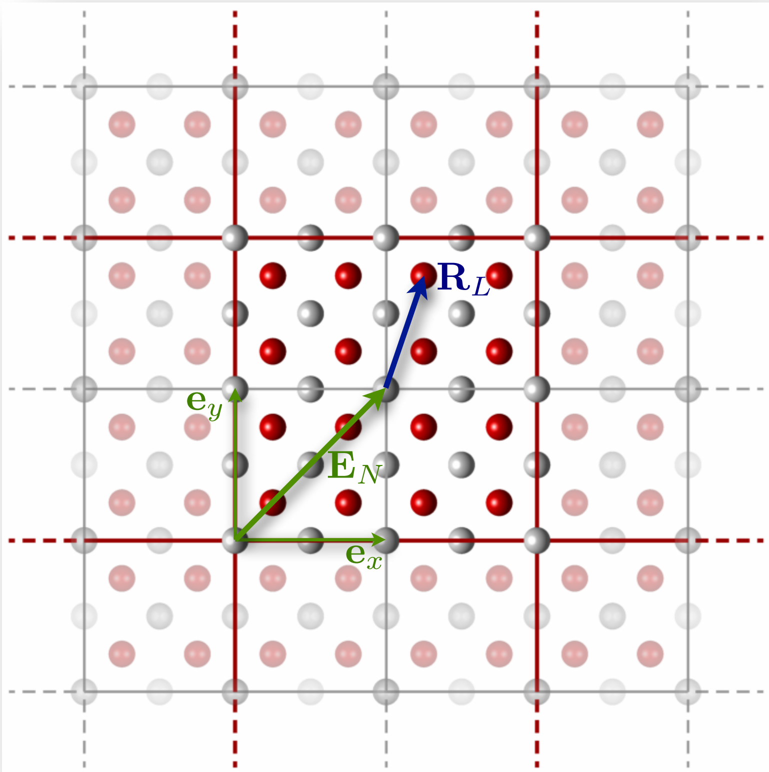
Hands-On DFT and Beyond Workshop
September 3 2019, Barcelona

Electron-Phonon Coupling and Electronic Transport in Solids from First Principles

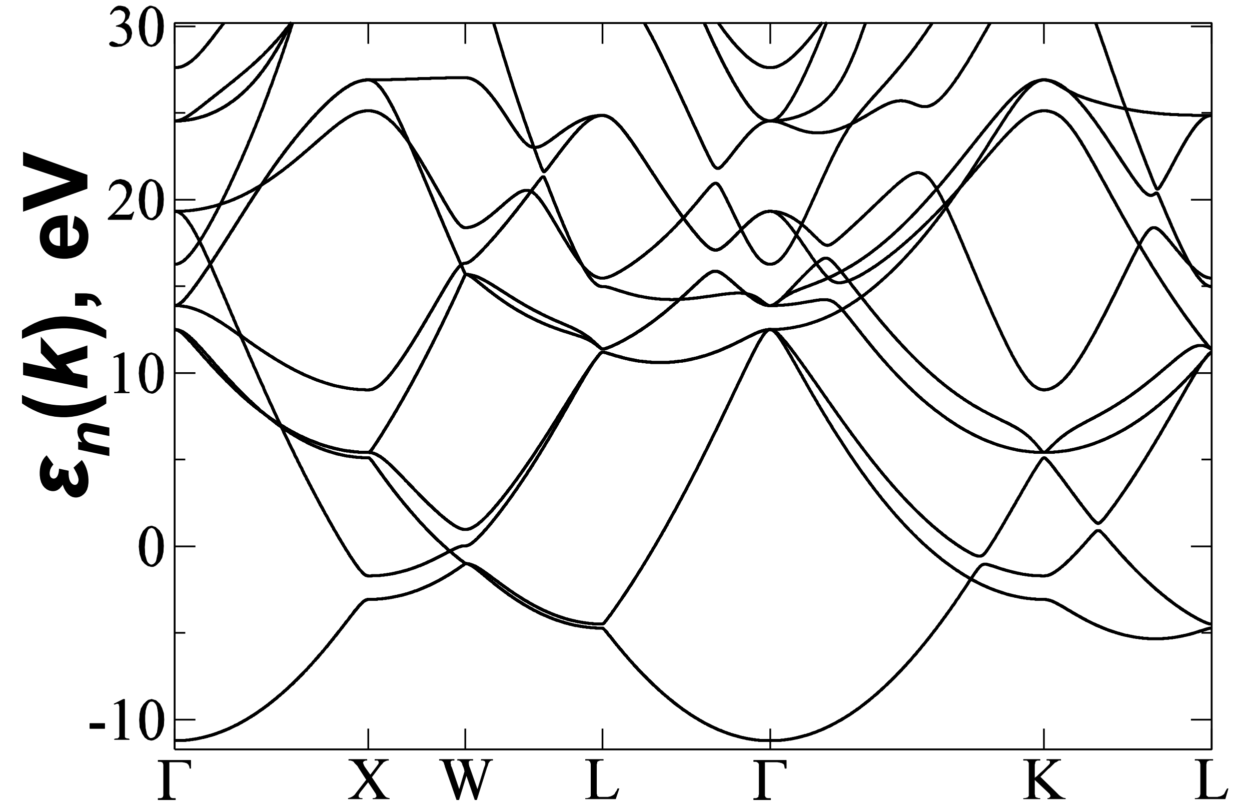
Christian Carbogno

Fritz-Haber-Institut
Max-Planck-Gesellschaft

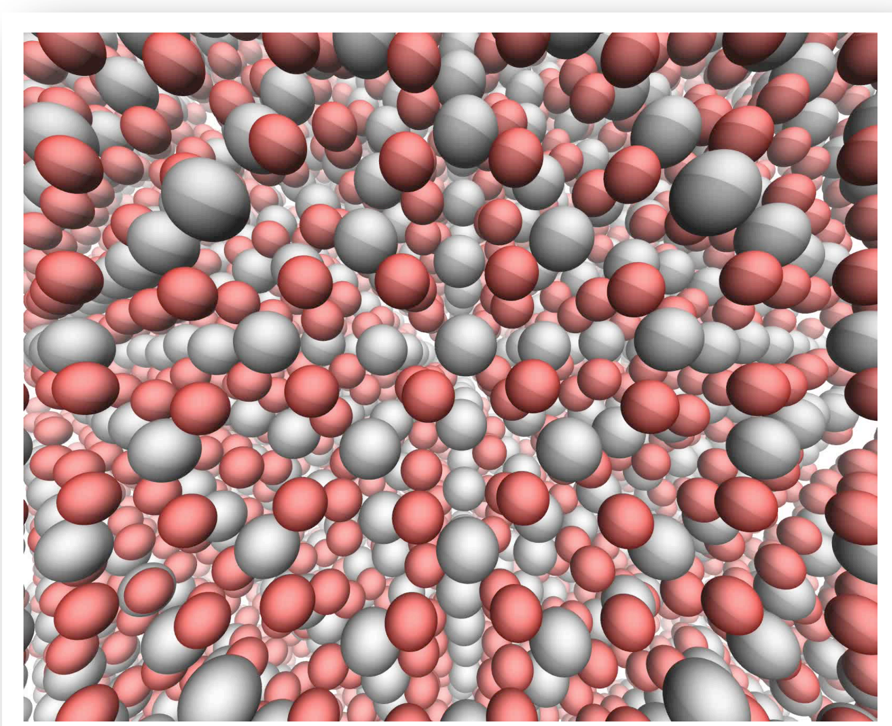
Idealized Crystal Structure



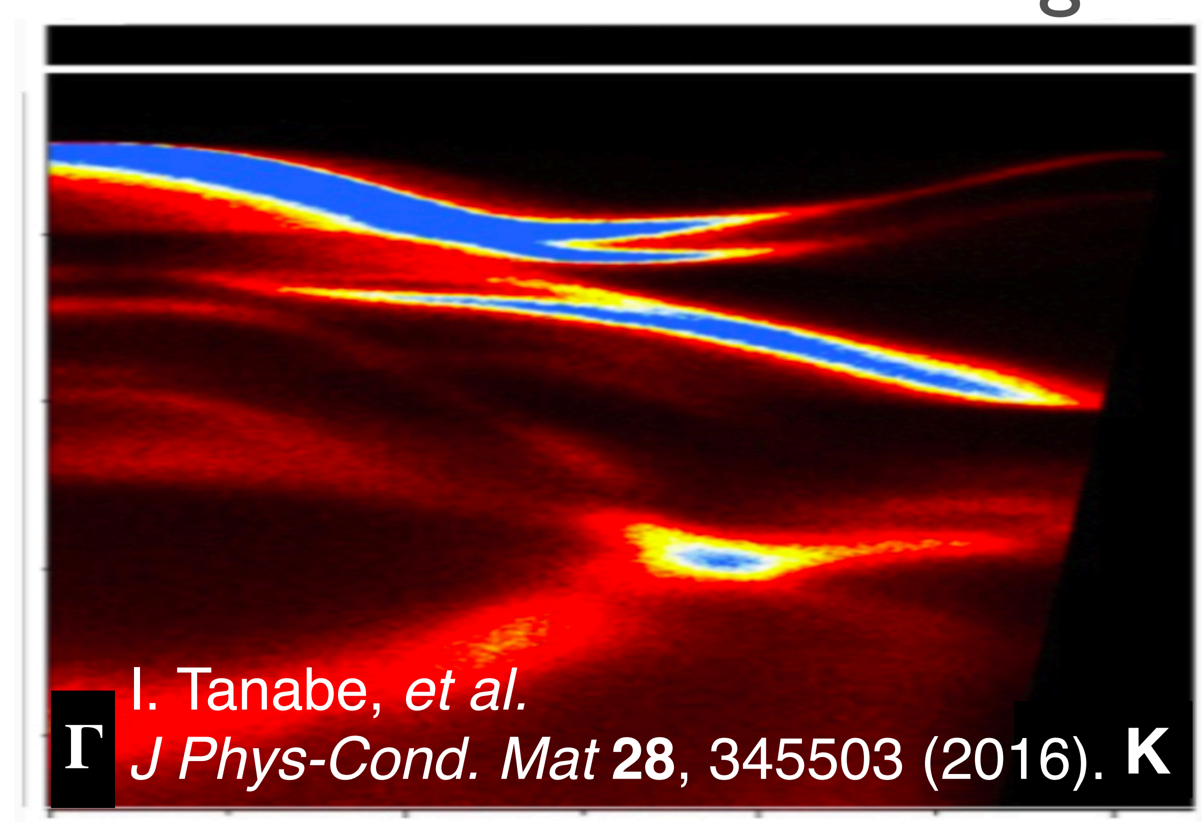
Perfectly Symmetric Band Structure



Real Materials

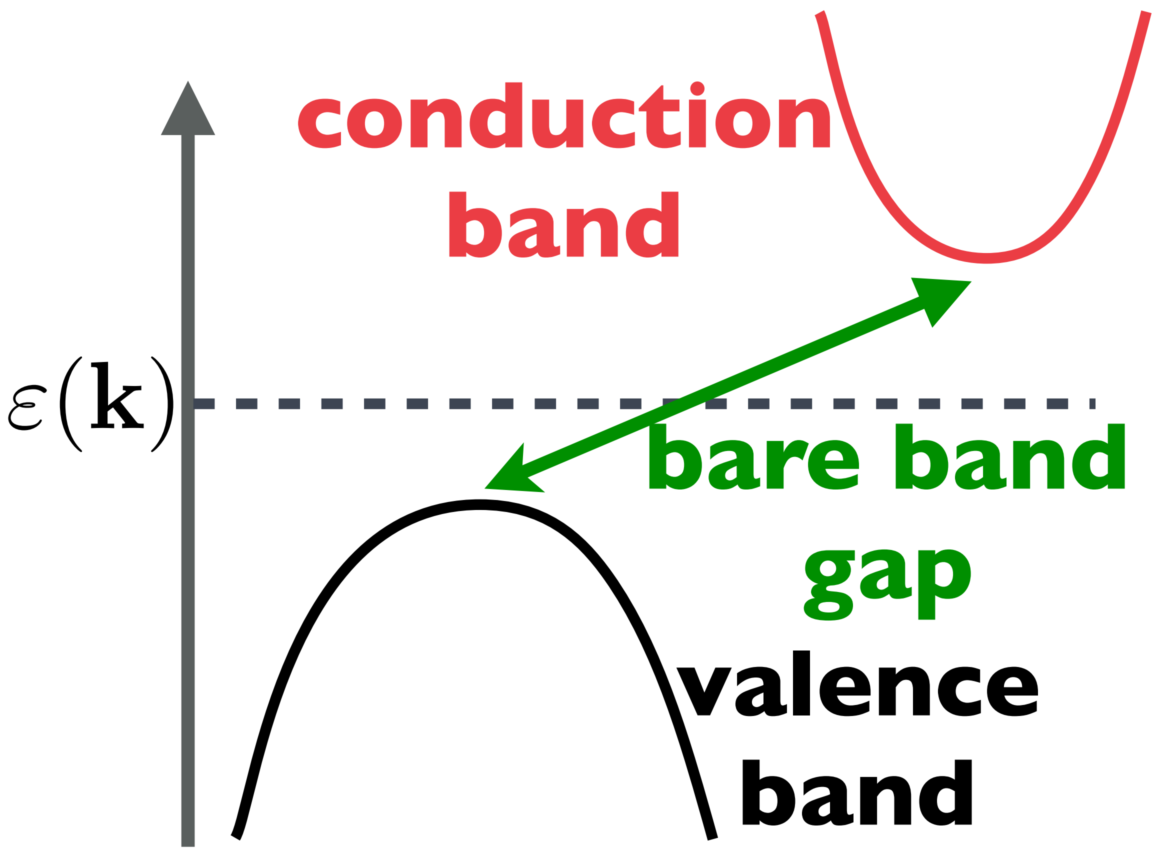


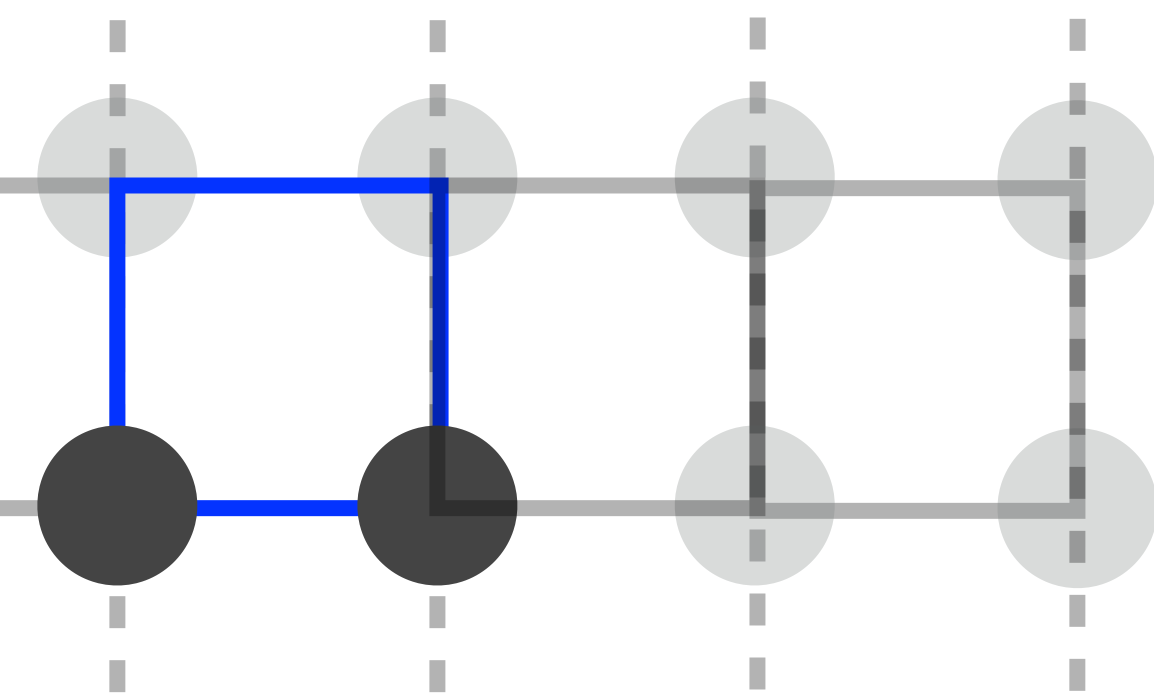
“Smeared-Out” Self-Energies



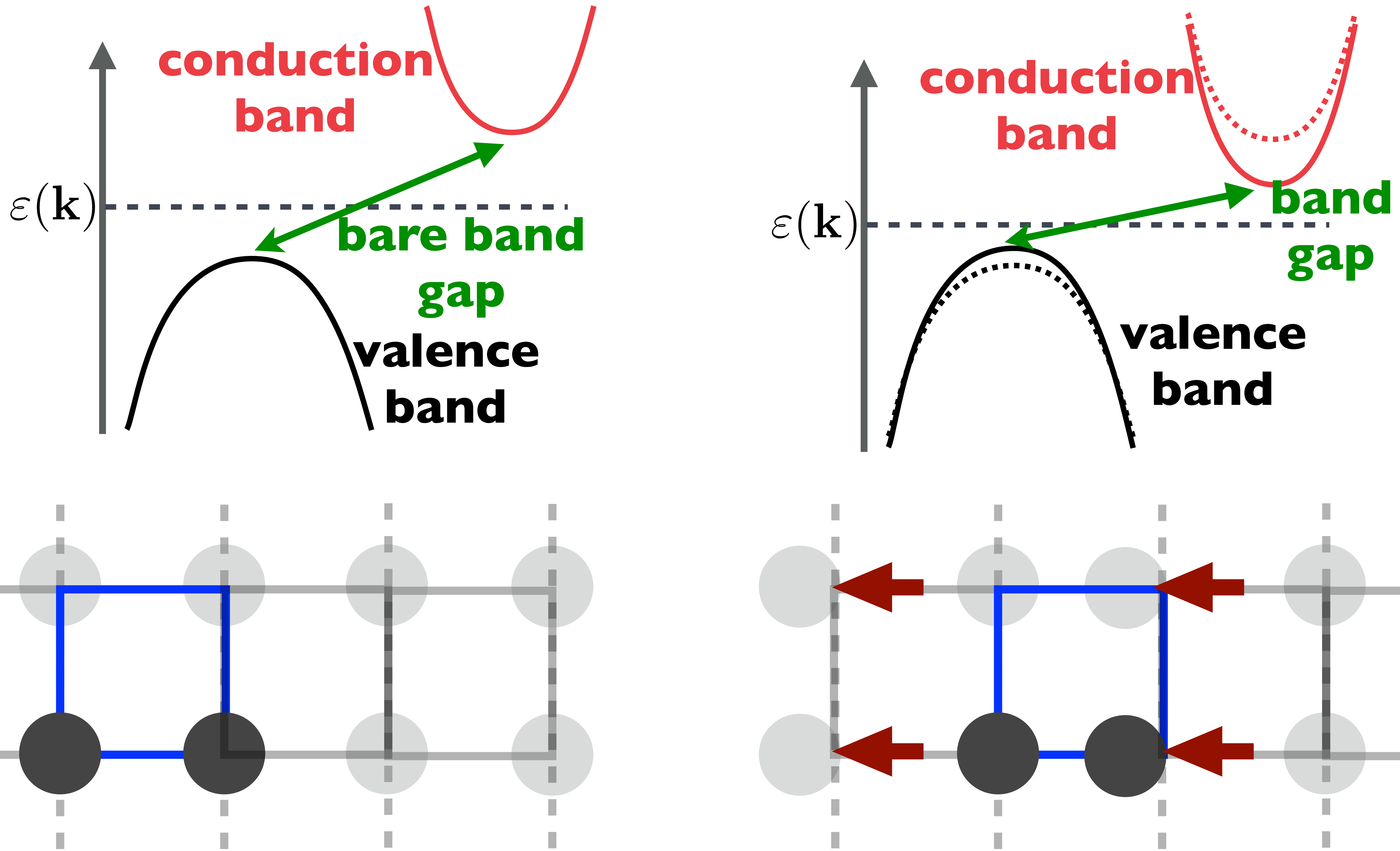
ELECTRON-PHONON COUPLING

Electron-Phonon Coupling





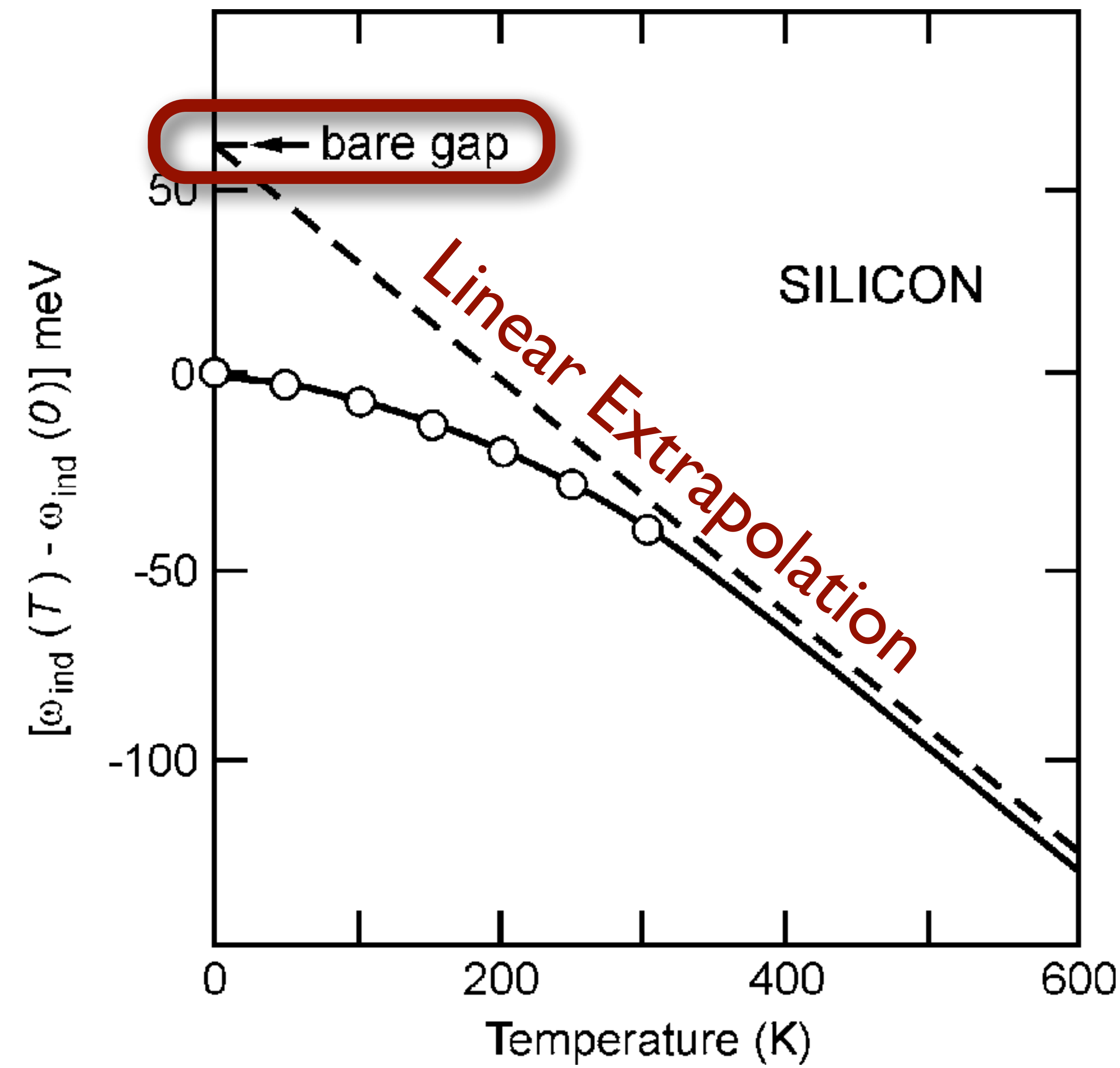
Electron-Phonon Coupling



BAND GAP RENORMALIZATION

Electronic band gaps often exhibit a distinct **temperature dependence**

Linear extrapolation yields the **bare gap at 0K**, i.e., the gap for immobile nuclei **(classical limit)**



M. Cardona,
Solid State Comm. **133**, 3 (2005).

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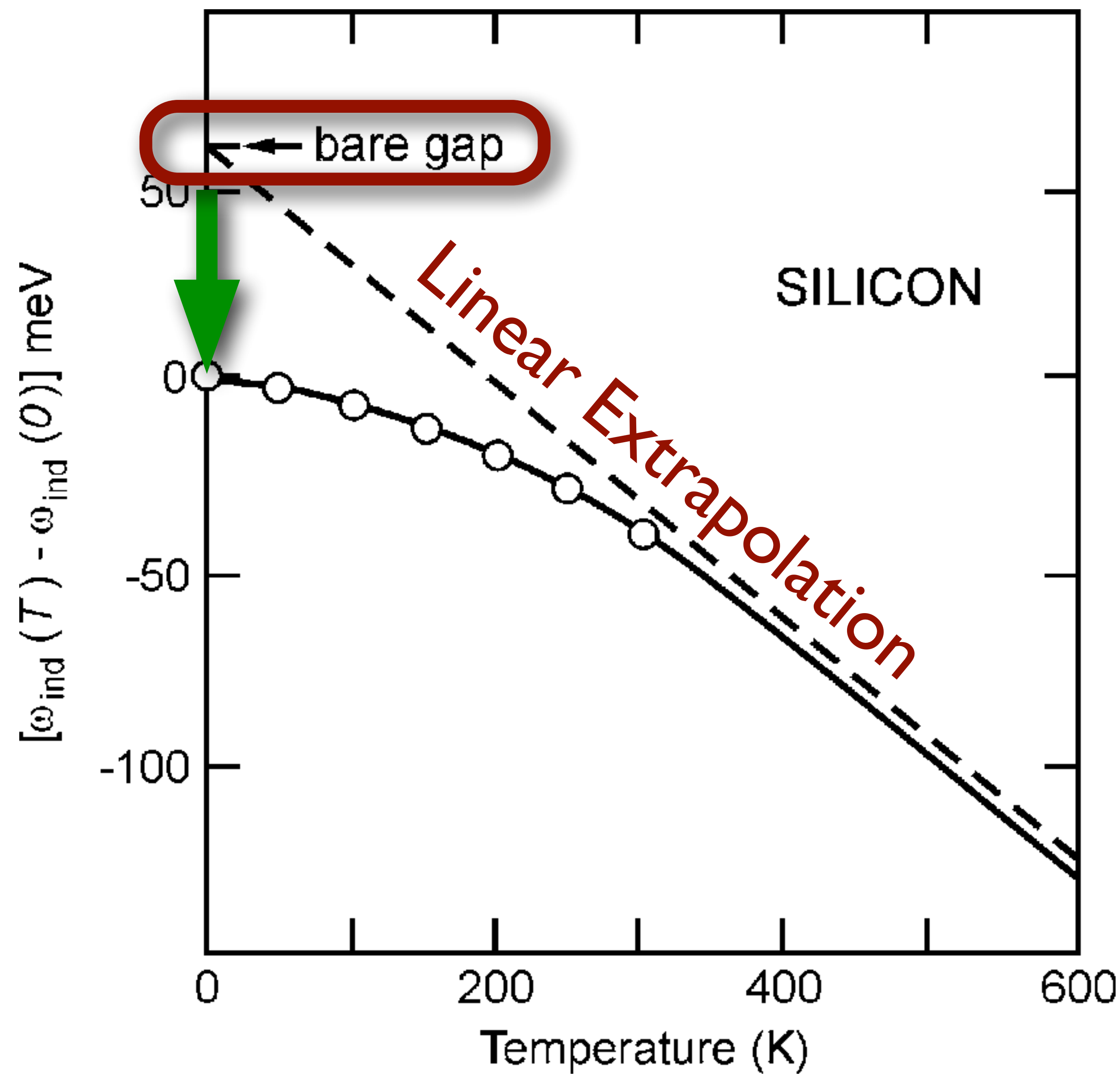
Actual band gap at 0K differs from the **bare gap**:
⇒ **Band gap renormalization**

due to 0K phonon motion



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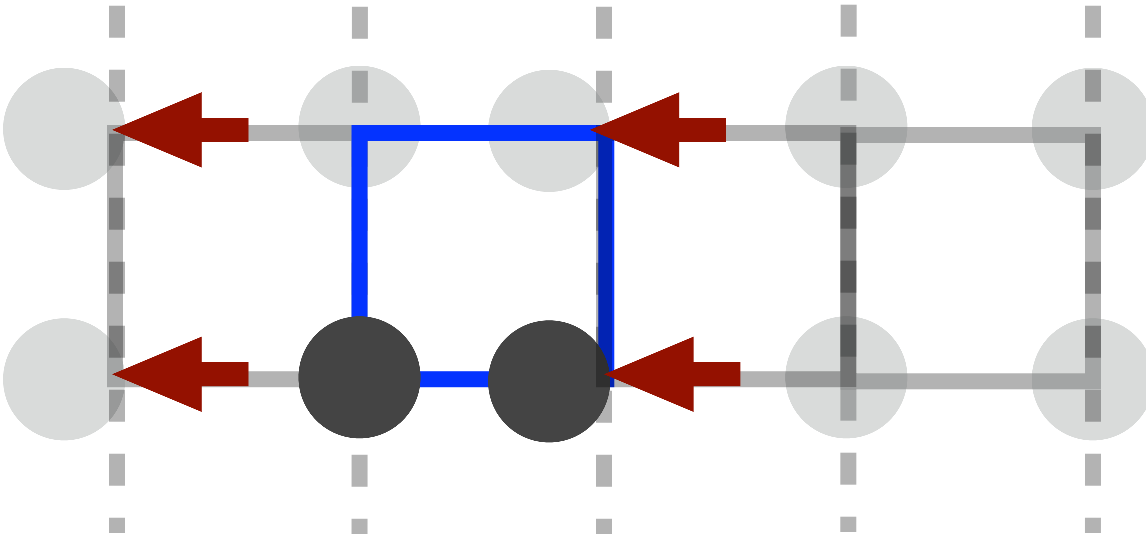
Electron-phonon interactions from first principles

F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).



Harmonic Approximation for Nuclear Motion

$$E\left(\{\Delta\mathbf{R}\}\right) \approx \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial\mathbf{R}_i\partial\mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i\Delta\mathbf{R}_j$$

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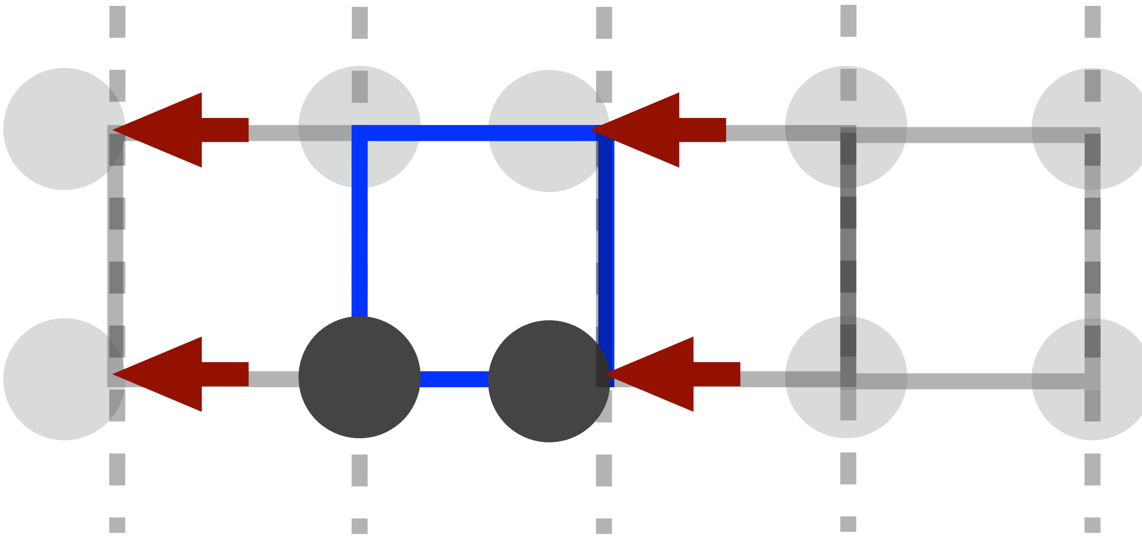

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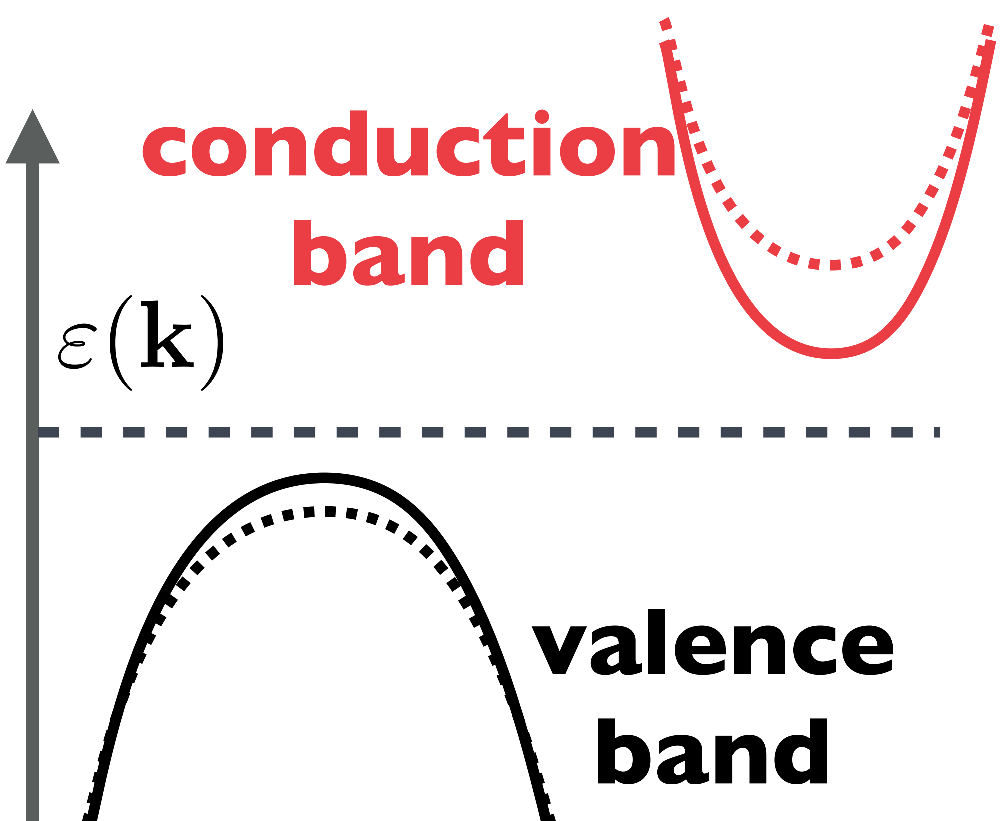
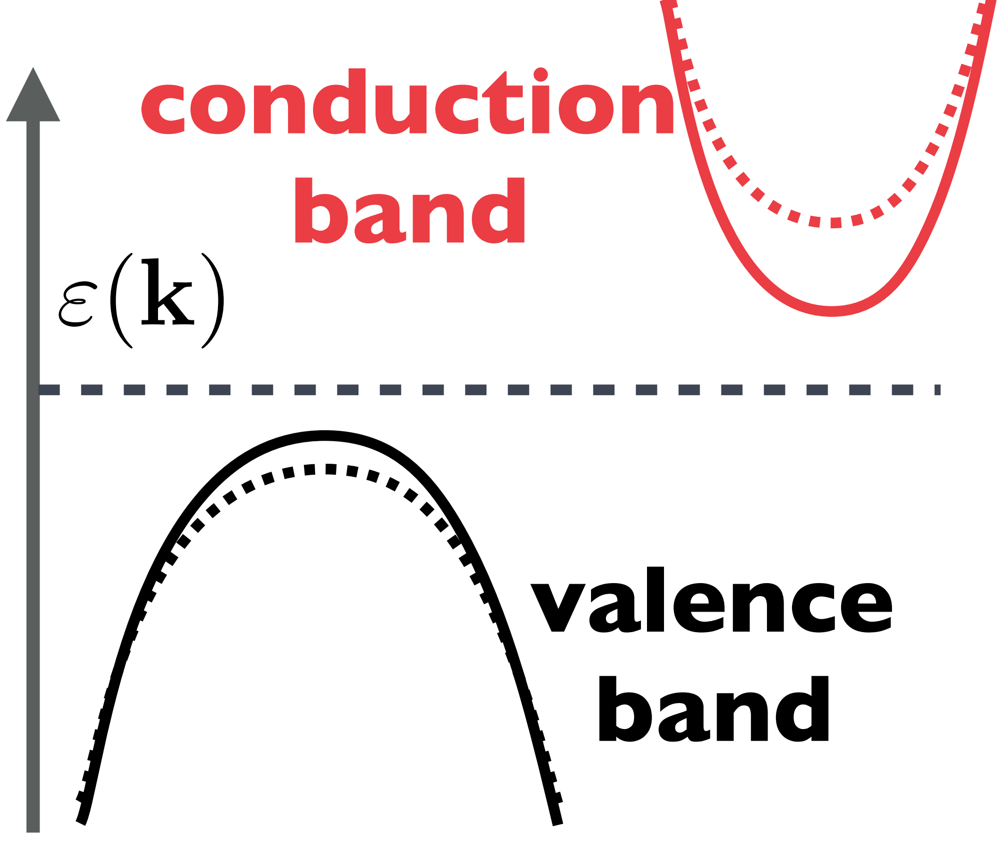


