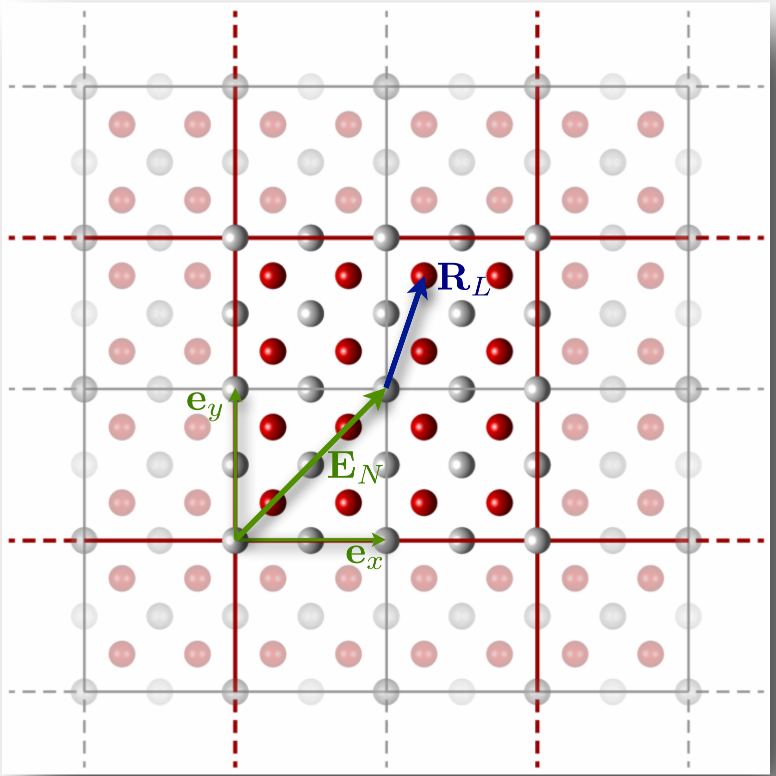
Virtual FHI-aims Tutorial Series 2021
March 23 2022

