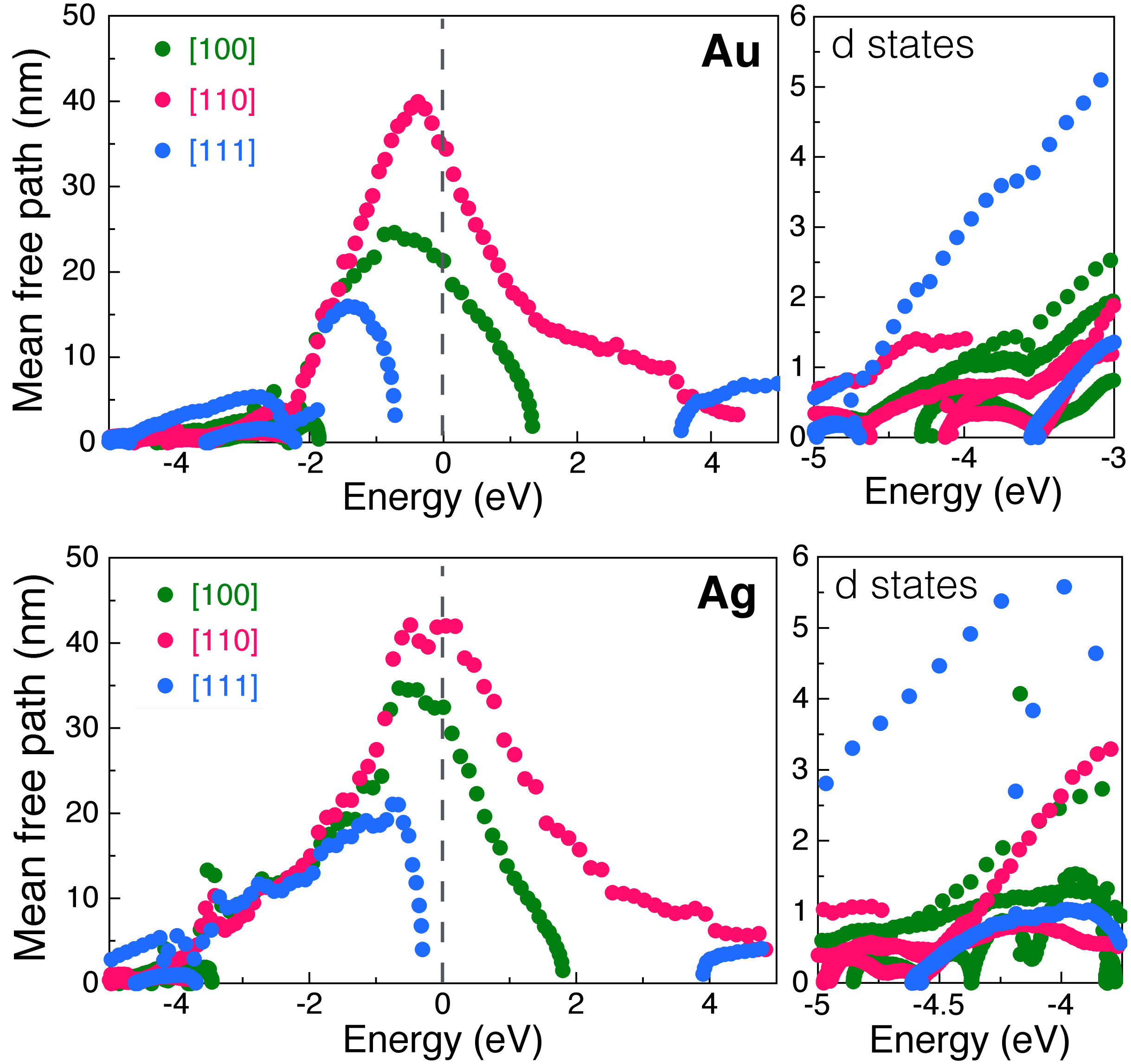




Similar population distributions for Ag

M. Bernardi et al., Nature Communications 6, 7044 (2015)

Hot Carrier Mean Free Path