"Harmonic" Expansion for Electronic Structure

$$\varepsilon_n(\mathbf{k})\left(\{\Delta\mathbf{R}\}\right) \approx \frac{1}{2}\sum_{i,j}\left.\frac{\partial^2 \varepsilon_n(\mathbf{k})}{\partial\mathbf{R}_i\partial\mathbf{R}_j}\right|_{\mathbf{R}_0}\Delta\mathbf{R}_i\Delta\mathbf{R}_j$$



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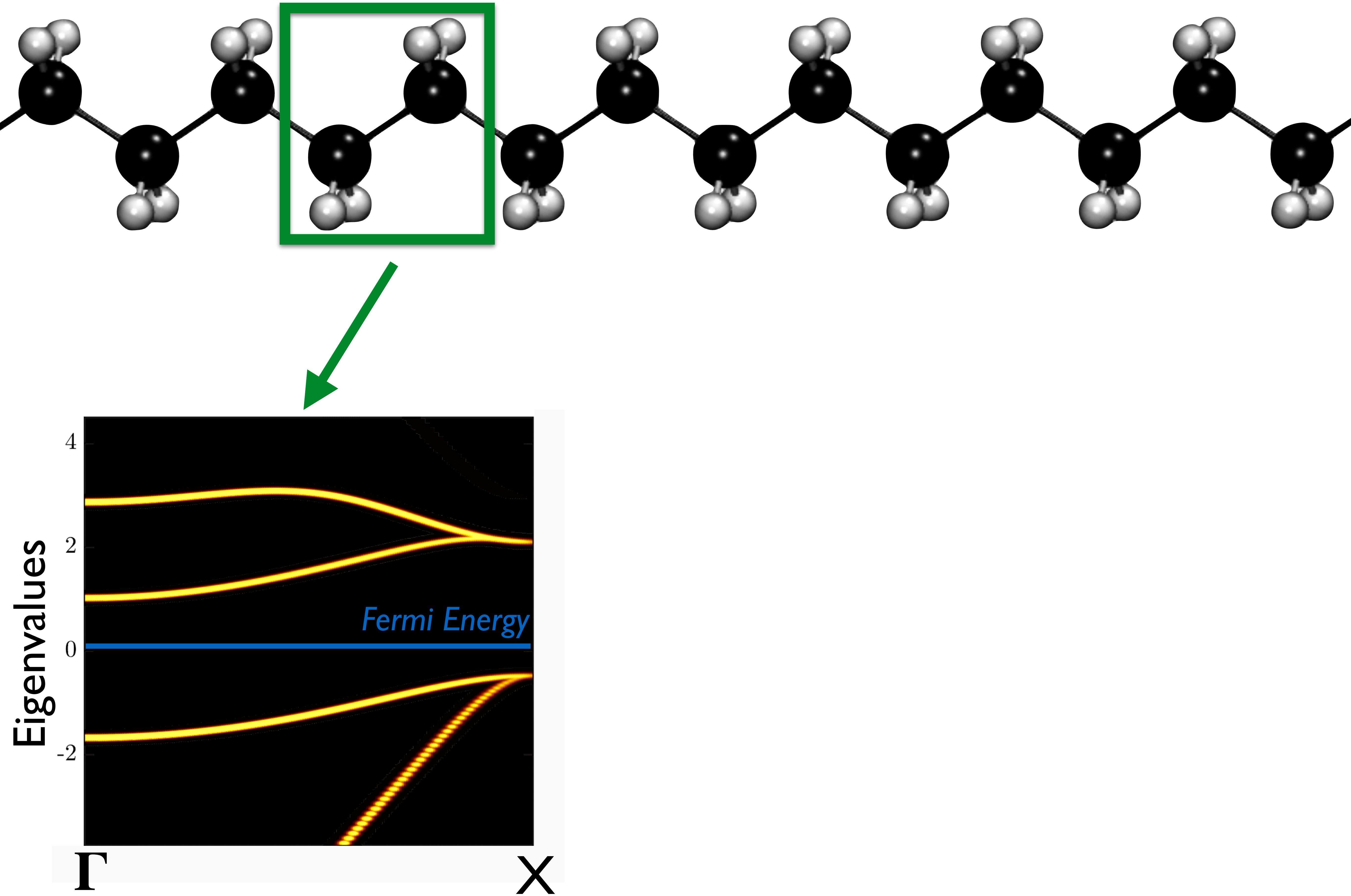
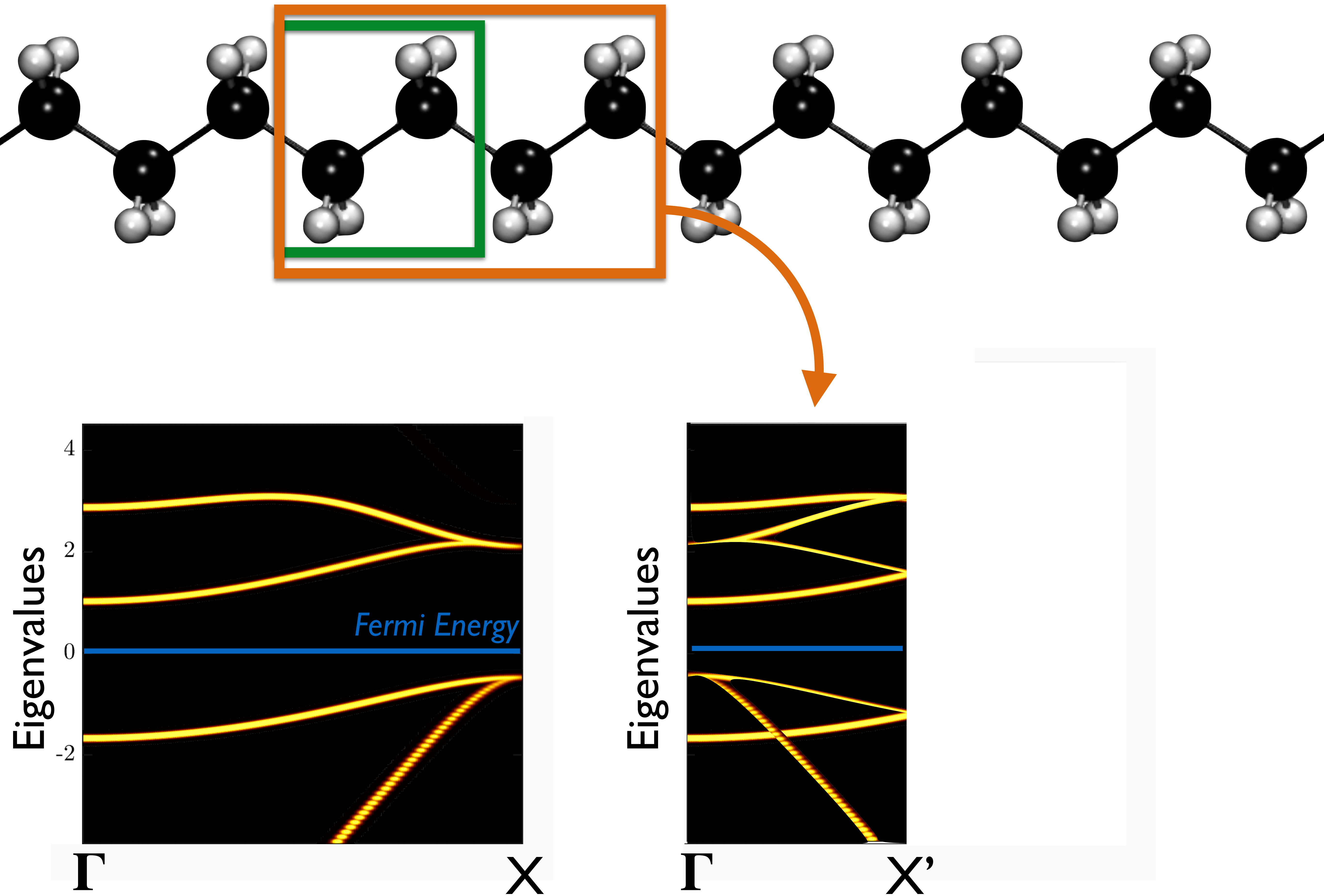
G. Antonius, *et al.*, *Phys. Rev. Lett.* **112**, 215501 (2014).

➜ Tricky in Supercells



Fermi Energy
4
2
0
-2
Eigenvalues
Γ
X



4
2
0
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Eigenvalues
Fermi Energy
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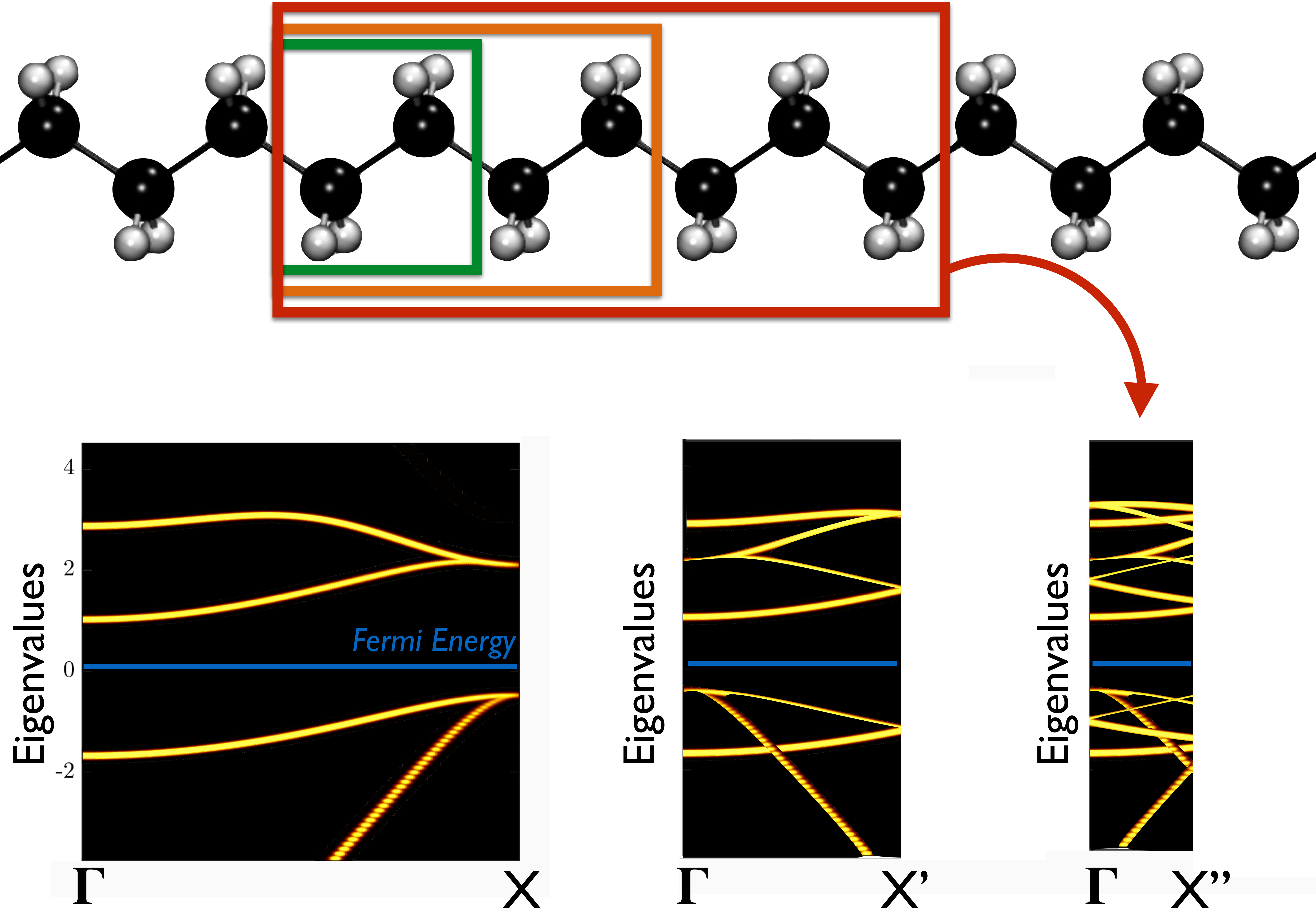
Eigenvalues
Γ
X'



4
2
0
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Eigenvalues
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Γ
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Eigenvalues
Γ
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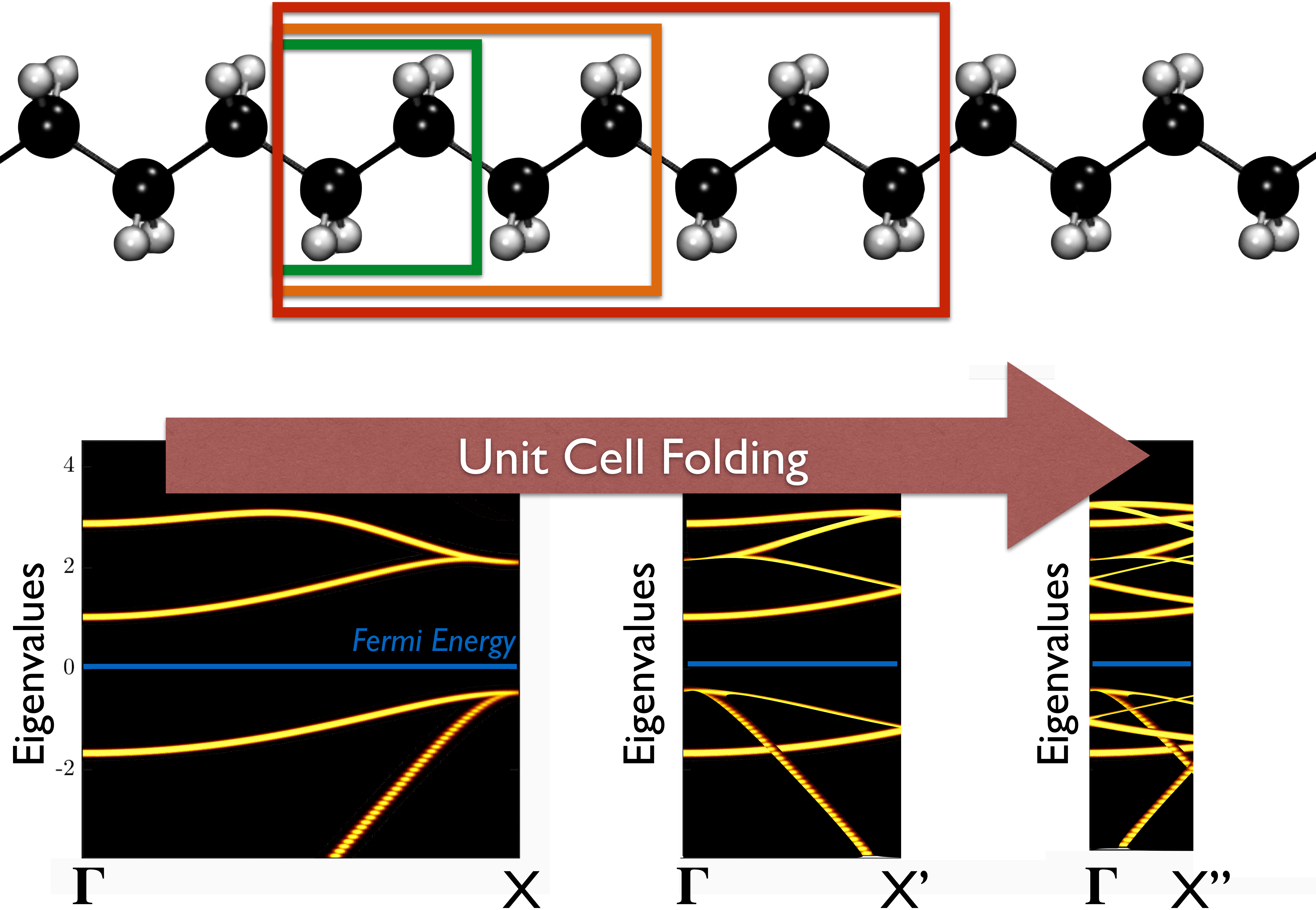
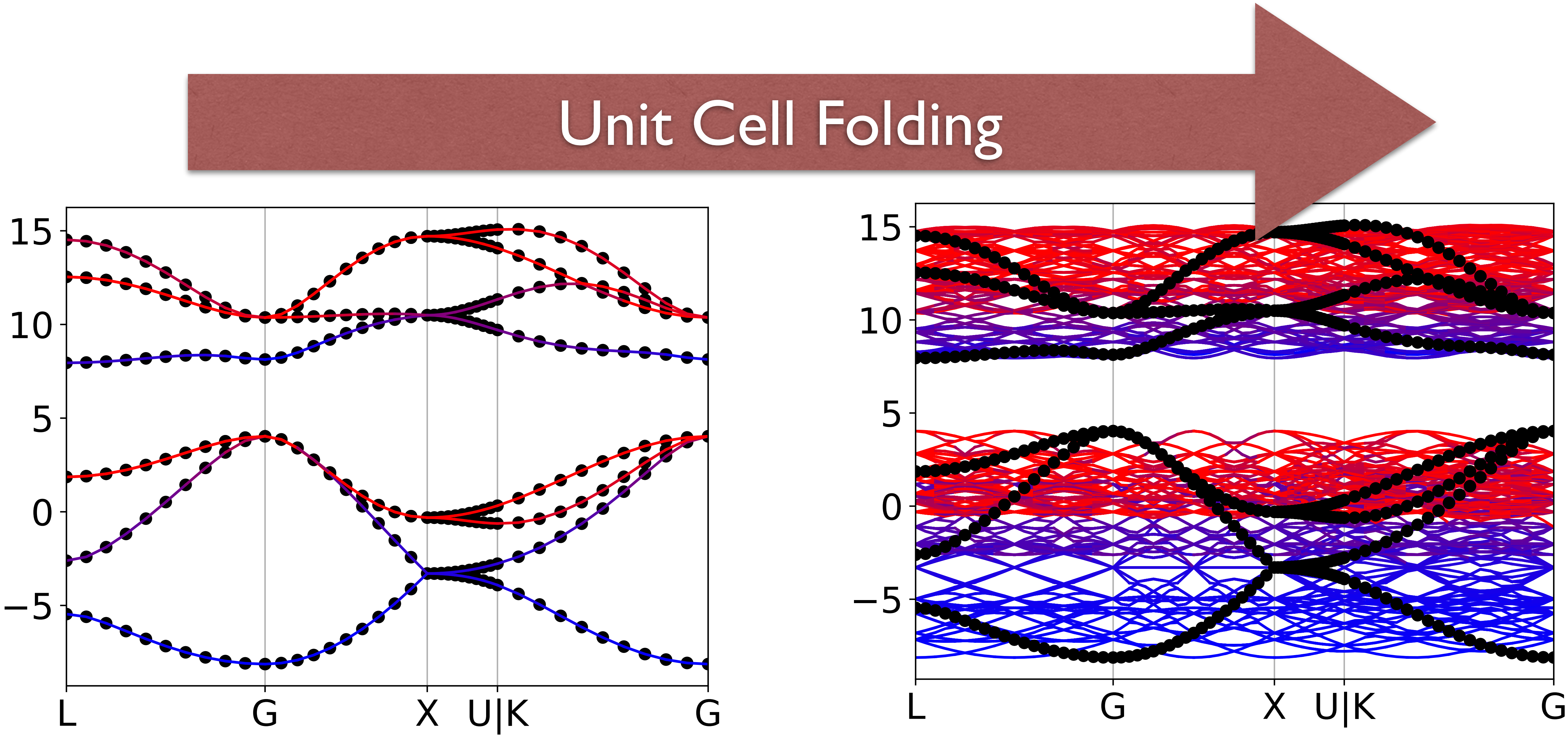
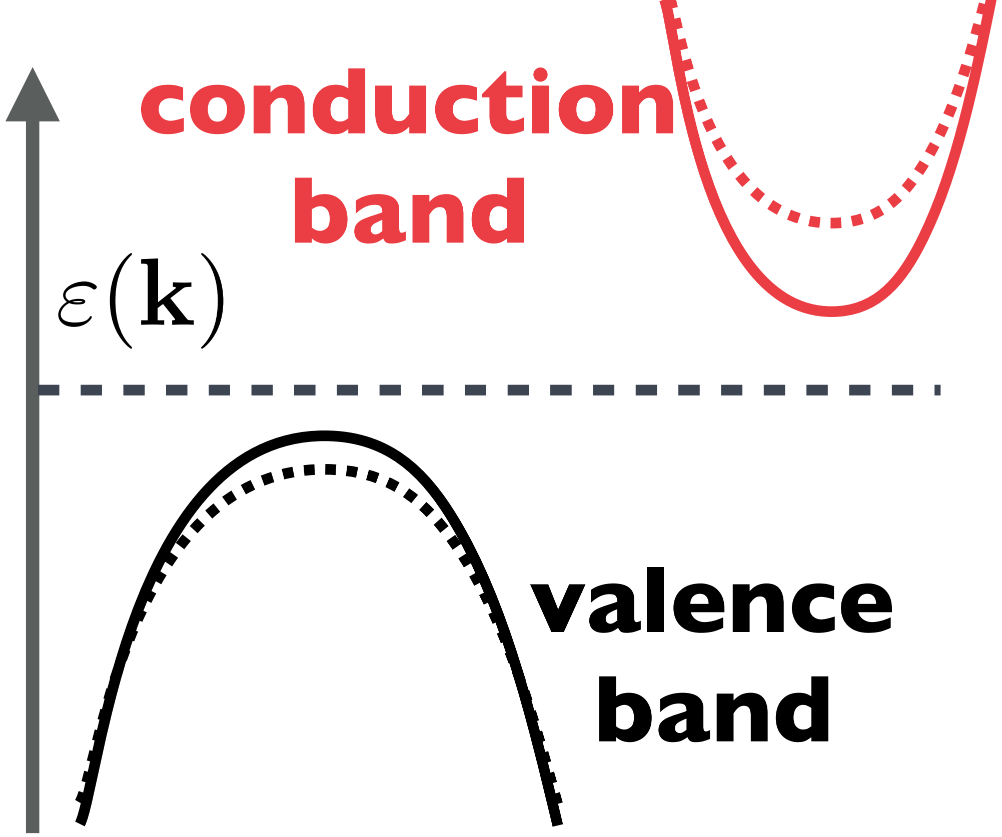
Eigenvalues
Γ
X''



Unit Cell Folding
Eigenvalues
4
2
0
-2
Fermi Energy
Γ
X
Eigenvalues
Γ
X’
Eigenvalues
Γ
X”

A Real Example: 4x4x4 Si





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➜ **Tricky in Supercells**

2*n*+1 Theorem:

$(2n+1)^{th}$ derivative of the **energy** requires the n^{th} derivative of the **wave function / electron density**.

X. Gonze and J.-P. Vigneron, *Phys. Rev. B* **39, 13120** (1989).

Density-Functional Perturbation Theory

S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987) &
S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).

Starting Point:
Kohn-Sham Equations

$$\hat{h}_{\mathrm{KS}}\psi_i = \left[\hat{t} + \hat{v}_{\mathrm{ext}}(r) + \hat{v}_{\mathrm{H}} + \hat{v}_{\mathrm{xc}}\right]\psi_i = \epsilon_i\psi_i$$

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First-order expansion of all relevant quantities with respect to a perturbation λ

$$\begin{aligned} \hat{h}_{\mathrm{KS}}(\lambda) &= \hat{h}_{\mathrm{KS}}^{(0)} + \overbrace{\frac{d\hat{h}_{\mathrm{KS}}}{d\lambda}}^{\hat{h}_{\mathrm{KS}}^{(1)}}\Delta\lambda + \cdots \\ \psi_i(\lambda) &= \psi_i^{(0)} + \psi_i^{(1)}\Delta\lambda + \cdots \\ \varepsilon_i(\lambda) &= \varepsilon_i^{(0)} + \varepsilon_i^{(1)}\Delta\lambda + \cdots \end{aligned}$$

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\varepsilon_i(\lambda) &= \varepsilon_i^{(0)} + \varepsilon_i^{(1)}\Delta\lambda + \cdots
\end{aligned}$$

Solve: *Sternheimer Equation*

$$\hat{h}_{\mathrm{KS}}(\lambda)\,\psi_i(\lambda) = \varepsilon_i(\lambda)\psi_i(\lambda) \Rightarrow \left(\hat{h}_{\mathrm{KS}}^{(0)} - \varepsilon_i^{(0)}\right)\psi_i^{(1)} = -\left(\hat{h}_{\mathrm{KS}}^{(1)} - \epsilon_i^{(1)}\right)\psi_i^{(0)} + \mathcal{O}(\lambda^2)$$

R.M. Sternheimer, *Phys. Rev.* **96** 951 (1954).

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Route A: *Density-functional Perturbation Theory* $\psi_i^{(1)} = \sum_l C_{il}\psi_l^{(0)}$

Route B: *Coupled-Perturbed Self-Consistent Field* $\psi_i^{(1)} = \sum_l C_{il}\varphi_l$

Additional Self-Concistency Cycle
required **per perturbation**!

Density-Functional Perturbation Theory

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R. M. Sternheimer, Phys. Rev. 96 951 (1954)

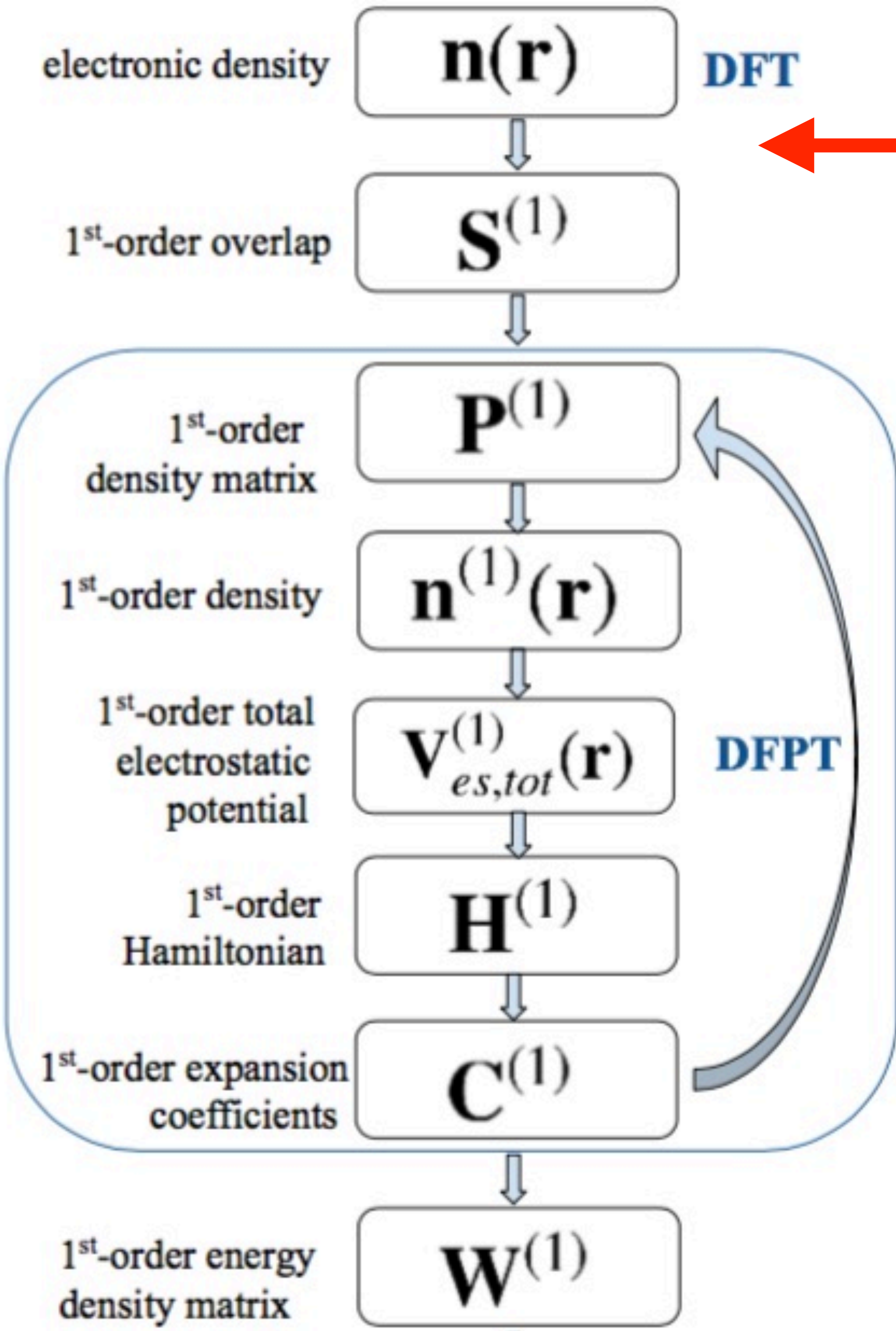
Normalization Conditions:

$$\left\langle \psi_i^{(0)} \middle| \psi_i^{(0)} \right\rangle = 1 \qquad \left\langle \psi_i^{(1)} \middle| \psi_i^{(0)} \right\rangle + \left\langle \psi_i^{(0)} \middle| \psi_i^{(1)} \right\rangle = 0$$

Phase Freedom: The phase of the perturbation can be freely chosen.

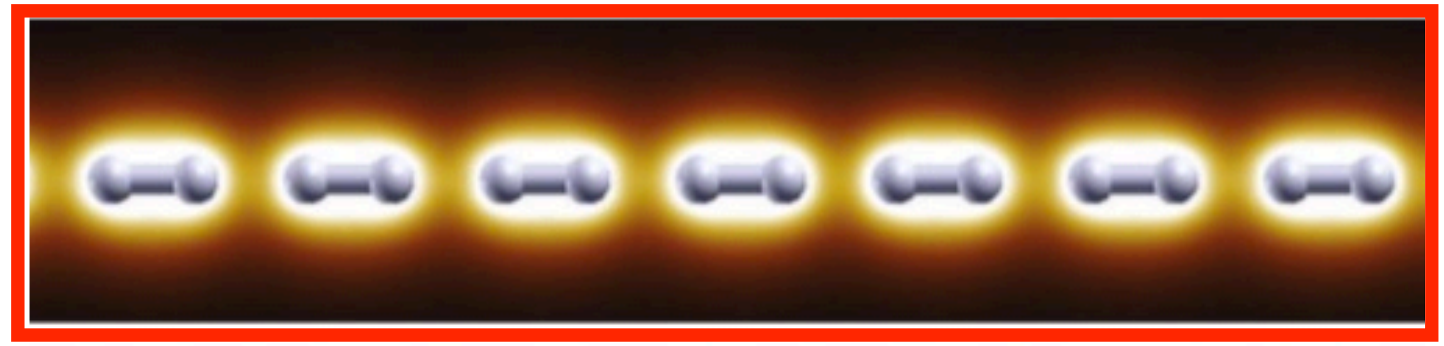
⇒ Extended Perturbations $\lambda(\mathbf{q})$ can be treated

in the unit cell!



Density Functional Theory:

*density n(**r**)*



Electric Field Perturbation Theory:

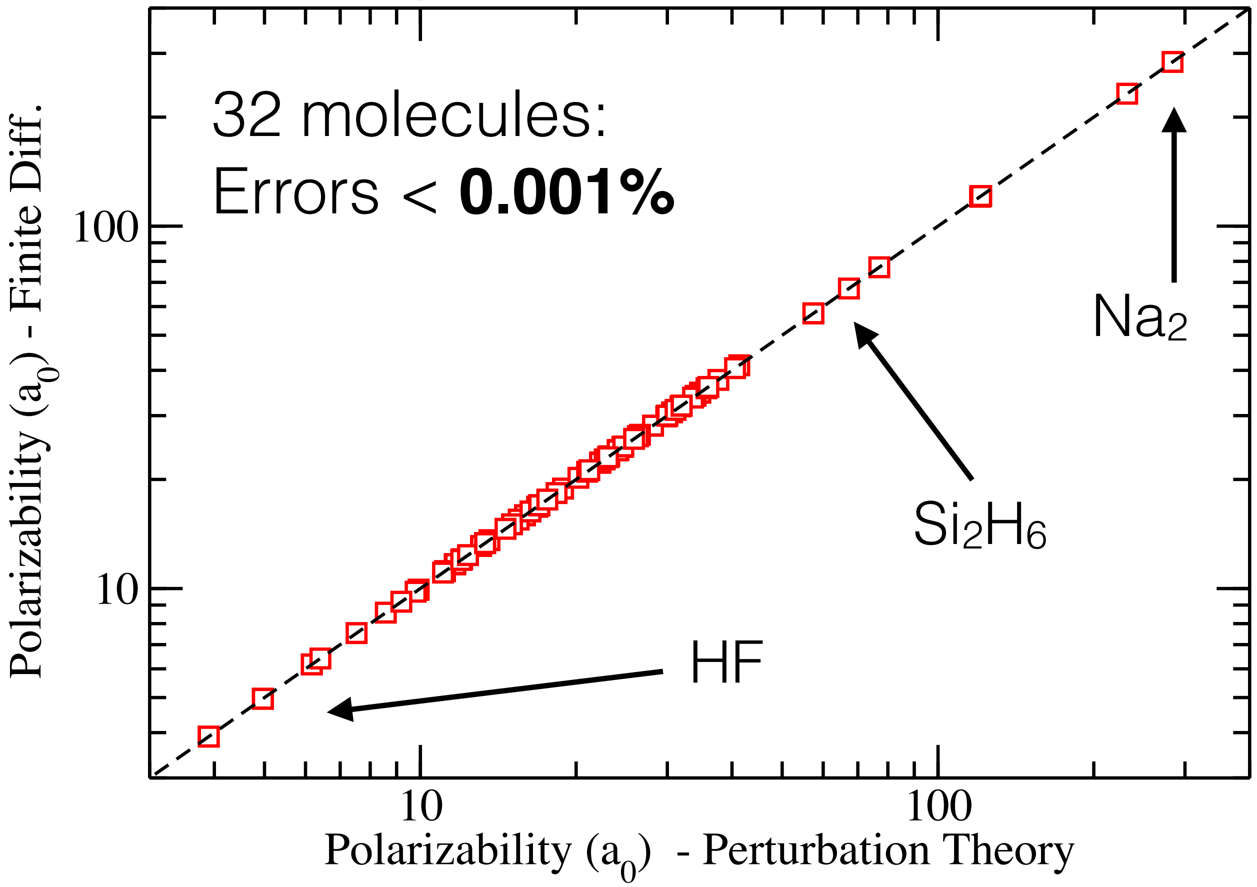
density response $dn(\mathbf{r})/d\mathbf{E}$

Polarizabilities & Dielectric Constants

Extensions: Response to Electric Fields

H. Shang, *et al.*, *New Journal of Physics* ***20****, 073040 (2018).*

Finite Systems: Polarizability



Validation:
Comparison **DFPT**
and **finite differences**

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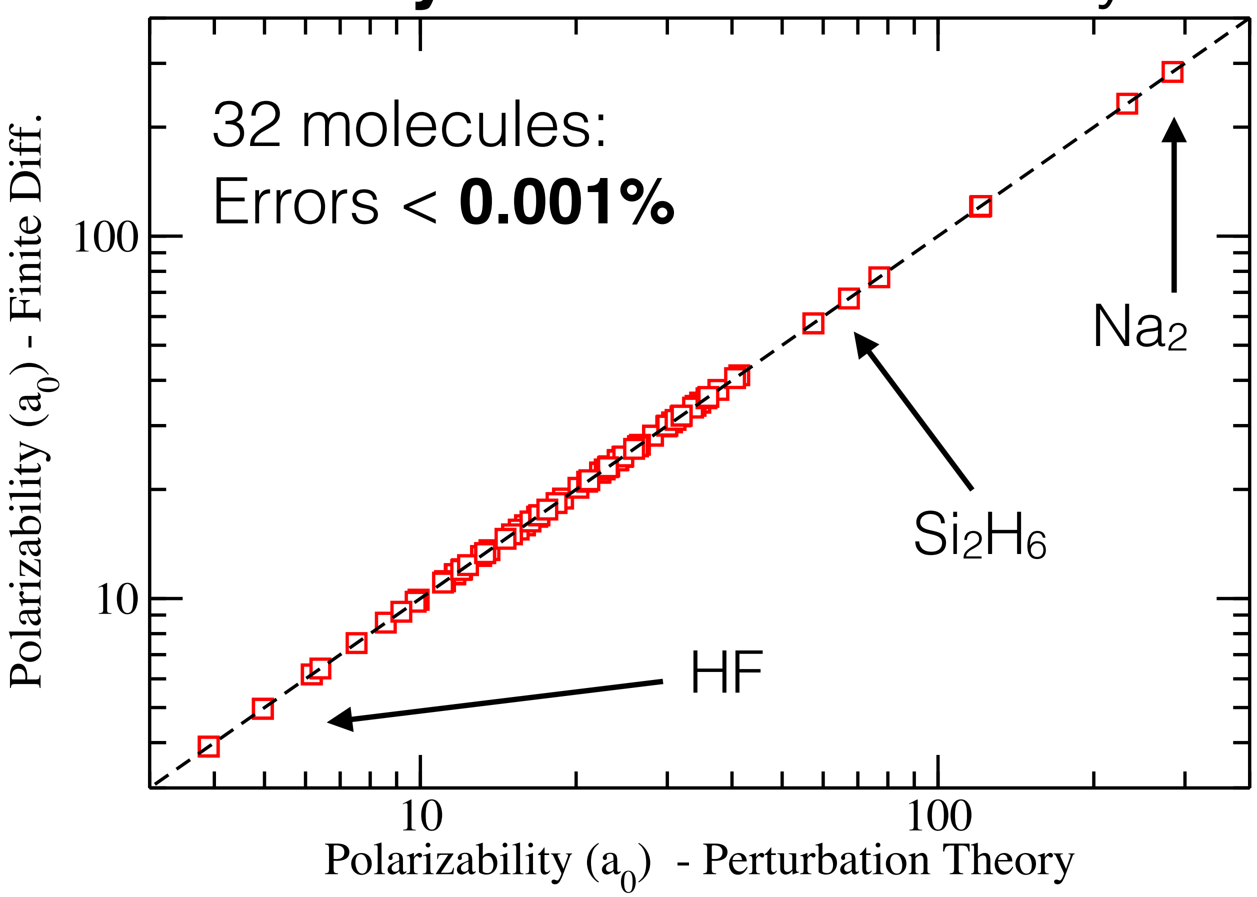

Periodic Systems: Dielectric Constant

	Exp.	this work (all electron) LDA	this work (all electron) PBE	Petousis *et al.*, 2016 PBE
Si	12.1	13.2	12.9	13.1
AlP	7.5	8.4	8.2	8.1
AlAs	8.2	9.5	9.5	9.5
AlSb	10.24	11.7	11.9	12.1
GaP	9.0	10.6	10.6	10.6

Theory Ref.: Petousis *et al.*, *Phys. Rev. B* **93**, 115151 (2016).