Phonons, electron-phonon coupling, heat and charge transport

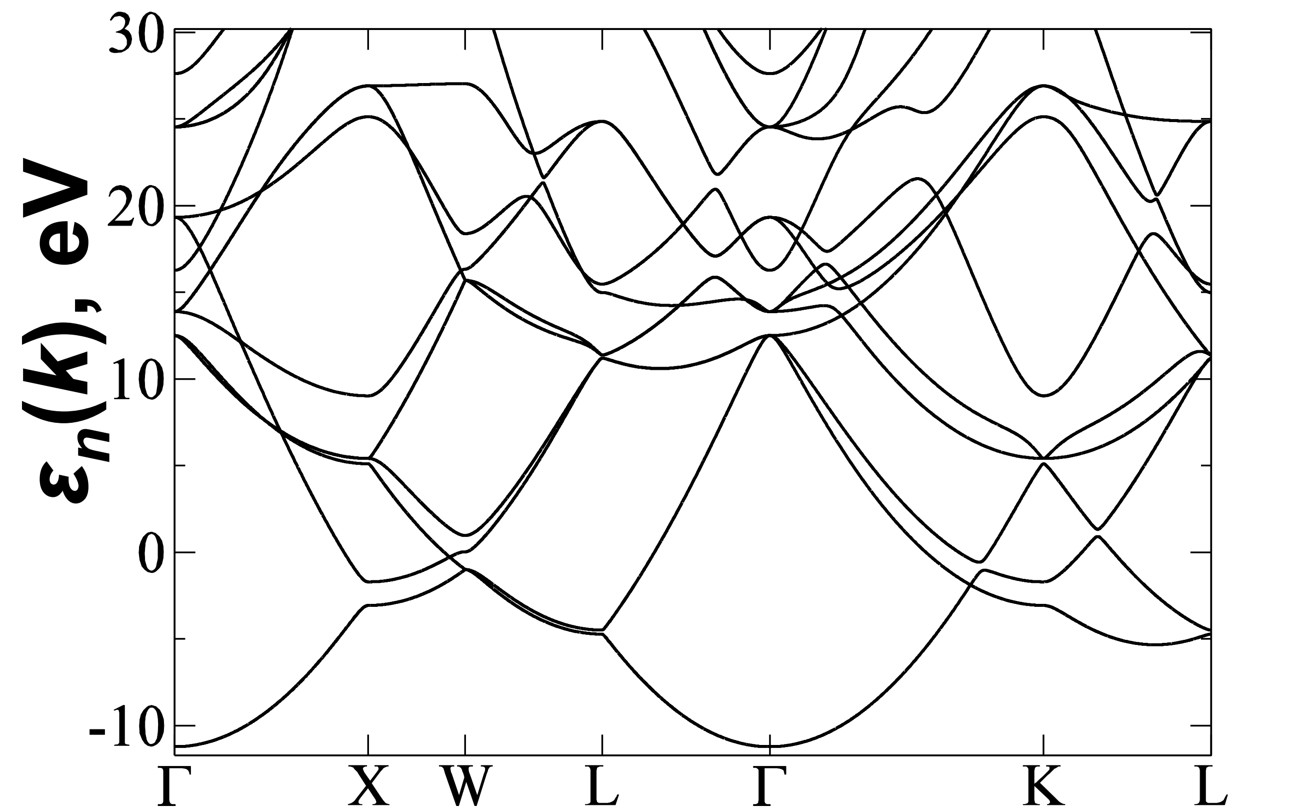
Christian Carbogno

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

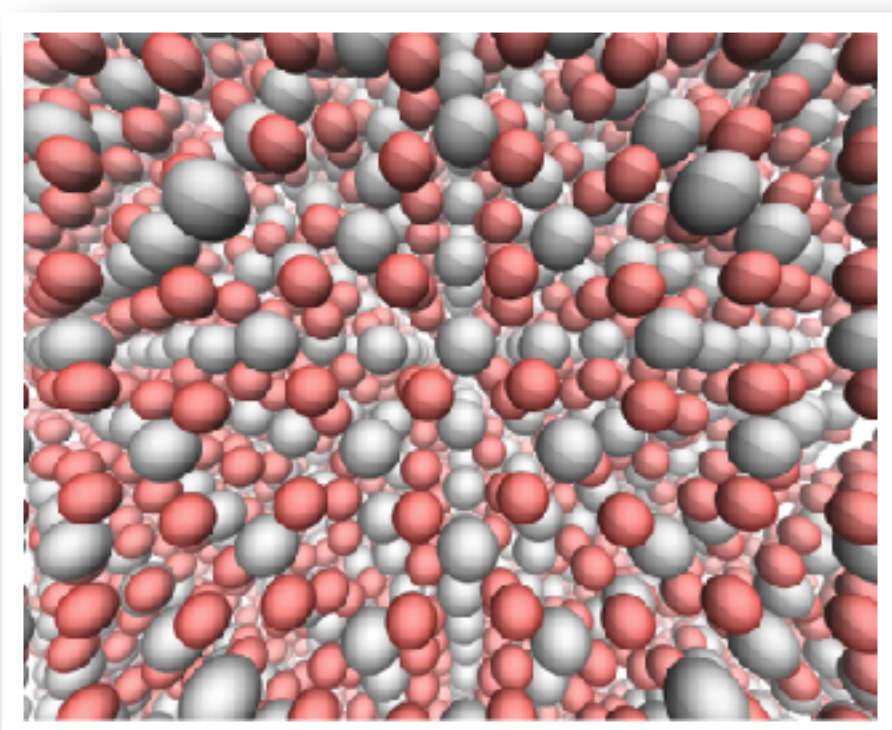
Idealized Crystal Structure



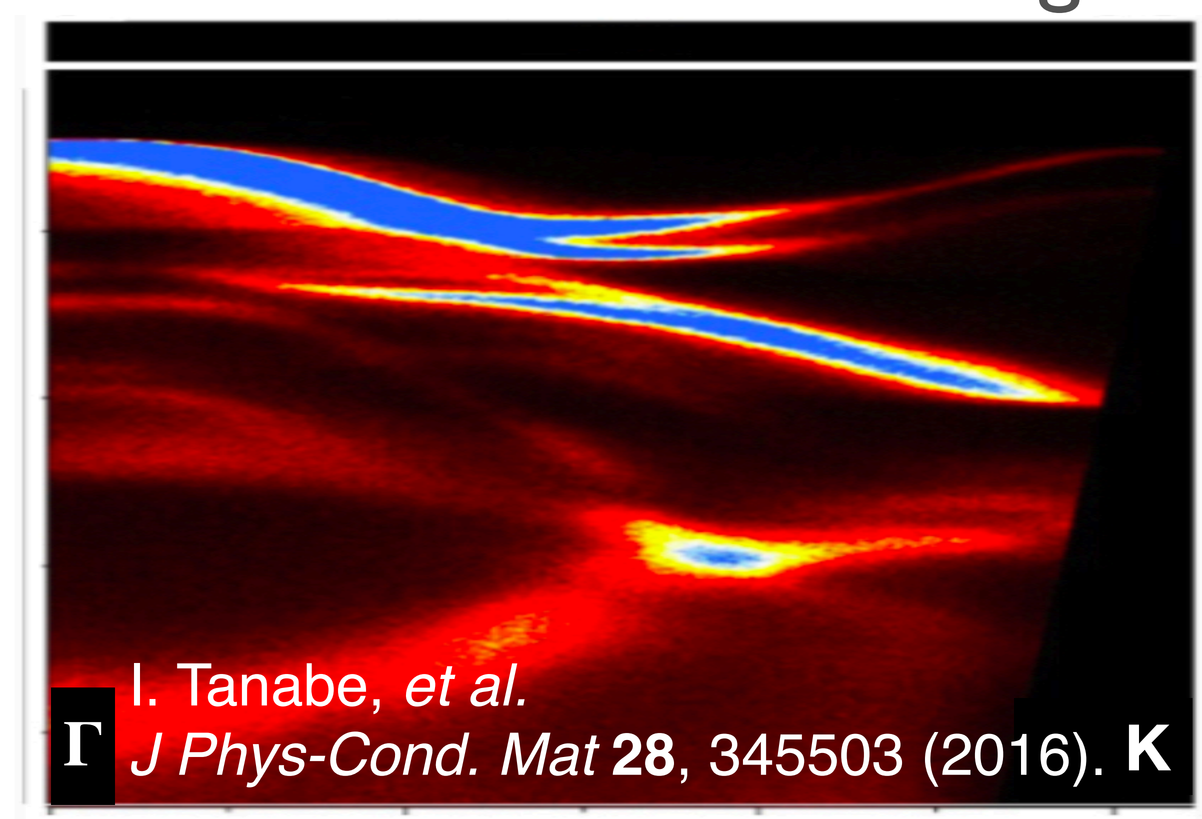
Perfectly Symmetric Band Structure



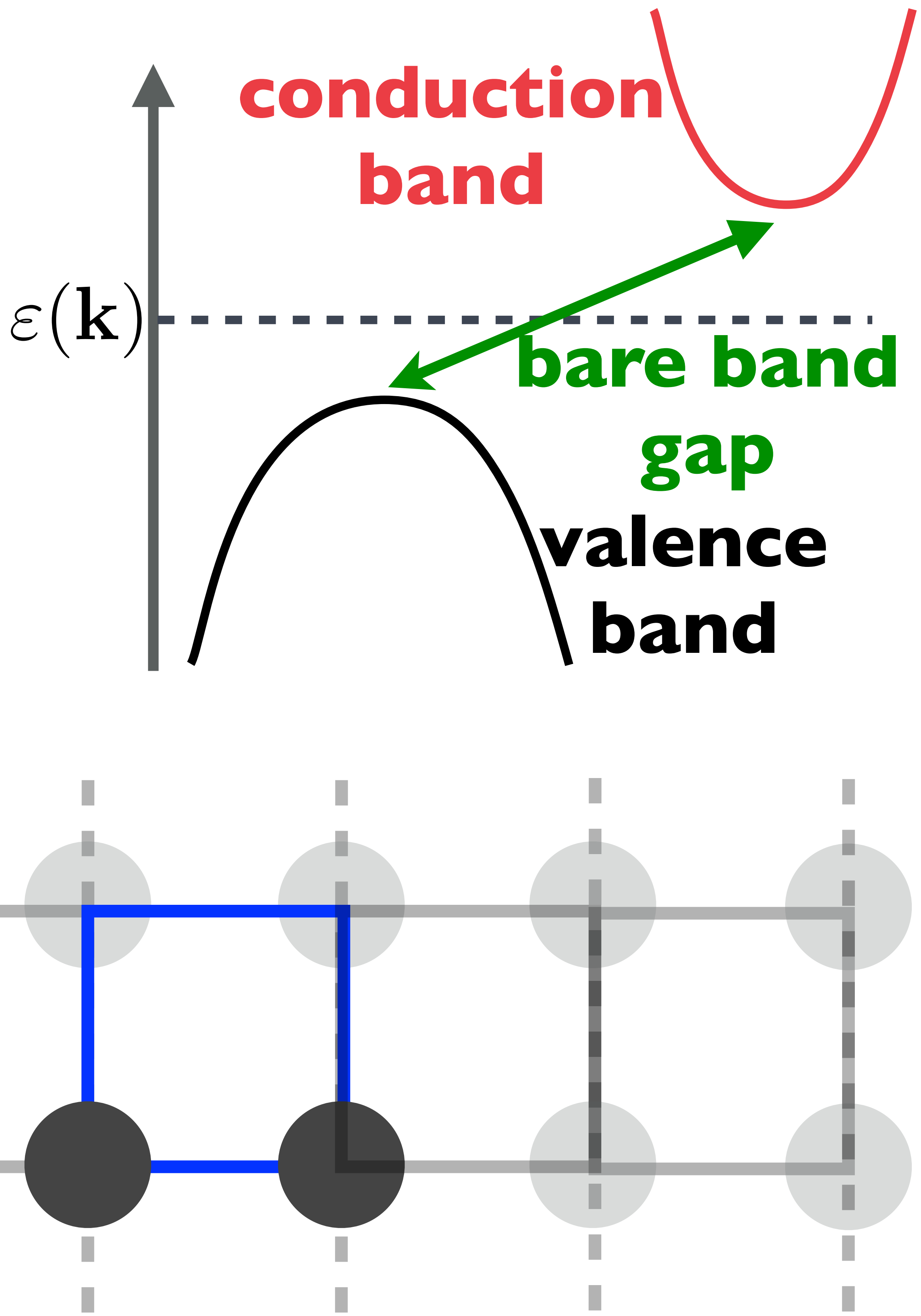
Real Materials



“Smeared-Out” Self-Energies



Electron-Phonon Coupling



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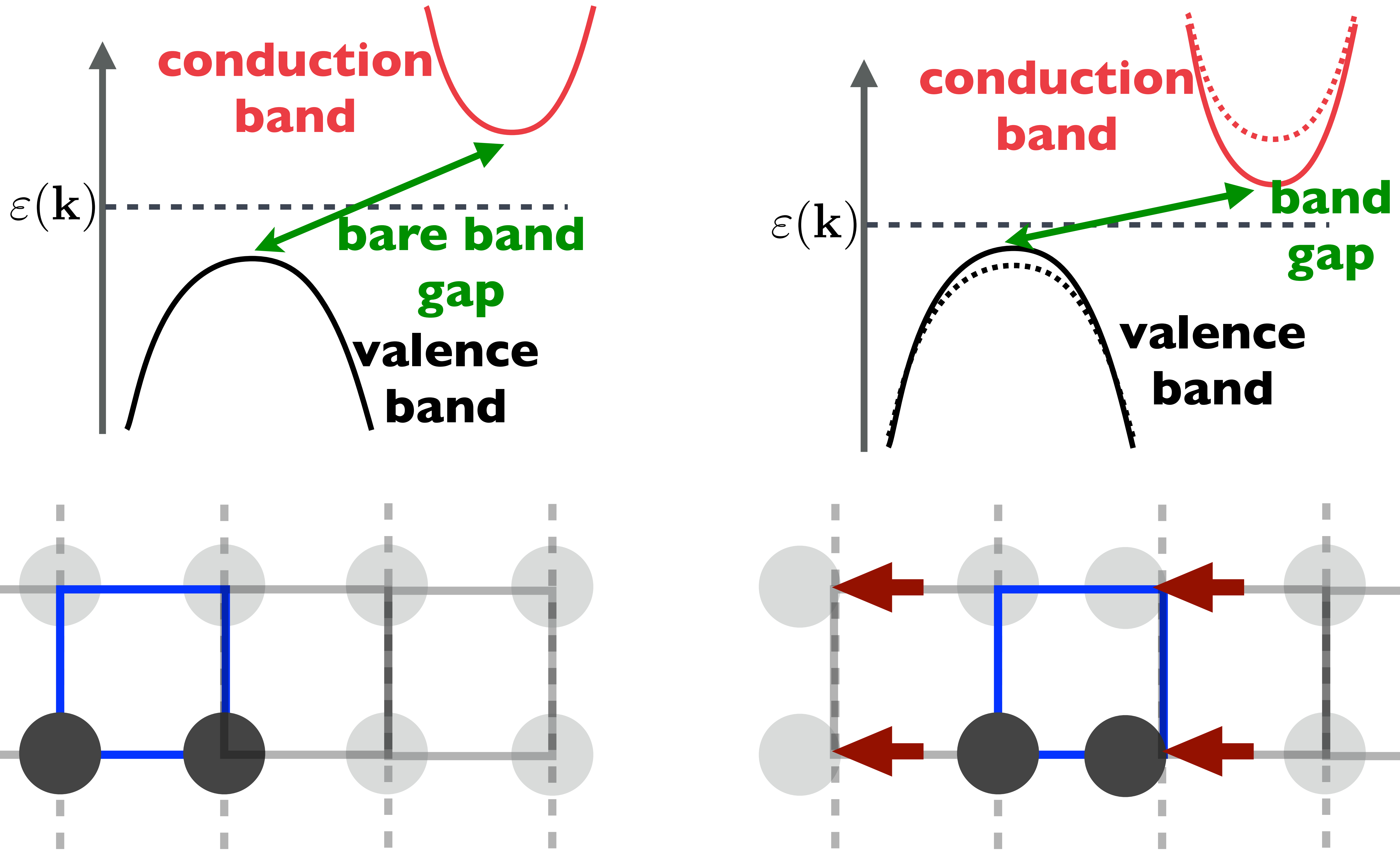
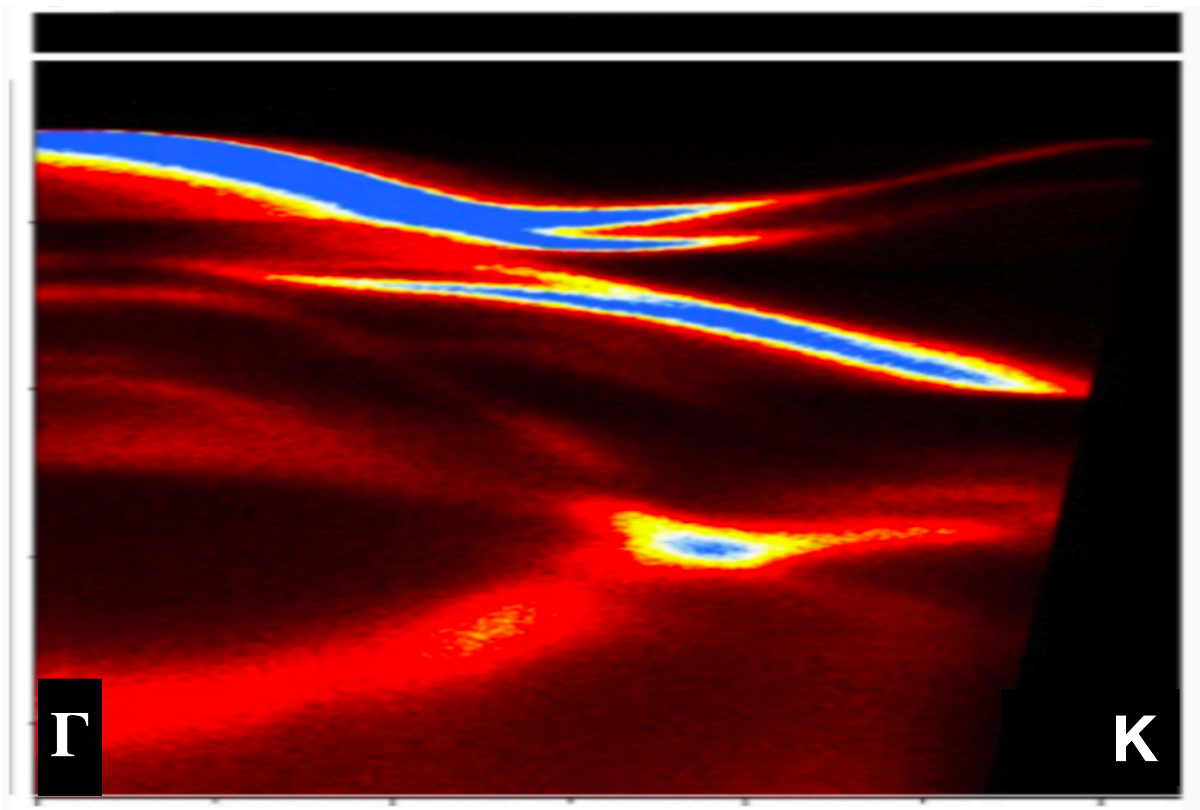
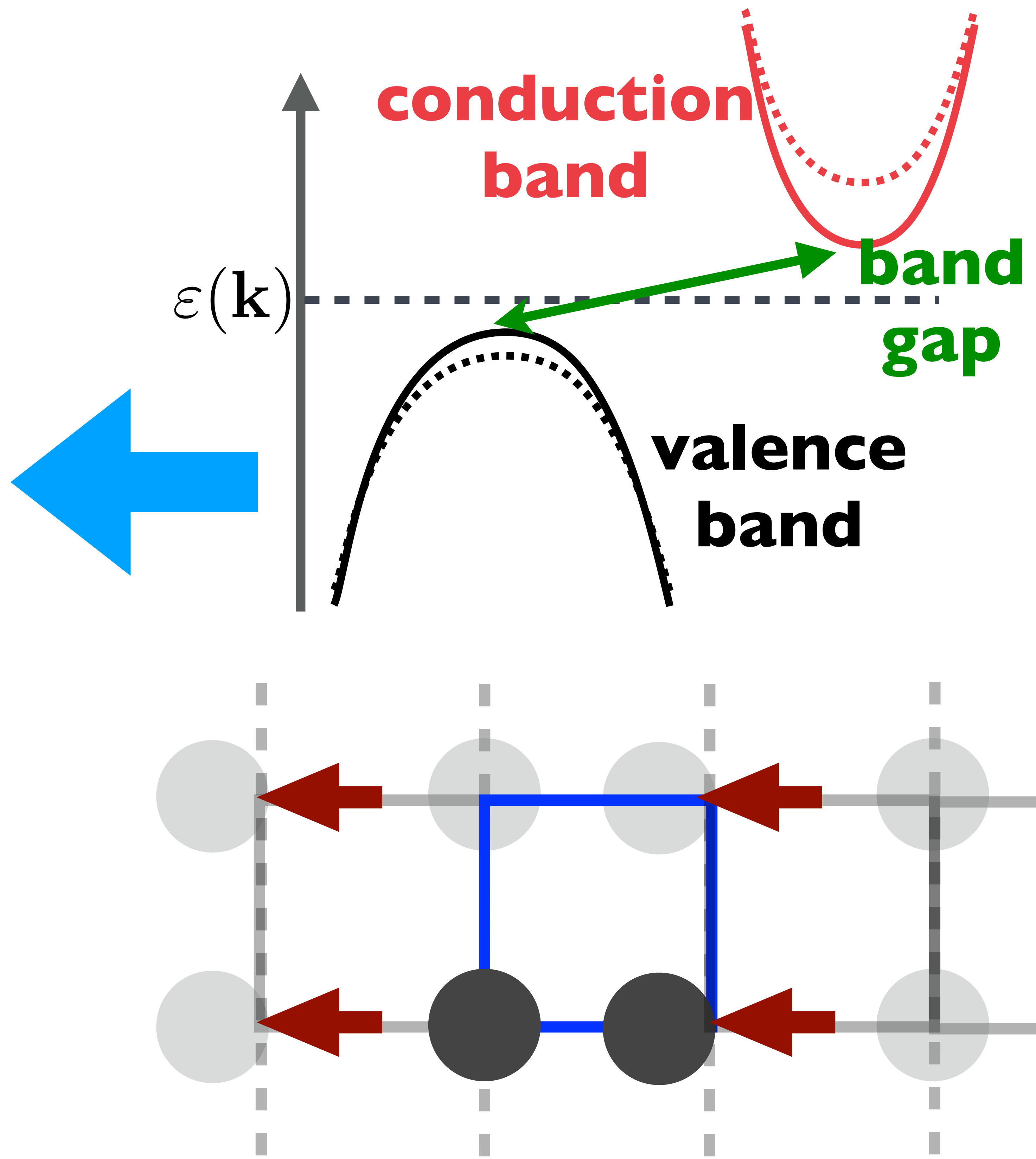


Electron-Phonon Coupling

Thermodynamic Average yields
“Smeared-Out” Self-Energies

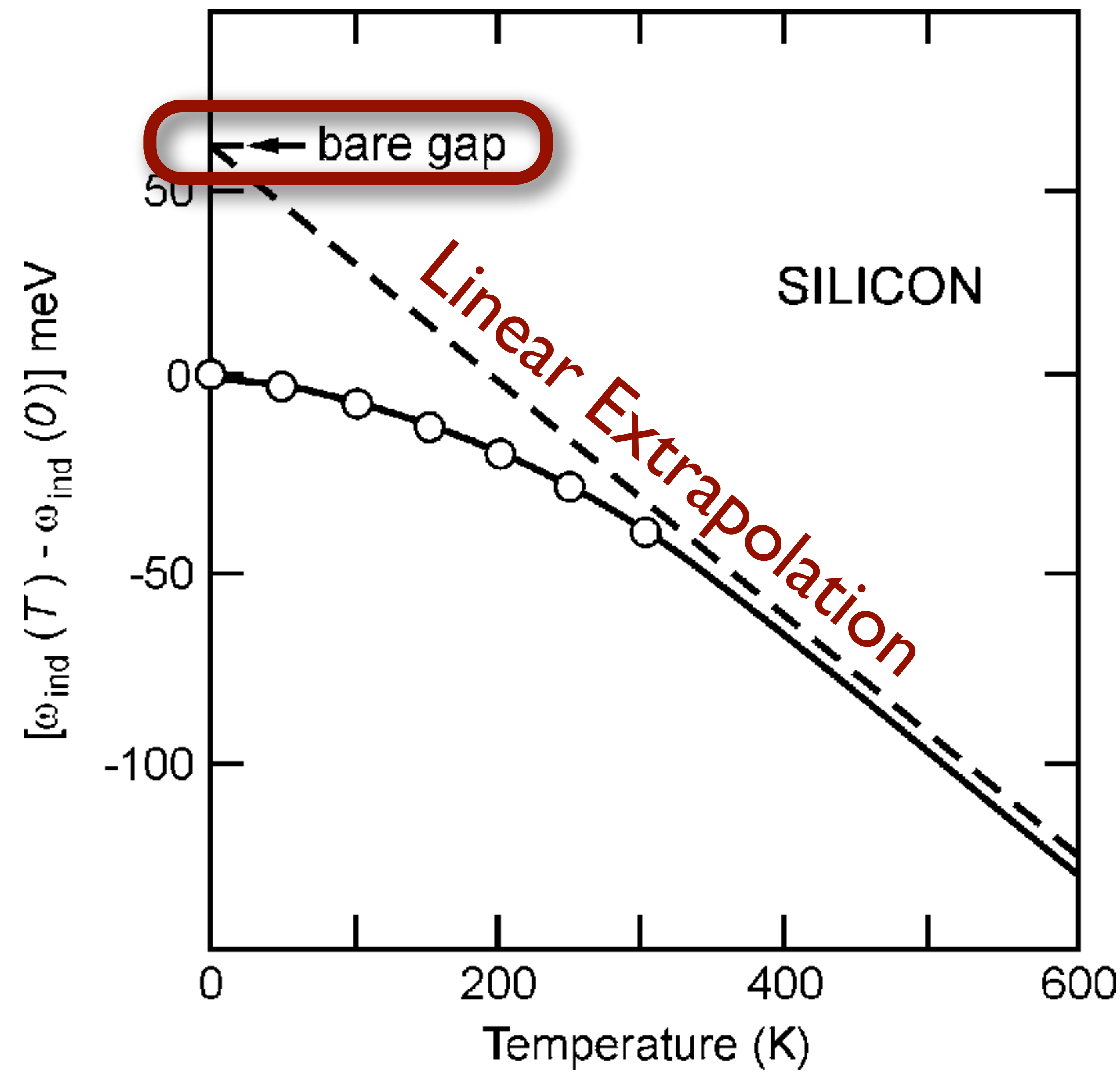




BAND GAP RENORMALIZATION

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).

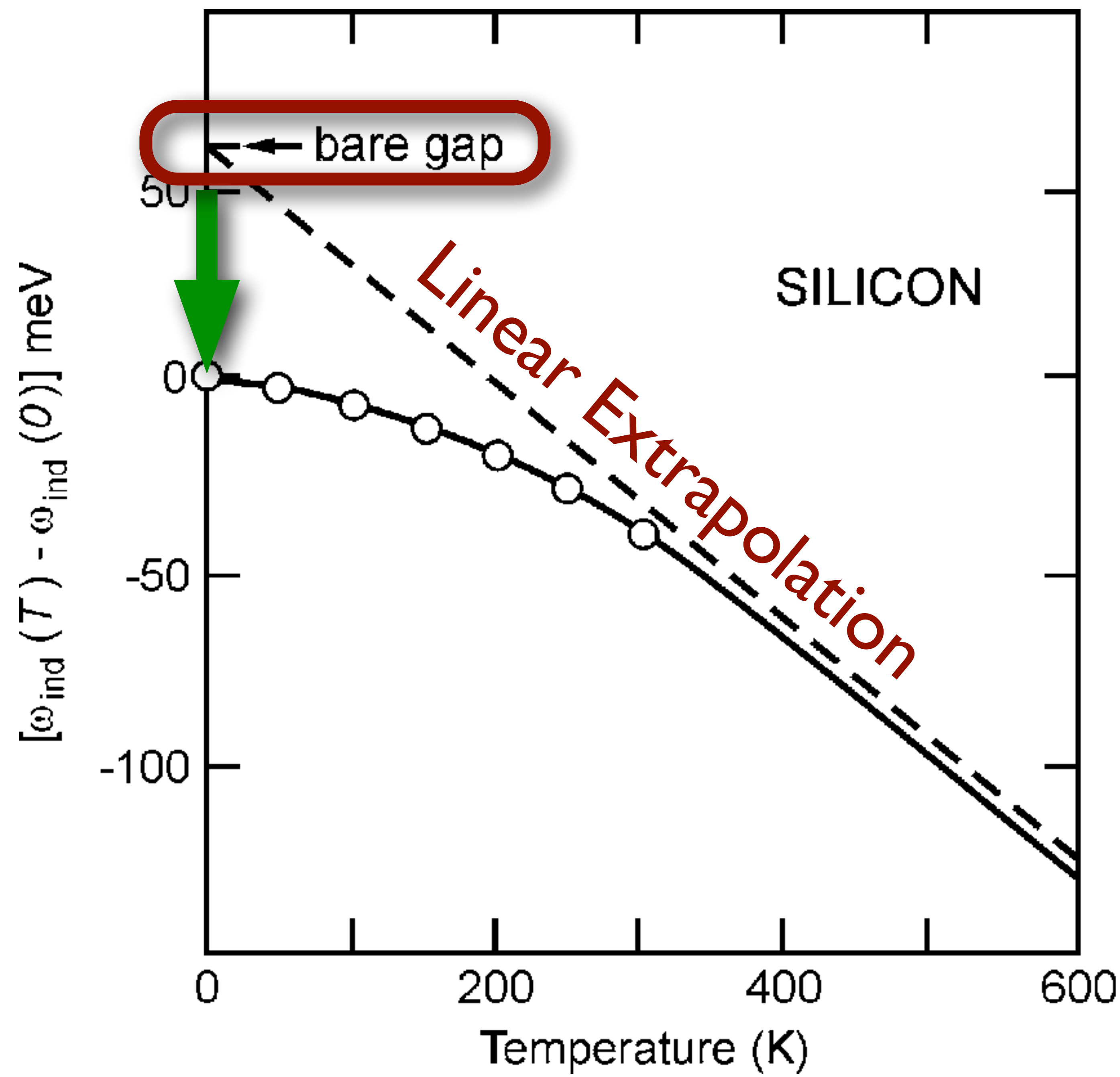
BAND GAP RENORMALIZATION

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)**

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

due to 0K phonon motion



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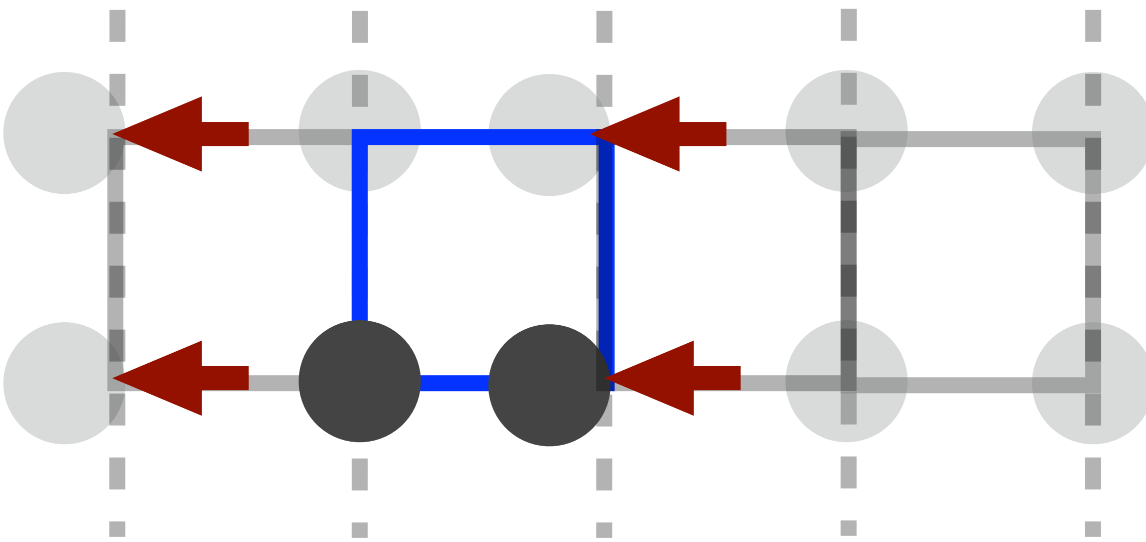
Solid State Comm. **133**, 3 (2005).

ELECTRON-PHONON COUPLING

Electron-phonon interactions from first principles

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



Harmonic Approximation for Nuclear Motion

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

Electron-phonon interactions from first principles

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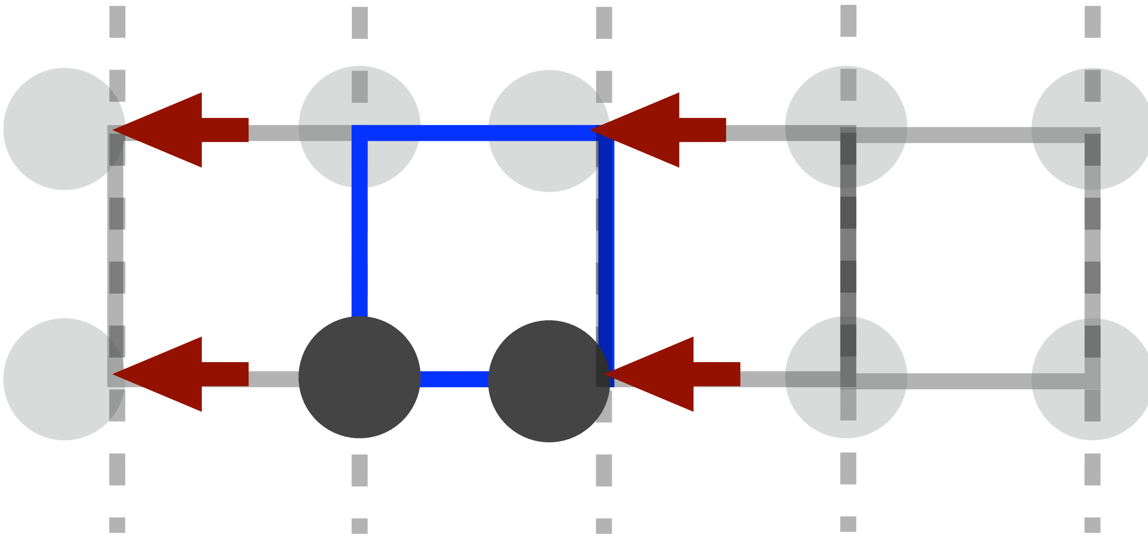