Volcano shape due to strong scattering at E>2 eV away from Fermi energy

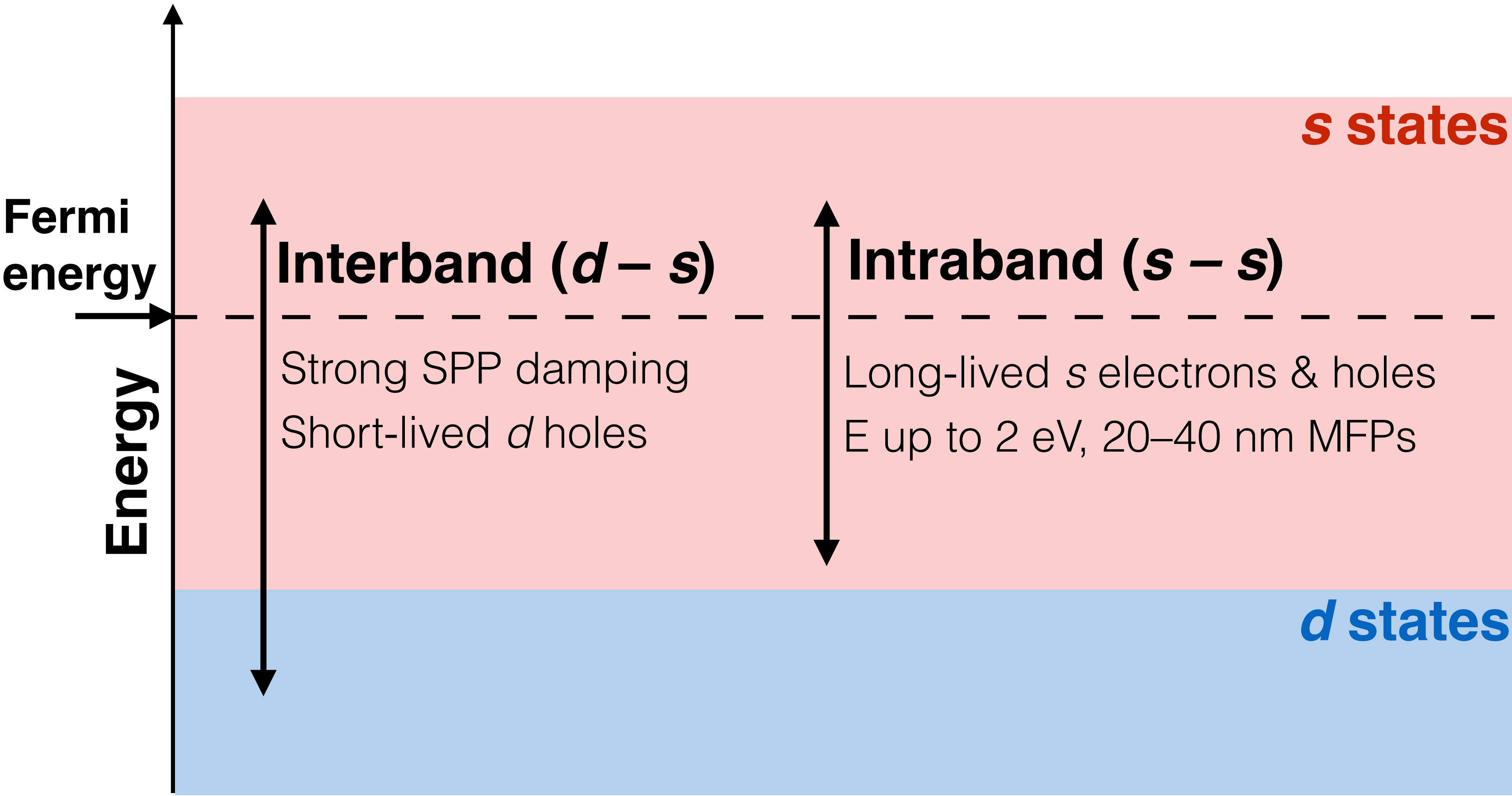
s holes ~isotropic, *s* electrons and *d* holes anisotropic, consistent with experiments