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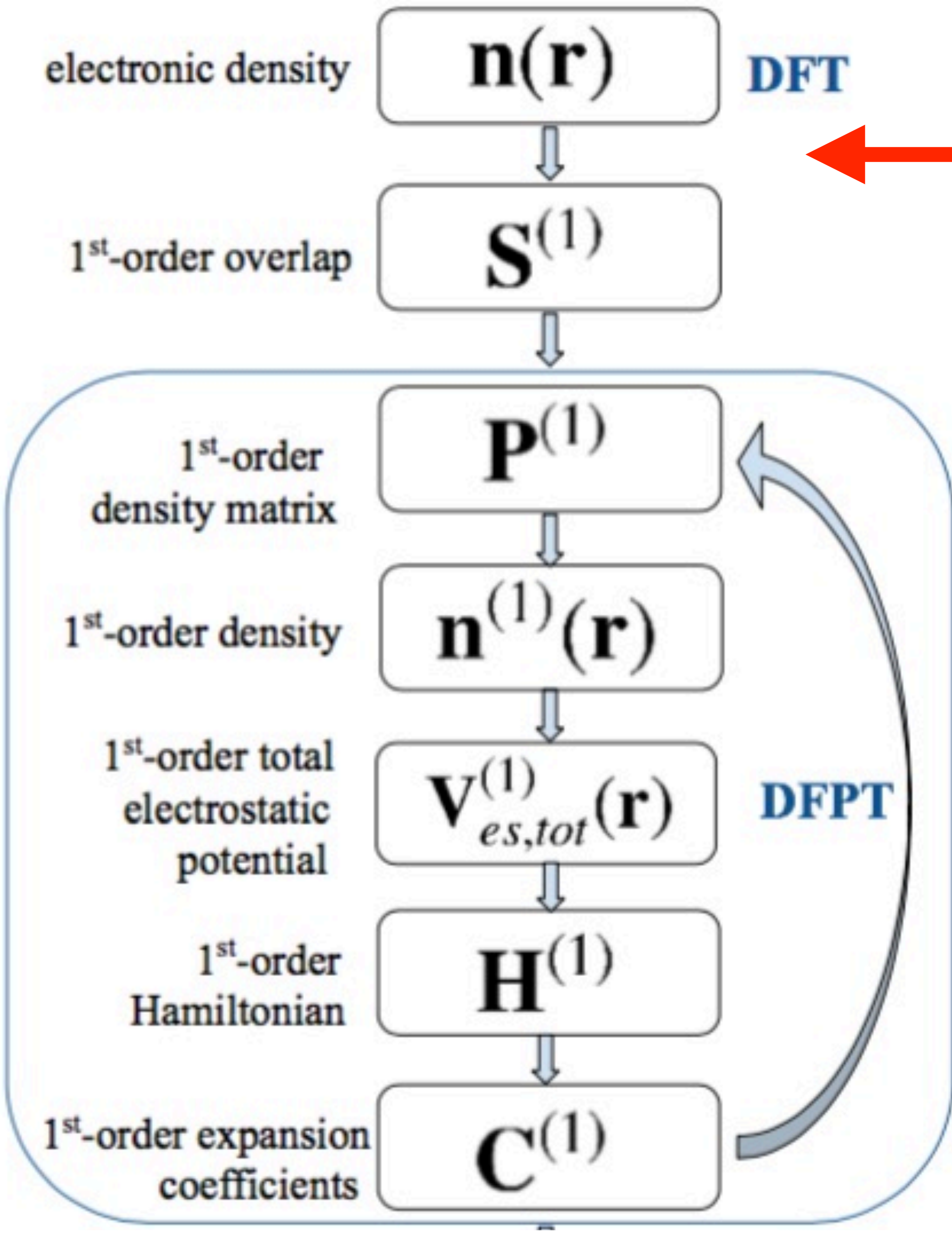
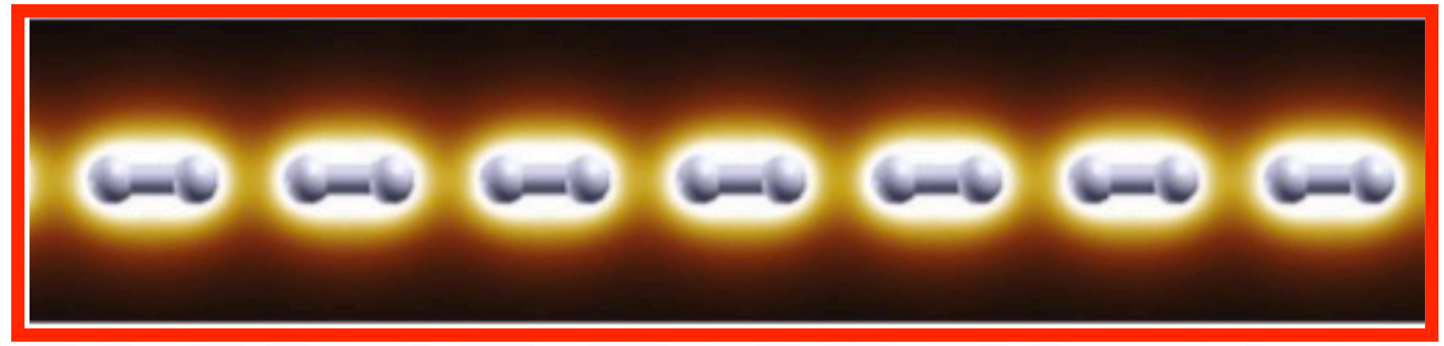
Comparison **DFPT** and **finite differences**

Validation:
Comparison **DFPT** with **exp.**/**theo.** literature



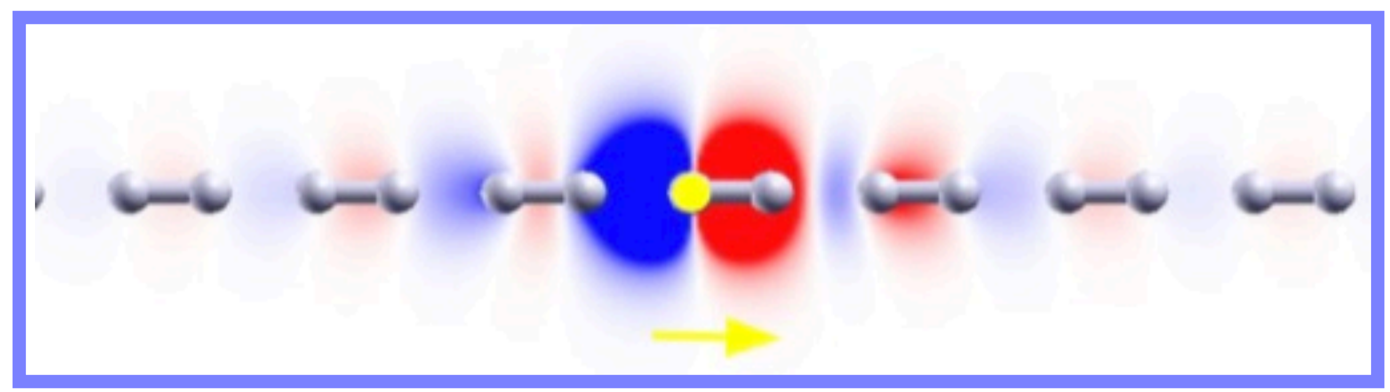
Density Functional Theory:

density $n(\mathbf{r})$



Density Functional Perturbation Theory:

density response $dn(\mathbf{r})/d\mathbf{R}_I$



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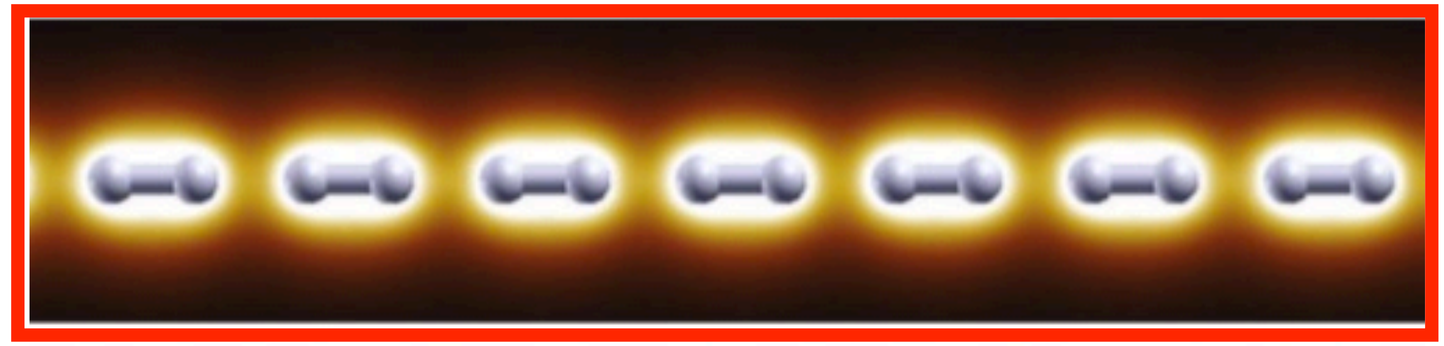

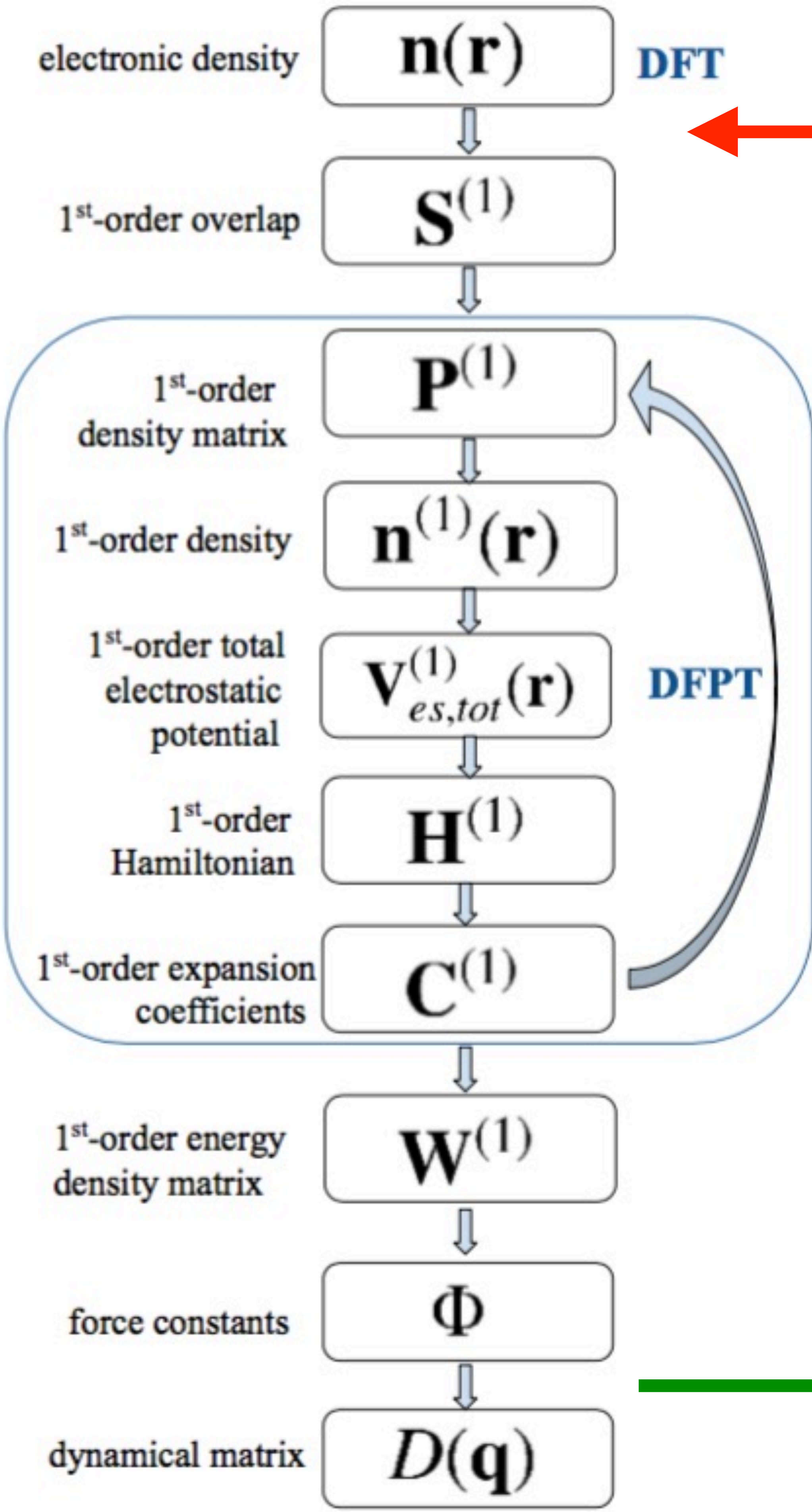

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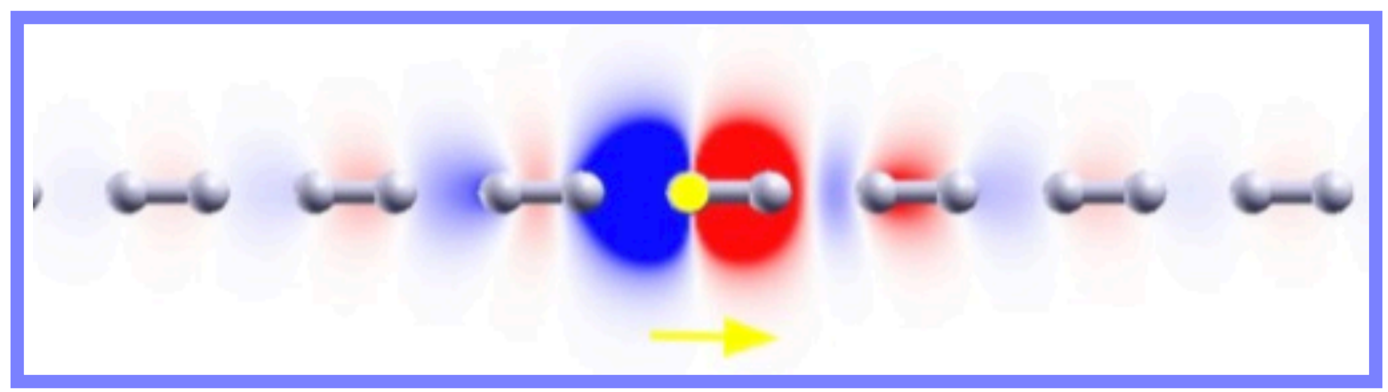
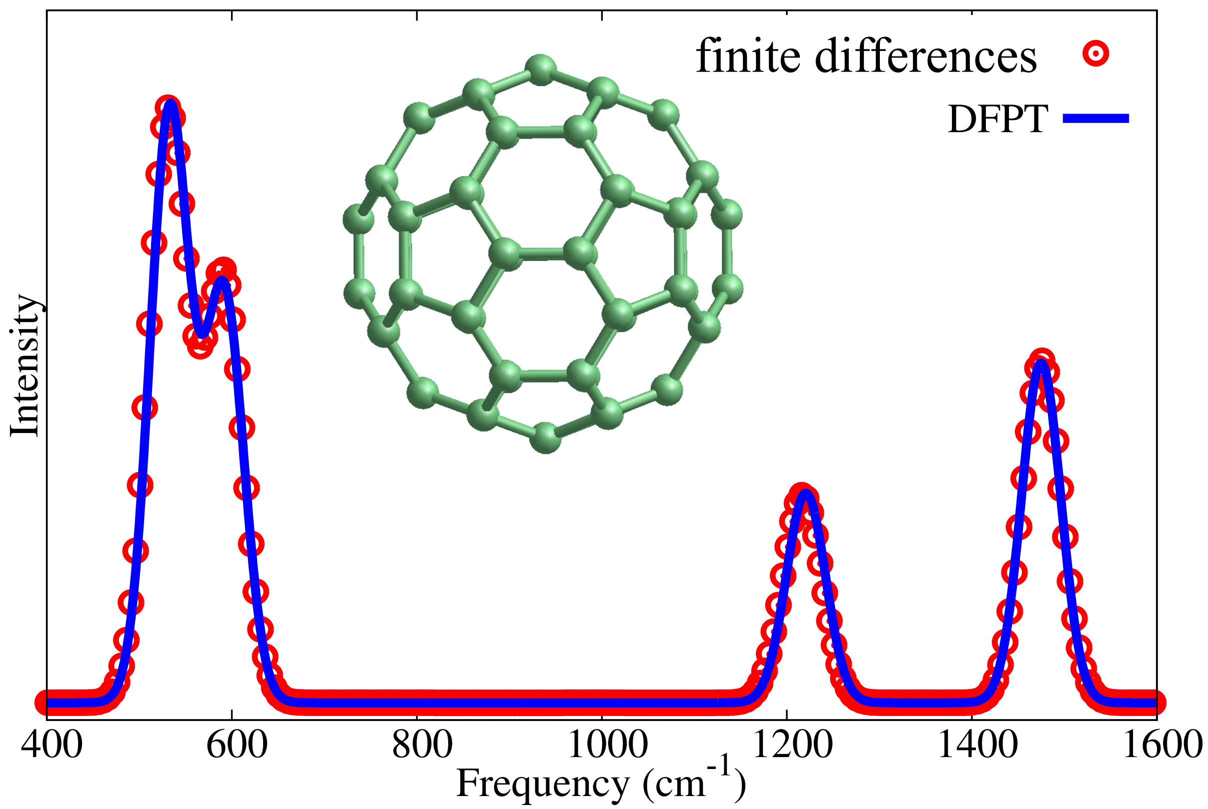


All phonon properties!

DF-Perturbation Theory in *FHI-aims*

H. Shang, C. Carbogno, P. Rinke, and M. Scheffler, Comp. Phys. Comm. ***215****, 26 (2017).*

Finite Systems: C_{60}



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Comparison **DFPT** and **finite differences** for vibrational properties

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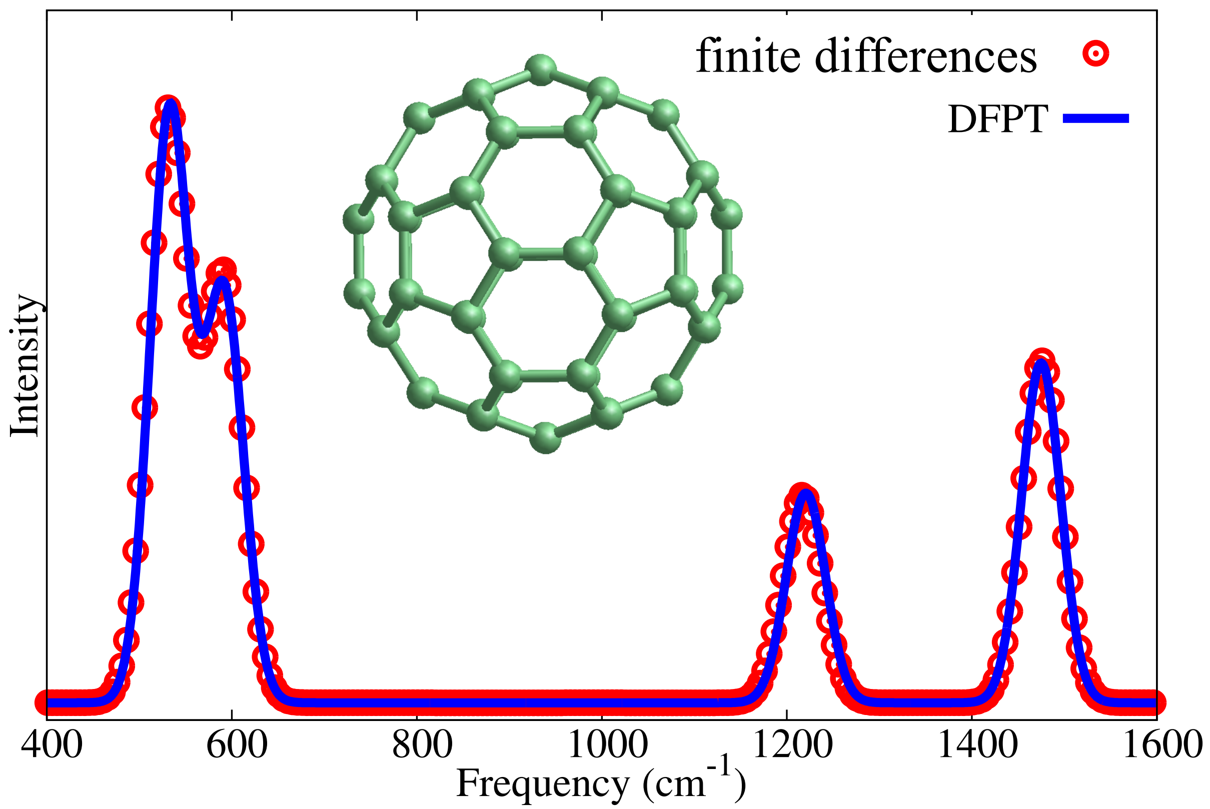
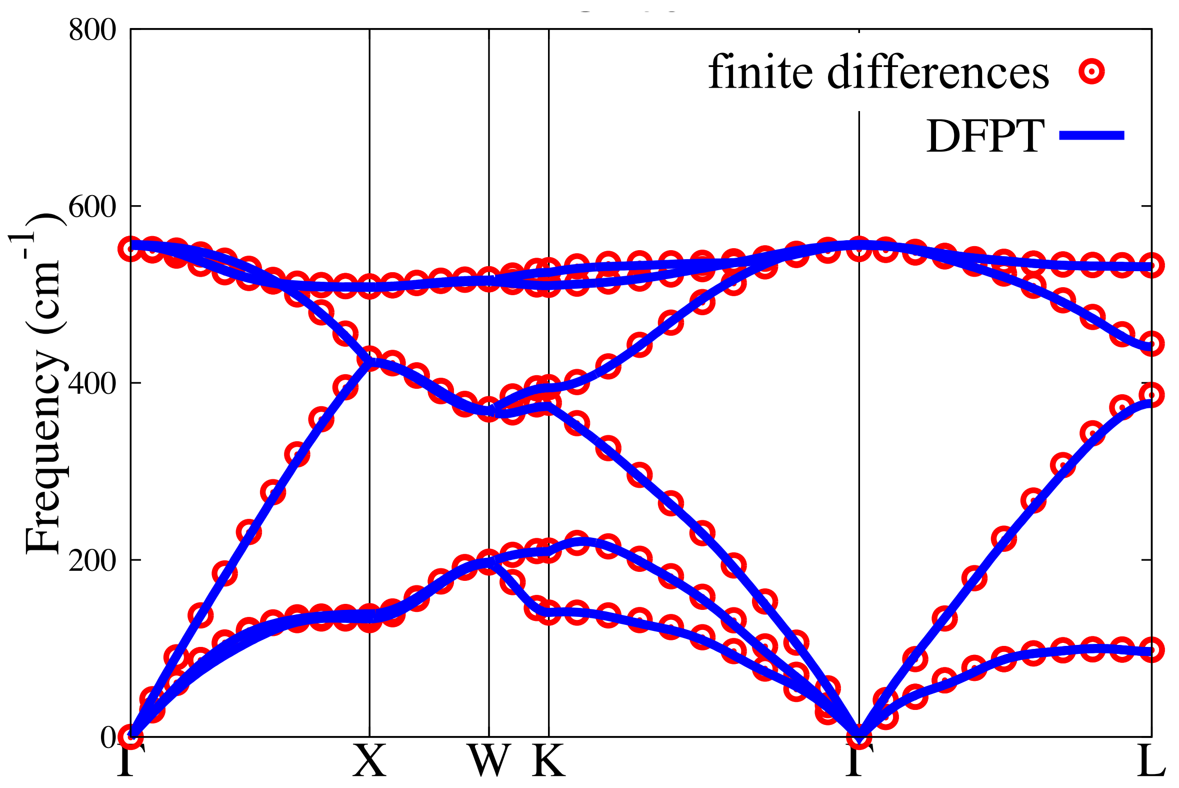


Periodic Systems: Silicon



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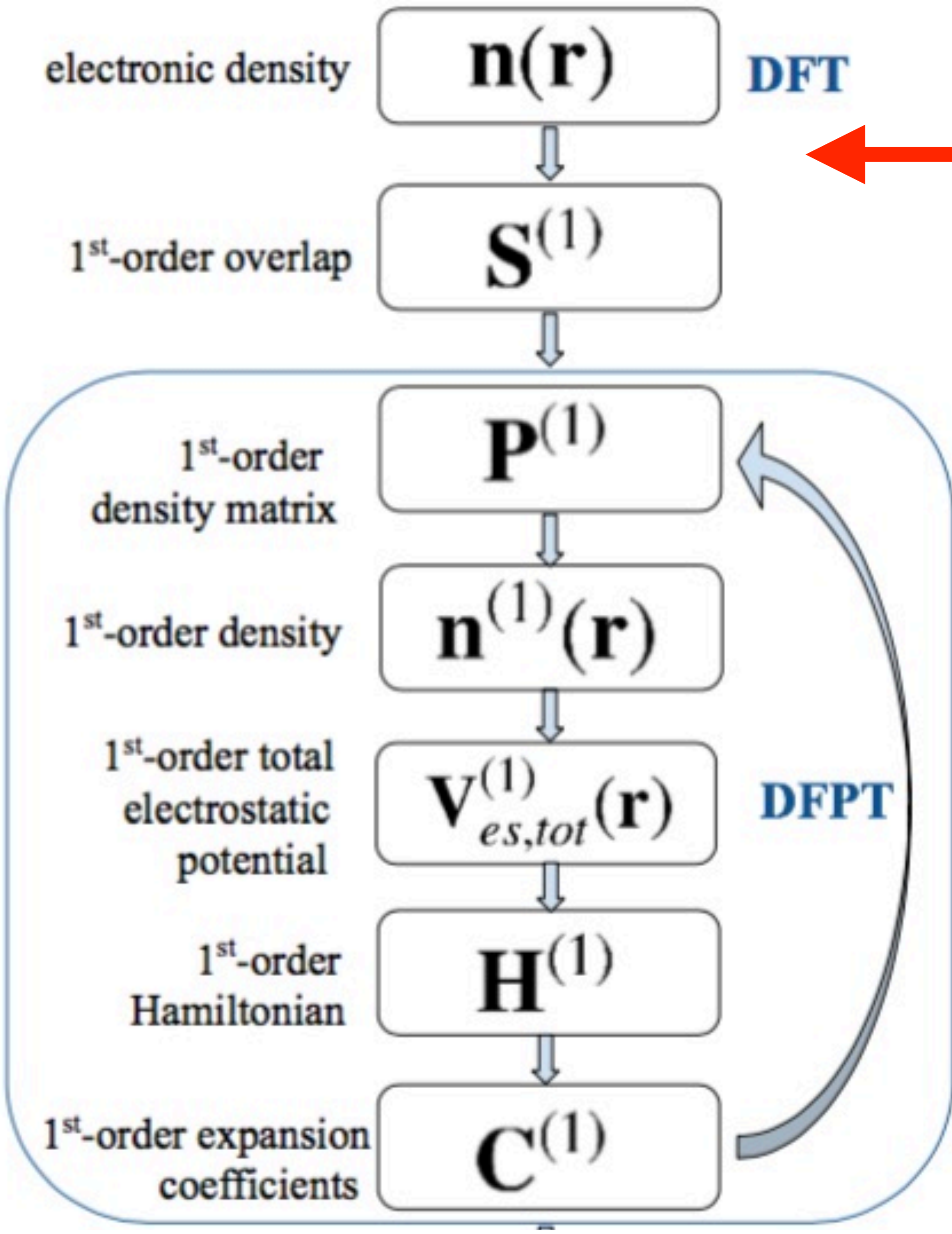

Density Functional Theory:

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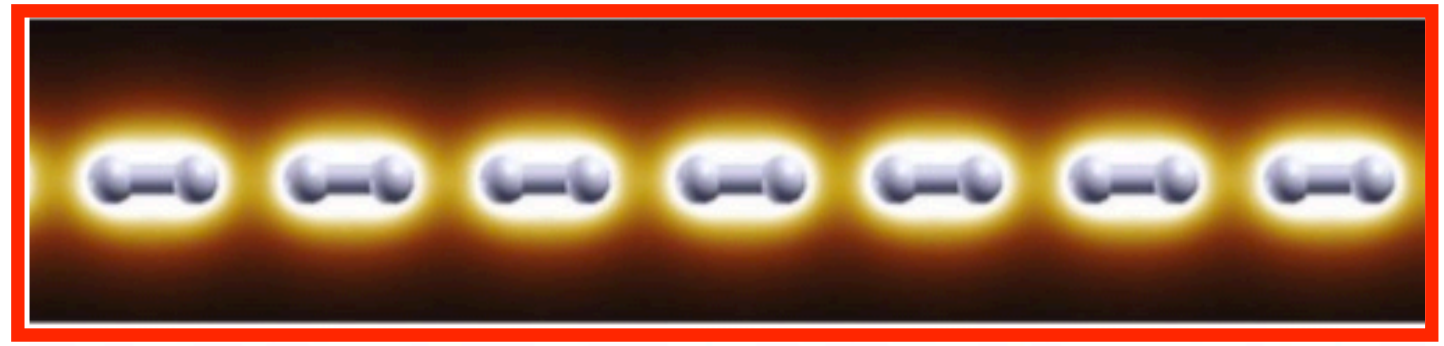

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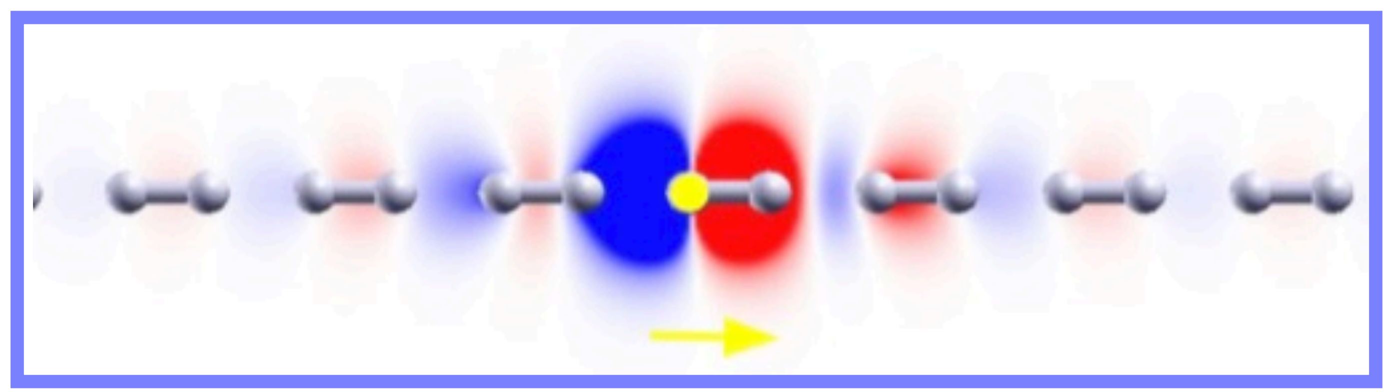
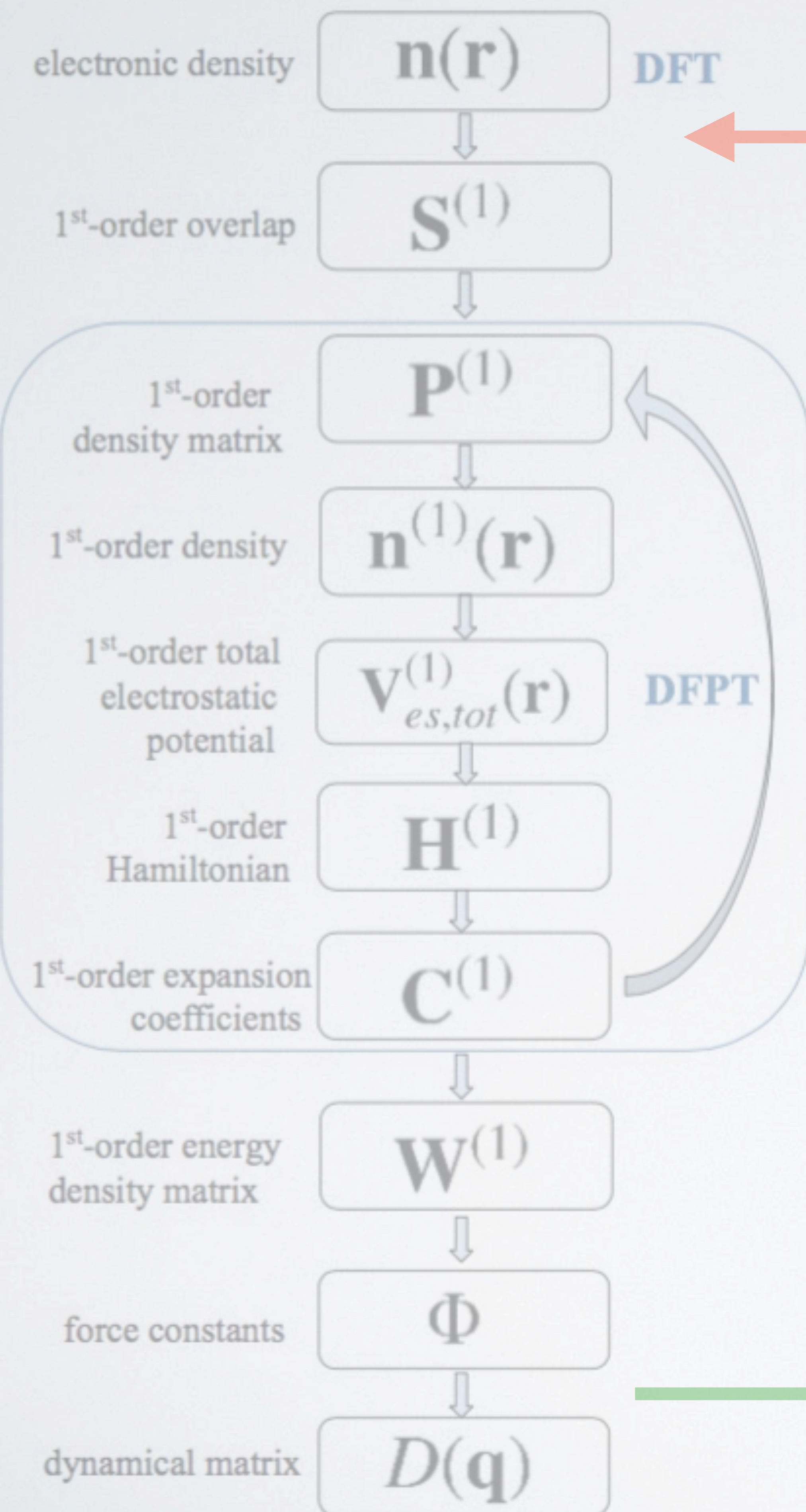


Electron-Phonon Coupling

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = \left\langle \Psi^{(0)}_{m\mathbf{k}+\mathbf{q}} \middle| \underbrace{\Delta_{\mathbf{q}\nu} v^{\mathrm{KS}}}_{\hat{h}^{(1)}_{\mathrm{KS}}(\nu,\mathbf{q})} \middle| \Psi^{(0)}_{n\mathbf{k}} \right\rangle_{\mathrm{uc}}$$



Density Functional Theory:

*density n(**r**)*

Density Functional Perturbation Theory:

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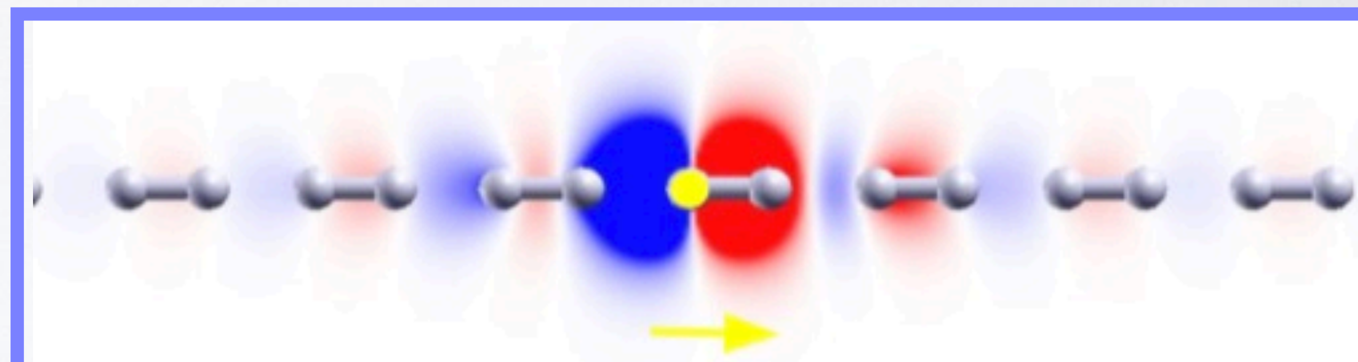

Density response is localized in real space.