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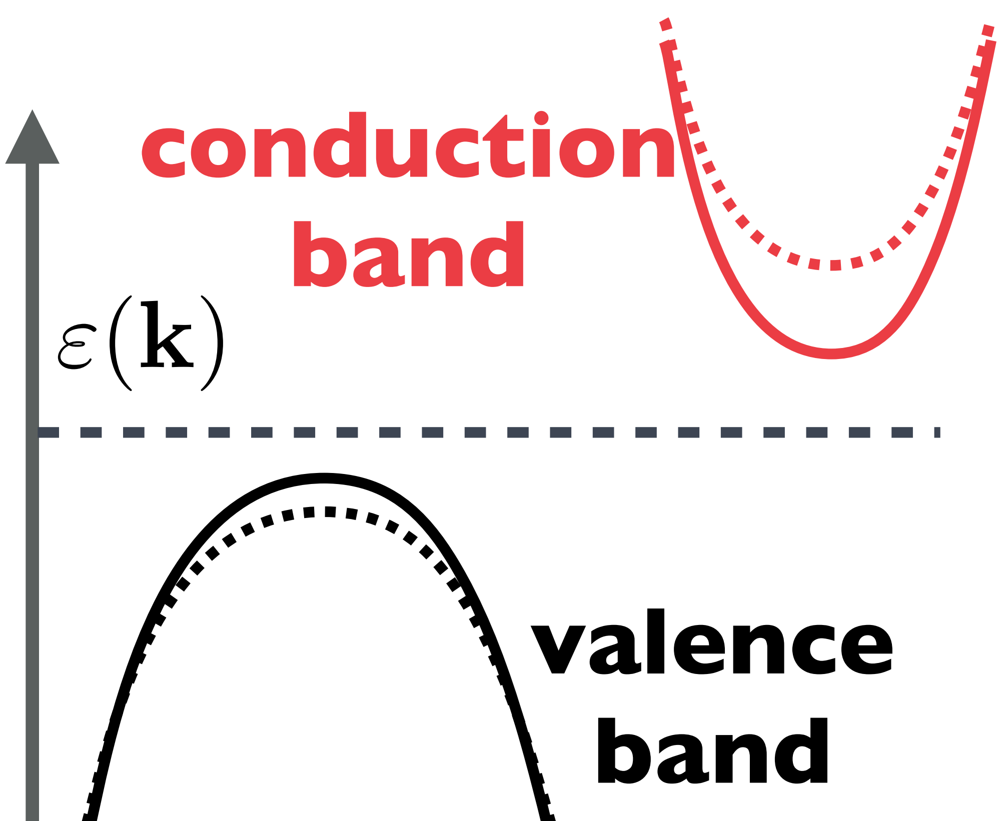
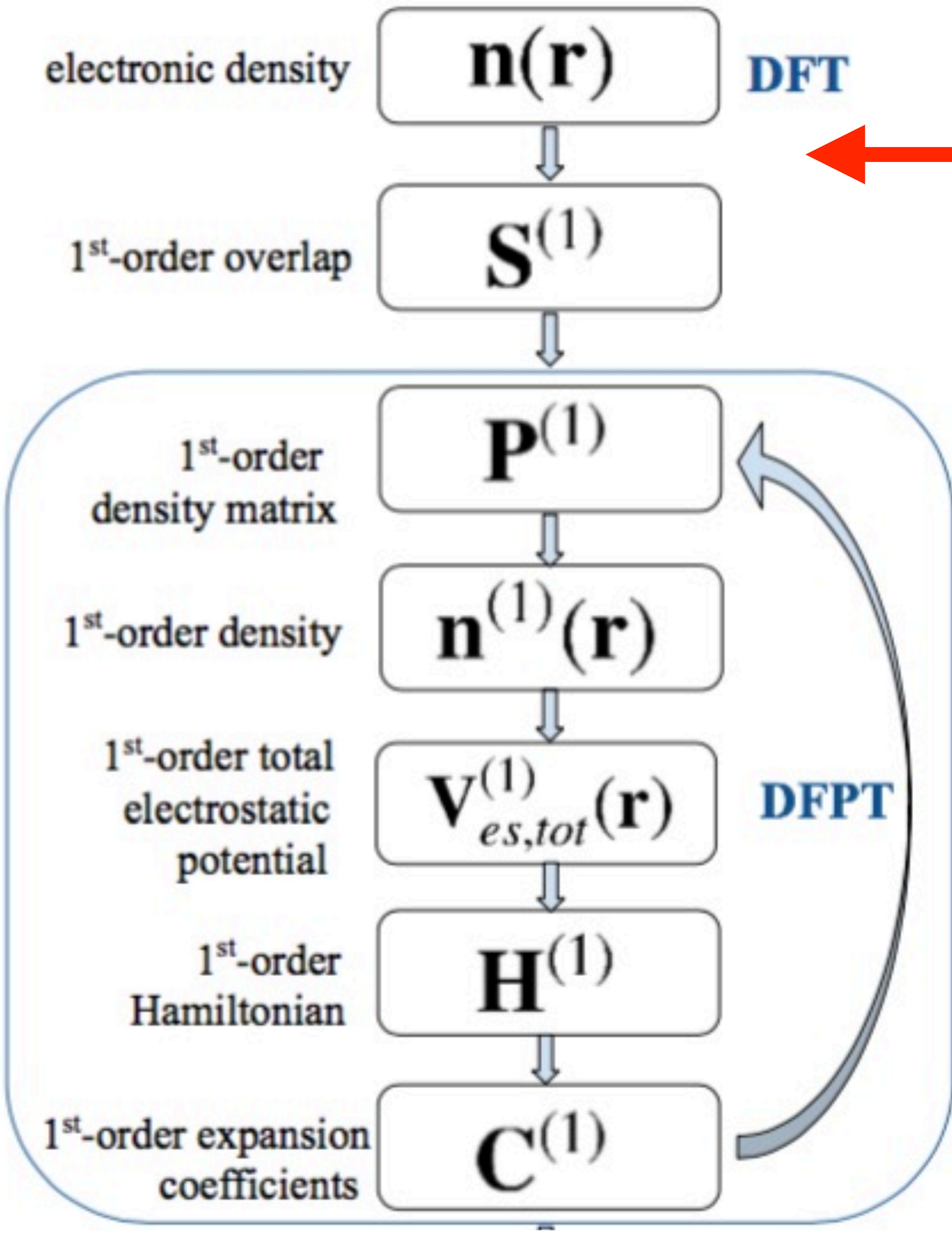


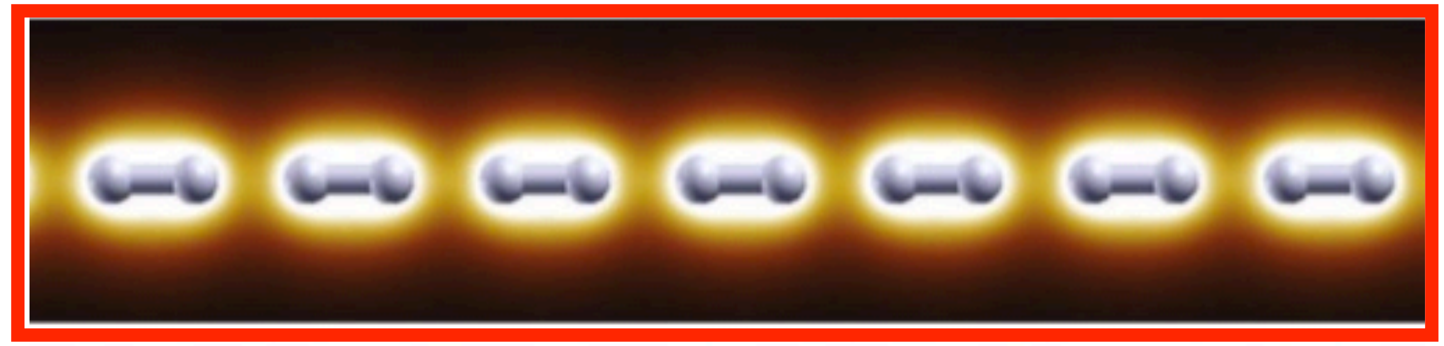
"Harmonic" Expansion for Electronic Structure

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



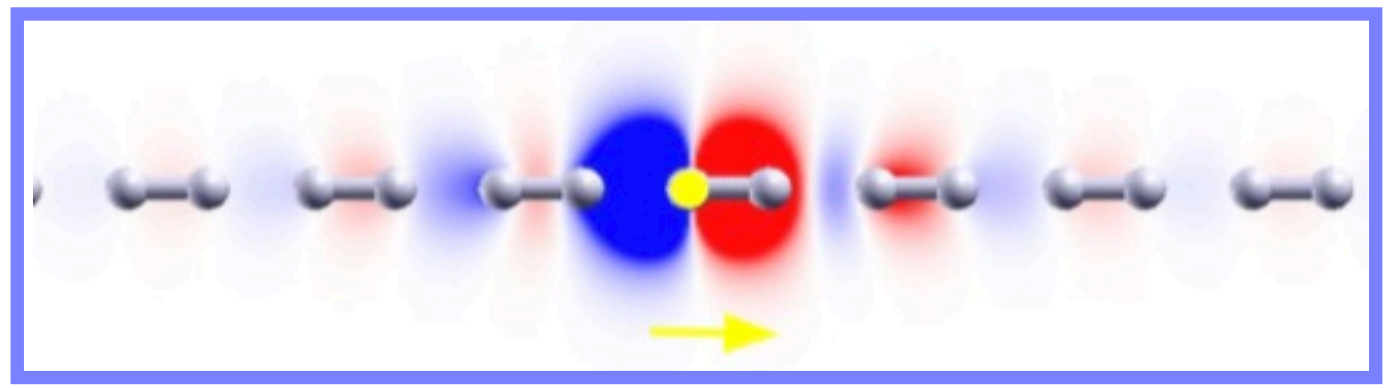
Density Functional Theory:

density $n(\mathbf{r})$



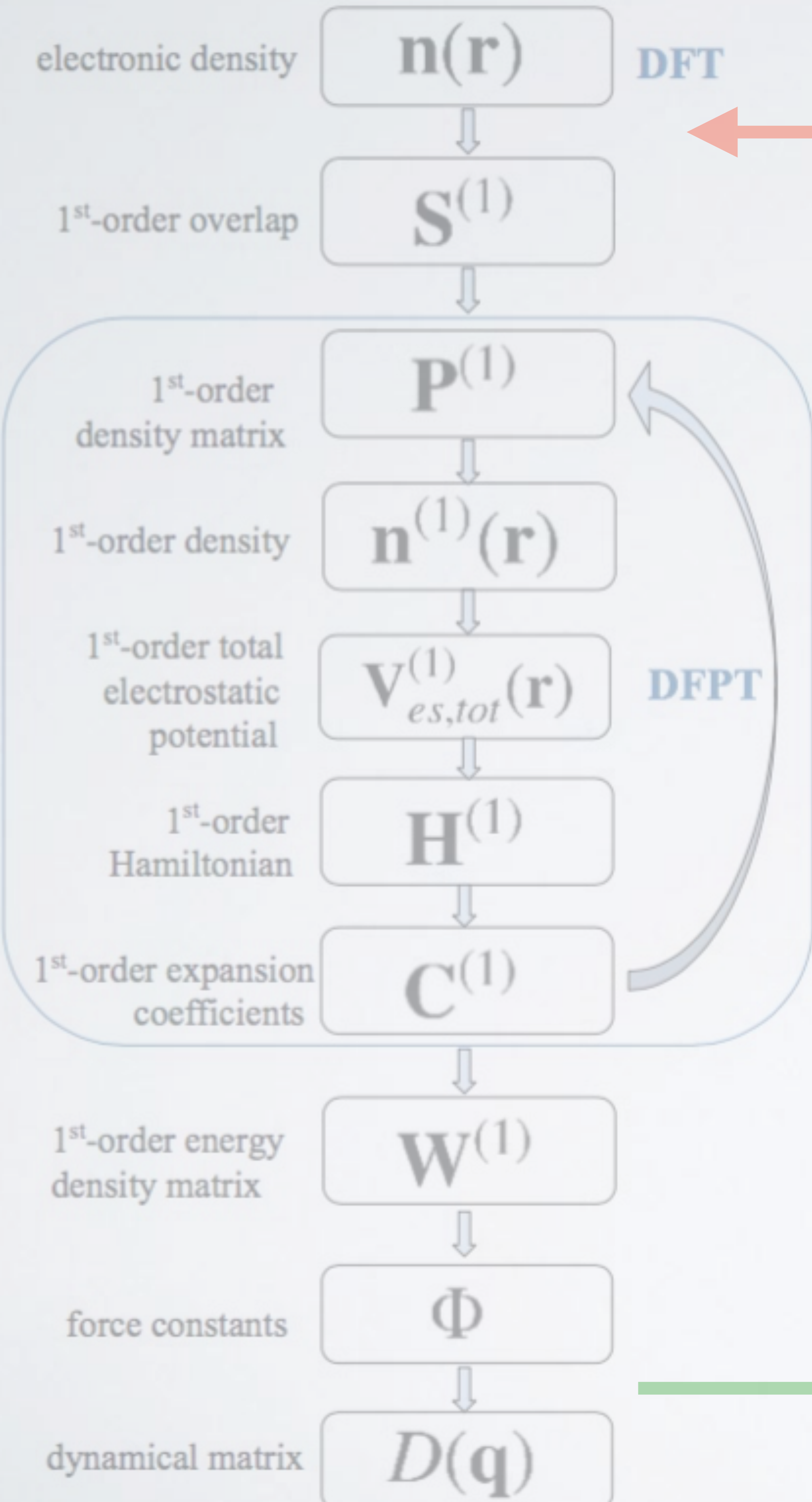
Density Functional Perturbation Theory:

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



Electron-Phonon Coupling

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



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Density Functional Perturbation Theory:

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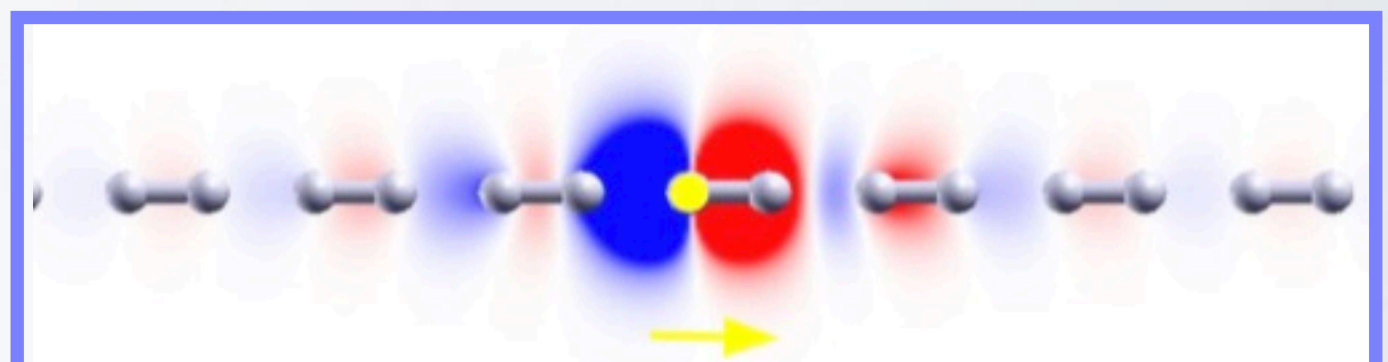


Density response is localized in real space.

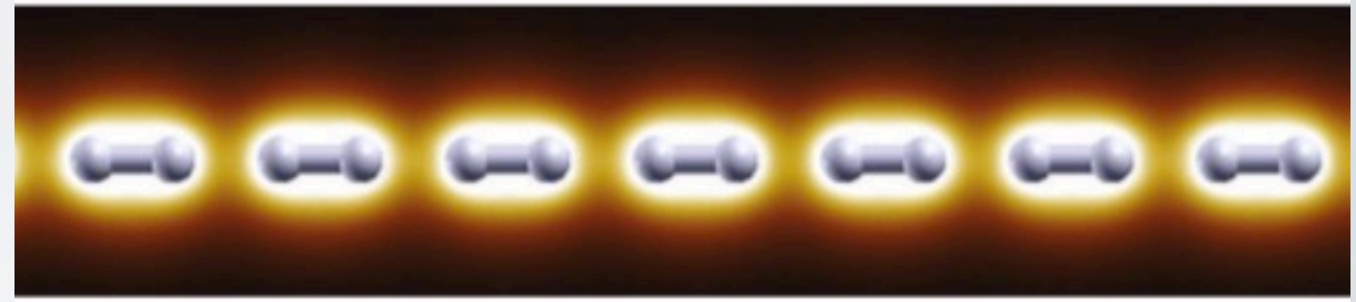
F. Giustino, M. Cohen, and S. Louie, *Phys. Rev. B* **76** 165108 (2007).

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

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

Density Functional Theory:

density $n(\mathbf{r})$

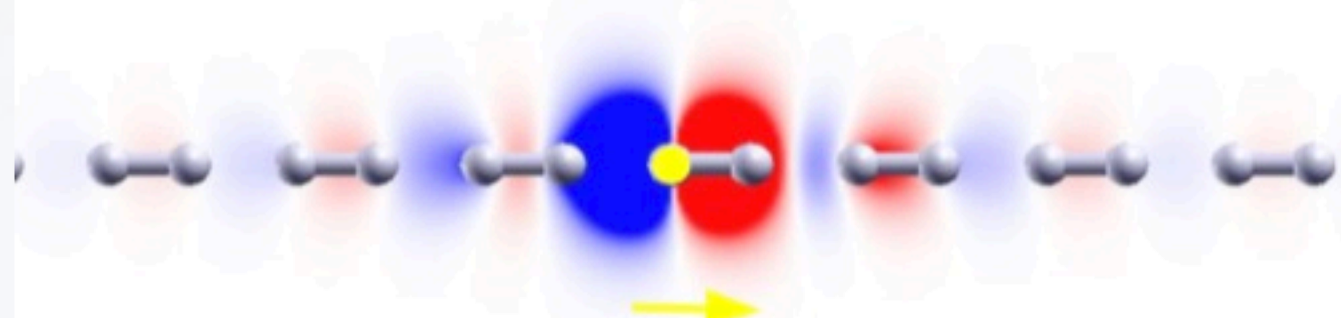


Using techniques developed for describing **delocalized properties** to describe a **localized response** is **not efficient**!

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

Density Functional Perturbation Theory:

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



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

force constants Φ

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

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.)

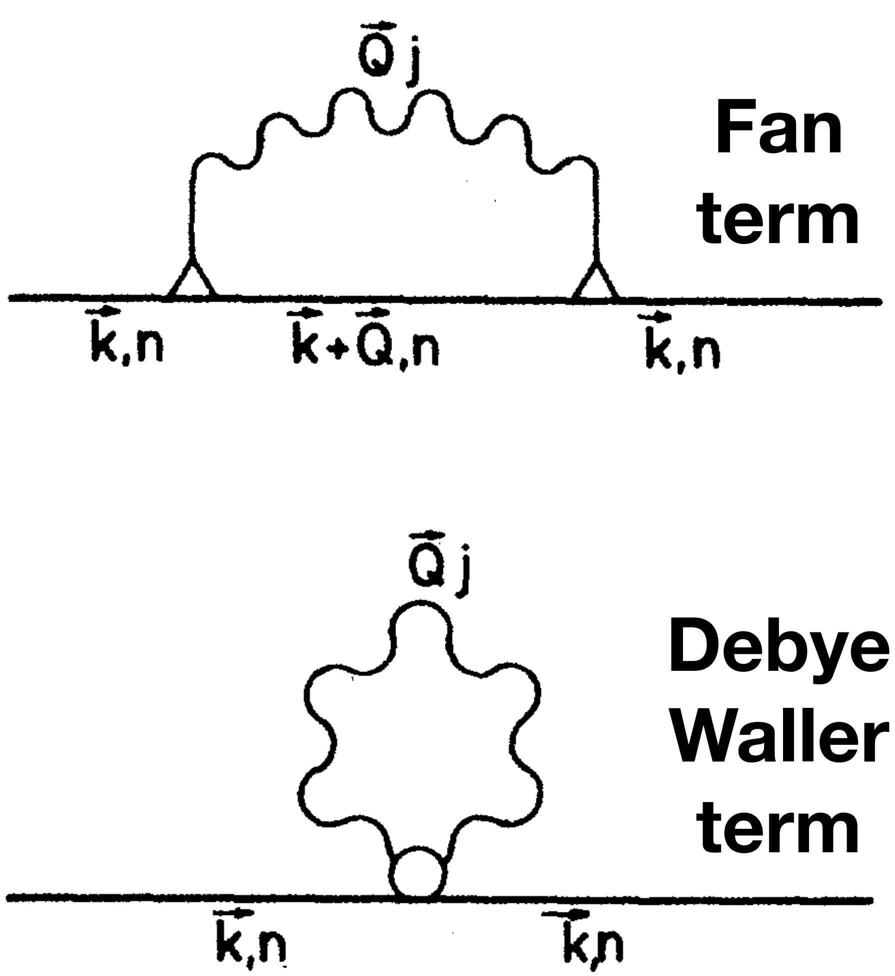
Truncated Fourier-Transform back to **reciprocal-space**.