M. Bernardi et al., Nature Communications 6, 7044 (2015)

Optimization of Hot Carrier Extraction

Two regimes for SPP-to-hot carrier conversion: intraband vs. interband

SPP with $E < E_{INT}$ can be tuned to generate HCs with ~2 eV energy & 20-40 nm MFPs

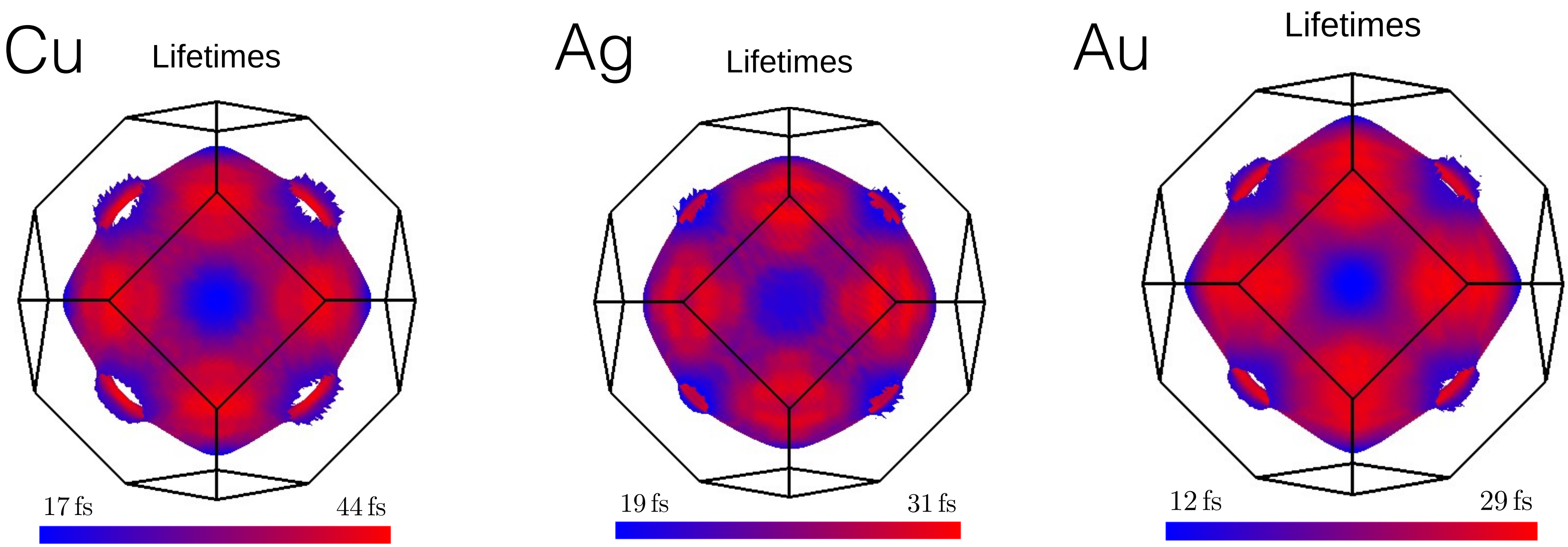


Silver may be better than gold for hot carriers from SPPs

M. Bernardi et al., Nature Communications 6, 7044 (2015)

Application to Carrier Transport

"… The conduction electrons are a nuisance in metals" J. M. Ziman, 1964



Conductivity $\sigma_{i,j} = e^2 \sum_{n,\mathbf{k}} \tau_{n,\mathbf{k}} v_{n,\mathbf{k},\mathbf{i}} v_{n,\mathbf{k},\mathbf{j}} \left(-\partial f / \partial E\right)$

Can predict resistivity within 10% of experiment

Can be applied to metals, semiconductors, insulators

Jamal Mustafa, M. Bernardi, S.G. Louie (to be submitted)

Summary

Carrier dynamics and scattering by electrons and phonons

Design hot carrier devices and experiments

Microscopic understanding of time-resolved experiments

Perturbation theory is promising for excited state timescales

Non-equilibrium theories necessary for coherent / driven dynamics

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