F. Giustino, M. Cohen, and S. Louie, *Phys. Rev. B* **76** 165108 (2007).

electronic density $\mathbf{n(r)}$ DFT

1st-order overlap $\mathbf{S}^{(1)}$

Using techniques developed for describing **delocalized properties** to describe a **localized response** is **not efficient**!

F. Giustino, M. Cohen, and S. Louie, *Phys. Rev. B* **76** 165108 (2007).

force constants Φ

dynamical matrix $D(\mathbf{q})$

Density Functional Theory:

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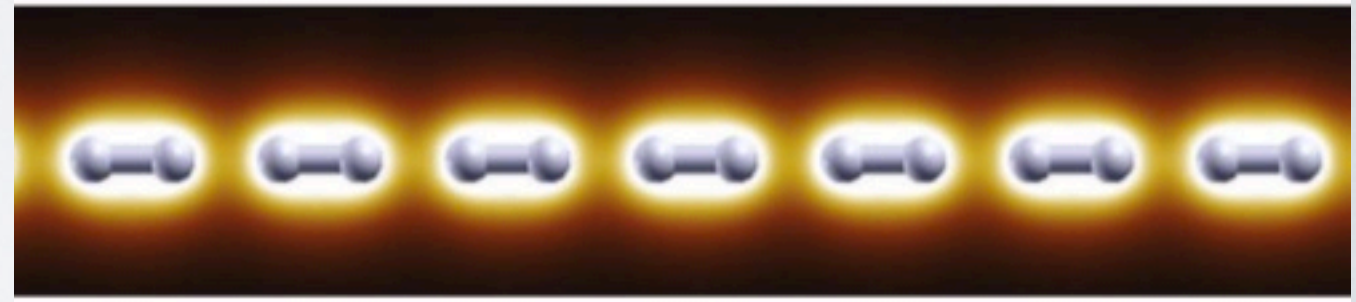

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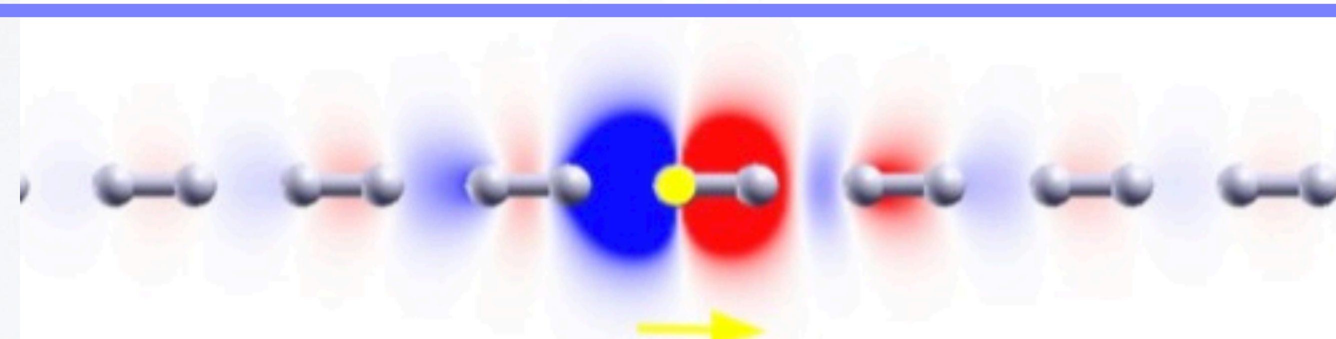

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F. Giustino, M. Cohen, and S. Louie, *Phys. Rev. B* **76** 165108 (2007).

Accelerating DFPT

e.g.: F. Giustino, M. Cohen, and S. Louie, *Phys. Rev. B* **76** 165108 (2007).
EPW Software: Ponce, *et al.*, *Comp. Phys. Comm.* **209**, 116 (2016).

Response computed in **reciprocal-space** on a finite **q-grid.**

Truncated Fourier-Transform to **real-space**.

Localization enables **real-space interpolation**
(e.g. *Wannier:* Vanderbilt, Marzari, Giustino, etc.)

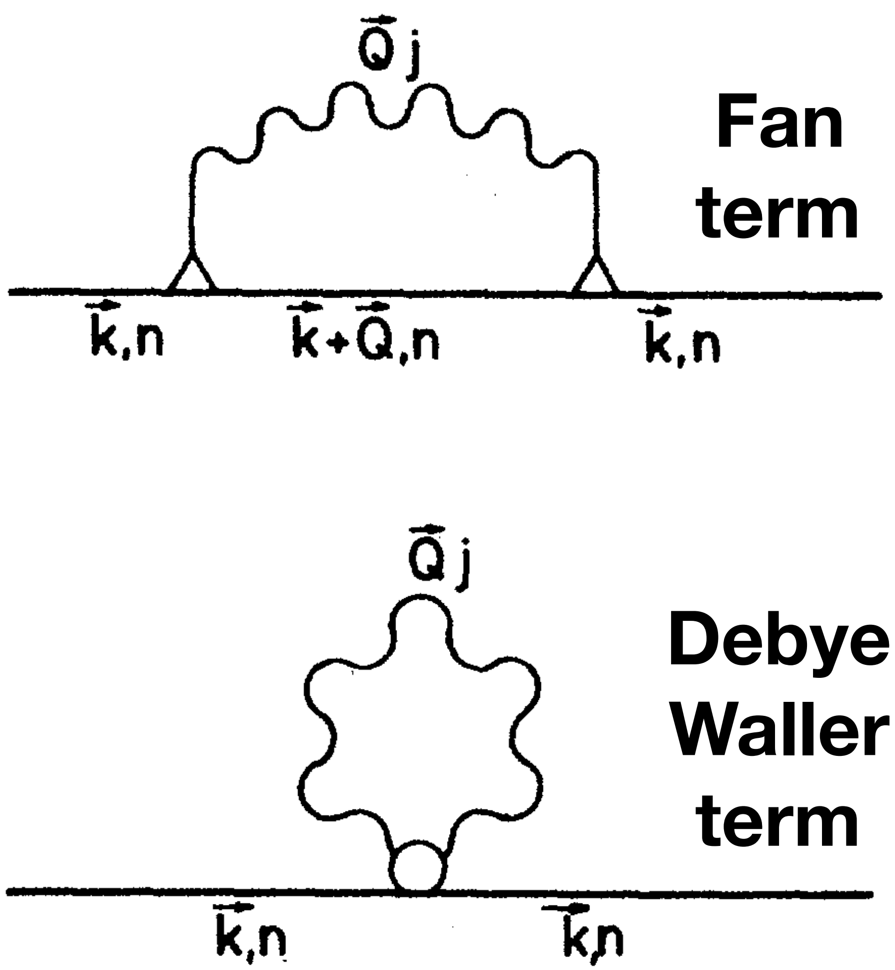
Truncated Fourier-Transform back to **reciprocal-space**.

Heine-Allen-Cardona Theory

P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).

Electron-Phonon Couplings $g_{mn\nu}(\mathbf{q},\mathbf{k})$

Many-Body Perturbation Theory



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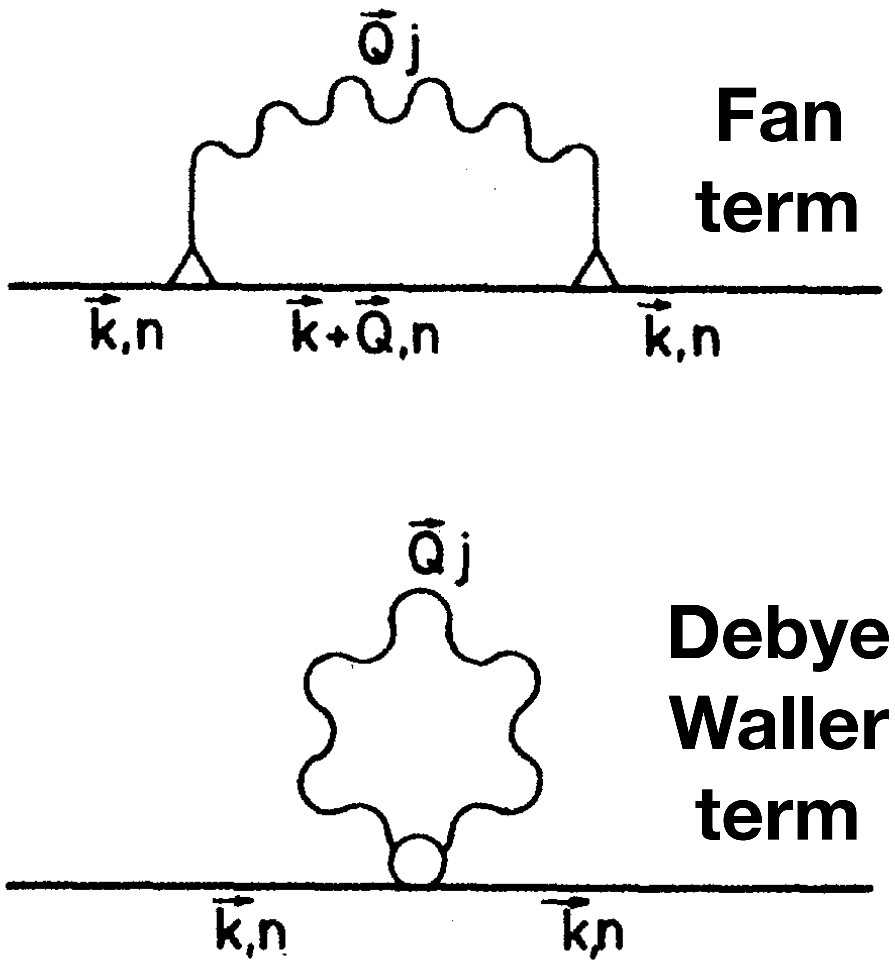
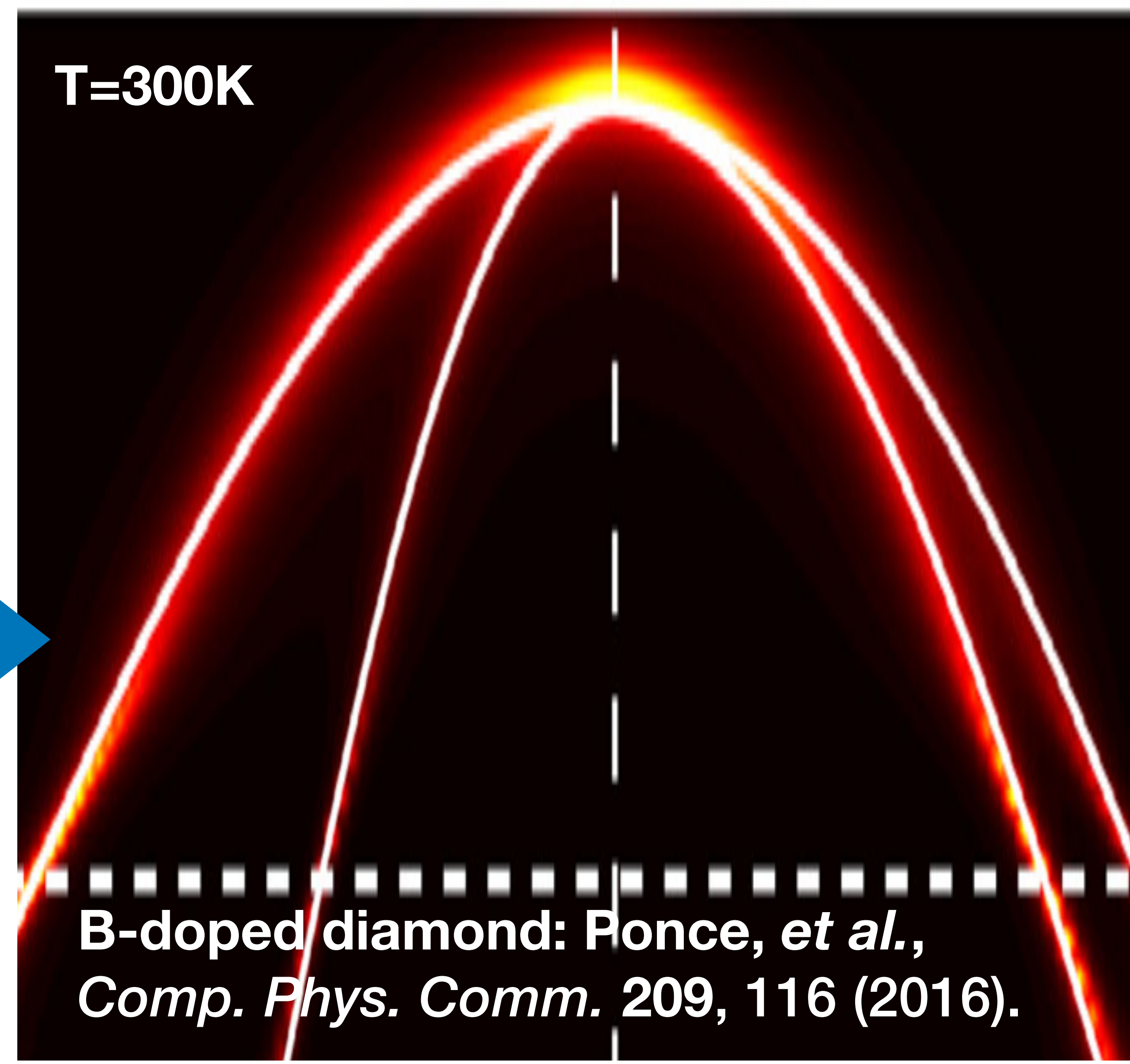
P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).

Electron-Phonon Couplings $g_{mn\nu}(\mathbf{q},\mathbf{k})$

Electronic Self-energies

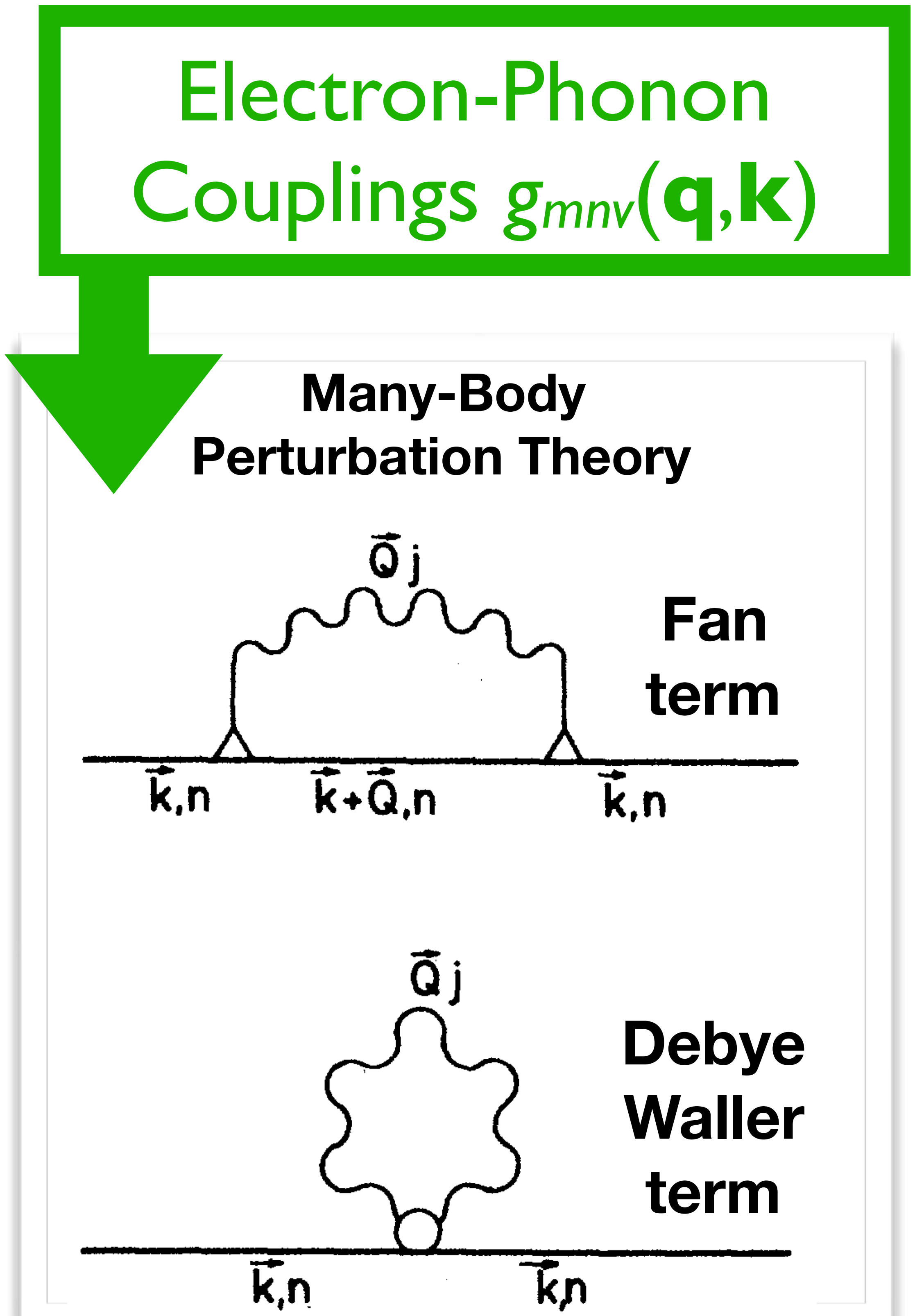
Many-Body Perturbation Theory

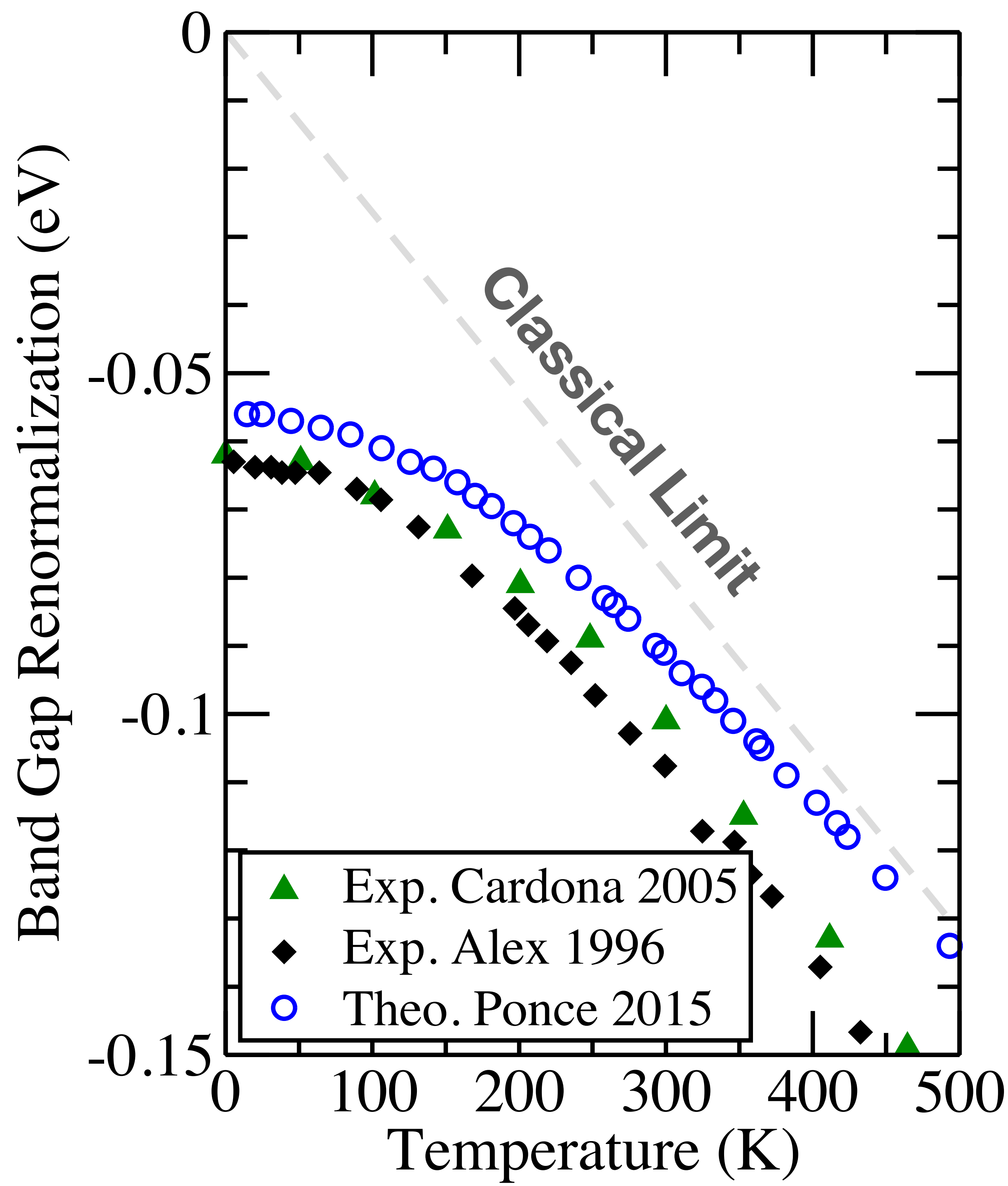




Heine-Allen-Cardona Theory

P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).

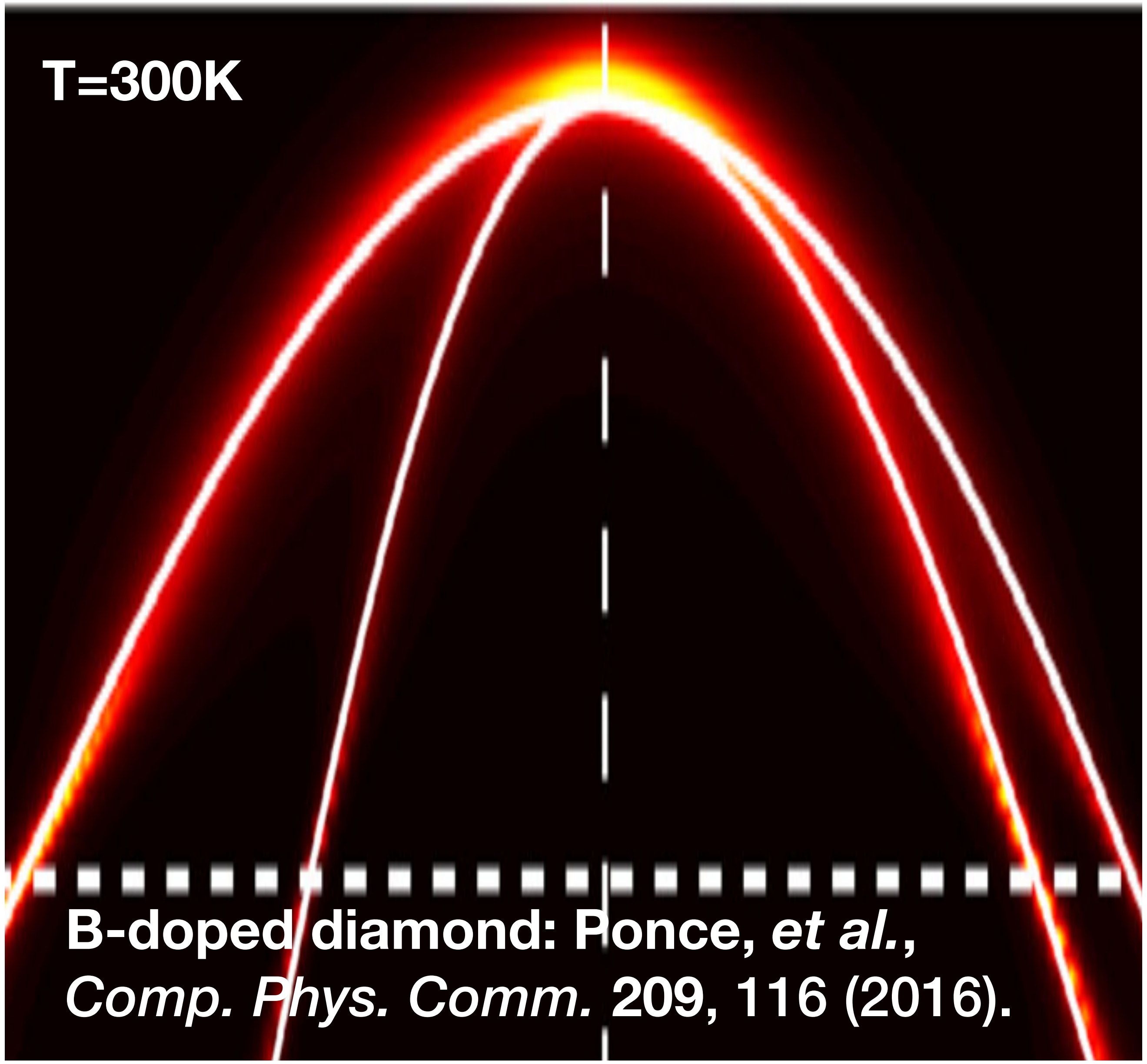




Heine-Allen-Cardona Theory

P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).

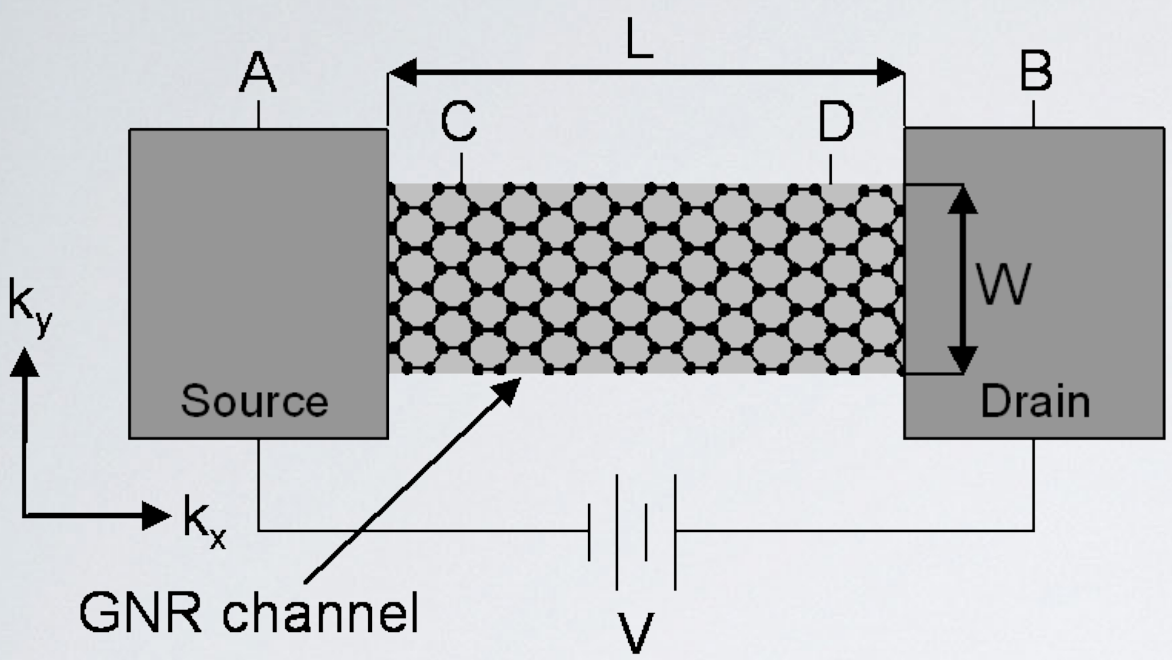
Imaginary Electronic Self-energies



B-doped diamond: Ponce, *et al.*,
***Comp. Phys. Comm.* 209, 116 (2016).**

III. CHARGE TRANSPORT

Microscopic



Length-scale: $L < 1\,\mu m$

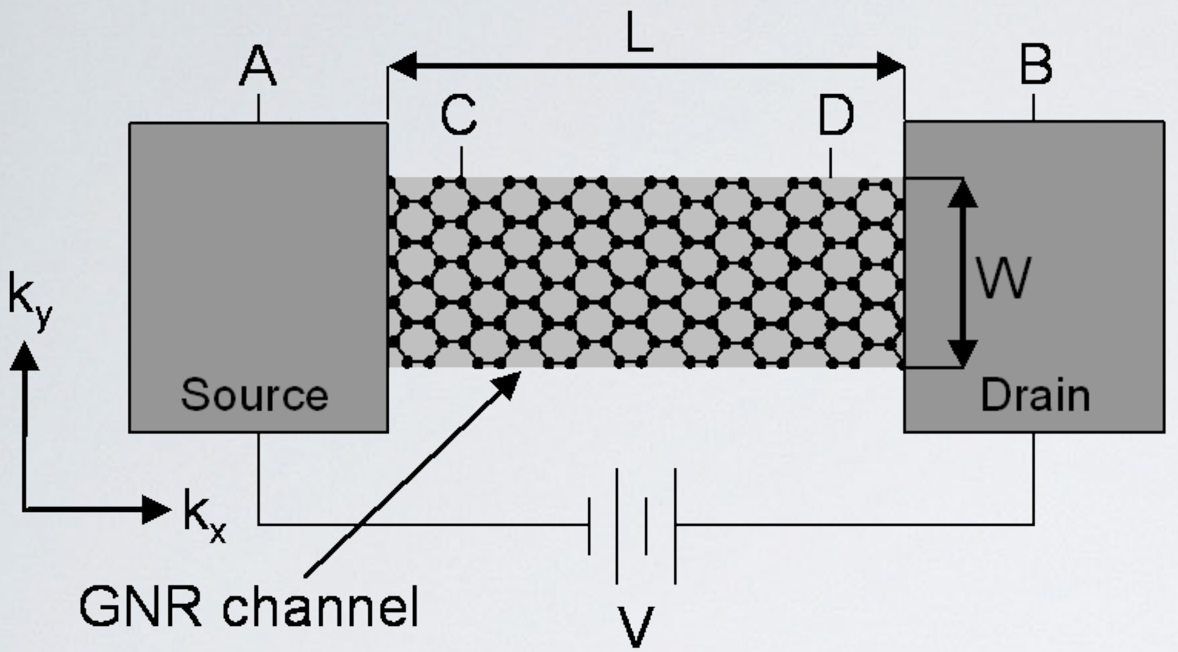
Potential: $U_1 - U_2 \sim 1\,V$

Field: $\nabla U \gg 10^{-6}\,V/Å$

Flux: $J \sim G(U_1 - U_2)$

local non-equilibrium

Microscopic



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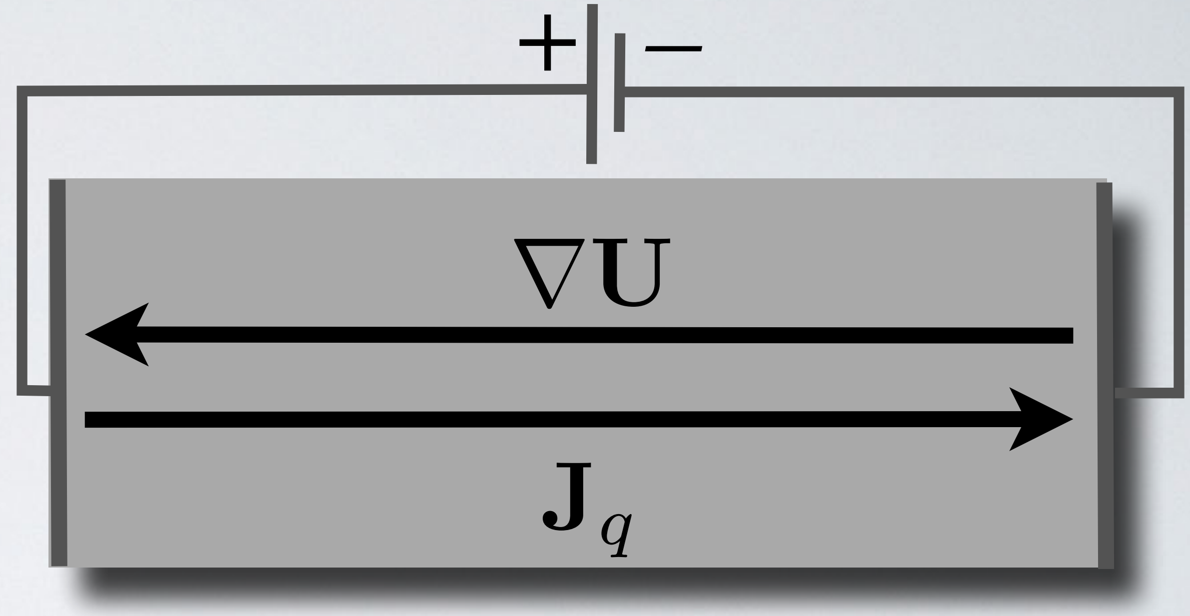
Macroscopic