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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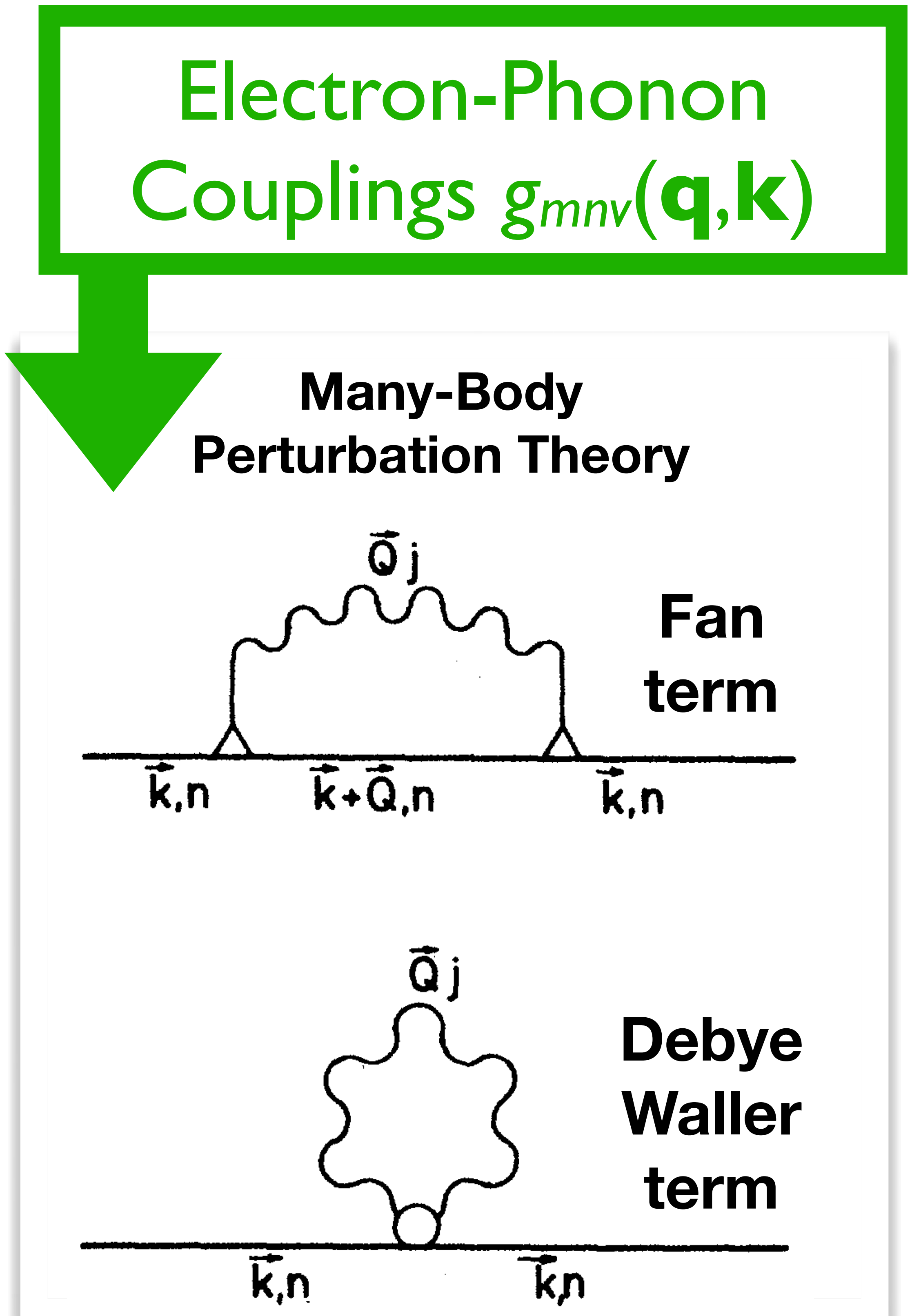

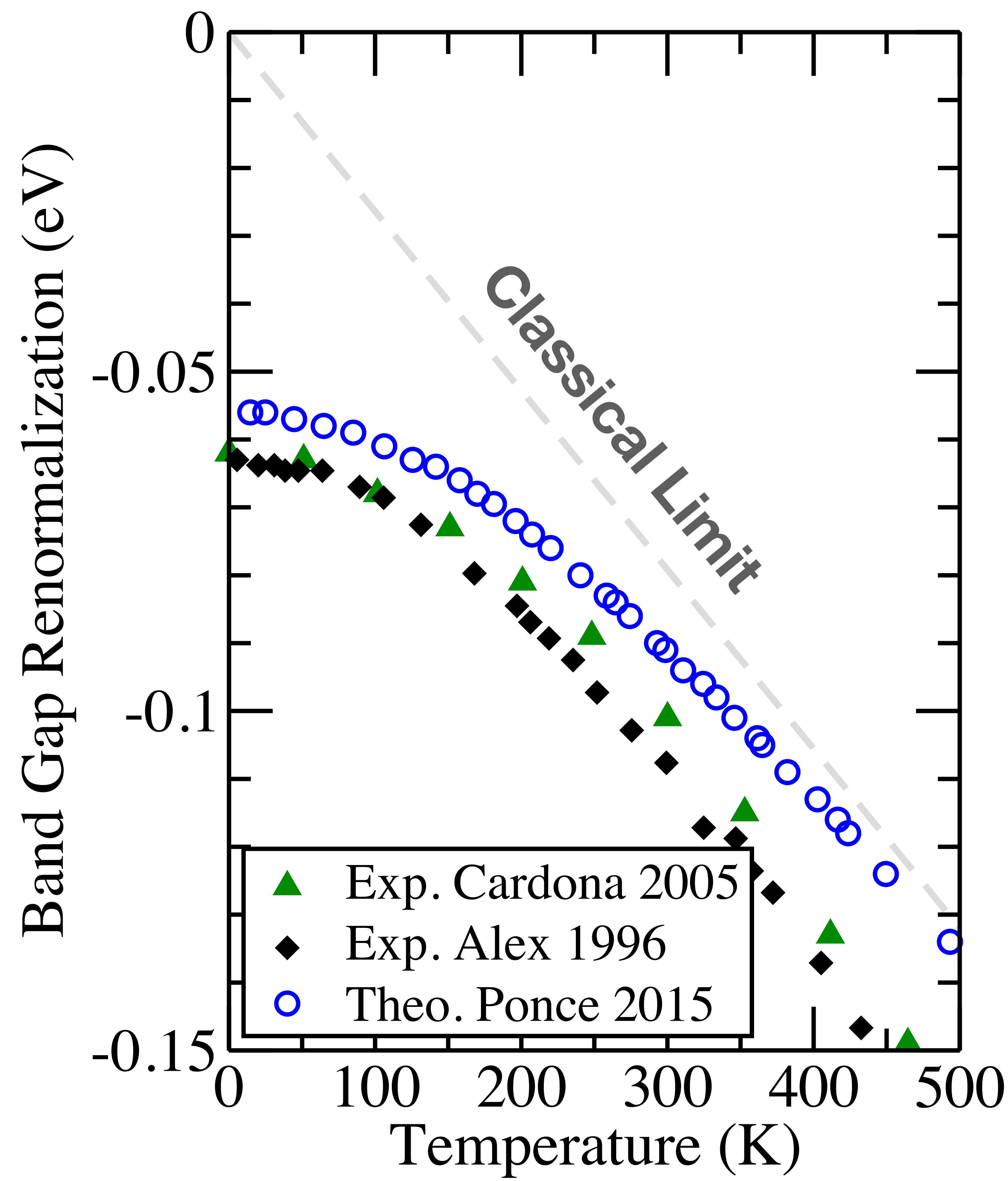

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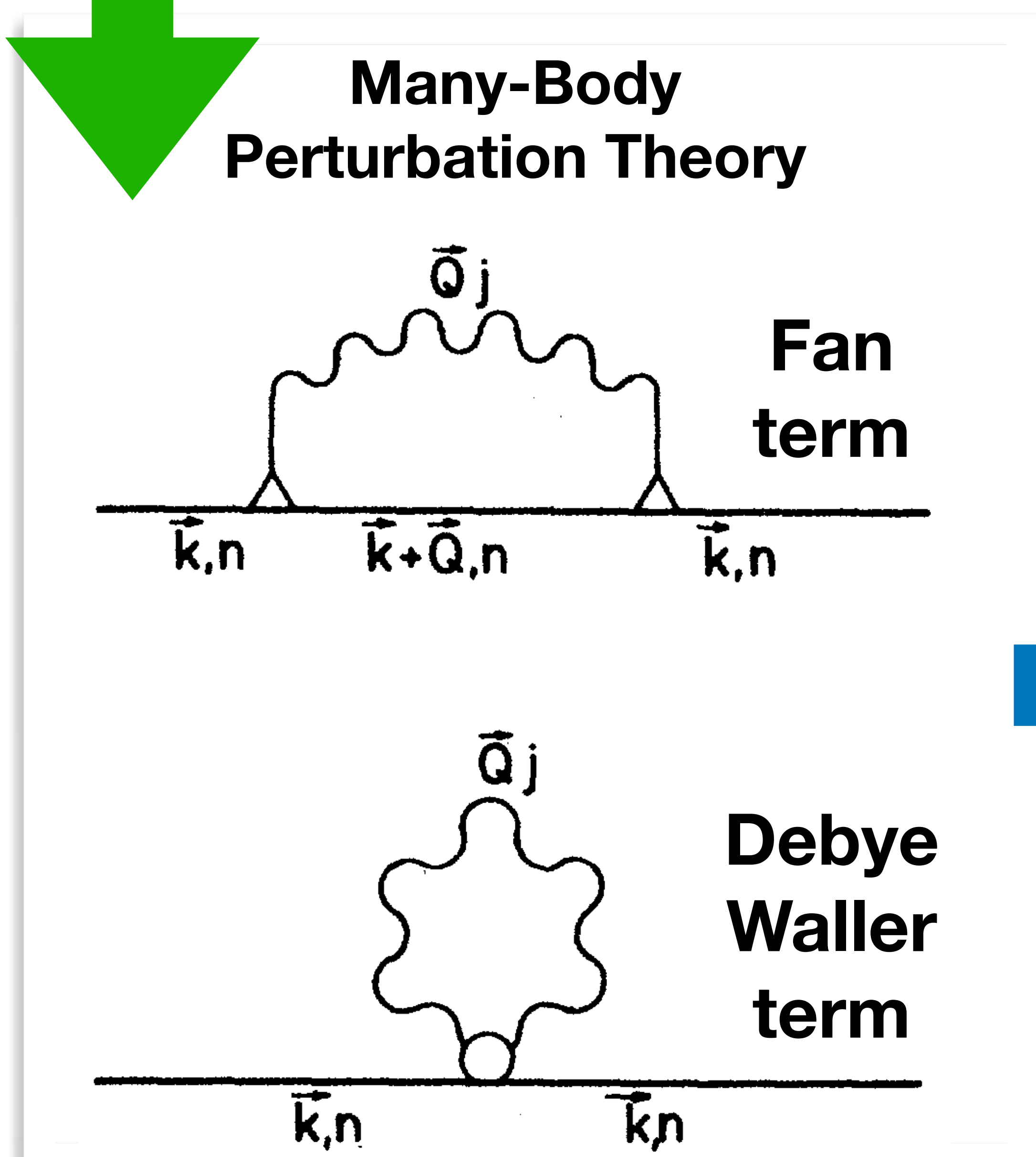
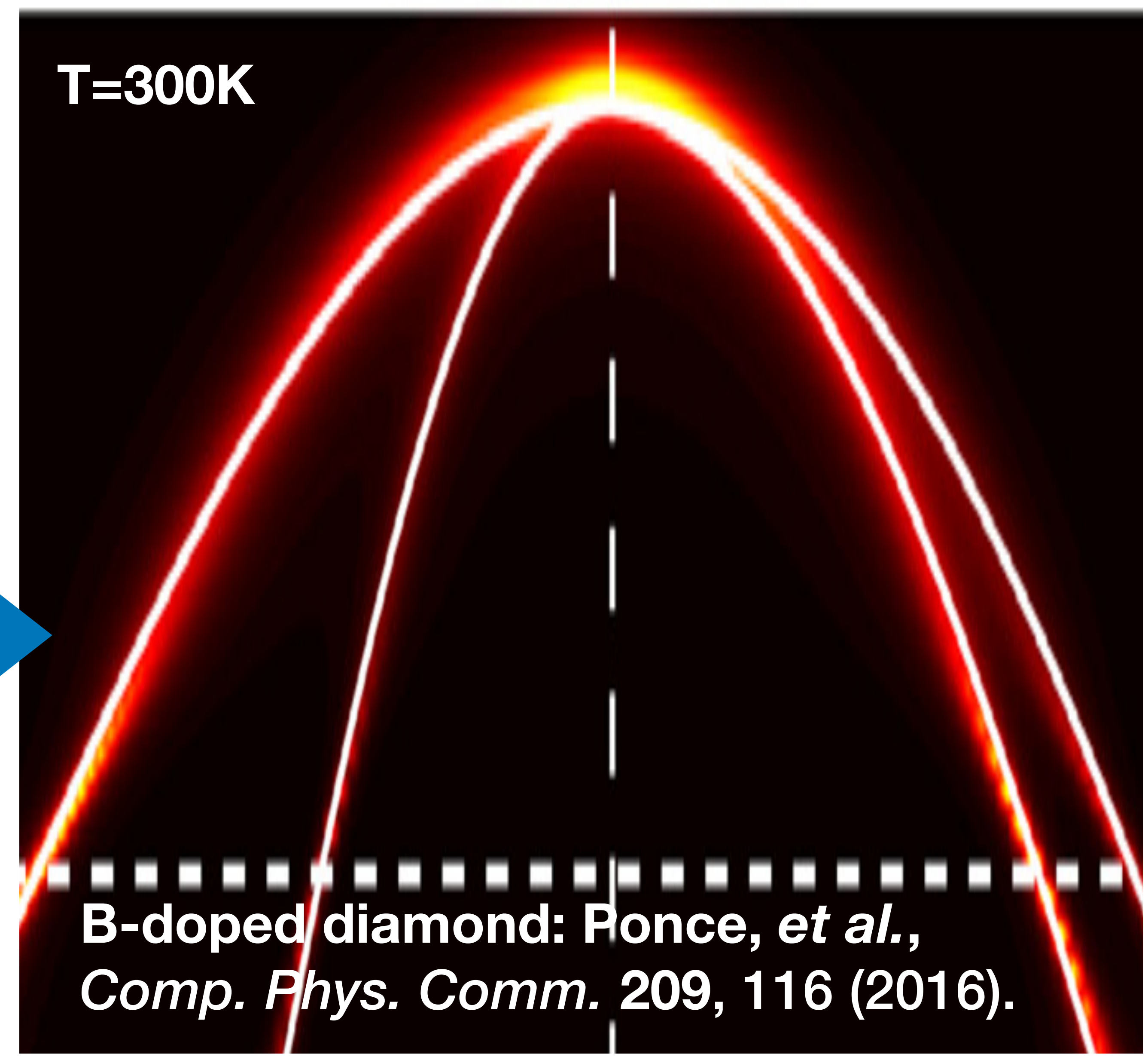
Electron-Phonon Couplings $g_{mn\nu}(\mathbf{q},\mathbf{k})$

Electronic Self-energies



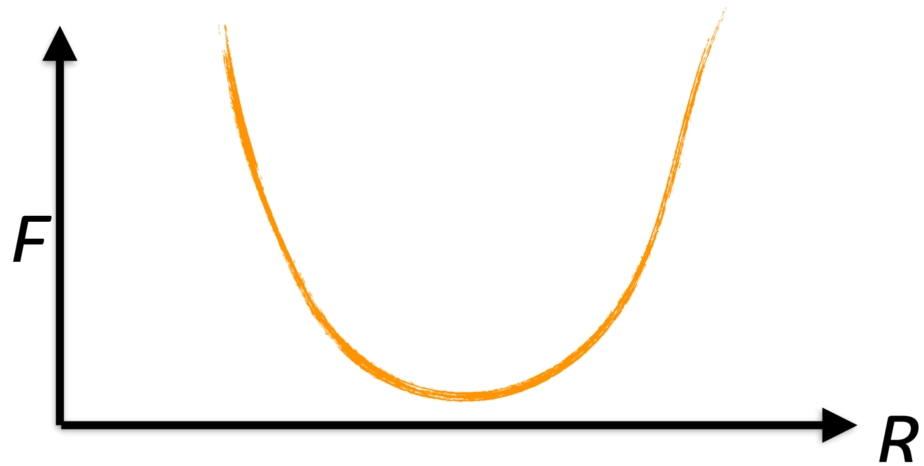


II. WHAT ABOUT ANHARMONICITY?

Vibronic Coupling

Traditional Perturbation Theory

P. B. Allen and V. Heine, *J. Phys. C* **9**, 2305 (1976).
F. Giustino, M. L. Cohen, and S. G. Louie,
Phys. Rev. B **76**, 165108 (2007).