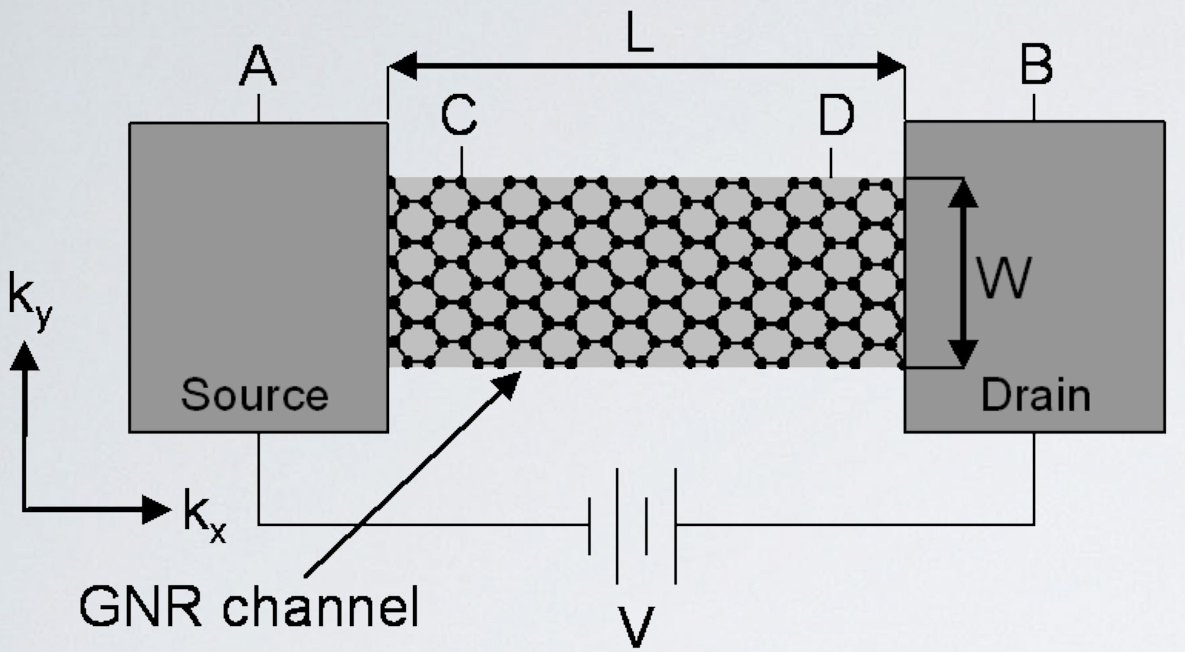


Length-scale: L > 1mm

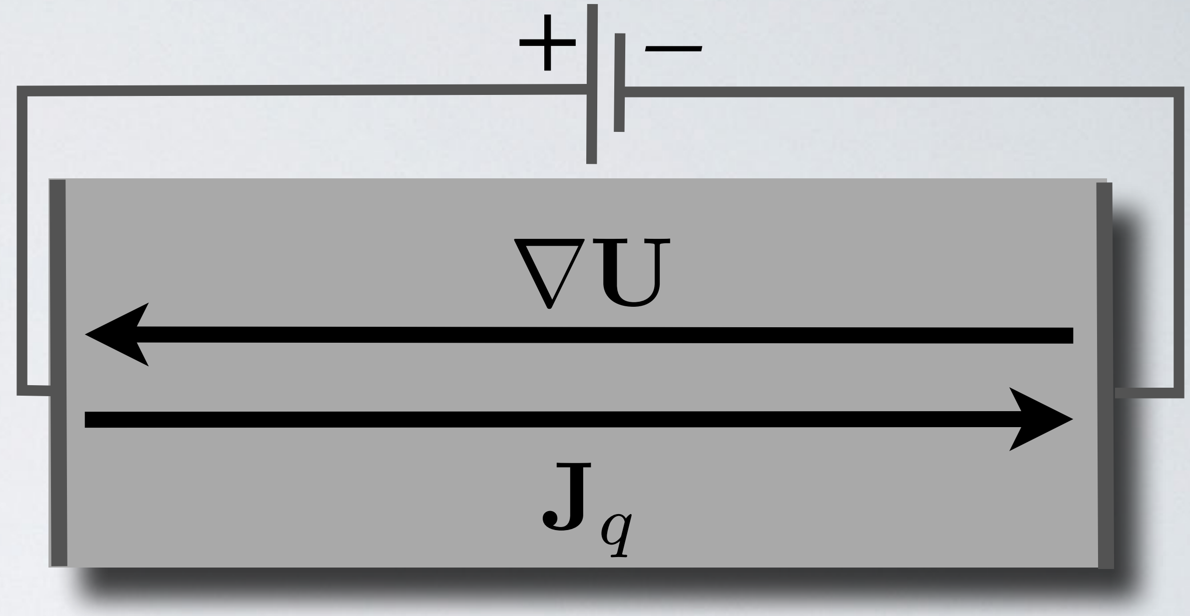
Potential: $U_1 - U_2 \sim 100V$

Field: $\nabla U \ll 10^{-6}\,V/Å$

Microscopic



Macroscopic



Length-scale:	L < 1 μm
Potential:	$U_1 - U_2 \sim 1$ V
Field:	$\nabla U \gg 10^{-6}$ V/Å
Flux:	$J \sim G(U_1 - U_2)$

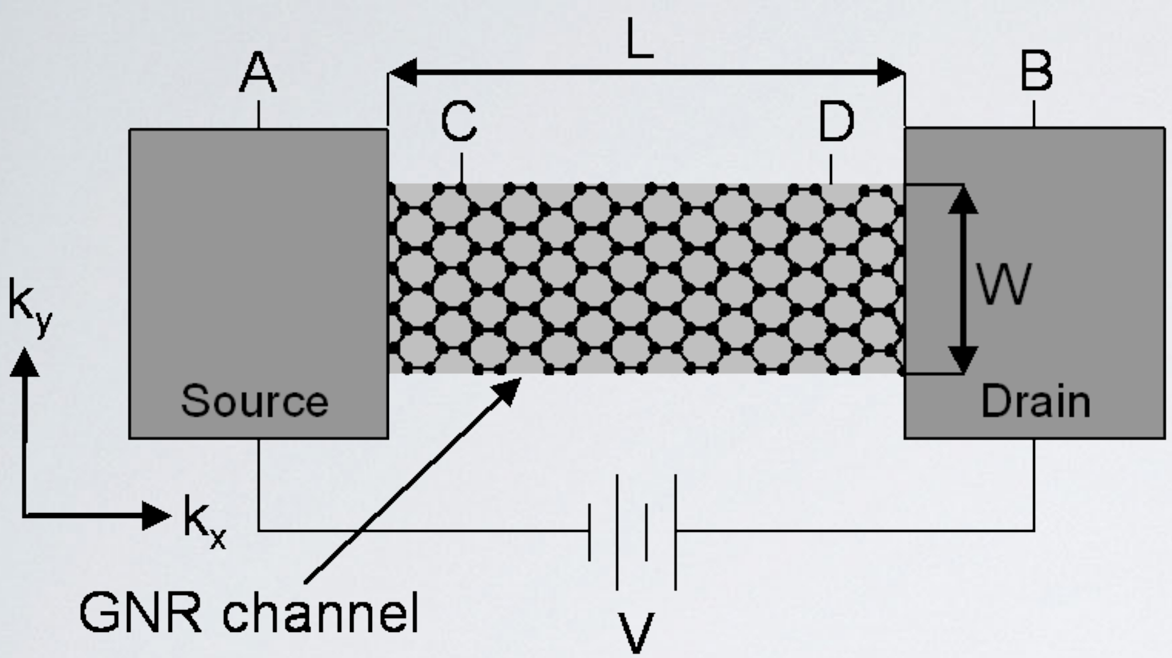
local non-equilibrium

Length-scale:	L > 1mm
Potential:	$U_1 - U_2 \sim 100$V
Field:	$\nabla U \ll 10^{-6}$ V/Å
Flux:	$j(r) \sim \sigma \nabla U(r)$

local equilibrium

L. Onsager, *Phys. Rev.* **37**, 405 (1931).

Microscopic



Length-scale: L < 1 μm

Potential: $U_1 - U_2 \sim 1$ V

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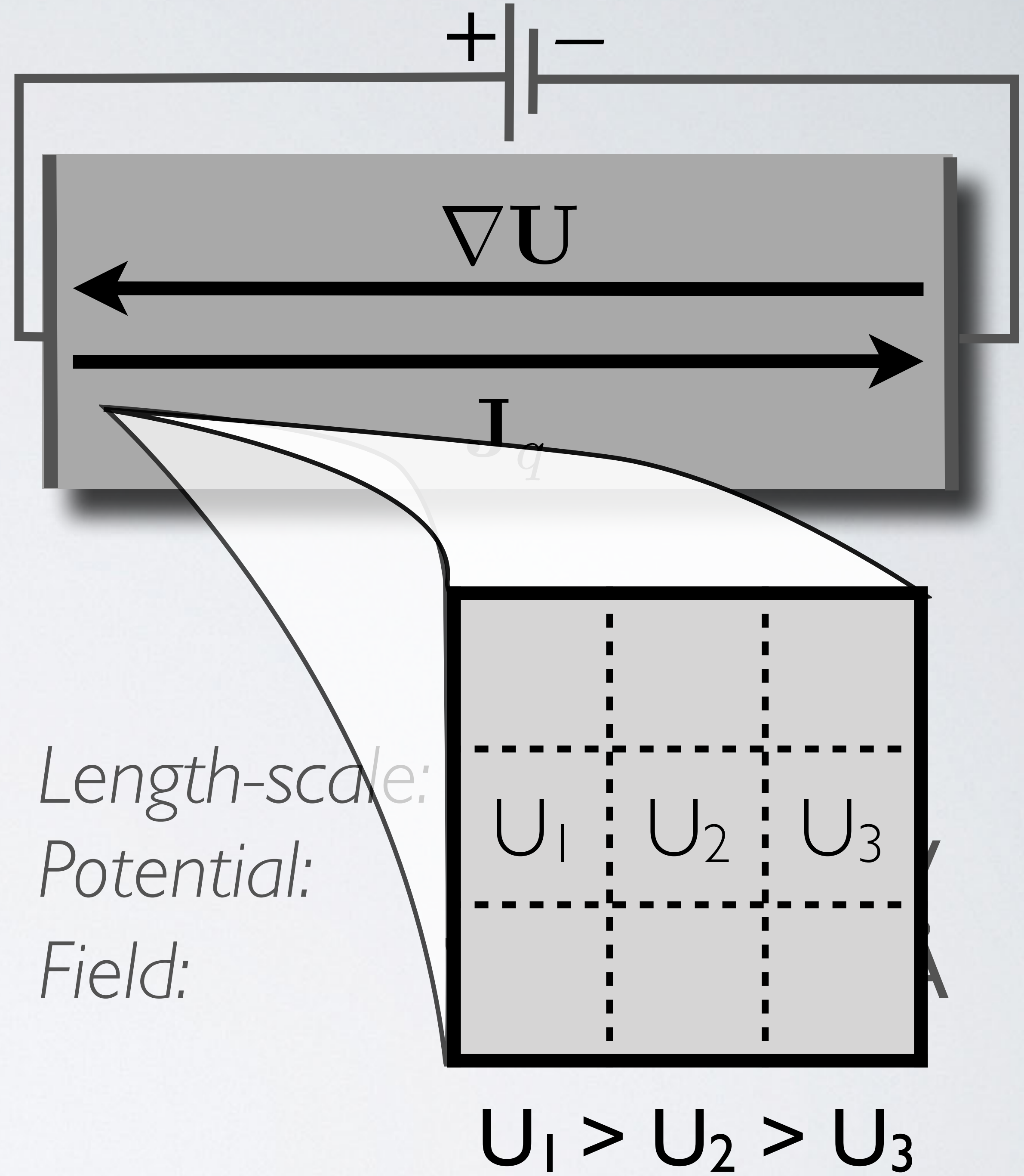
Macroscopic



Length-scale:

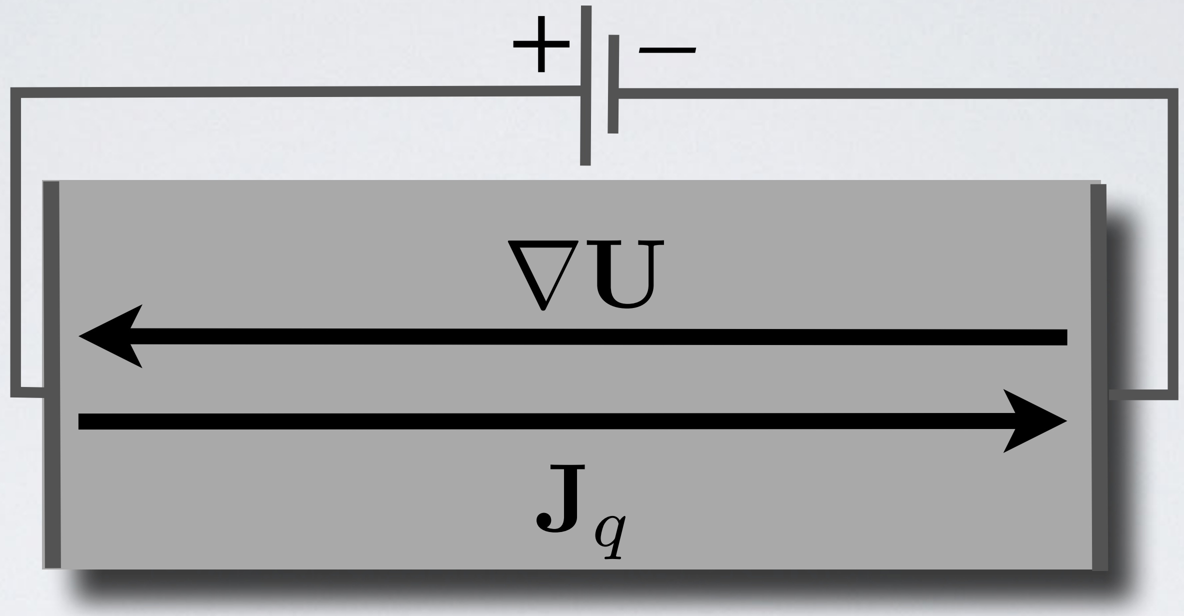
Potential:

Field:

Global non-equilibrium,
but local equilibrium!

L. Onsager, *Phys. Rev.* **37**, 405 (1931).

Macroscopic Electronic Transport Coefficients



Charge Transport ⇔ Electrical Conductivity $$J_q = -\sigma_{el} \nabla U$$

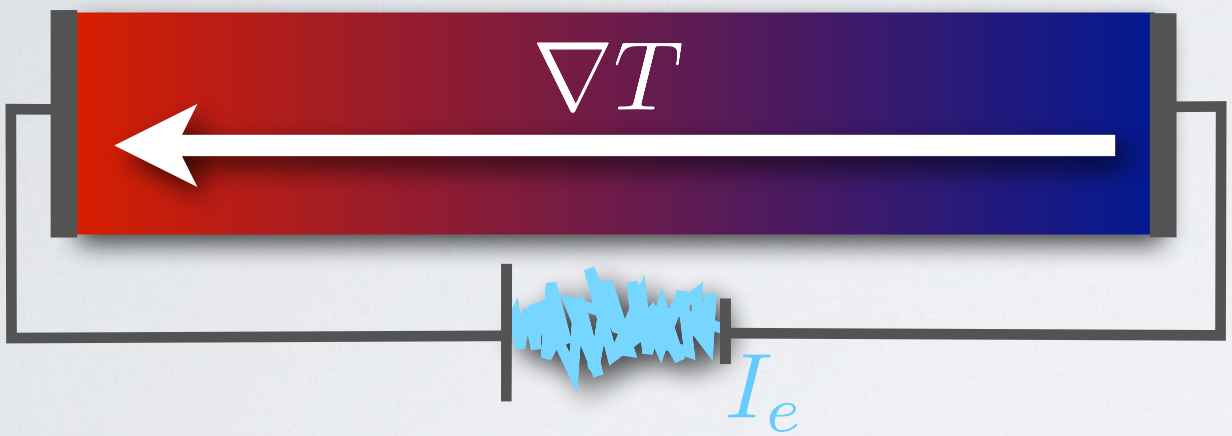
Heat Transport ⇔ Thermal Conductivity $$J_h = -\kappa_{el} \nabla T$$

Coupling of Charge & Heat Transport
⇒**Thermopower** *(Seebeck Coefficient)* $$\nabla U = -S \nabla T$$

Conversion Efficiency
⇒**thermoelectric figure of merit** $$zT = \frac{S^2 \sigma T}{\kappa_{el} + \kappa_{nu}}$$

Thermoelectric Elements

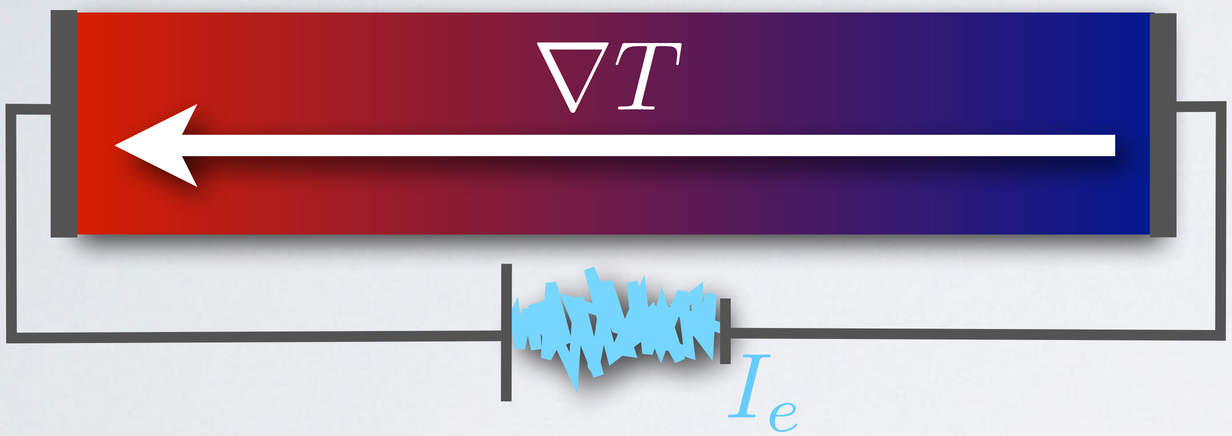
Conversion of **temperature gradient** into **electric current**.



Efficiency $\propto \dfrac{S_{el}^2\,\sigma_{el}\,T}{\kappa_{ph} + \kappa_{el}}$

Thermoelectric Elements

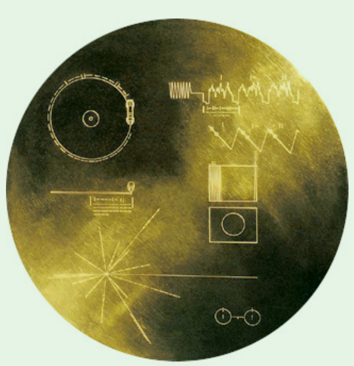
Conversion of **temperature gradient** into **electric current.**



Efficiency $\propto \dfrac{S_{el}^2\, \sigma_{el}\, T}{\kappa_{ph} + \kappa_{el}}$

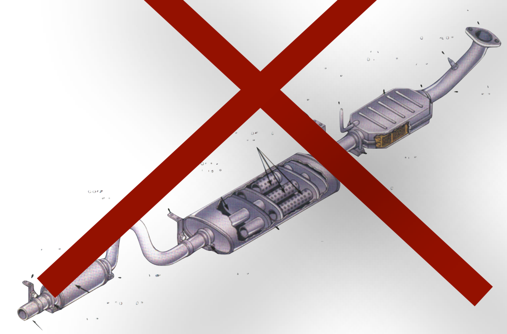
Potential *"waste heat recovery"* device!

Spacecraft



Industrial plants

Car exhausts



Personal Computing

Too low efficiency inhibits a large scale, economically attractive deployment of **thermoelectric devices.**

Phonon-Glass-Electron-Crystal-Paradigm

G.A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).

$$zT = \frac{S_{el}^2 \, \sigma_{el} \, T}{\kappa_{ph} + \kappa_{el}}$$

Minimize phonon heat conductivity,
but ***do not disturb*** *electronic transport!*

Phonon-Glass-Electron-Crystal-Paradigm

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Minimize phonon heat conductivity,
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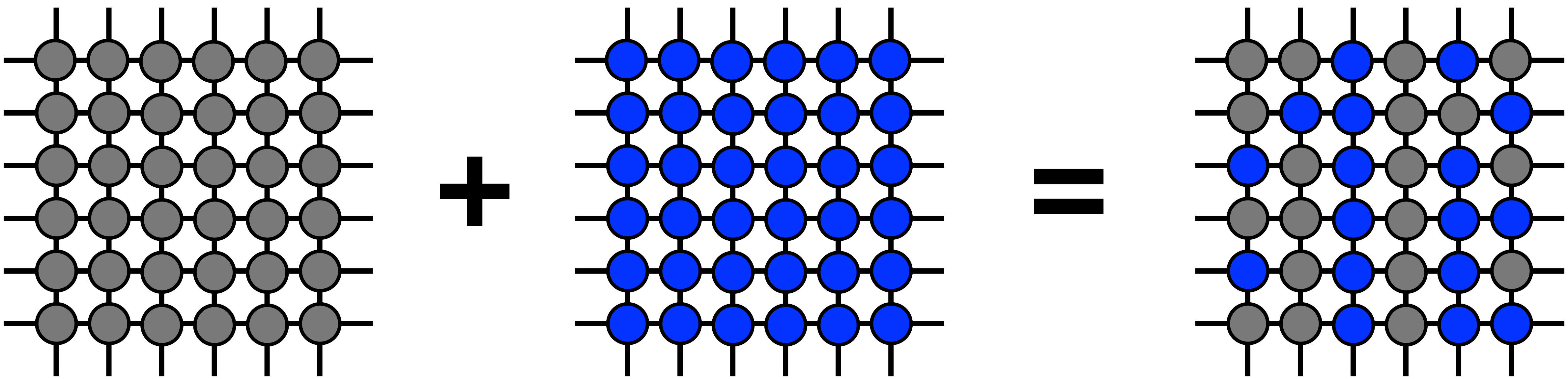
Example: $Si_xGe_{(1-x)}$ Random Alloys



Silicon $\kappa_{ph} \approx 130\ \mathrm{W/mK}$

Germanium $\kappa_{ph} \approx 55\ \mathrm{W/mK}$

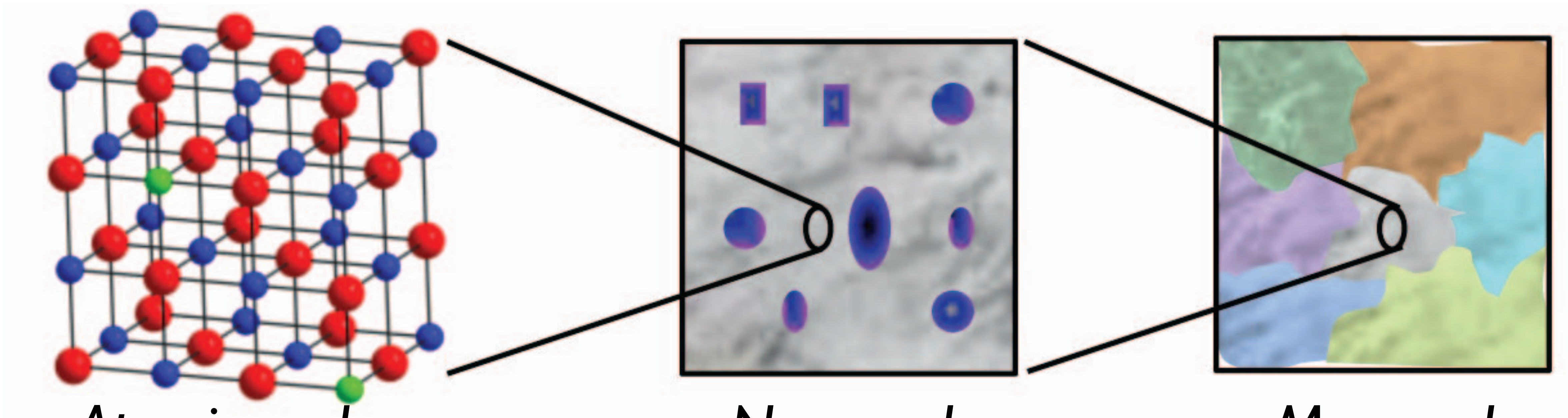
SiGe $\kappa_{ph} \approx 10\ \mathrm{W/mK}$

J. Garg, N. Bonini, B. Kozinsky, and N. Marzari, *Phys. Rev. Lett.* **106**, 045901 (2011).

Phonon-Glass-Electron-Crystal-Paradigm

G. A. Slack, *CRC Handbook of Thermoelectrics*, CRC Press (1995).

Hierarchically structured PbTe

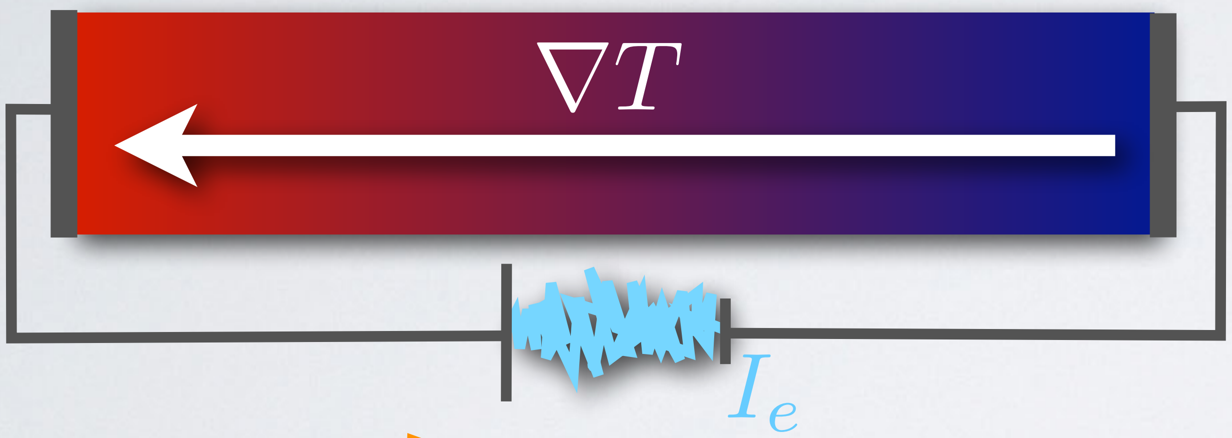


Atomic scale:	*Nanoscale:*	*Mesoscale:*
Lattice disorder	Precipitates	Grain boundaries
ZT≈1.1	**ZT≈1.7**	**ZT≈2.2**

K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, and M. G. Kanatzidis, *Nature* **489**, 414 (2012).

Thermoelectric Elements

Conversion of **temperature gradient** into **electric current.**

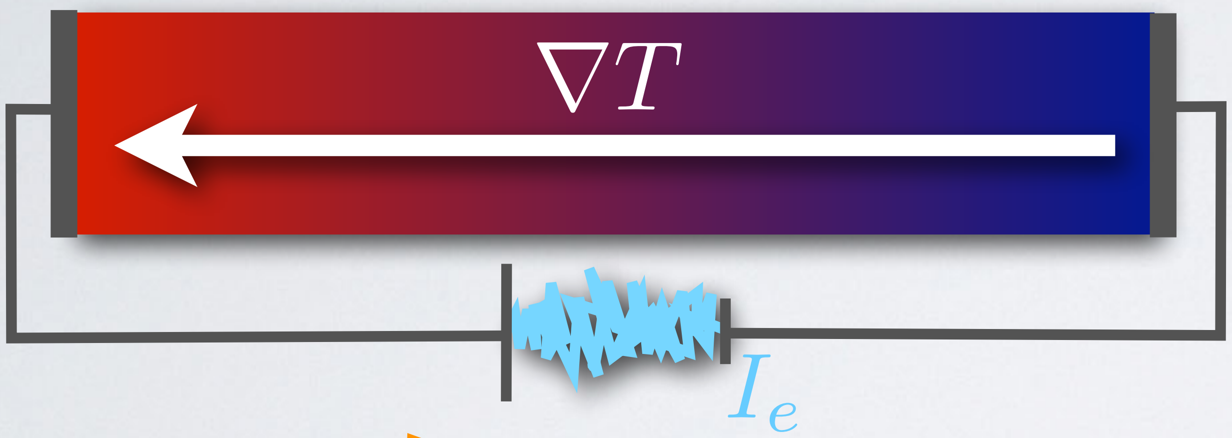


Efficiency $\propto \dfrac{S_{el}^2 \, \sigma_{el} \, T}{\kappa_{ph} + \kappa_{el}}$

We have learnt a lot about *phonon* heat transport in the last decay.

Thermoelectric Elements

Conversion of **temperature gradient** into **electric current.**

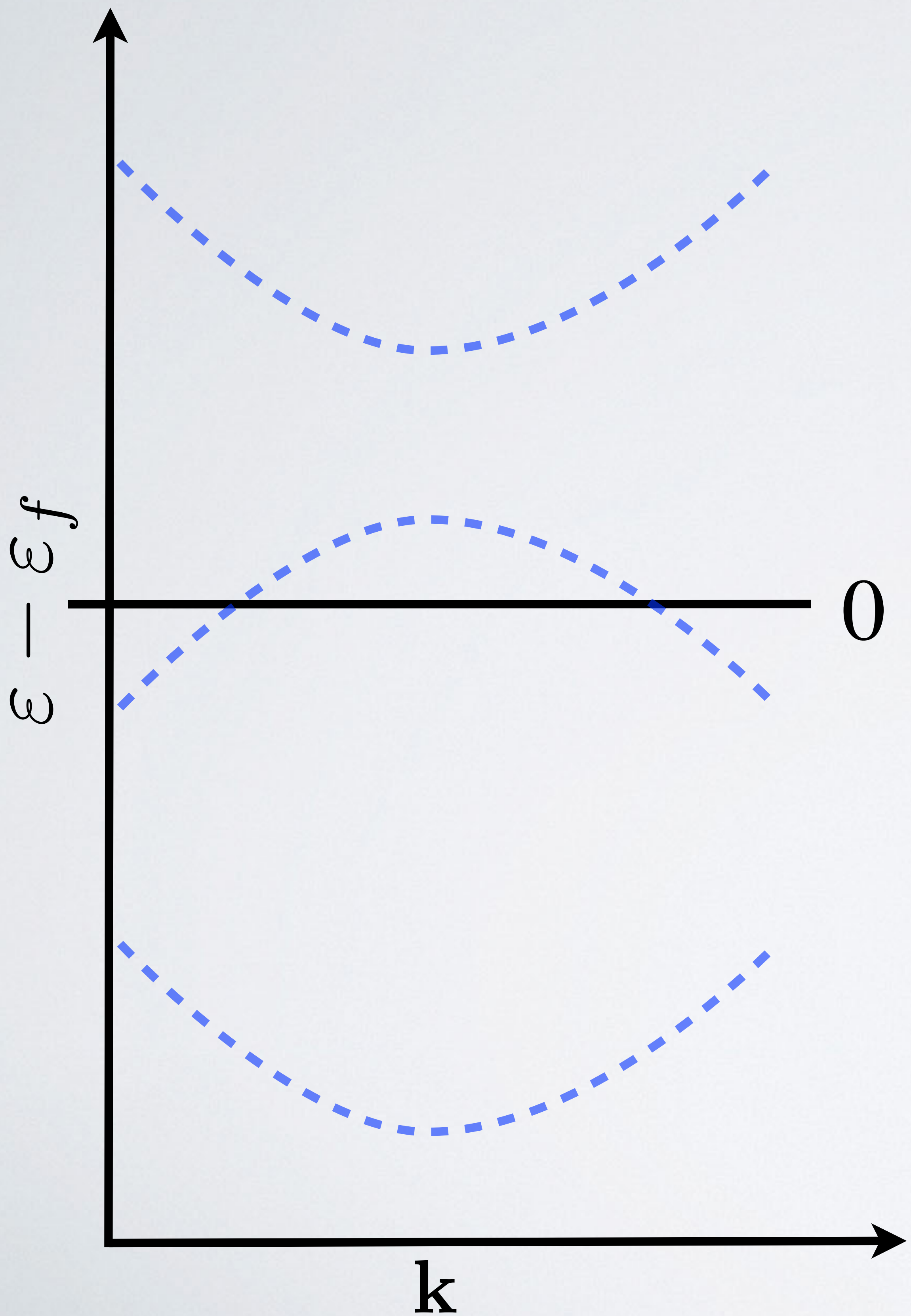


Efficiency $\propto \frac{S_{el}^2 \, \sigma_{el} \, T}{\kappa_{ph} + \kappa_{el}}$

We have learnt a lot about *phonon* heat transport in the last decay.

Electrical Transport even more tricky, since it enters both enumerator and denominator.

ELECTRONS IN A PERIODIC POTENTIAL

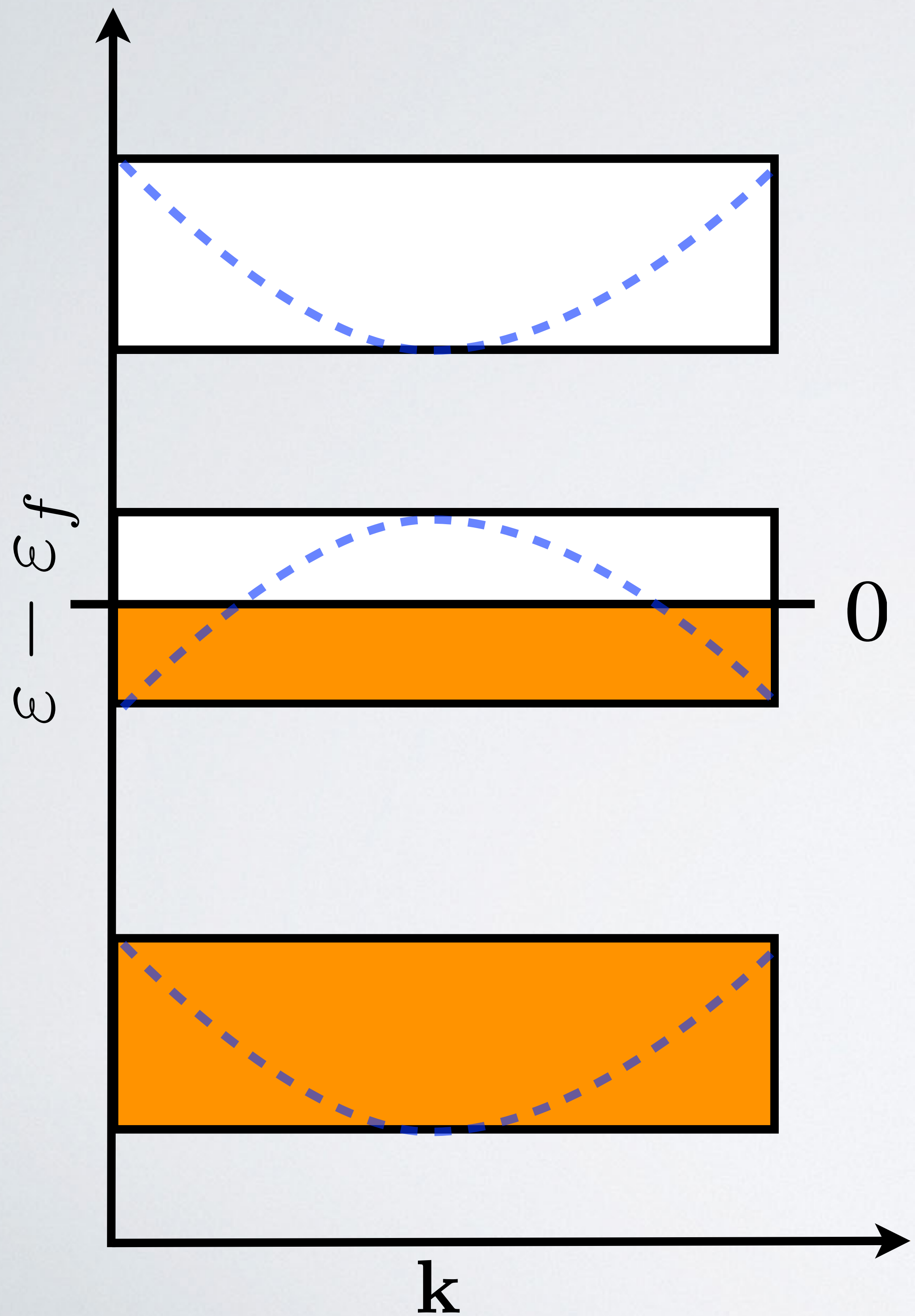


The Bloch Theorem:

F. Bloch, *Z. Physik* **52**, 555 (1929).

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) \cdot e^{i\mathbf{kr}}$$

ELECTRONS IN A PERIODIC POTENTIAL



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F. Bloch, *Z. Physik* **52**, 555 (1929).

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) \cdot e^{i\mathbf{kr}}$$

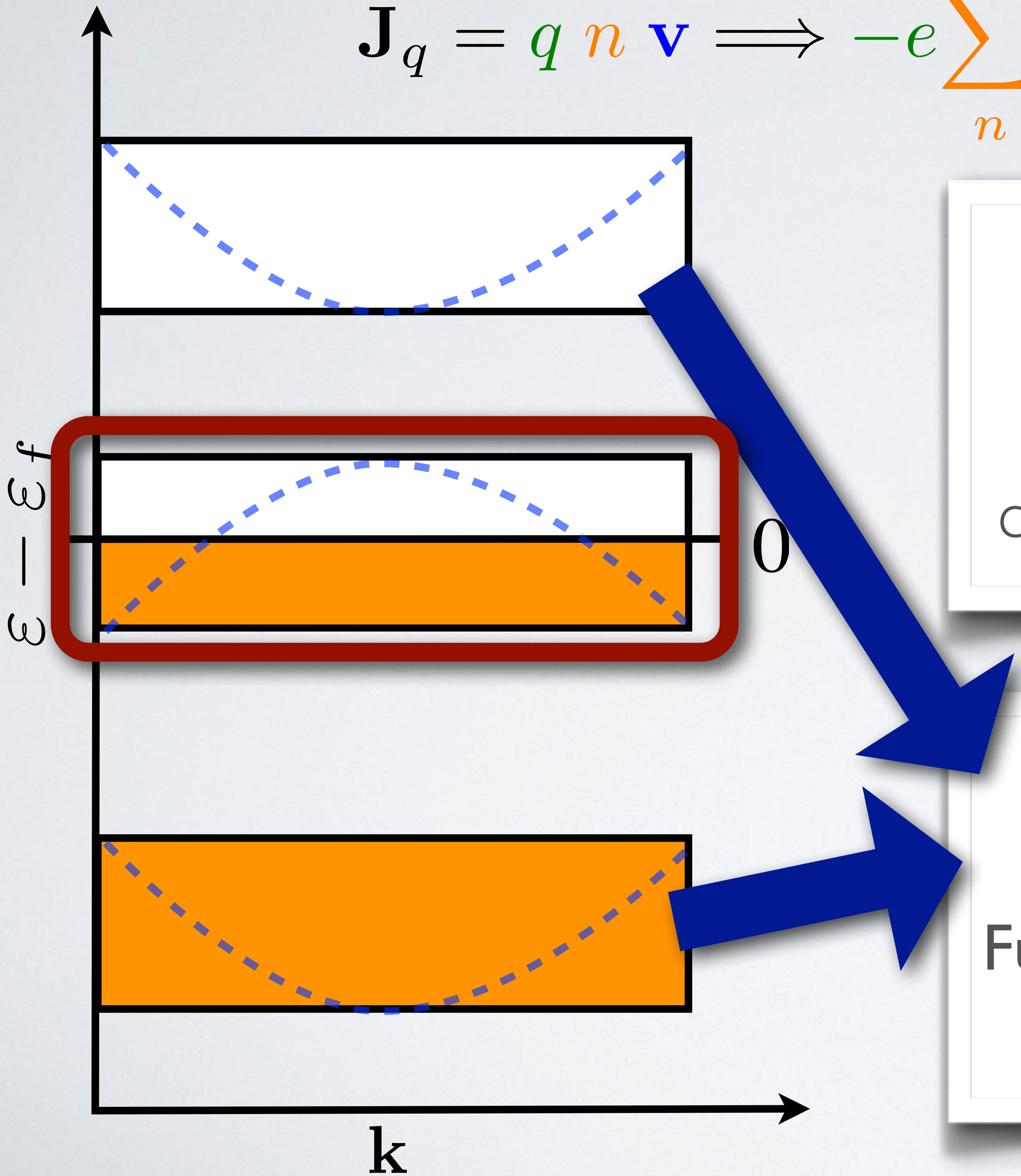
Fermi-Dirac Statistics:

E. Fermi, *Z. Physik* **36**, 902 (1926).
P. Dirac, *Proc. R. Soc. A* **112**, 661 (1926).

$$f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - \varepsilon_f}{k_B T}\right)}$$

ELECTRONS IN A PERIODIC POTENTIAL

$$\mathbf{J}_q = q\, n\, \mathbf{v} \Longrightarrow -e\sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n(\mathbf{k}))\, \mathbf{v}_n(\mathbf{k})$$



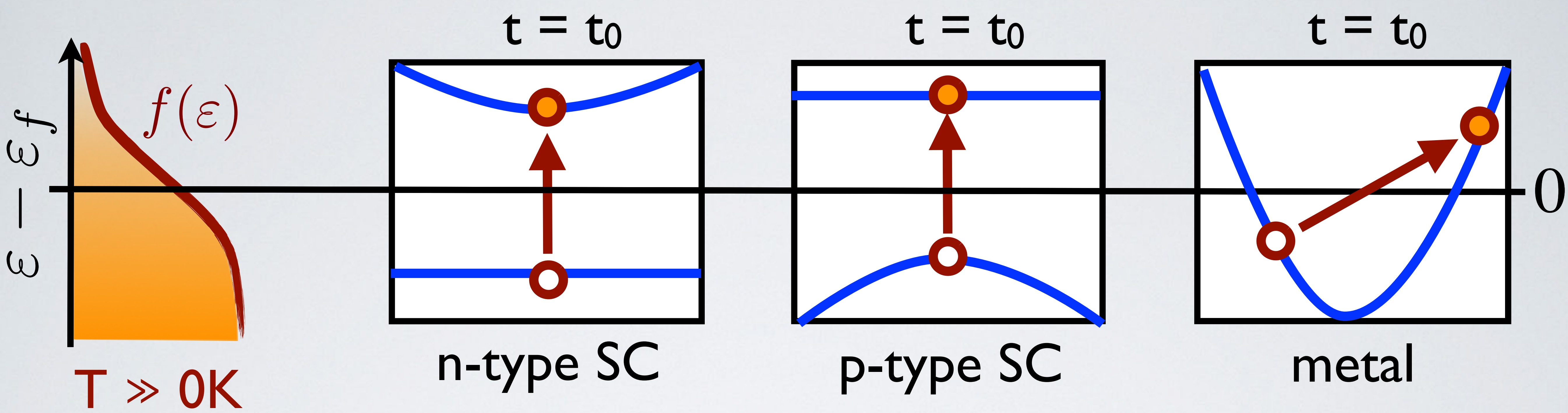
$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$$

Each electron ***(n,k)*** has a constant avg. velocity ***$v_n(k)$***.

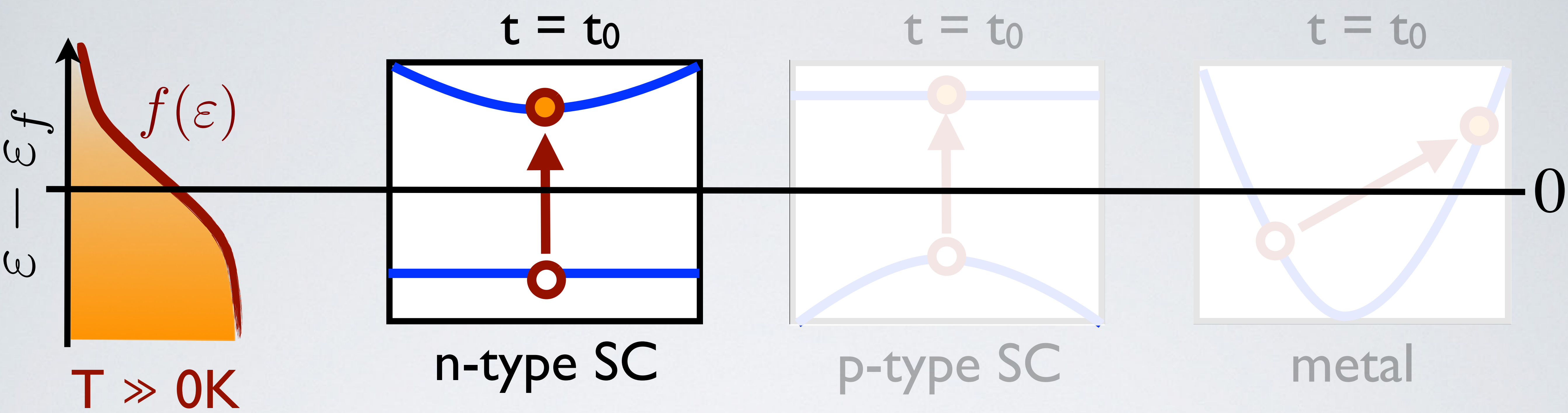
$$\int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k}) = 0$$

Fully filled and **empty** bands do not contribute to J_q

INSTANTANEOUS NON-EQUILIBRIUM



INSTANTANEOUS NON-EQUILIBRIUM

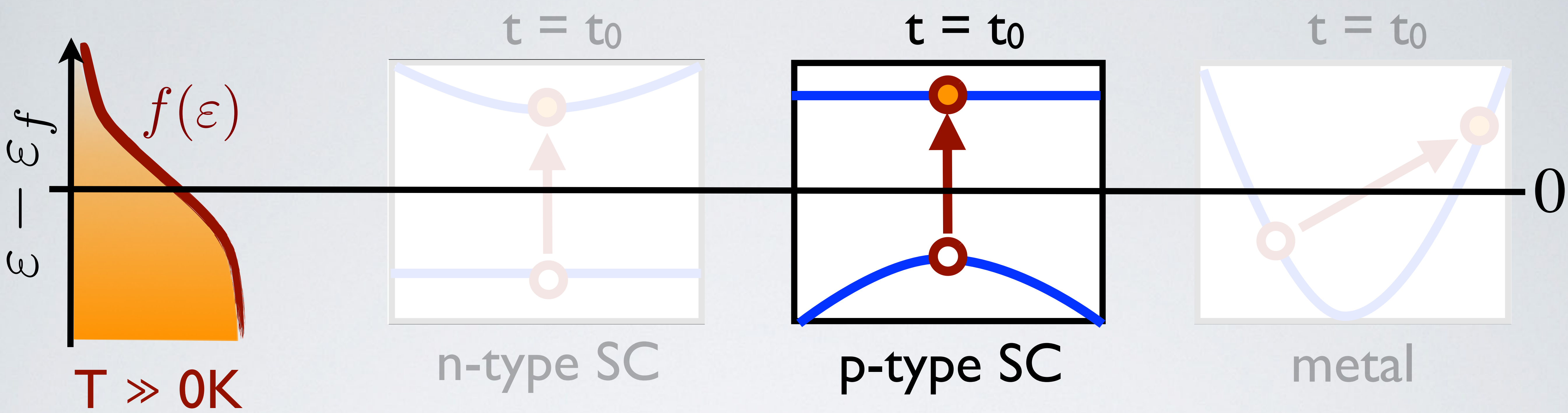


$$\mathbf{J}_q^{nk} = -e\,\mathbf{v}_n(\mathbf{k})$$

$$\mathbf{J}_e = -e\,\mathbf{v}_e(\mathbf{k_e}) \qquad \mathbf{J}_h = 0$$

In **n-type** semiconductors, **electrons** are the **majority charge carriers**.

INSTANTANEOUS NON-EQUILIBRIUM

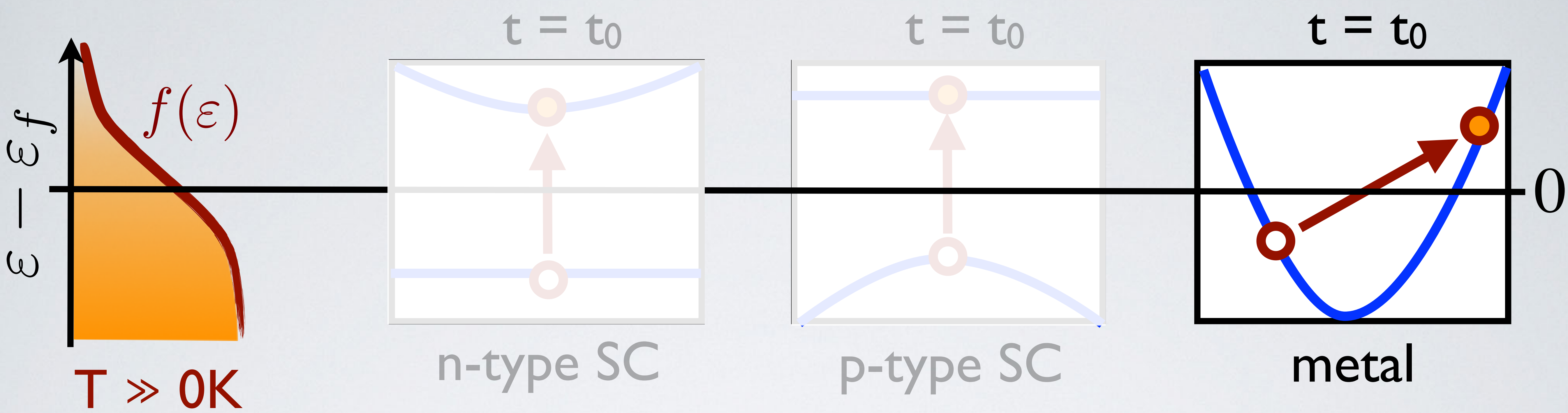


$$\mathbf{J}_q^{nk} = -e\,\mathbf{v}_n(\mathbf{k})$$

$$\mathbf{J}_e = 0 \qquad \mathbf{J}_h = +e\,\mathbf{v}_h(\mathbf{k_h})$$

In **p-type** semiconductors, **holes** are the **majority charge carriers**.

INSTANTANEOUS NON-EQUILIBRIUM



$$\mathbf{J}_q^{nk} = -e\,\mathbf{v}_n(\mathbf{k})$$

$$\mathbf{J}_e = -e\,\mathbf{v}_e(\mathbf{k_e}) \qquad \mathbf{J}_h = +e\,\mathbf{v}_h(\mathbf{k_h})$$

In typical **metals** with $\mathbf{v_e > v_h}$,
electrons are the **majority charge carriers**.

BOLTZMANN TRANSPORT EQUATION

N. W Ashcroft and N. D. Mermin, *"Solid State Physics"* (1976).

$$\sigma = -e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}}$$

$$S = -\frac{e k_B}{\sigma} \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}} \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)$$

$$\kappa_{el} = -k_B^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \tau_{n\mathbf{k}} \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)^2$$

Group velocity

Eq. population

scattering time

Band structure calculation

?

BOLTZMANN TRANSPORT EQUATION

N. W Ashcroft and N. D. Mermin, *"Solid State Physics"* (1976).

$$\sigma = -e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n}\right) \tau_{n\mathbf{k}}$$

$$S = -\frac{ek_B}{\sigma} \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n}\right) \tau_{n\mathbf{k}} \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T}\right)$$

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~~Electron-electron scattering~~

Electron-nuclei scattering

defects

phonons

SINGLE RELAXATION TIME APPROXIMATION

N.W Ashcroft and N. D. Mermin, *"Solid State Physics"* (1976).

$$\sigma = -e^2 \, \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \, \mathbf{v}_n(\mathbf{k}) \, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right)$$

$$S = -\frac{e k_B}{\sigma} \, \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \, \mathbf{v}_n(\mathbf{k}) \, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)$$

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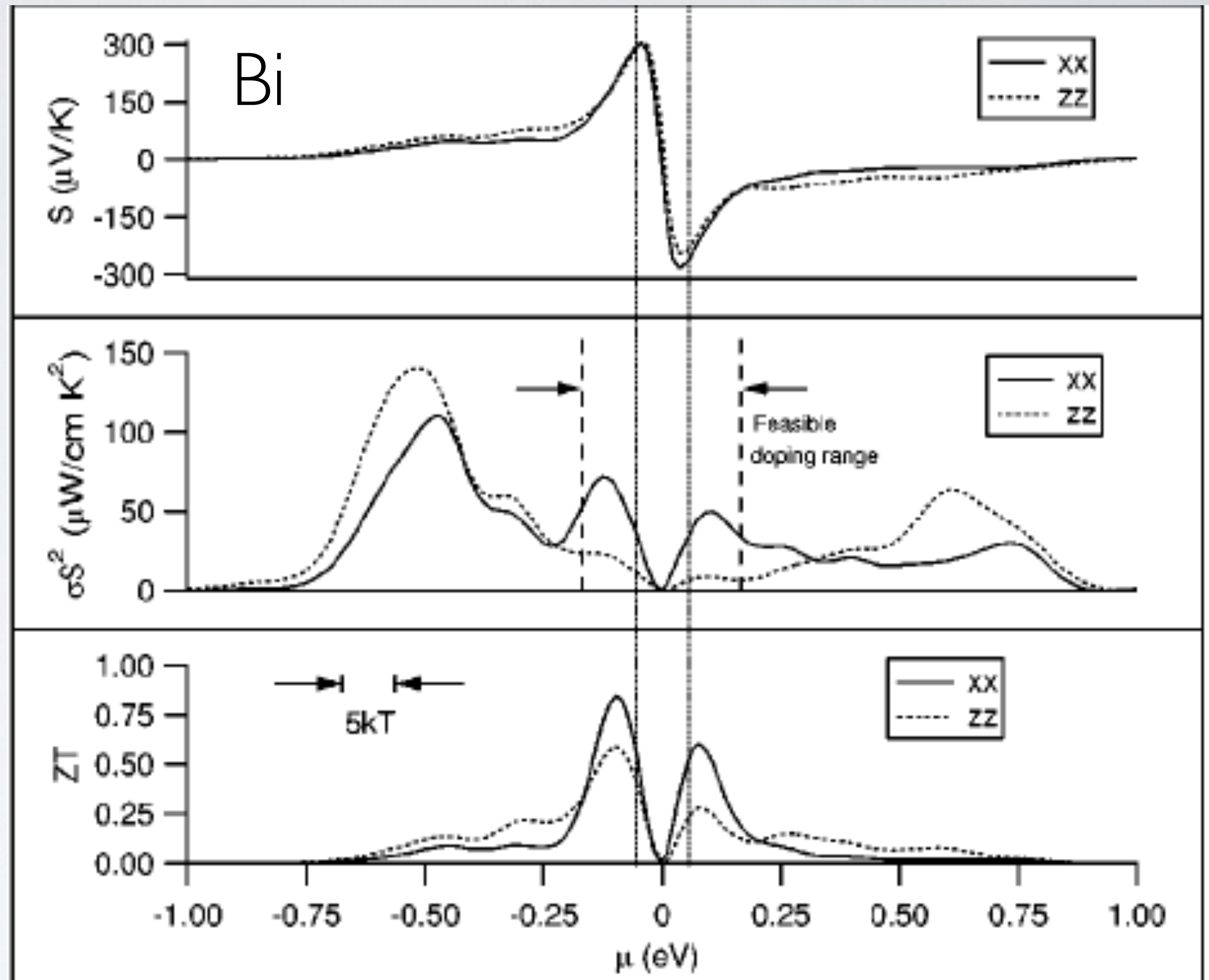
Energy and Crystal Momentum independent scattering time: SRTA

SINGLE RELAXATION TIME APPROXIMATION

- Accurate **band structure**
- *“Reasonable” relaxation time*

Electronic Transport Coefficients



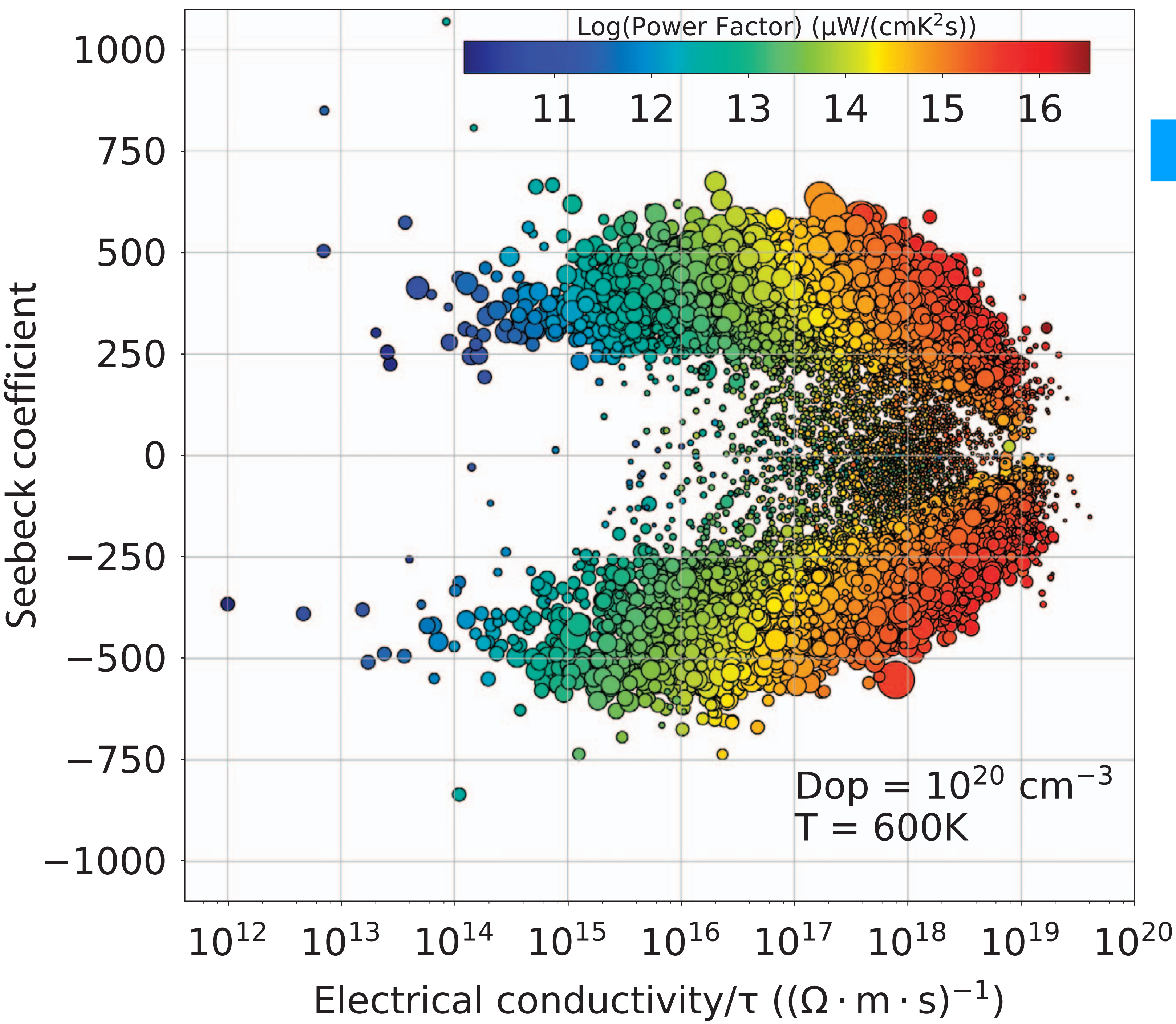
T. Thonhauser, T. J. Scheidemantel, and J. O. Sofo, *Appl. Phys. Lett.* **85**, 588 (2004).

T. J. Scheidemantel, *et al.* *Phys. Rev. B* **68**, 125210 (2003)

Ab initio electronic transport database

BoltzTrap Code: G. K. H. Madsen and D. J. Singh, *Comp. Phys. Comm.* **175**, 67 (2006).

F. Ricci, *et al.*, *Scientific Data* 4,170085 (2017).



~48,000 materials

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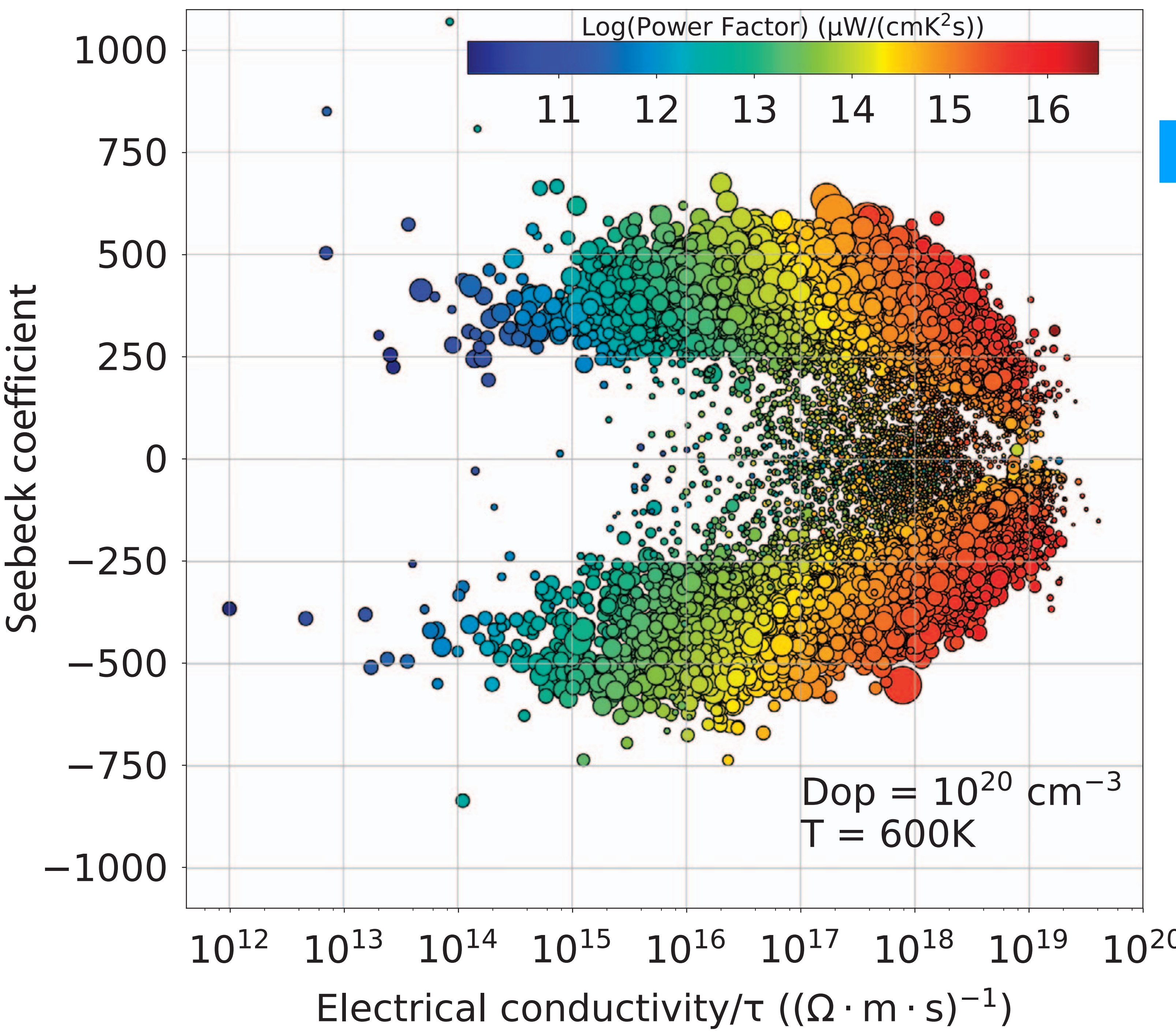

~48,000 materials

Why is the SRTA useful at all?

Ab initio electronic transport database

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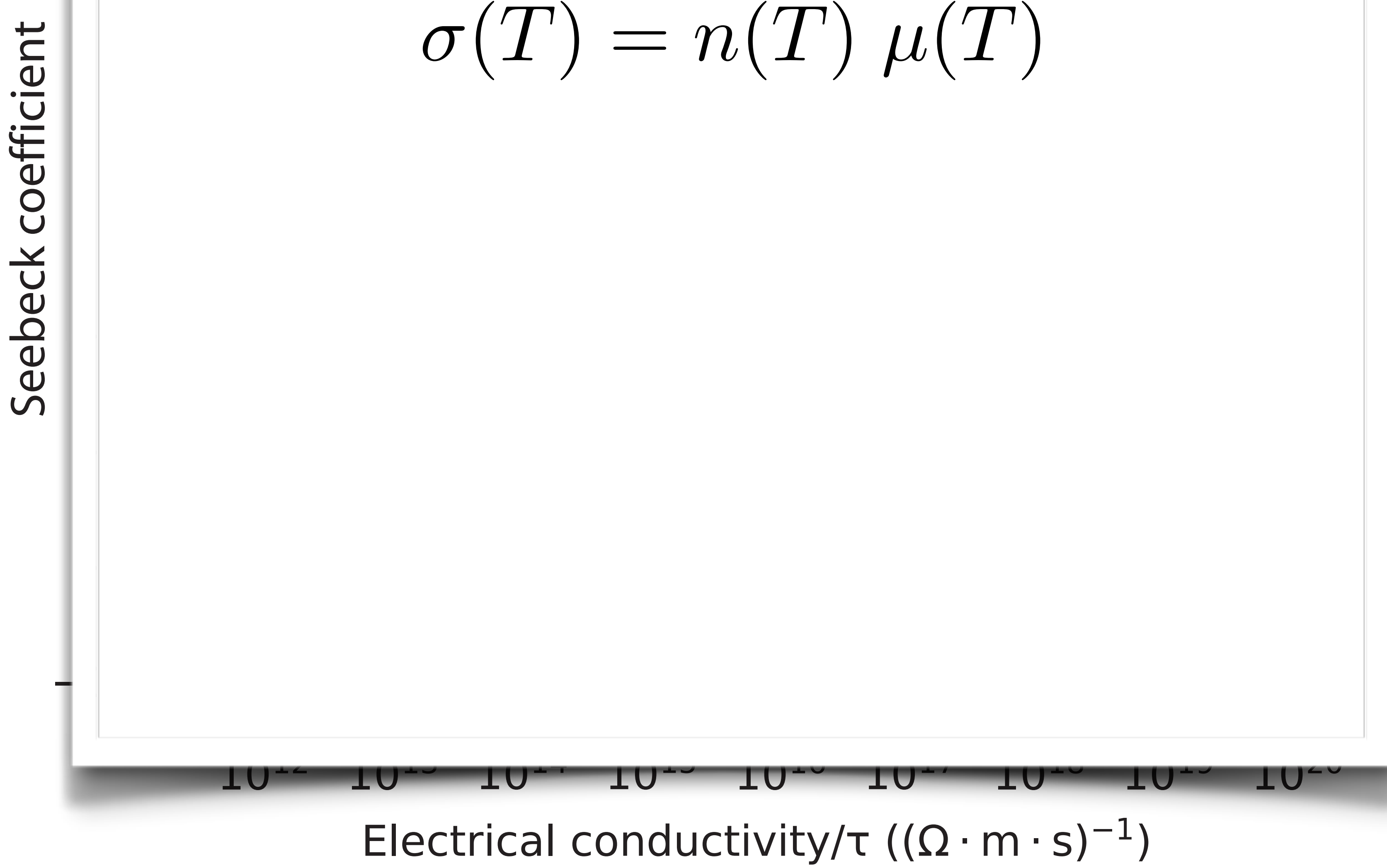

Remember:

Conductivity = Charge Carriers * Mobility

$$\sigma(T) = n(T)\ \mu(T)$$

~48,000 materials

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Remember:

Conductivity = Charge Carriers * Mobility

$$\sigma(T) = n(T)\ \mu(T)$$

Lifetime-independent contribution from

$$n(T) \sim \exp\left(-E_g/k_B T\right)$$

is the leading term.

Seebeck coefficient

Electrical conductivity/τ $((\Omega \cdot m \cdot s)^{-1})$

~48,000 materials

Why is the SRTA useful at all?

Ab initio electronic transport database

BoltzTrap Code: G. K. H. Madsen and D. J. Singh, *Comp. Phys. Comm.* **175**, 67 (2006).

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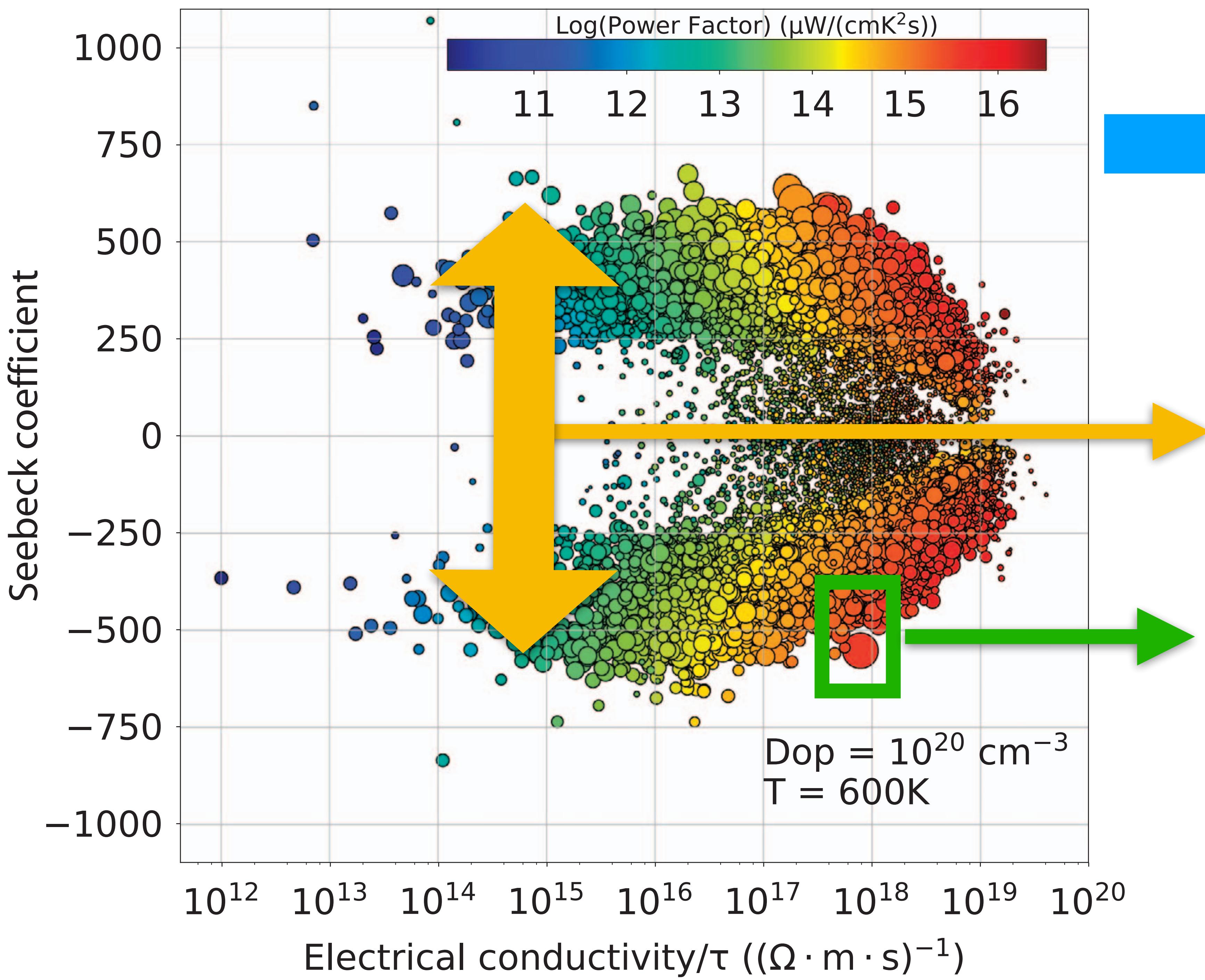


~48,000 materials

SRTA is good for trends over orders of magnitude

Mobility and lifetimes needed for accurate predictions

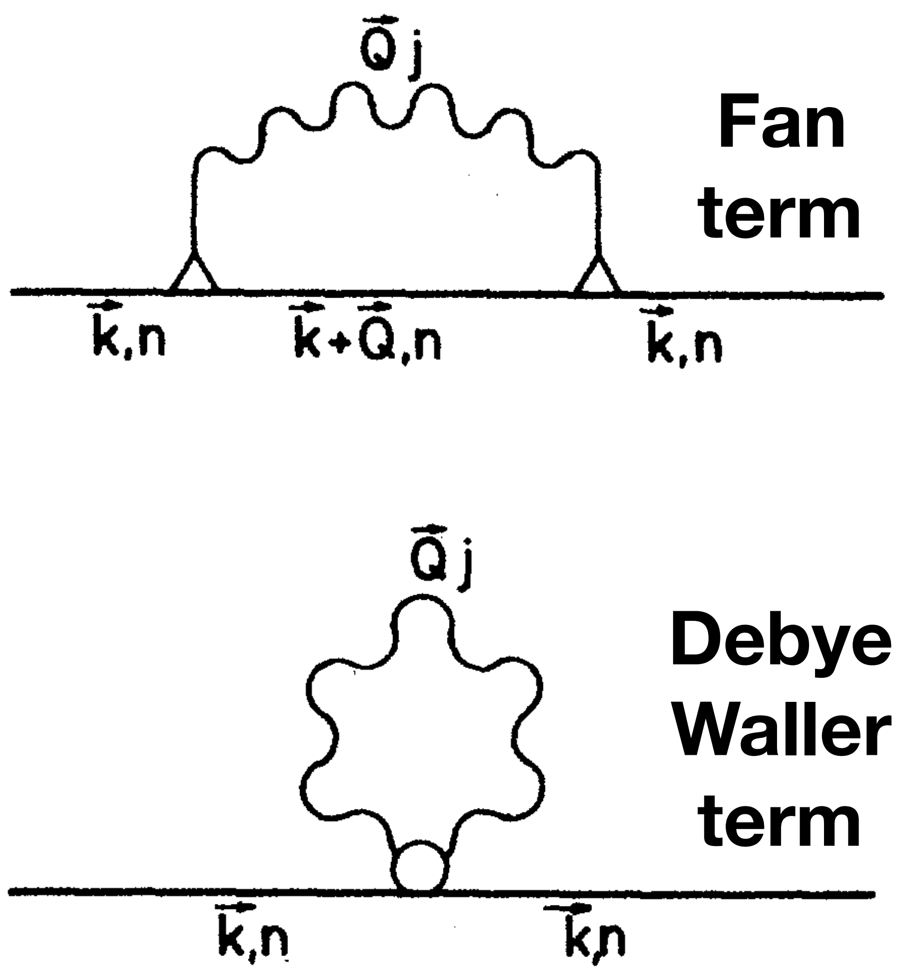
Heine-Allen-Cardona Theory

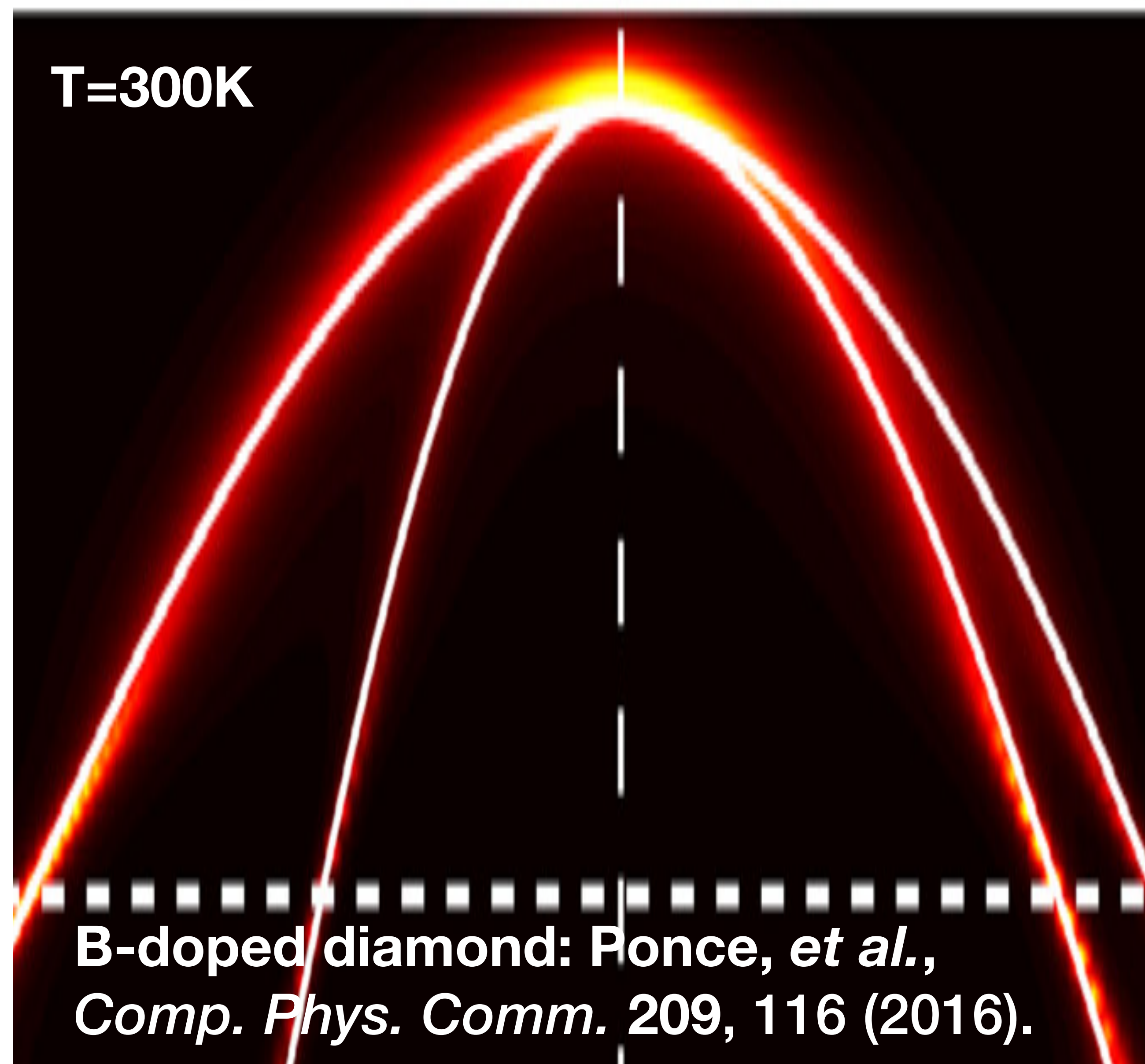
P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).