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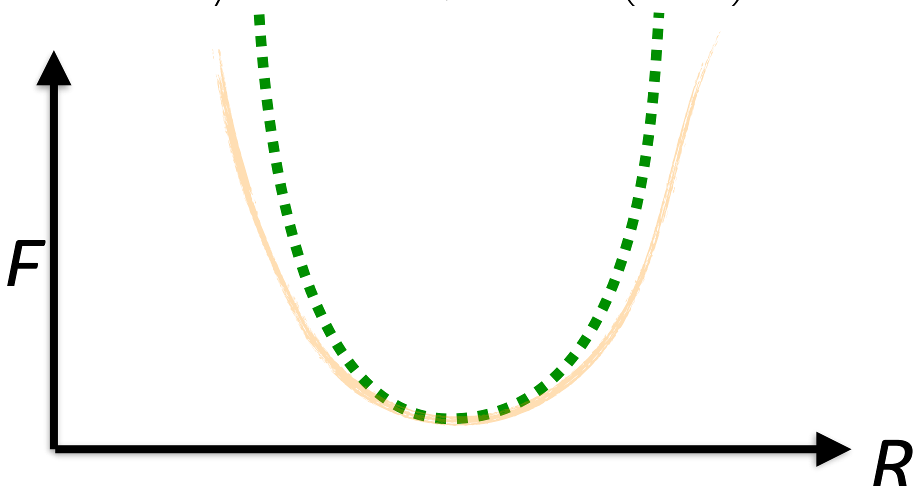

***Harmonic* Approximation for the PES**

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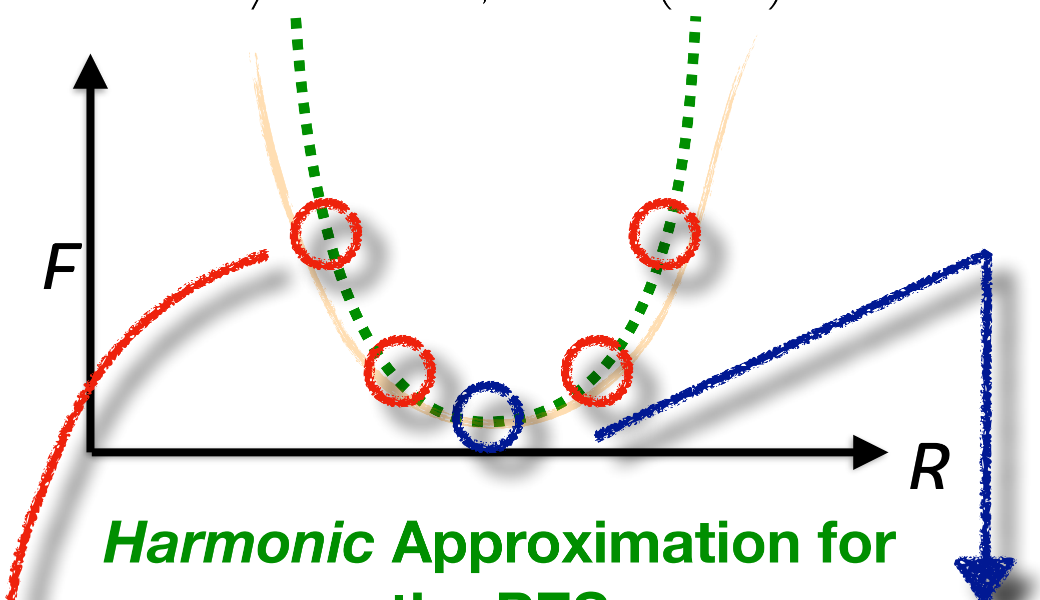

Harmonic **Approximation for the PES**

Equilibrium wavefunction $\Psi^{\rm eq}_{n\mathbf{k}}(\mathbf{R}^{\rm eq})$

Linear-Response Wavefunctions:

$$\begin{aligned} \Psi_{n\mathbf{k}}(\mathbf{R}) &\approx \Psi^{\rm pt}_{n\mathbf{k}}(\Delta\mathbf{R}) \\ &= \Psi^{\rm eq}_{n\mathbf{k}} + \sum_{l,\mathbf{k}'} \Delta\mathbf{R}\, C^{\mathbf{k}\mathbf{k}'}_{nl}\Big|_{\mathbf{R}^{\rm eq}} \cdot \Psi^{\rm eq}_{l\mathbf{k}'} \end{aligned}$$

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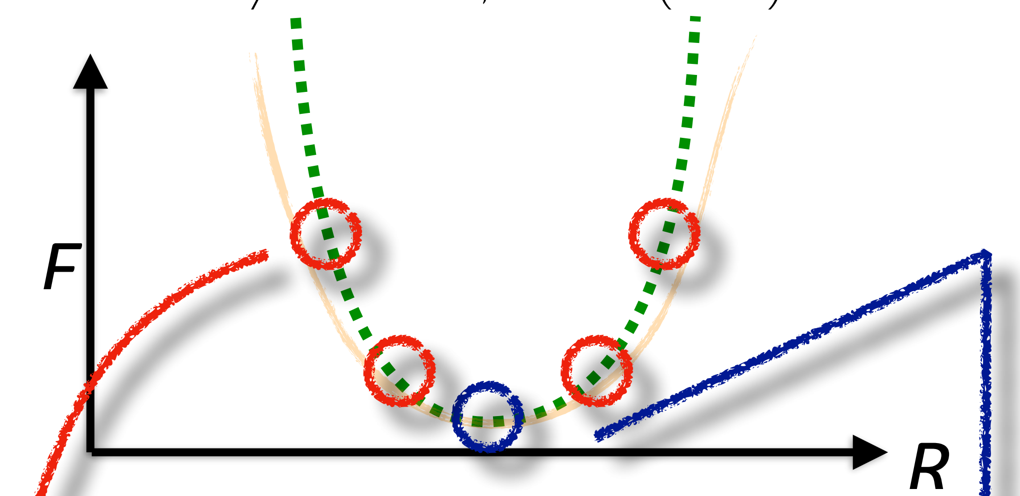

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Can we overcome these approximations?

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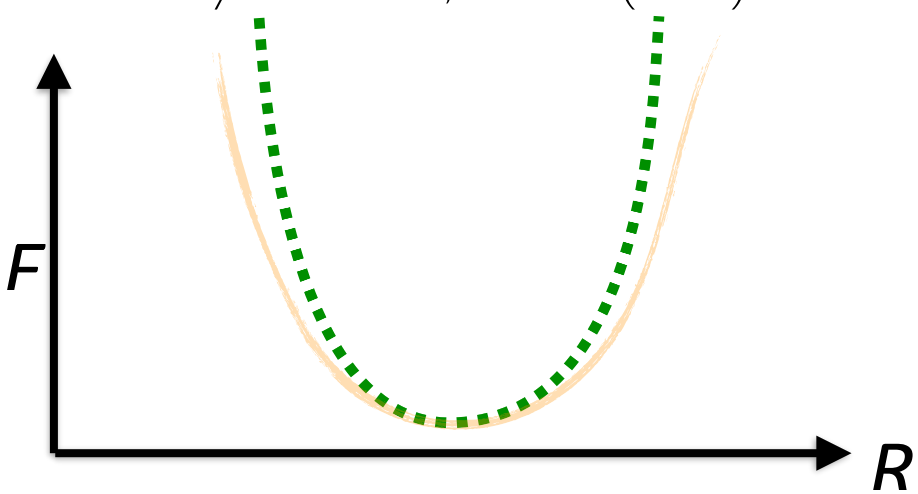
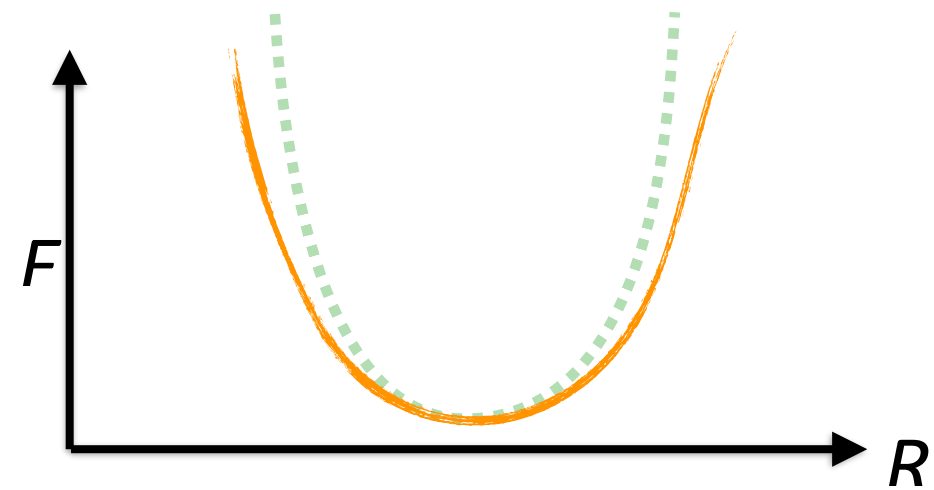


***Harmonic* Approximation for the PES**

This Work:

Non-Perturbative Theory



Fully *anharmonic* PES

Vibronic Coupling

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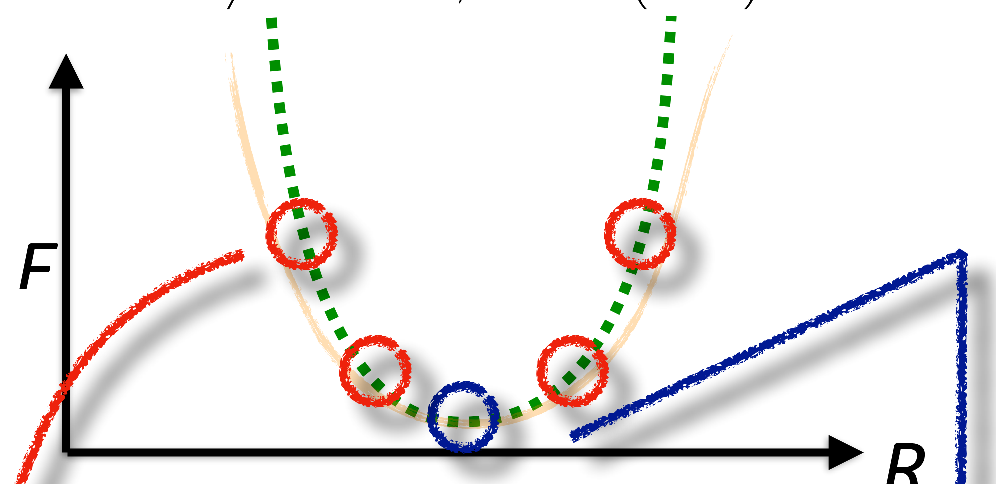

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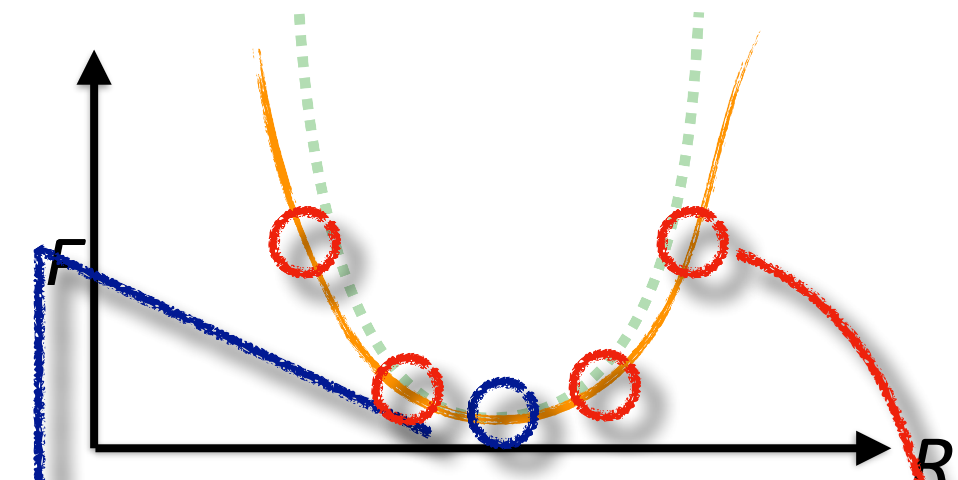

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Self-Consistent Wavefunctions:

$$\Psi_{n\mathbf{k}}(\mathbf{R}) = \Psi_{n\mathbf{k}}(\mathbf{R})$$

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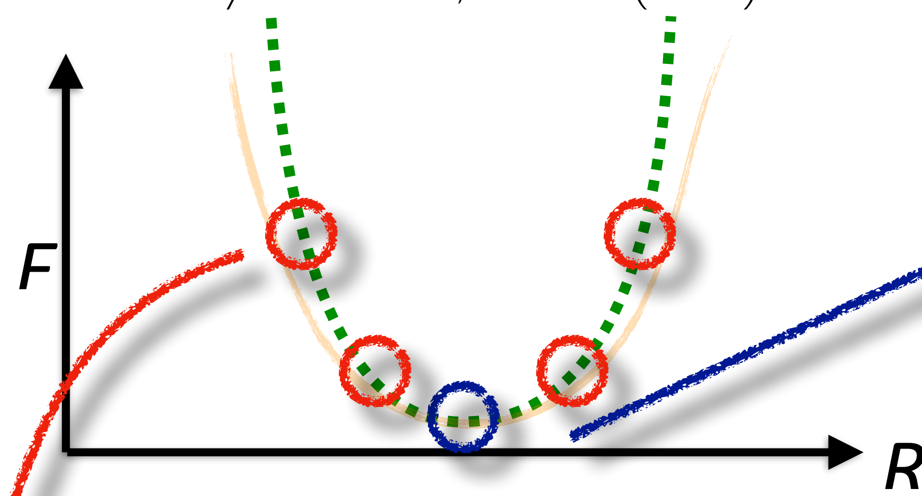

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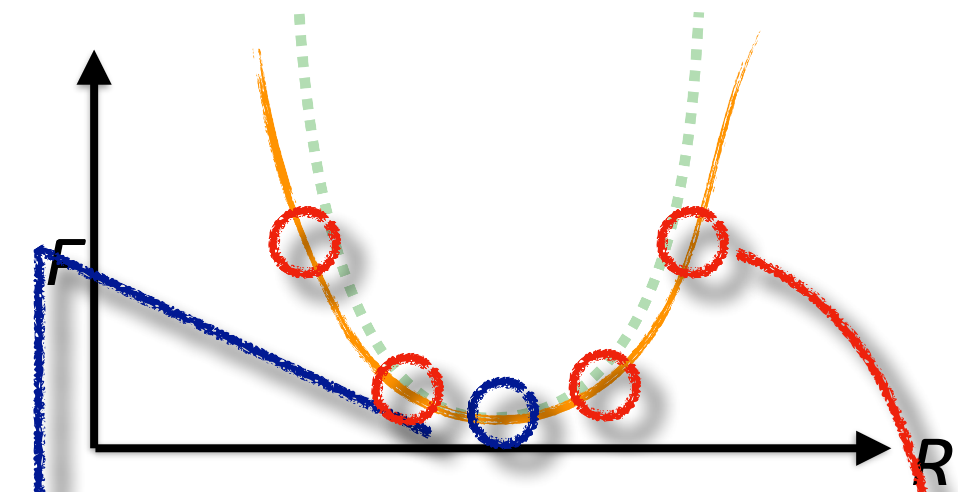

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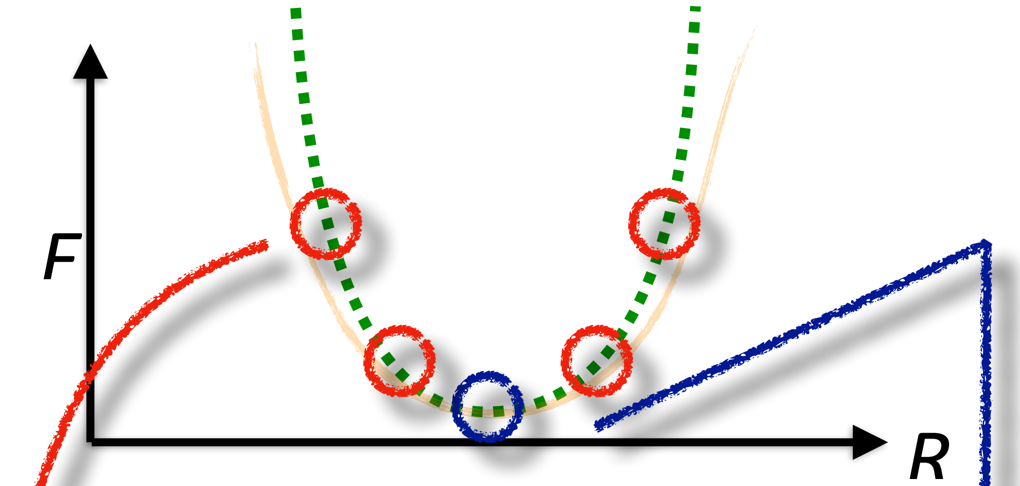
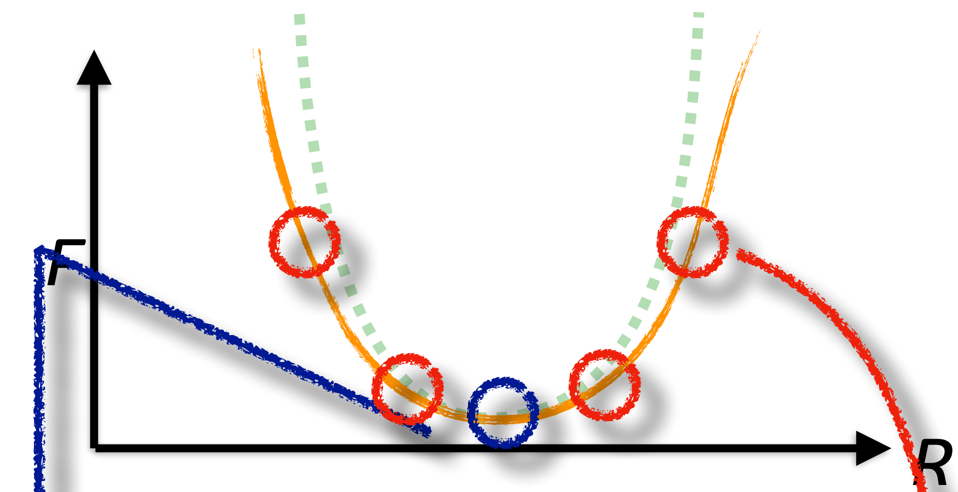


***Harmonic* Approximation for the PES**

This Work:

Non-Perturbative Theory



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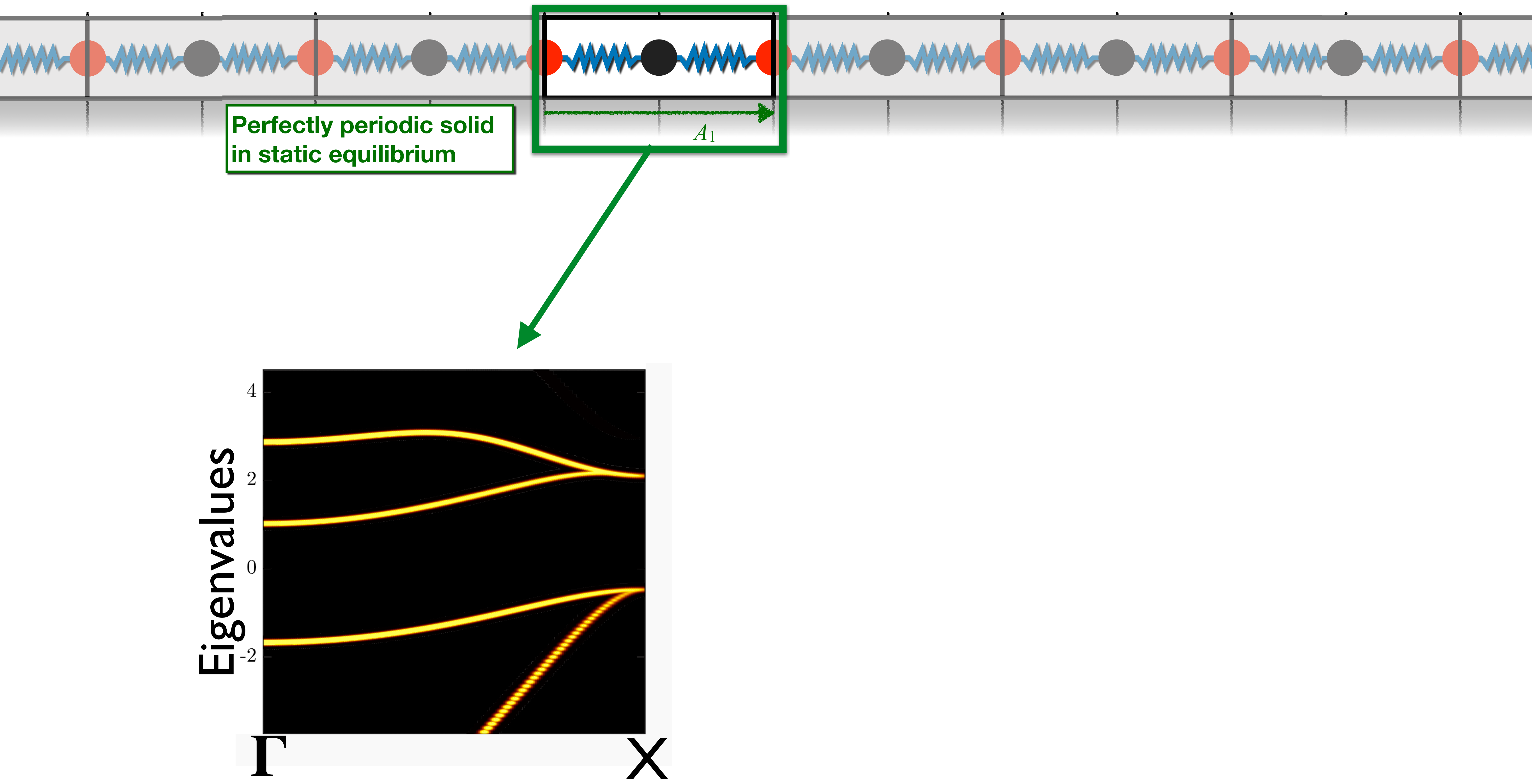
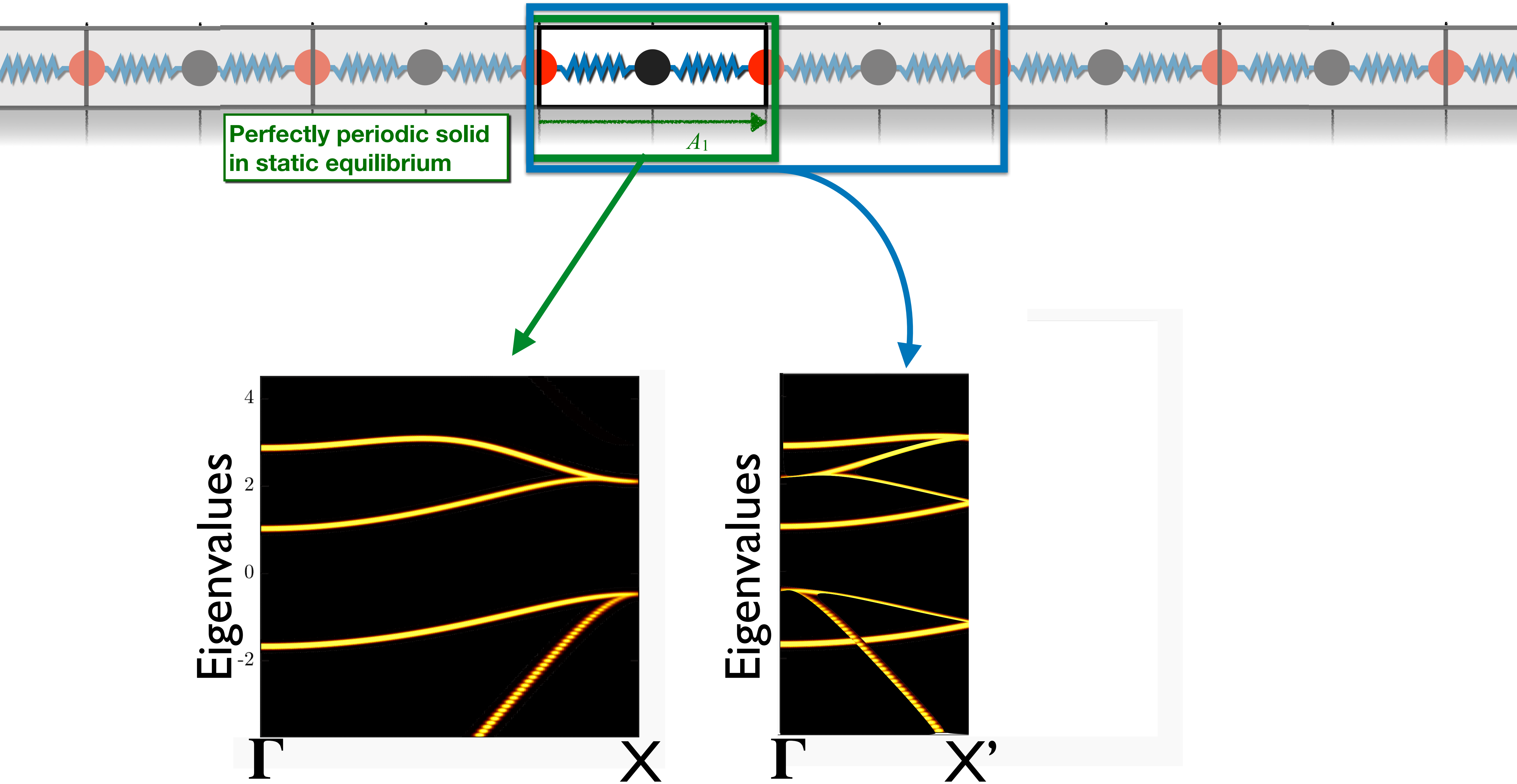

Perfectly periodic solid
in static equilibrium
A1
Eigenvalues
4
2
0
-2
Γ
X



Perfectly periodic solid
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A_1
Eigenvalues
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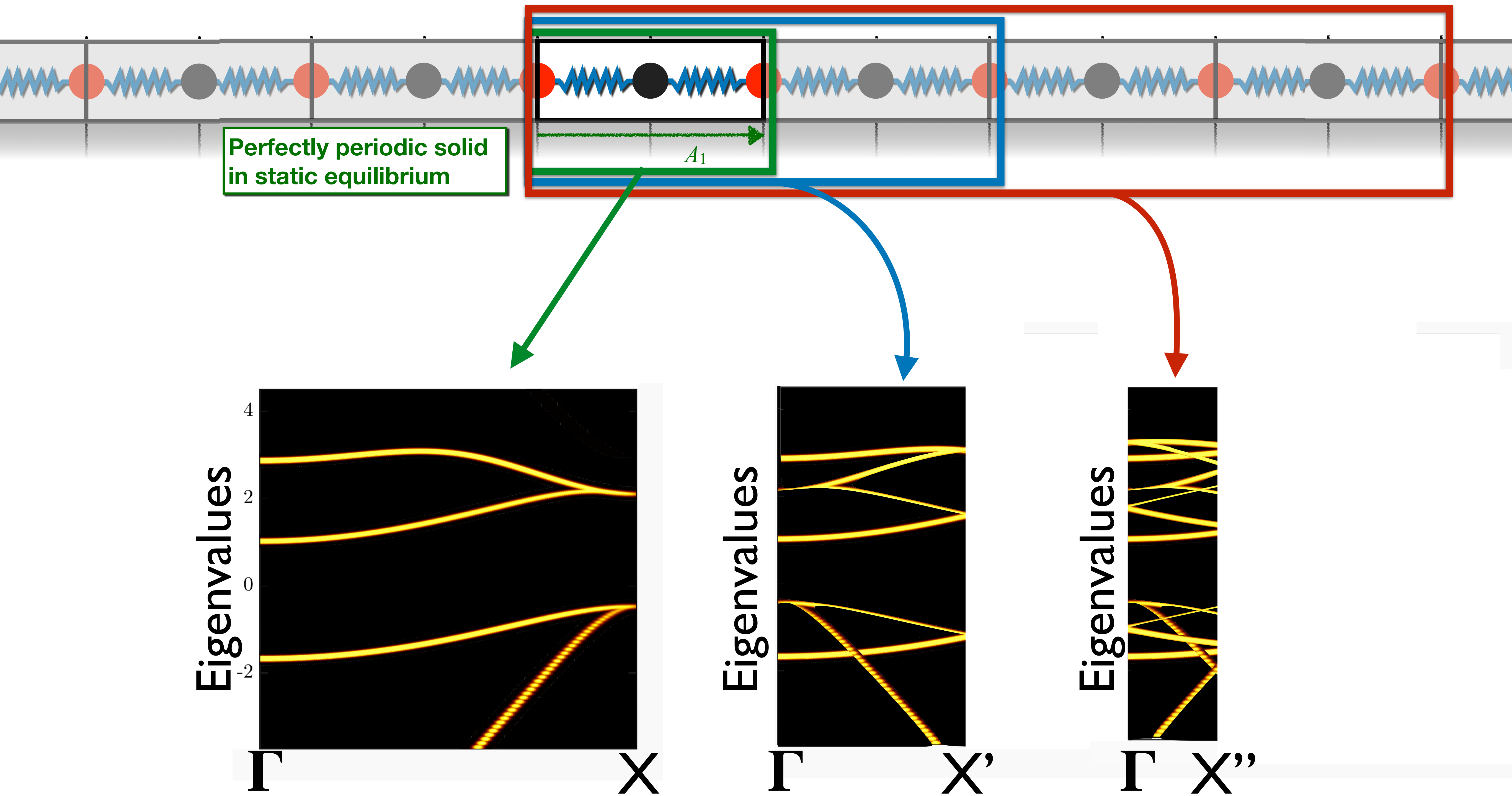
Eigenvalues
Γ
X'



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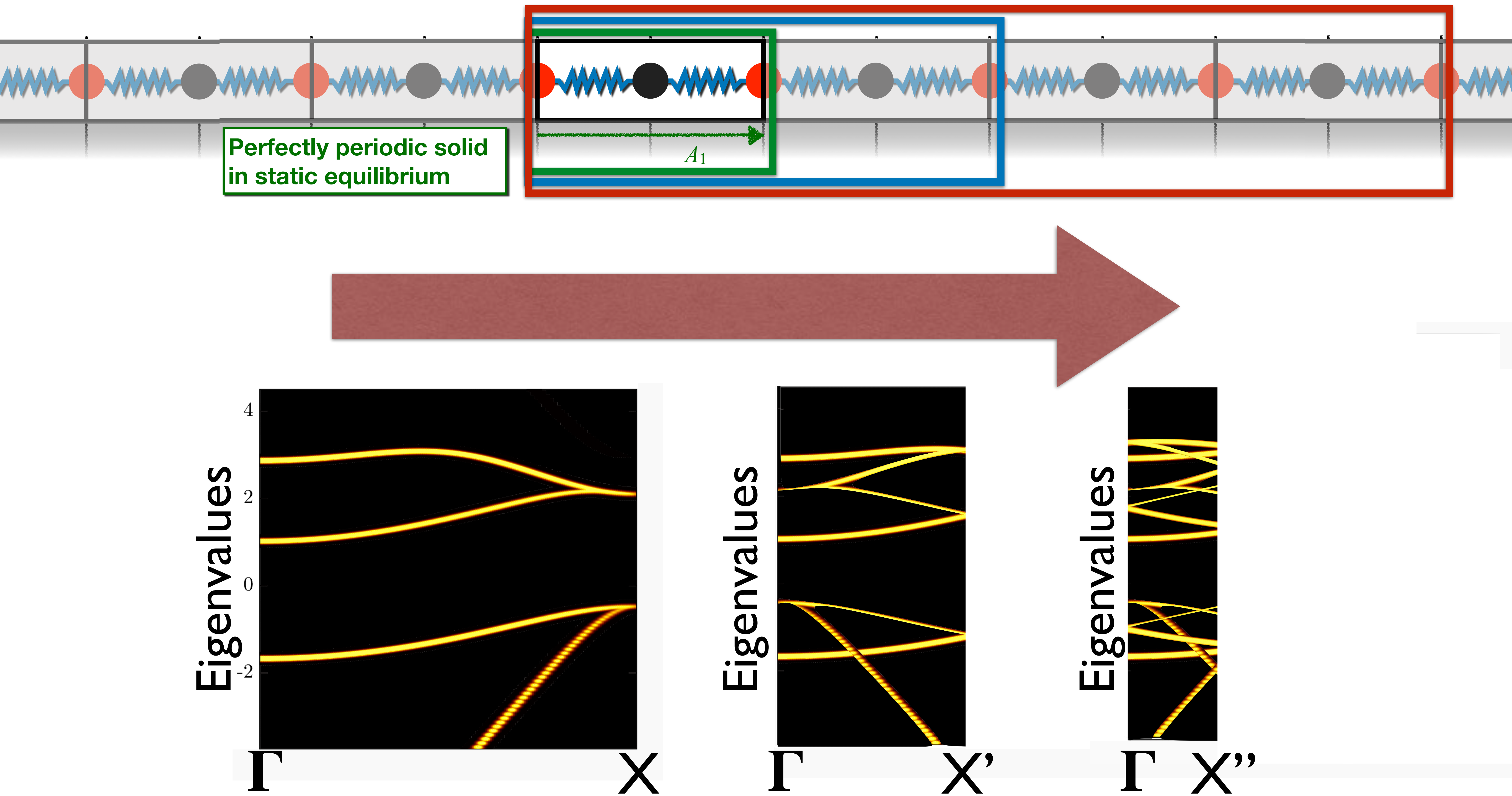
X''



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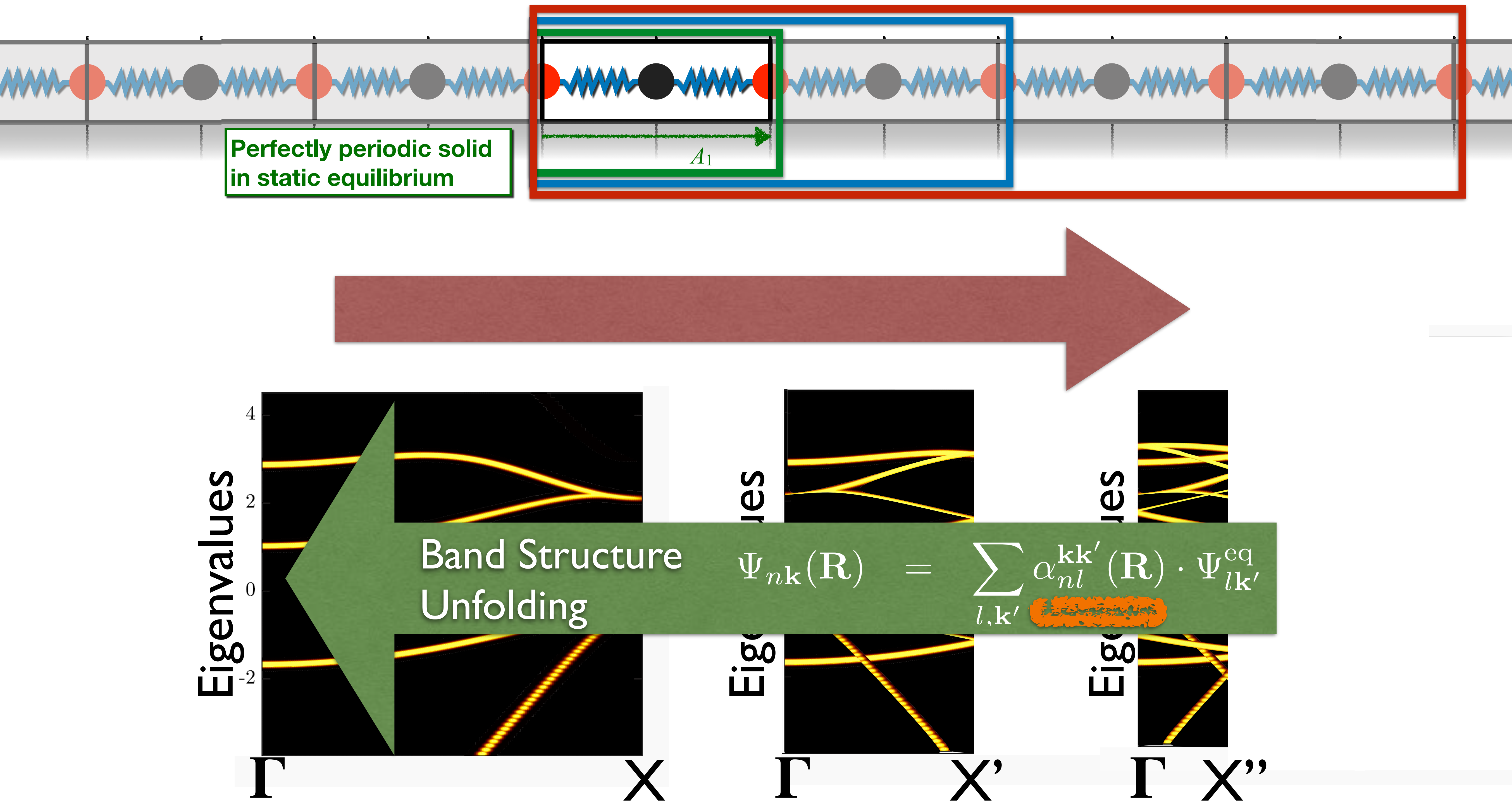

Perfectly periodic solid
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A_1
Band Structure
Unfolding
$\Psi_{n\mathbf{k}}(\mathbf{R}) = \sum_{l,\mathbf{k}'} \alpha_{nl}^{\mathbf{k}\mathbf{k}'}(\mathbf{R}) \cdot \Psi_{l\mathbf{k}'}^{\mathrm{eq}}$
Eigenvalues
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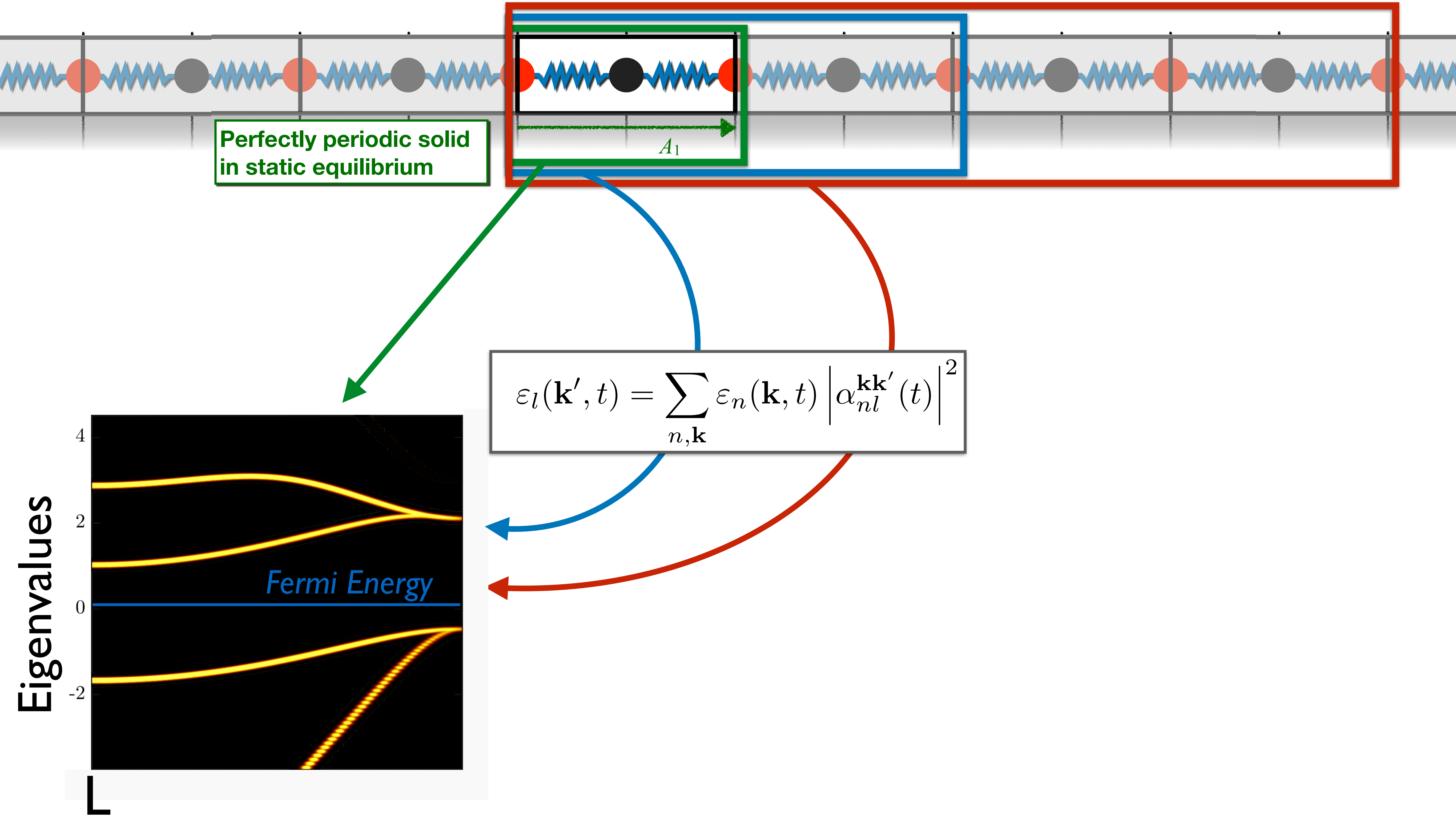
2
0
-2
Γ
X
Γ
X'
Γ
X''



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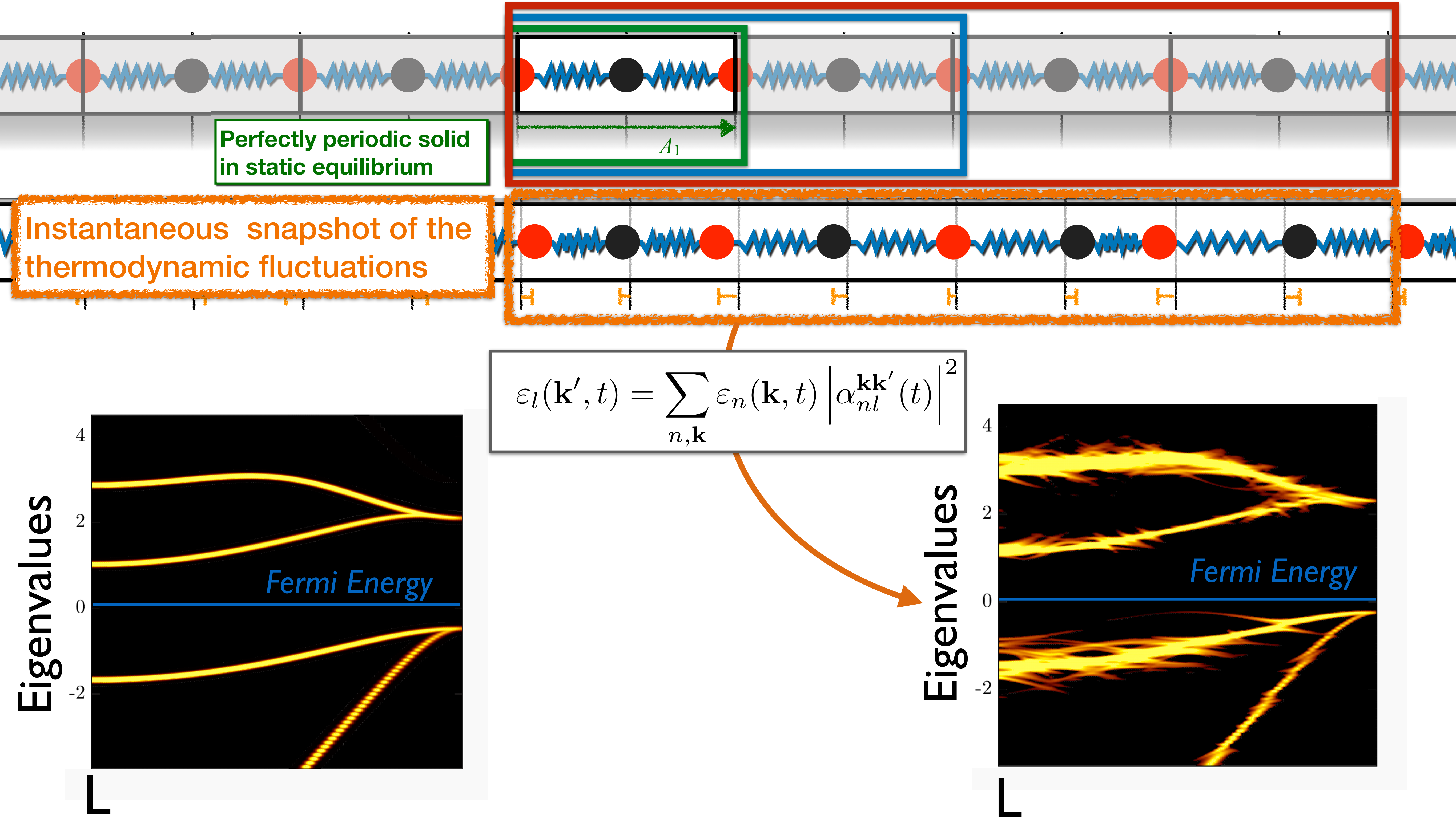
in static equilibrium
A_1
$$\varepsilon_l(\mathbf{k}',t) = \sum_{n,\mathbf{k}} \varepsilon_n(\mathbf{k},t) \left| \alpha_{nl}^{\mathbf{k}\mathbf{k}'}(t) \right|^2$$
Eigenvalues
4
2
0
-2
Fermi Energy
L



Perfectly periodic solid in static equilibrium
A_1
Instantaneous snapshot of the thermodynamic fluctuations
$\varepsilon_l(\mathbf{k}', t) = \sum_{n,\mathbf{k}} \varepsilon_n(\mathbf{k}, t) \left| \alpha_{nl}^{\mathbf{k}\mathbf{k}'}(t) \right|^2$
Eigenvalues
4
2
0
-2
Fermi Energy
L
Eigenvalues
4
2
0
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Fermi Energy
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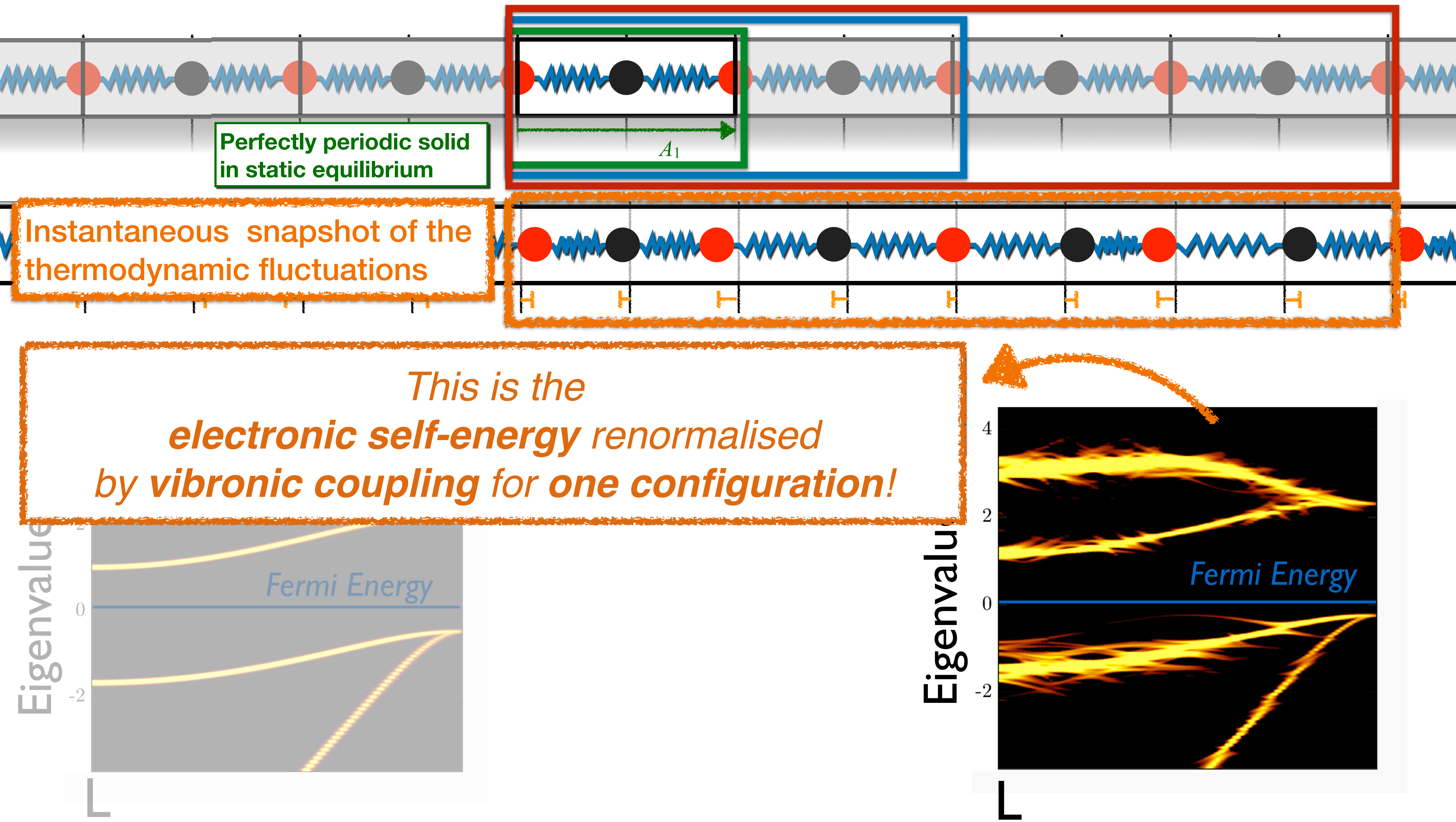
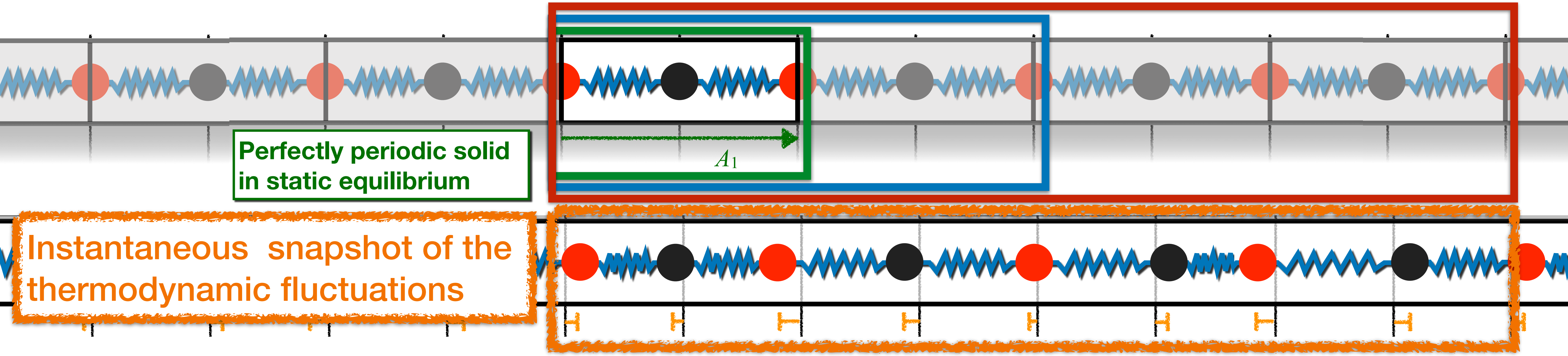
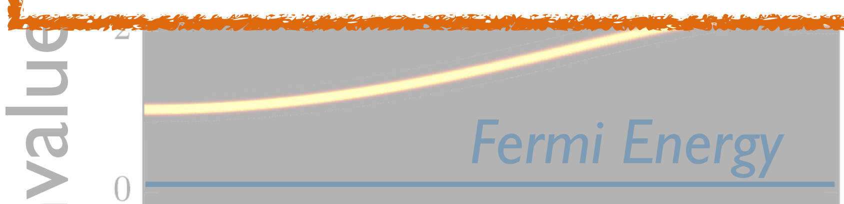
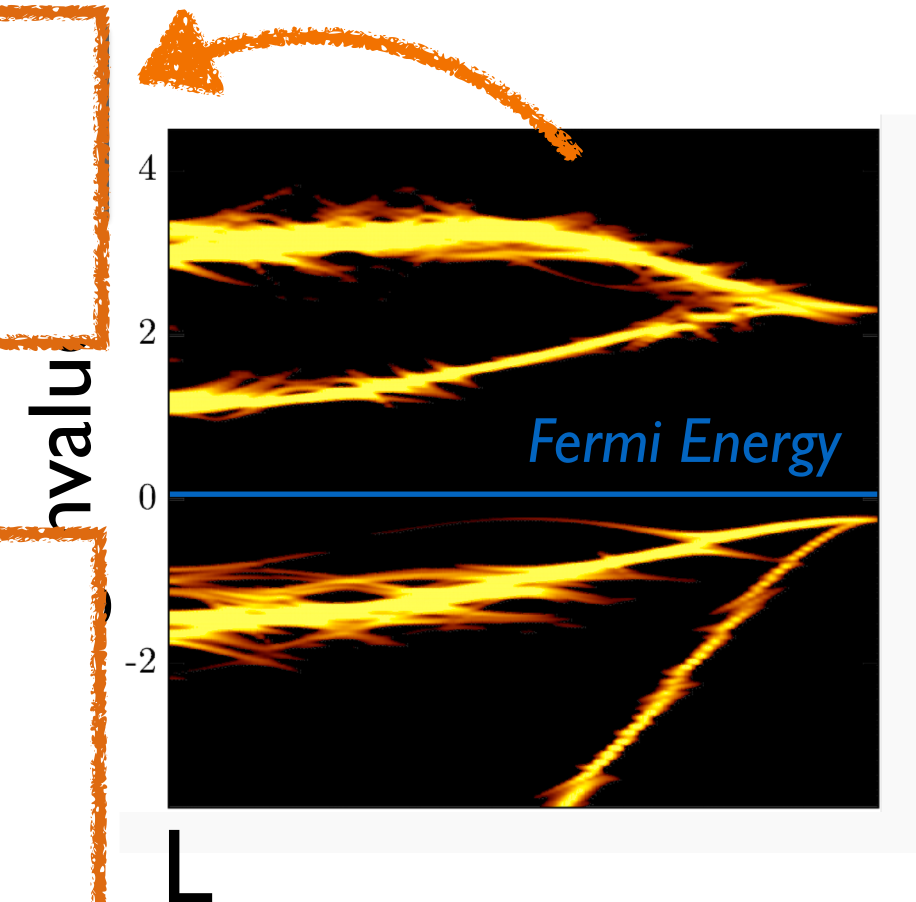

Perfectly periodic solid
in static equilibrium
A_1
Instantaneous snapshot of the
thermodynamic fluctuations
This is the
electronic self-energy renormalised
by vibronic coupling for one configuration!
Eigenvalue
Fermi Energy
0
-2
L
Eigenvalue
4
2
0
-2
Fermi Energy
L



This is the
electronic self-energy *renormalised*
by ***vibronic coupling*** *for* ***one configuration!***

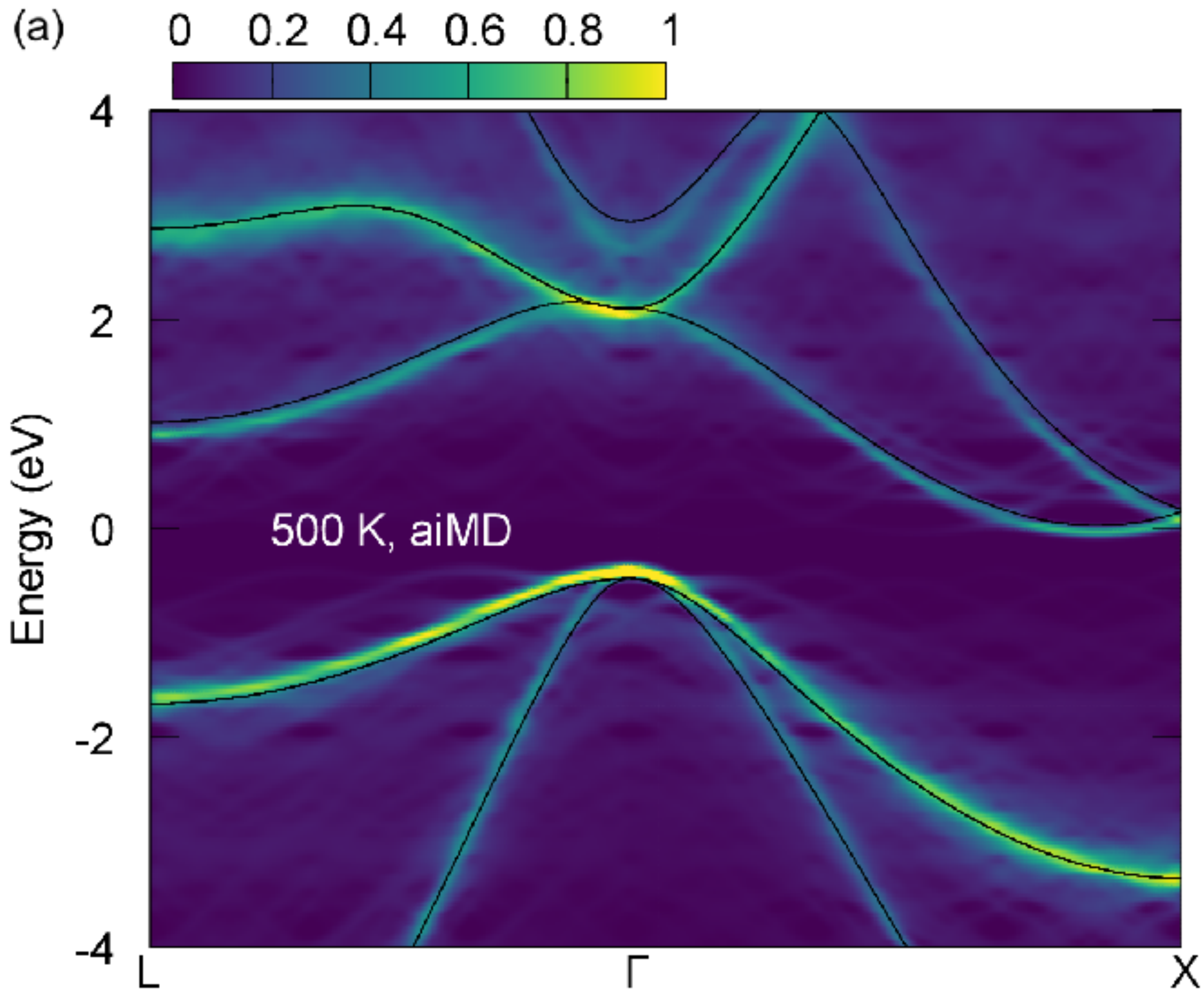


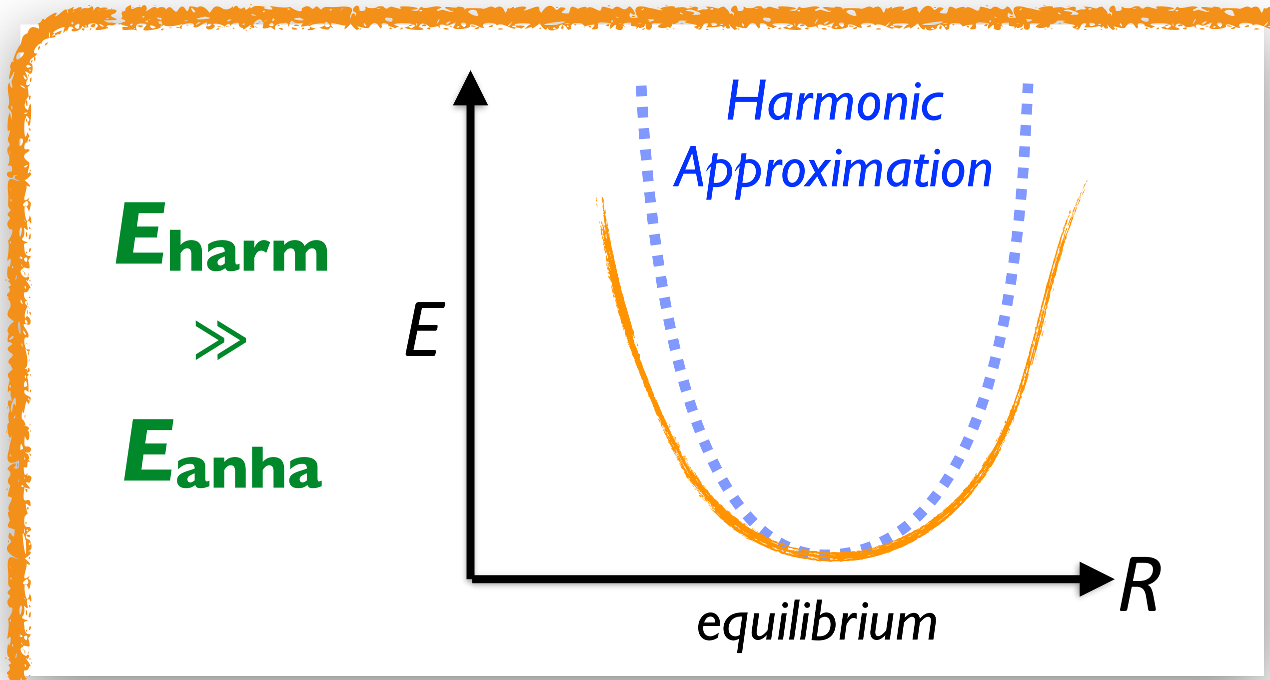


Thermodynamic *Average gives*
Expectation value:

$$\langle \varepsilon_l(\mathbf{k}') \rangle_T^{\mathrm{MD}} = \frac{1}{t_0} \int_0^{t_0} \varepsilon_l(\mathbf{k}', t)\, dt \;.$$