Electron-Phonon Couplings $g_{mn\nu}(\mathbf{q},\mathbf{k})$

Imaginary Electronic Self-energies

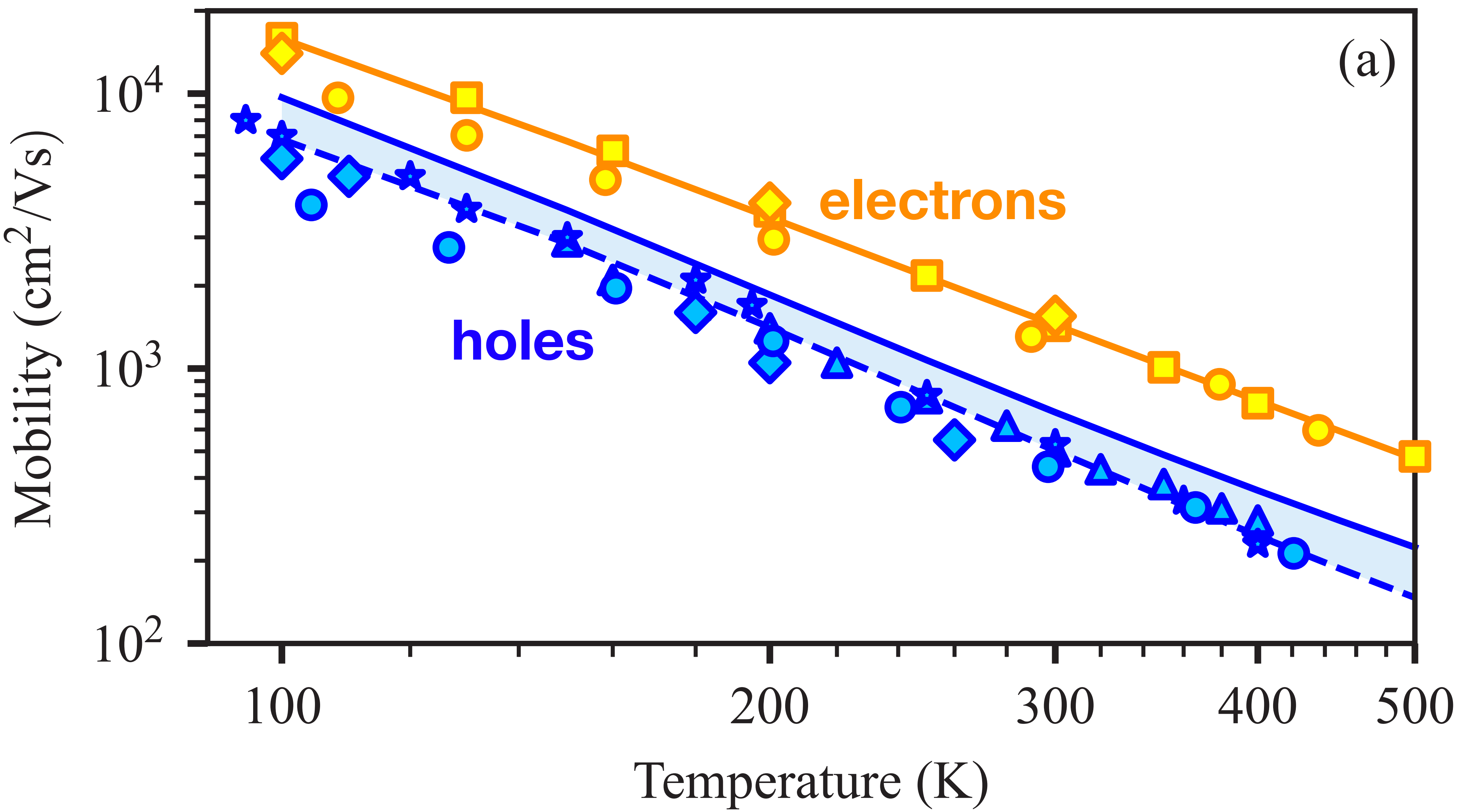
Many-Body Perturbation Theory





Heine-Allen-Cardona Theory

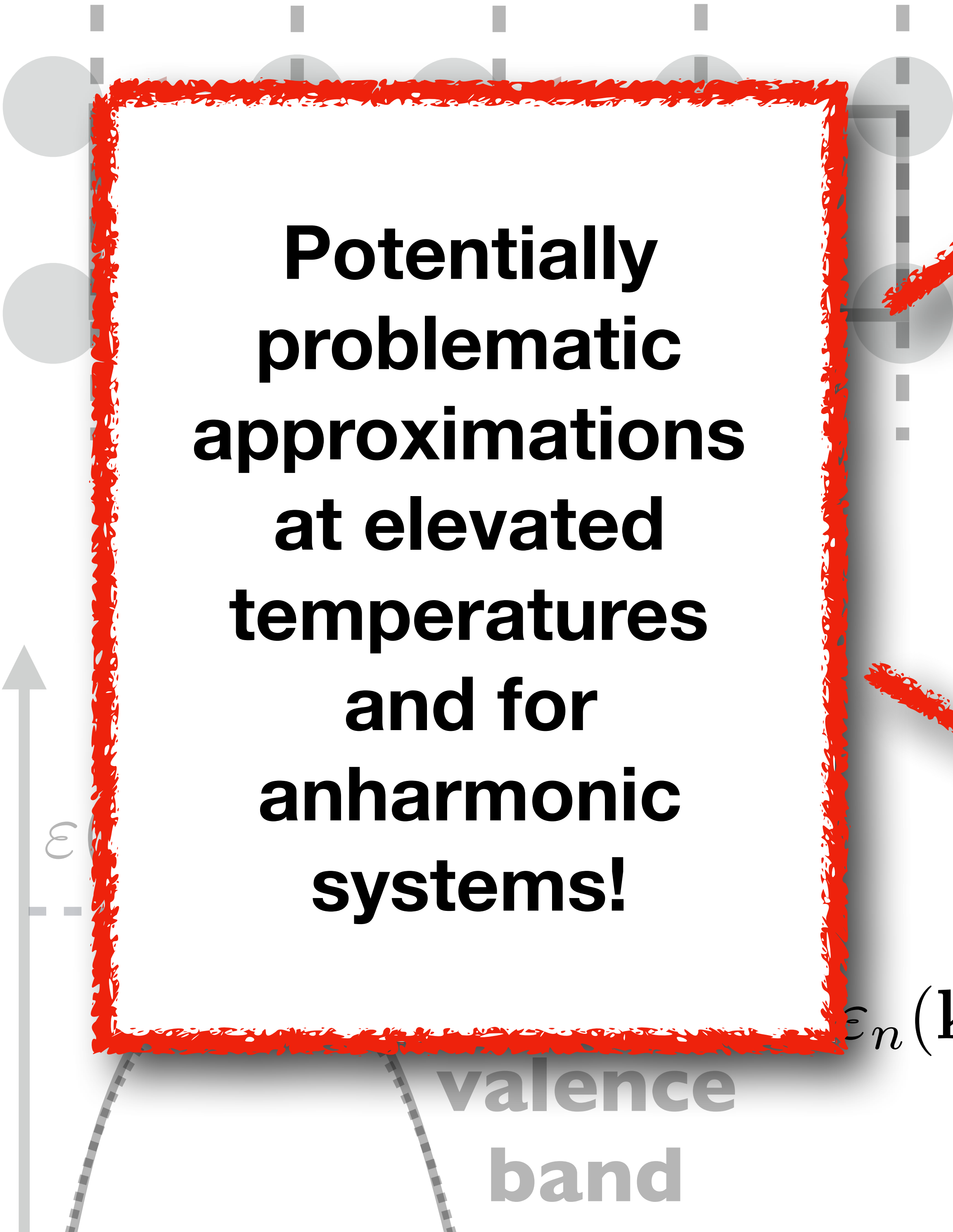
P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).



S. Poncé, E. R. Margine, and F. Giustino, *Phys. Rev. B* **97**, 121201 (2018).

Electron-phonon interactions from first principles

F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).



Potentially problematic approximations at elevated temperatures and for anharmonic systems!

Harmonic Approximation for Nuclear Motion

$$E\left(\{\Delta \mathbf{R}\}\right) \approx \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta \mathbf{R}_i \Delta \mathbf{R}_j$$

"Harmonic Approximation" for Electronic Structure

$$\varepsilon_n(\mathbf{k})\left(\{\Delta \mathbf{R}\}\right) \approx \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 \varepsilon_n(\mathbf{k})}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta \mathbf{R}_i \Delta \mathbf{R}_j$$

SINGLE RELAXATION TIME APPROXIMATION

N.W Ashcroft and N. D. Mermin, "*Solid State Physics*" (1976).

The **conductivity** is intrinsically related to the **effective mass**:

$$\sigma = -e^2\tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n}\right)$$

$$= -e^2\tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

The **AC conductivity** does not depend on the **relaxation time** τ for $\omega\tau \gg 1$

$$\sigma(\omega) = -\frac{e^2\tau}{1 - i\omega\tau} \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

$$\xrightarrow{\omega\tau \gg 1} \frac{e^2}{i\omega} \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

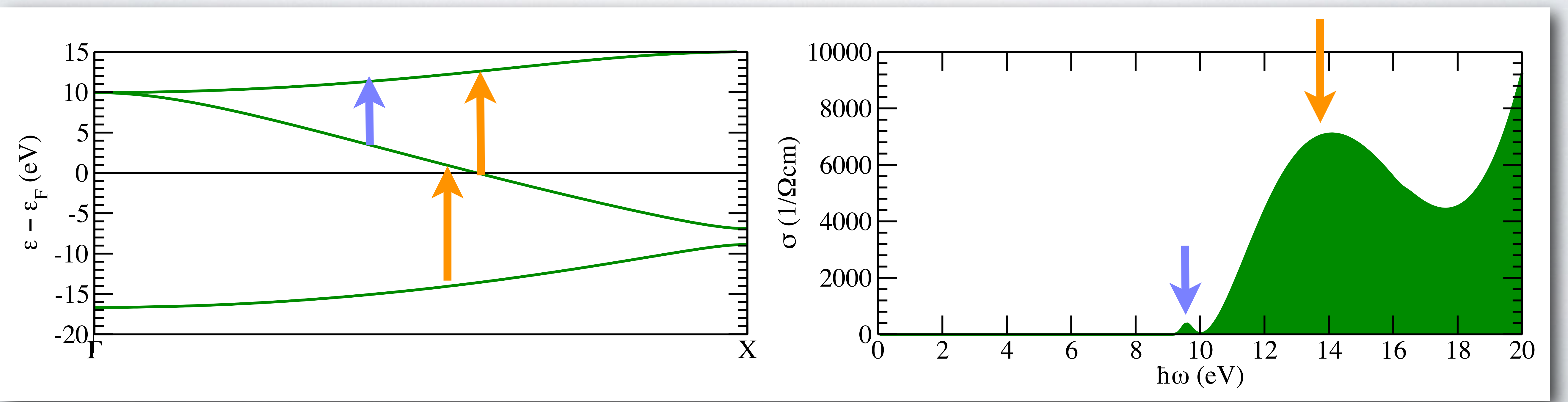
OPTICAL CONDUCTIVITY

N.W Ashcroft and N. D. Mermin, *"Solid State Physics"* (1976).

Using **perturbation theory,** we can thus compute the **AC (optical) conductivity** (in the independent particle approximation).

$$\sigma(\omega) \xrightarrow{\omega\tau \gg 1} \frac{e^2}{i\omega} \sum_n \int \frac{d\mathbf{k}}{4\pi^3} f(\varepsilon_n) \frac{1}{\hbar^2} \frac{\partial^2 \varepsilon}{\partial \mathbf{k}\, \partial \mathbf{k}}$$

$$= \frac{e^2\hbar^2}{i\omega m_e^2} \sum_{n,m\neq n} \int \frac{d\mathbf{k}}{4\pi^3} \left[f(\varepsilon_n) - f(\varepsilon_m)\right] \frac{|\langle nk|\, \nabla \,|mk\rangle|^2}{\varepsilon_n - \varepsilon_m - \hbar\omega}$$



ficticious sc-Aluminum along X direction

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

Kubo's Linear Response:

$$\sigma(\omega) = \frac{1}{V} \left\langle \lim_{\varepsilon \to 0} \int_0^\infty dt\, e^{i(\omega + i\varepsilon)t} \int_0^{(k_B T)^{-1}} d\tau\, \mathbf{Tr} \left[\hat{\rho}_0\, \mathbf{j}_c(t - i\hbar\tau) \cdot \mathbf{j}_c(t) \right] \right\rangle_T$$

Independent Particle Picture:

$$\mathbf{j}_c = -\frac{e}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} \xrightarrow{\text{Heisenberg picture}} \mathbf{j}_c(t)$$

$$\sigma(\omega) = \frac{e^2 \hbar^2}{m_e^2 \omega} \frac{2\pi}{V} \left\langle \sum_{n, n \neq m} \sum_{\mathbf{k}} w_k \left[f(\varepsilon_n) - f(\varepsilon_m) \right] \left| \langle n\mathbf{k} | \nabla | m\mathbf{k} \rangle \right|^2 \delta\left(\varepsilon_n - \varepsilon_m - \hbar\omega \right) \right\rangle_T$$

B. Holst, M. French, and R. Redmer, *Phys. Rev. B* **83**, 235120 (2011).

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

For **ω ≠ *0***, the **electrical conductivity** can be computed from the ***thermodynamic average* <>*T*** :

$$\sigma(\omega) = \frac{e^2\hbar^2}{m_e^2\omega}\frac{2\pi}{V}\left\langle \sum_{n,n\neq m}\sum_{\mathbf{k}} w_k \left[f(\varepsilon_n) - f(\varepsilon_m)\right] \left|\langle n\mathbf{k}|\nabla|m\mathbf{k}\rangle\right|^2 \delta\left(\varepsilon_n - \varepsilon_m - \hbar\omega\right)\right\rangle_T$$

(a) Thermodynamic average of the band structure is sampled
⇒ no rigid band approximation

(b) Full adiabatic electron-phonon coupling is accounted for if the thermodynamic average is perfomed via ab initio MD
⇒ no perturbative approximation

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D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

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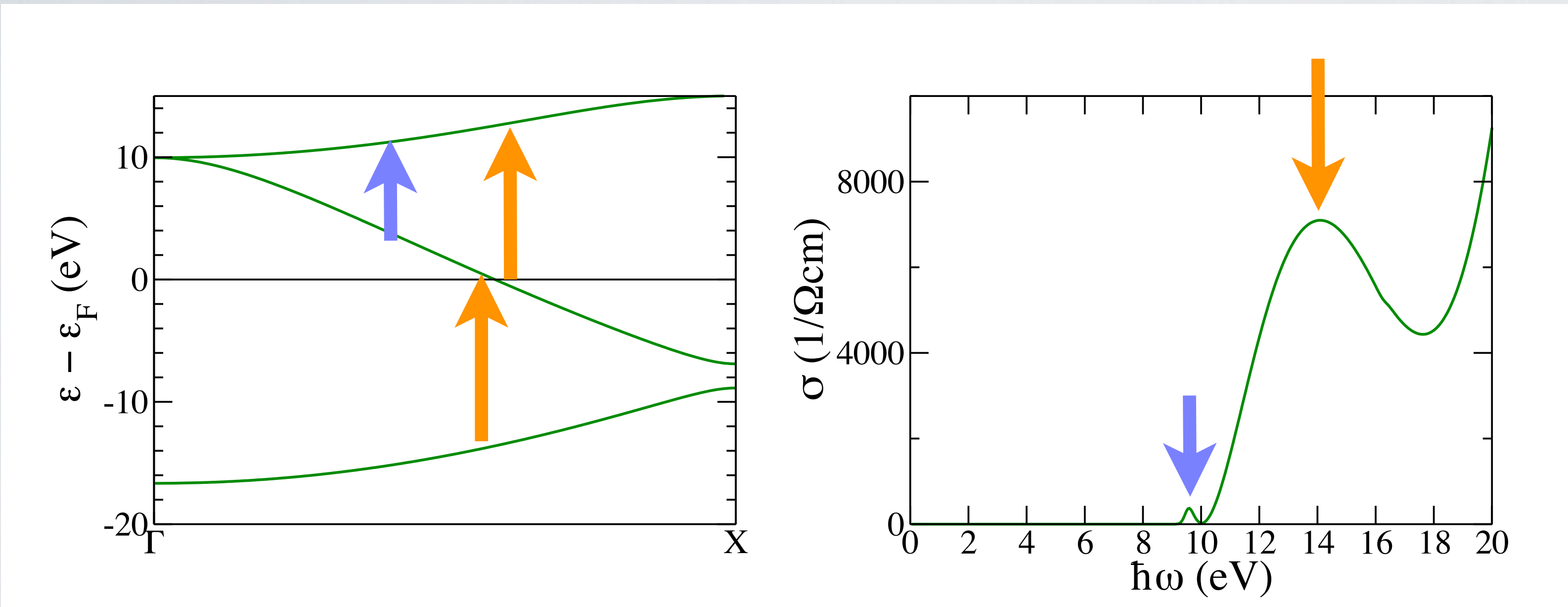
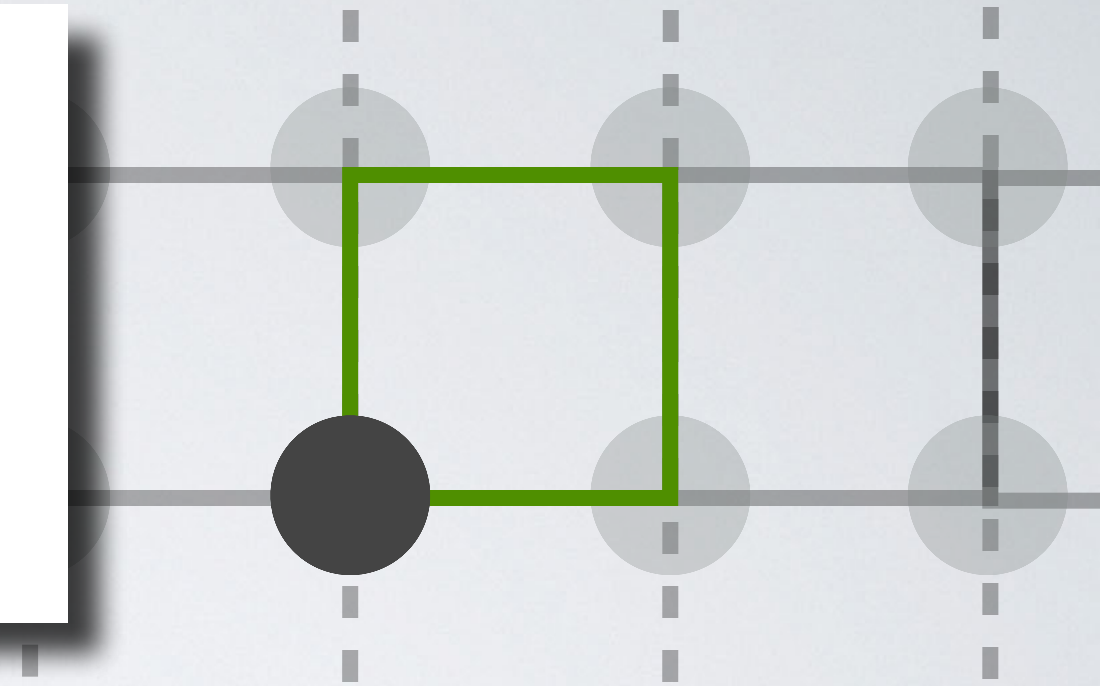
Compare: Optical conductivity in **SRT approximation**

$$\sigma(\omega) \xrightarrow{\omega\tau \gg 1} \frac{e^2\hbar^2}{m_e^2\omega}\sum_{n,m\neq n}\int \frac{d\mathbf{k}}{4\pi^3}\left[f(\varepsilon_n) - f(\varepsilon_m)\right]\frac{|\langle nk|\nabla|mk\rangle|^2}{\varepsilon_n - \varepsilon_m - \hbar\omega}$$

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).





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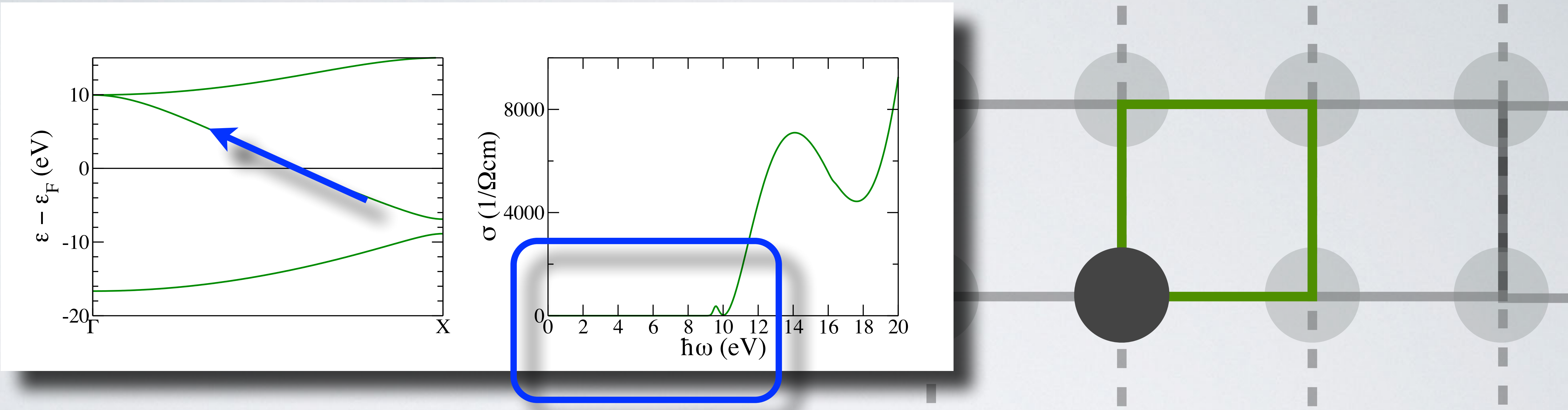
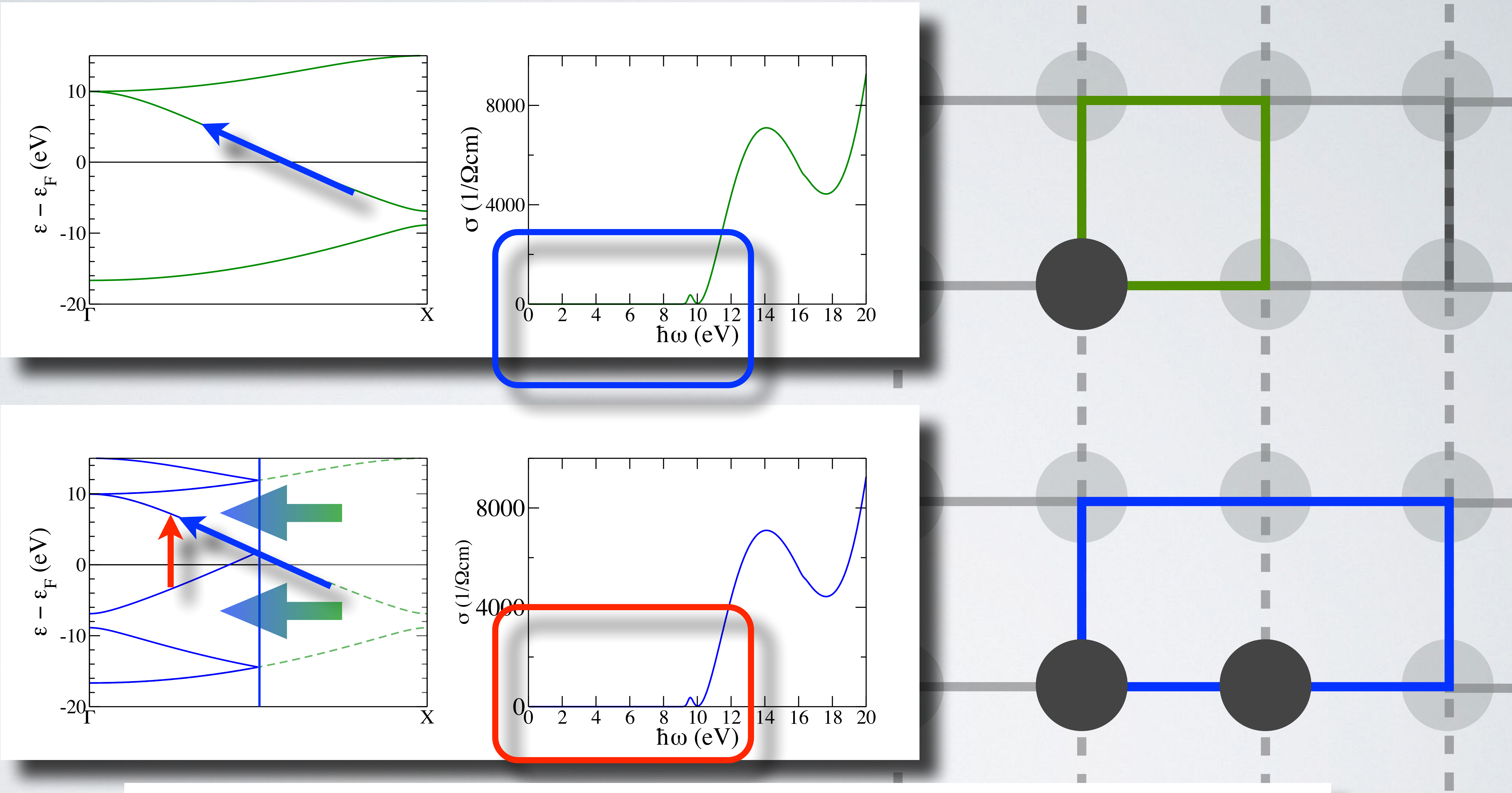


Crystal Momentum Conservation:
Non-vertical transitions require **phonons**

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

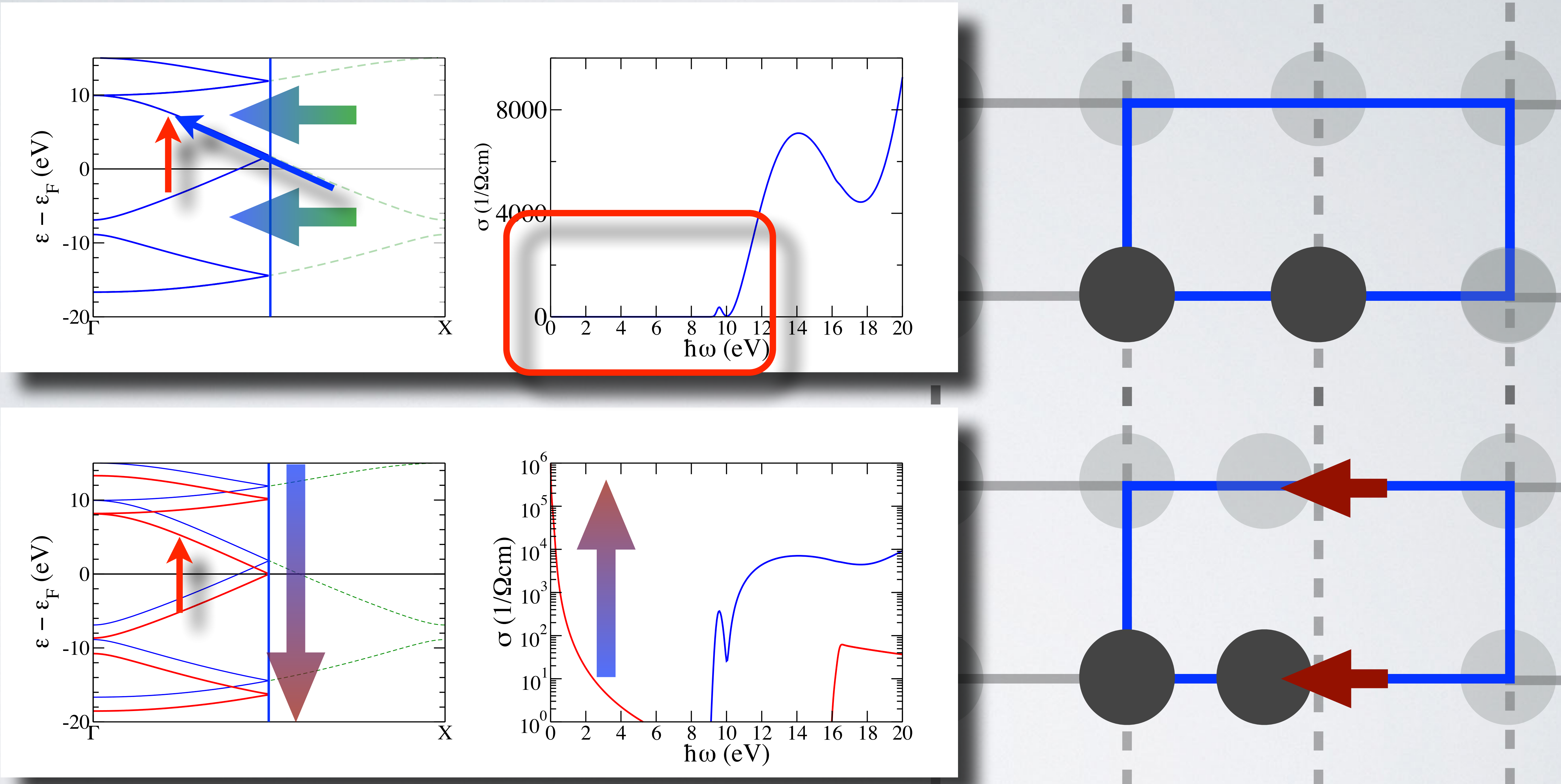


Brillouin zone folding:

Larger supercells allow for **direct transitions** that are however suppressed by **symmetry**.

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).

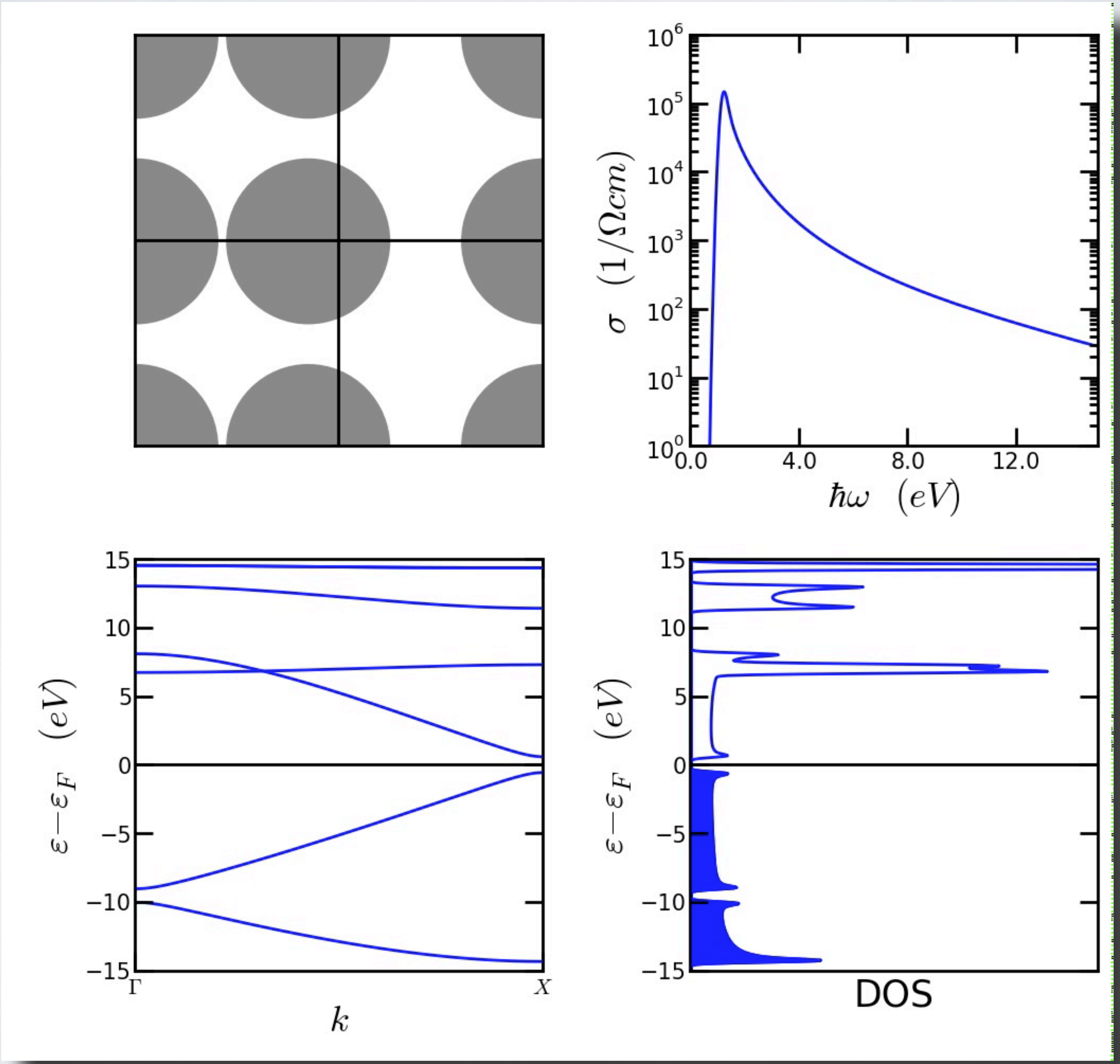


Thermal Motion of the nuclei:

Phonons momentarily break the **symmetry** and thus allow the **direct transitions** to become **active**.

GREENWOOD-KUBO FORMALISM

D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).



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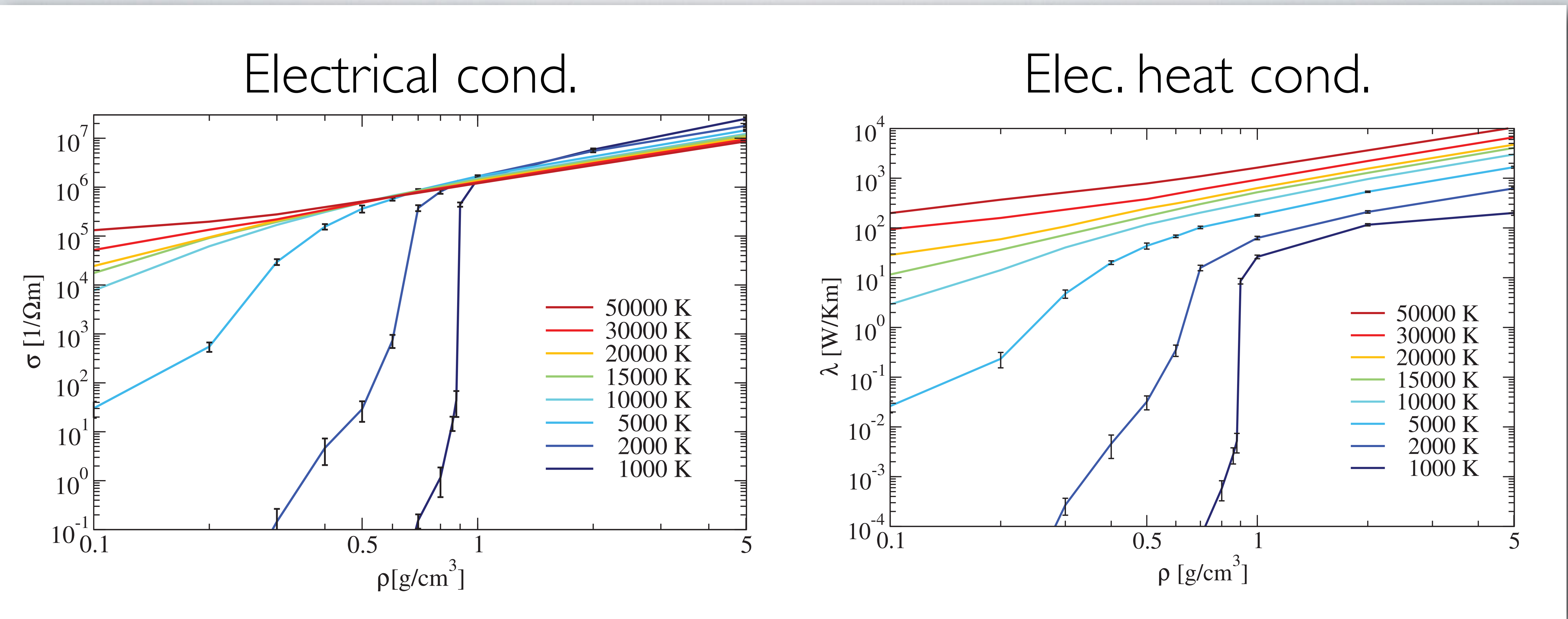

Non-metal to metal transition in dense liquid hydrogen

B. Holst, M. French, and R. Redmer, *Phys. Rev. B* **83**, 235120 (2011).

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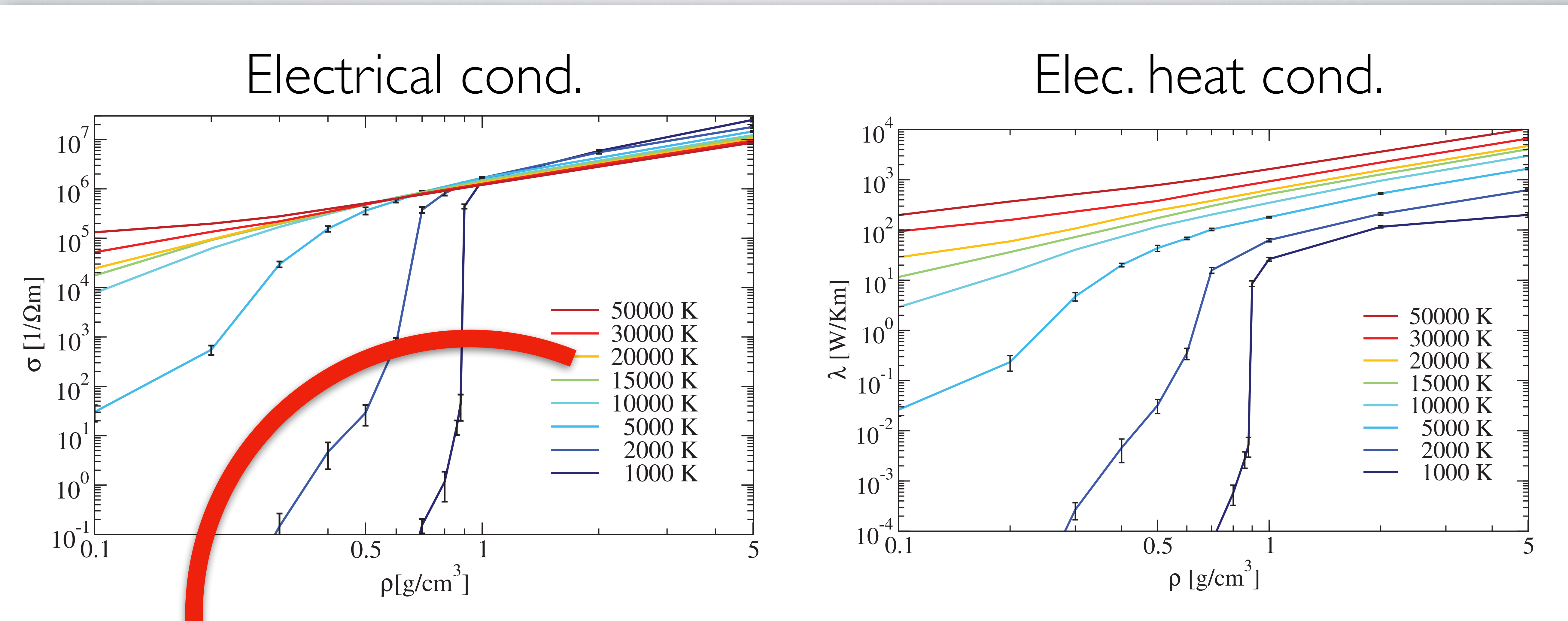
D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).



Non-metal to metal transition in dense liquid hydrogen

B. Holst, M. French, and R. Redmer, *Phys. Rev. B* **83**, 235120 (2011).

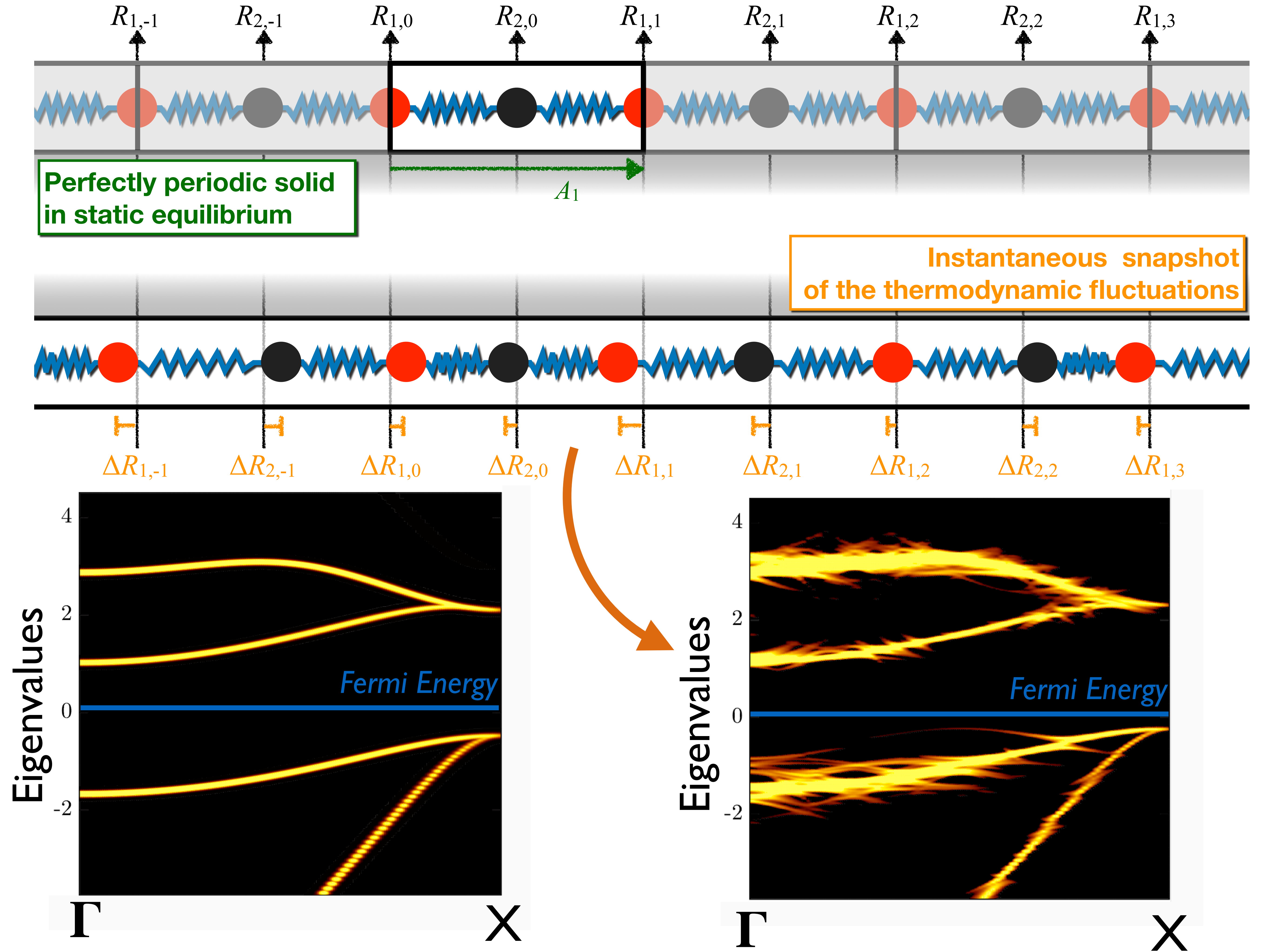
Hard to converge for reasonable temperatures in crystalline materials.

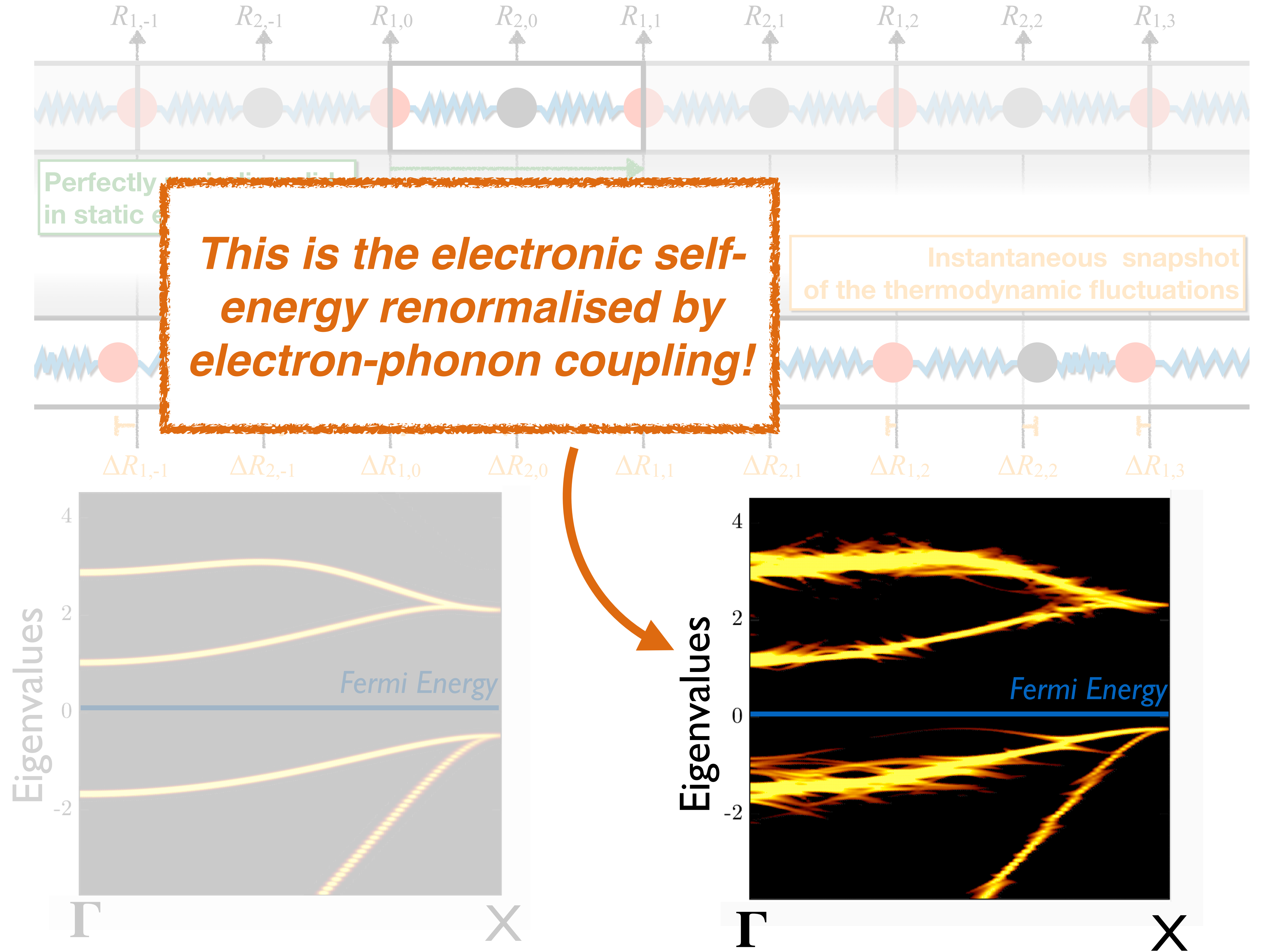
SUMMARY

The **nuclear motion** affects the **electronic structure:**
Real-part of the self-energy: renormalization of the eigenvalues
Imaginary-part of the self-energy: finite lifetimes/broadening

Perturbative approaches have reached a **maturity** level that allows the routinely assessment of electron-phonon coupling.

Anharmonic effects are still a massive challenge in this field.


$R_{1,-1}$ $R_{2,-1}$ $R_{1,0}$ $R_{2,0}$ $R_{1,1}$ $R_{2,1}$ $R_{1,2}$ $R_{2,2}$ $R_{1,3}$
Perfectly periodic solid in static equilibrium
A_1
Instantaneous snapshot of the thermodynamic fluctuations
$\Delta R_{1,-1}$ $\Delta R_{2,-1}$ $\Delta R_{1,0}$ $\Delta R_{2,0}$ $\Delta R_{1,1}$ $\Delta R_{2,1}$ $\Delta R_{1,2}$ $\Delta R_{2,2}$ $\Delta R_{1,3}$
Eigenvalues
Fermi Energy
4
2
0
-2
Γ
X
Eigenvalues
Fermi Energy
4
2
0
-2
Γ
X


$R_{1,-1}$ $R_{2,-1}$ $R_{1,0}$ $R_{2,0}$ $R_{1,1}$ $R_{2,1}$ $R_{1,2}$ $R_{2,2}$ $R_{1,3}$
Perfectly
in static e
This is the electronic self-energy renormalised by electron-phonon coupling!
Instantaneous snapshot
of the thermodynamic fluctuations
$\Delta R_{1,-1}$ $\Delta R_{2,-1}$ $\Delta R_{1,0}$ $\Delta R_{2,0}$ $\Delta R_{1,1}$ $\Delta R_{2,1}$ $\Delta R_{1,2}$ $\Delta R_{2,2}$ $\Delta R_{1,3}$
Eigenvalues
4
2
0
-2
Fermi Energy
Γ
X
Eigenvalues
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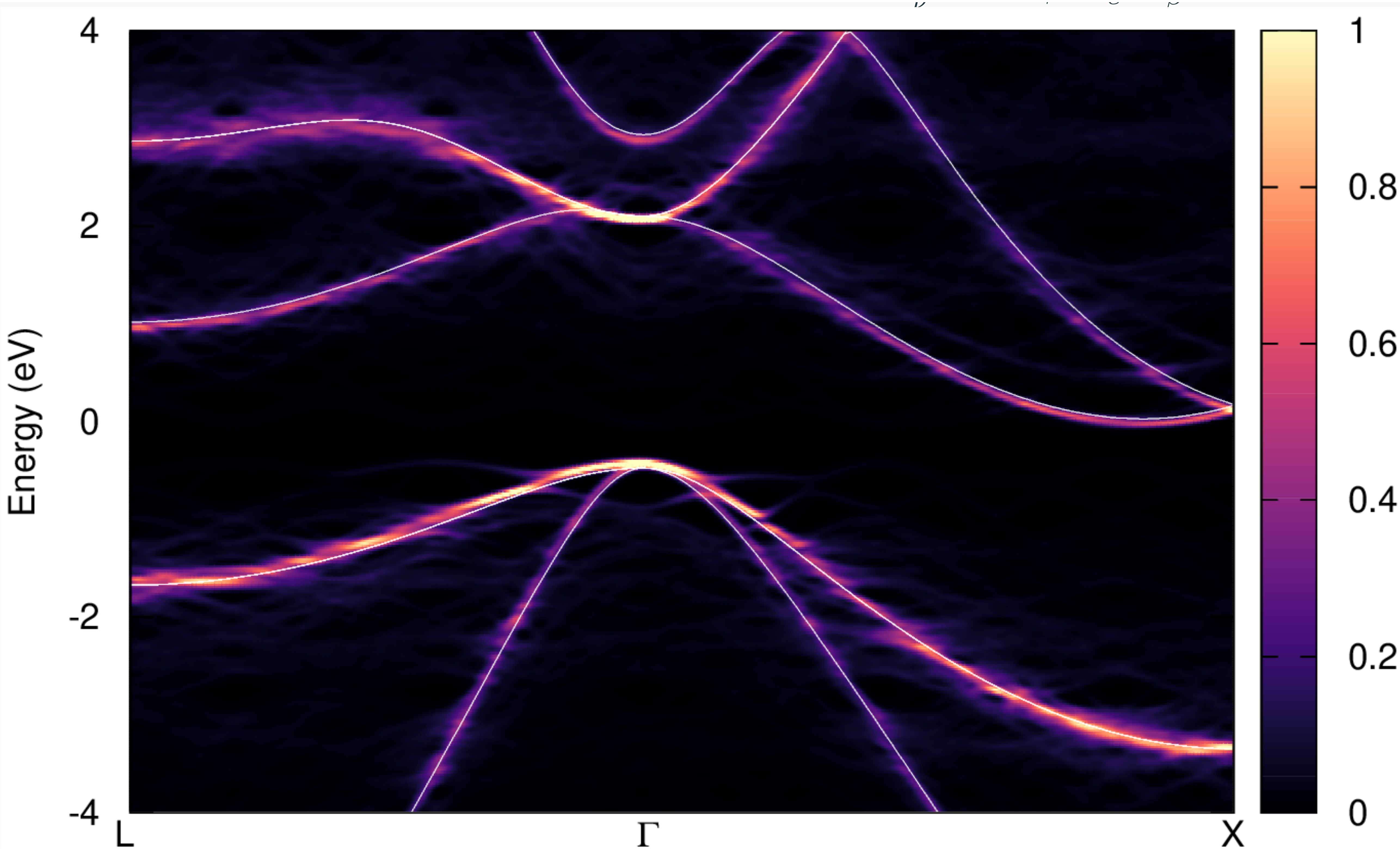
-2
Fermi Energy
Γ
X

A Real Example: 7x7x7 Si



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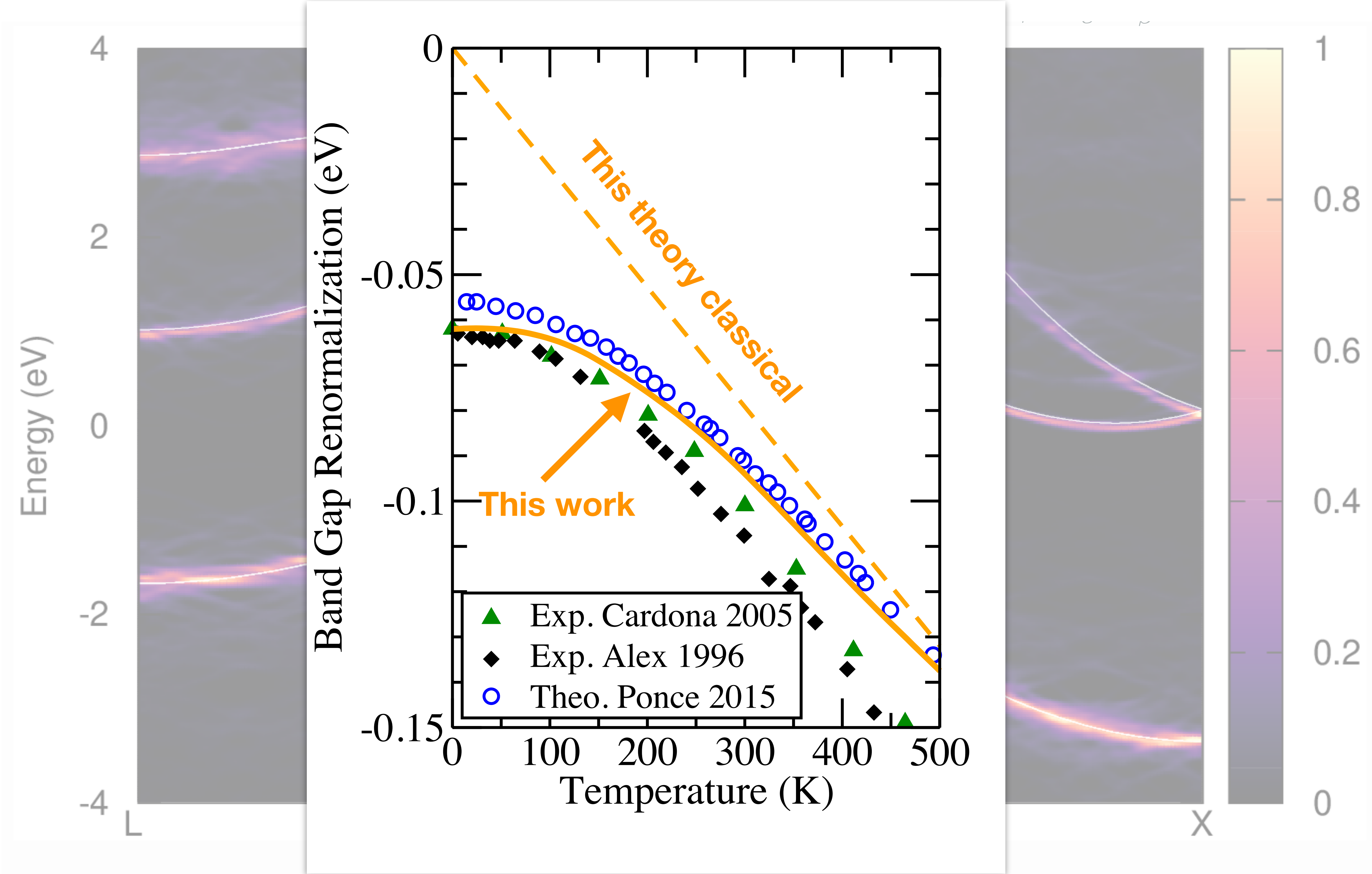

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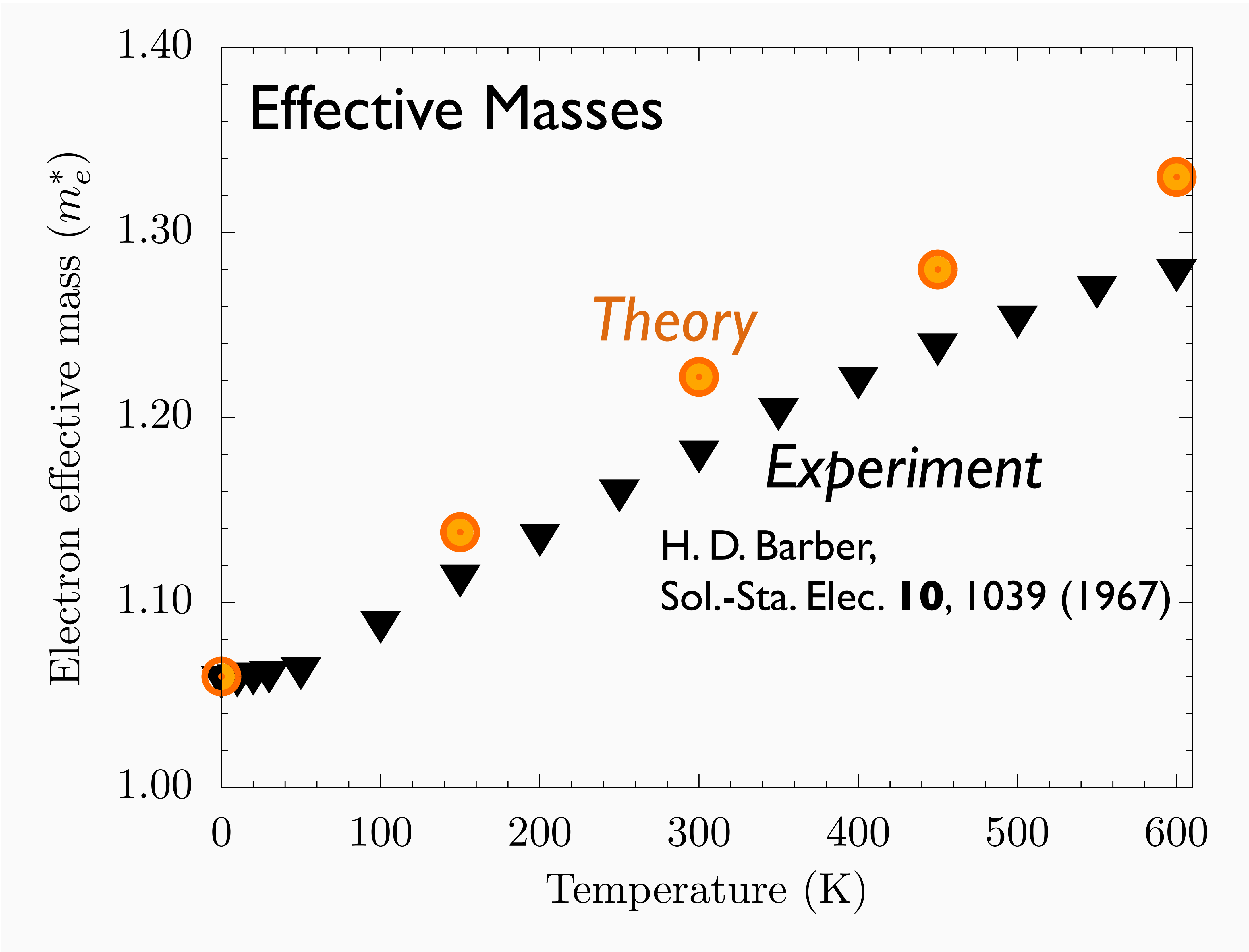

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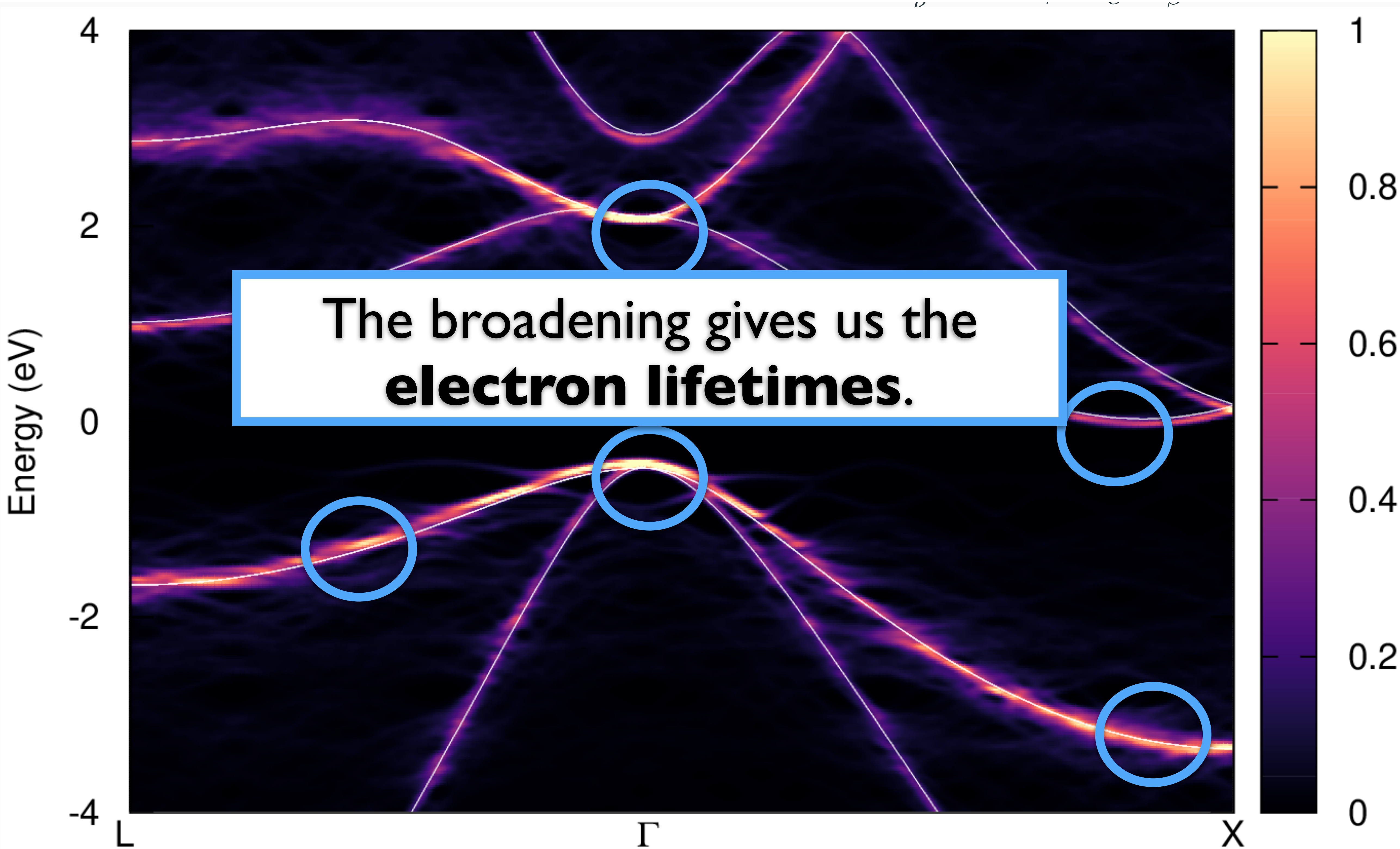

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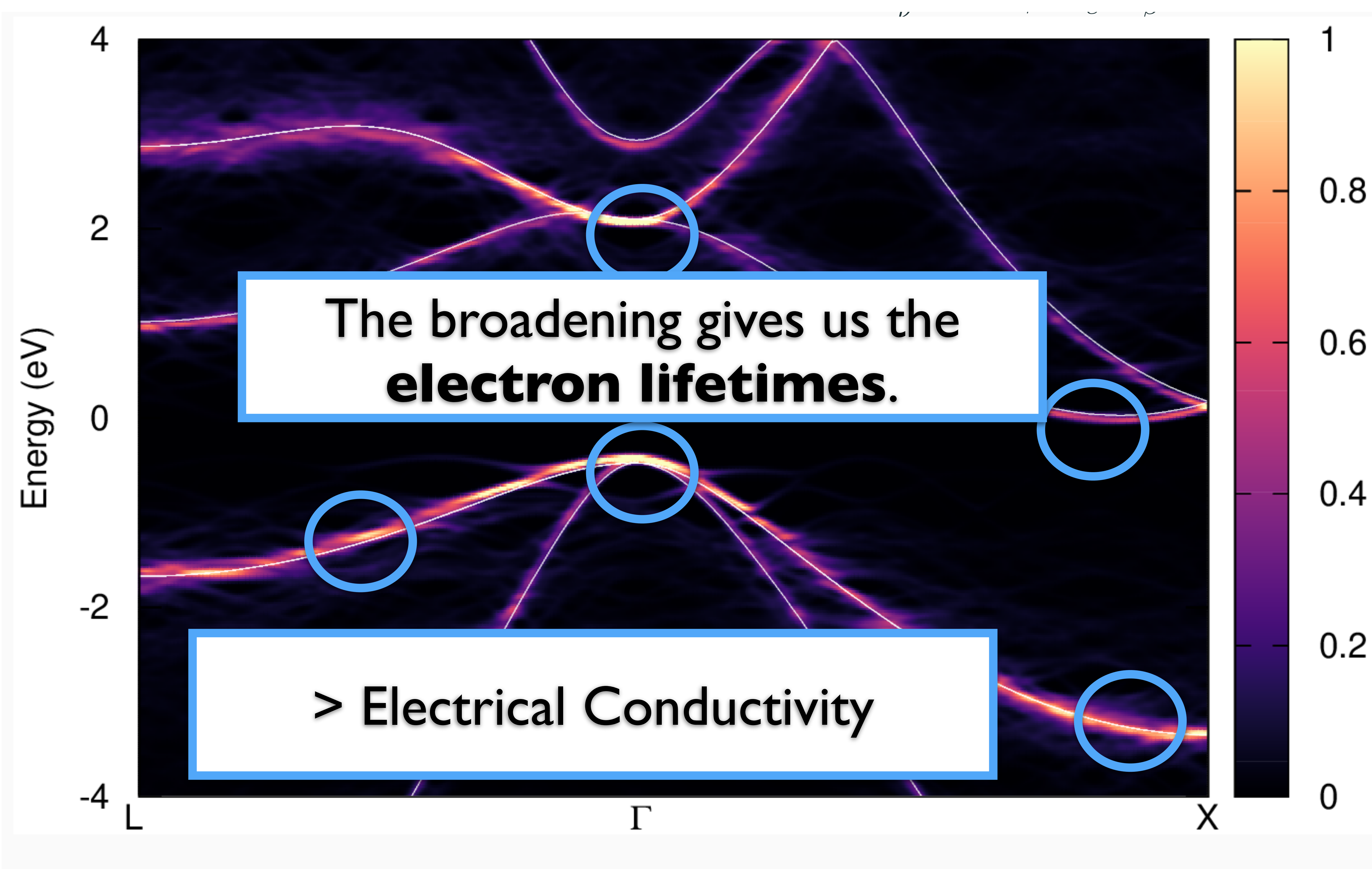

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