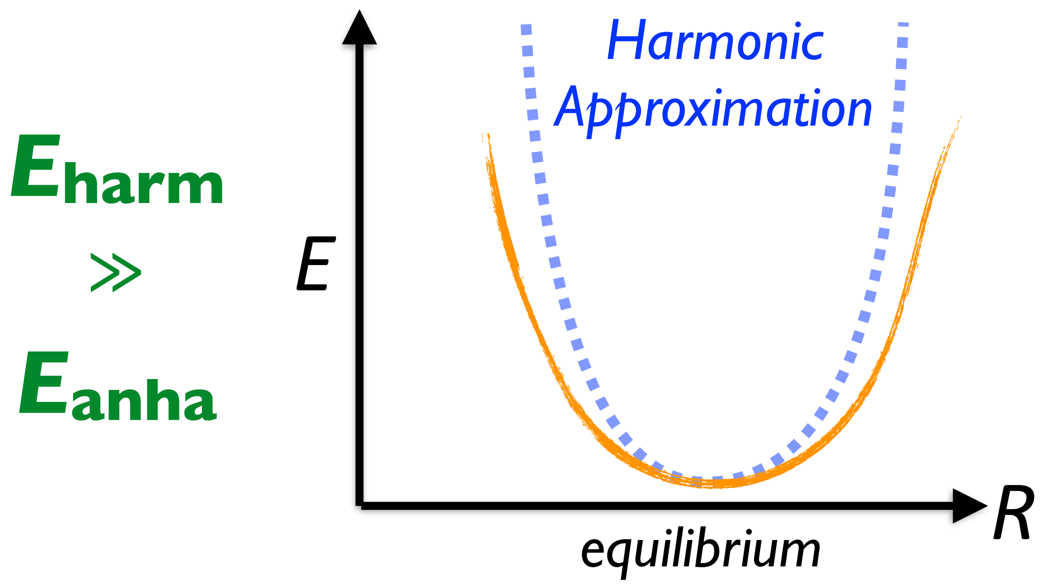
A Real Example: 7x7x7 Si





Si: very harmonic

M. Zacharias, M. Scheffler, and C. Carbogno, *Phys. Rev. B* **102**, 04526 (2020).



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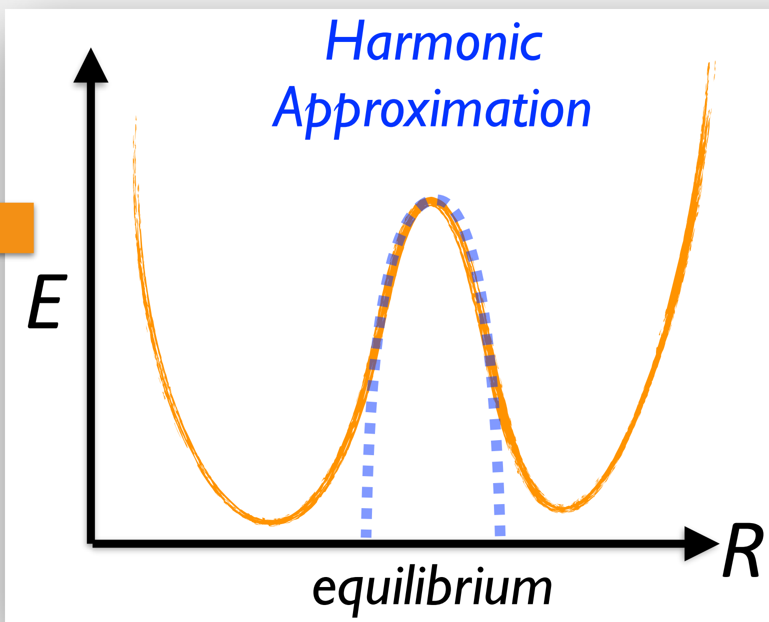
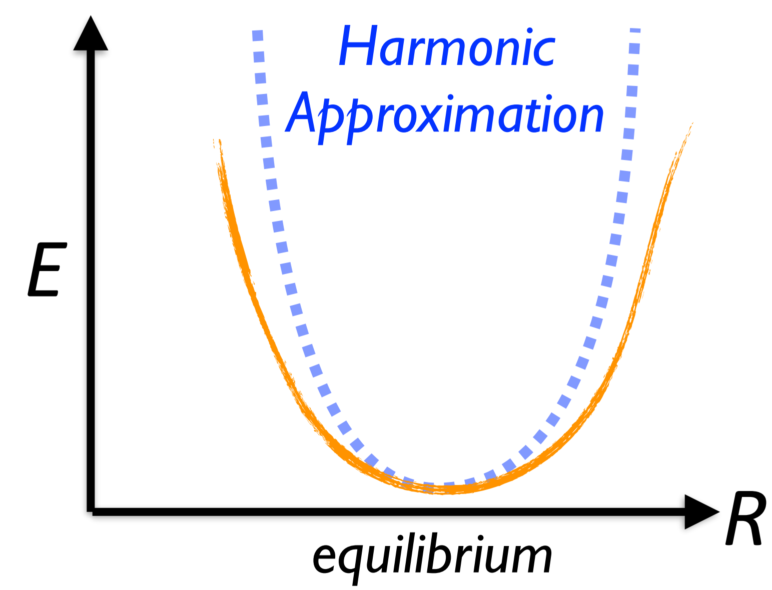


What about anharmonic systems?

E_{harm} ≫ E_{anha}



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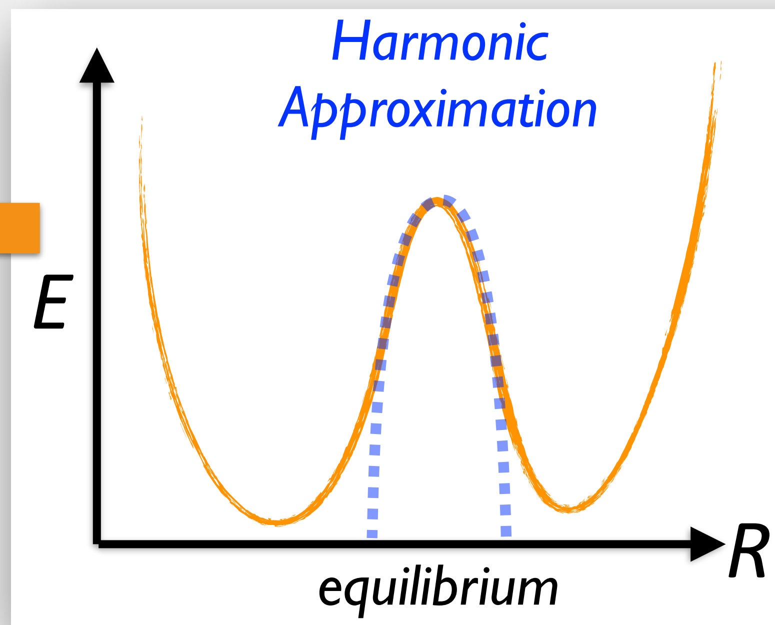
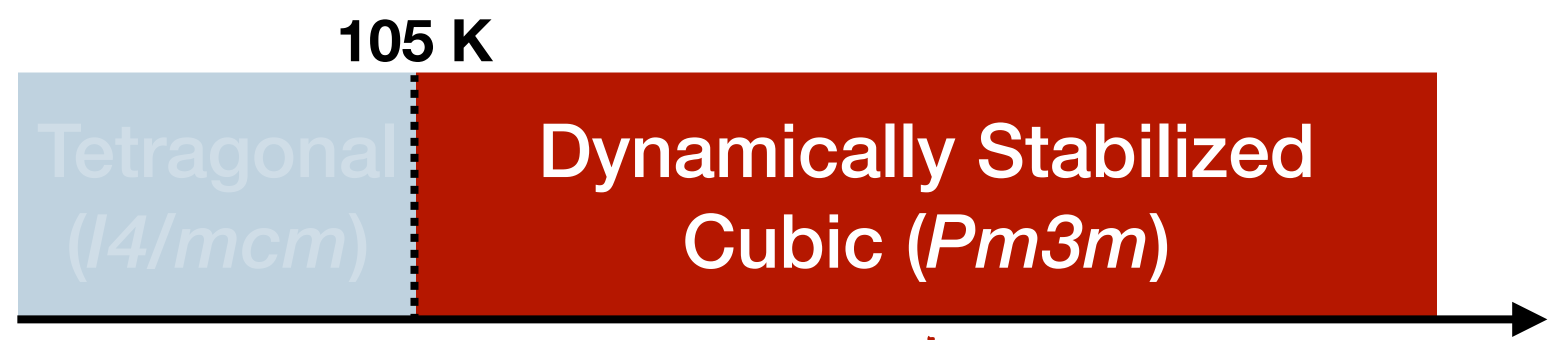
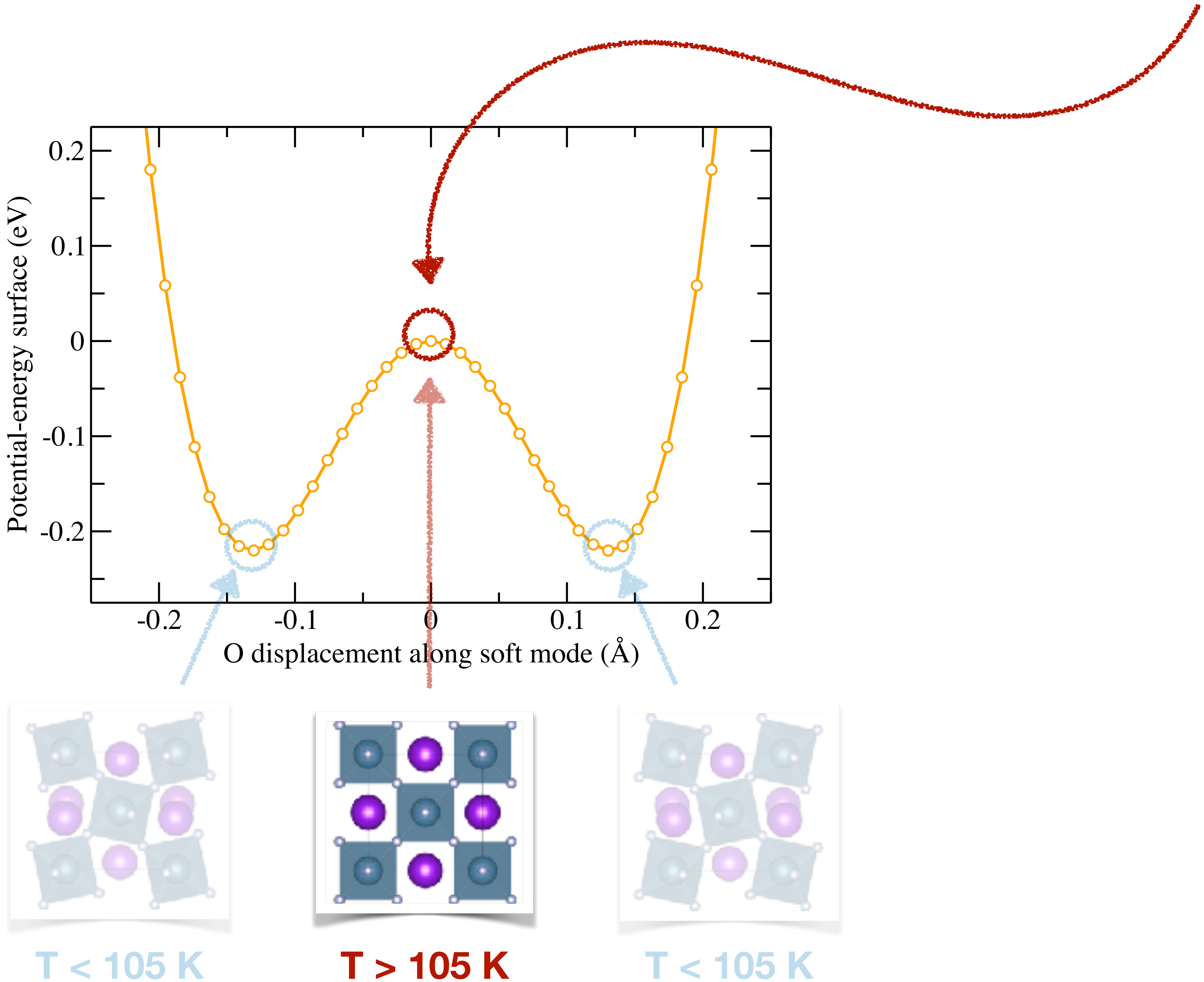


Cubic $SrTiO_3$: A Real Challenge

R. Lötzsch, *et al.*, *Appl. Phys. Lett.* **96**, 071901 (2010).
P. K. Gogoi and D. Schmidt, *Phys. Rev. B* **93**, 075204 (2016).

Cubic $SrTiO_3$: A Real Challenge





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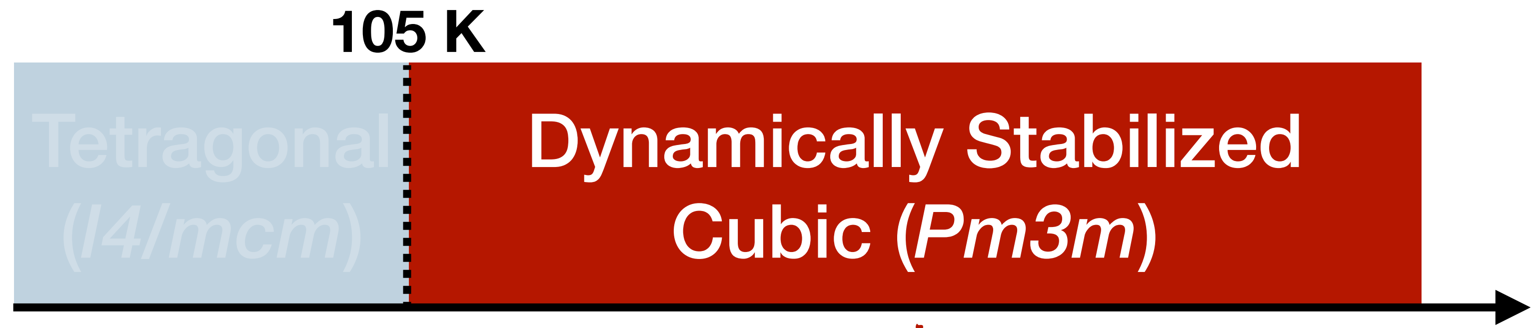
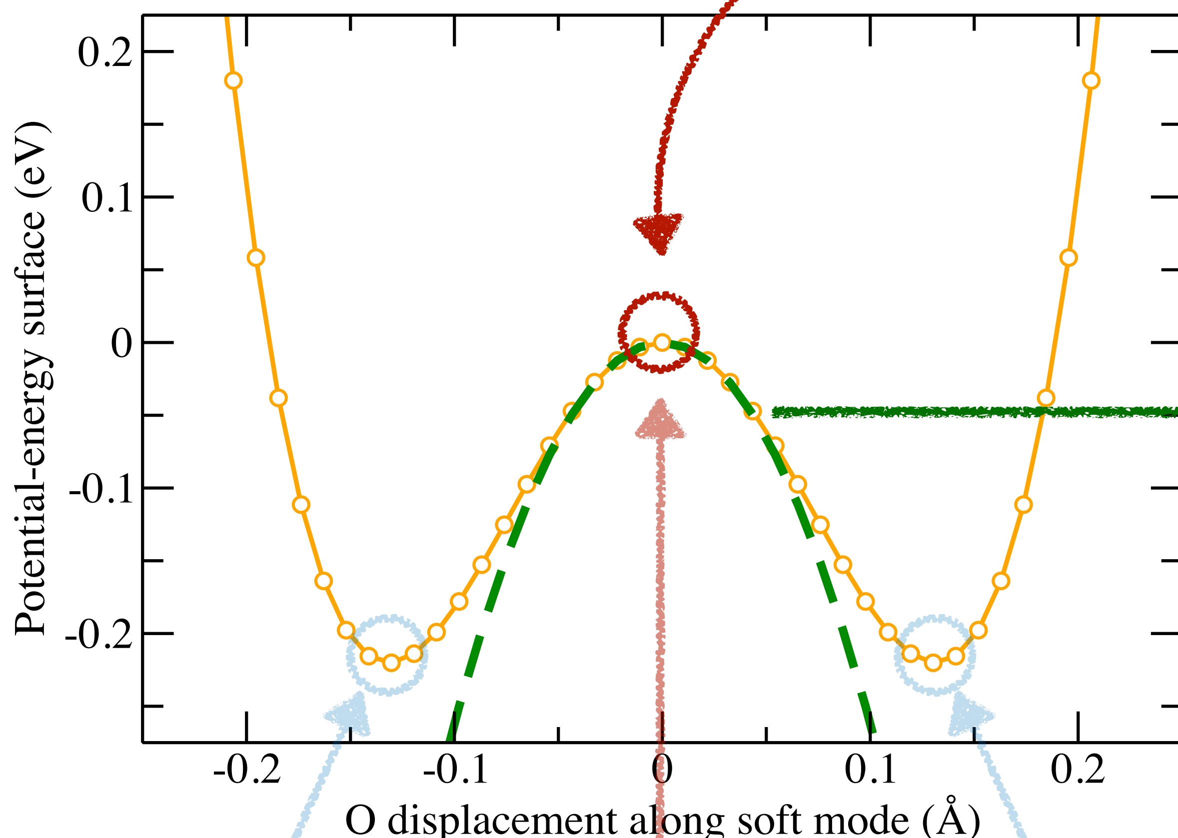
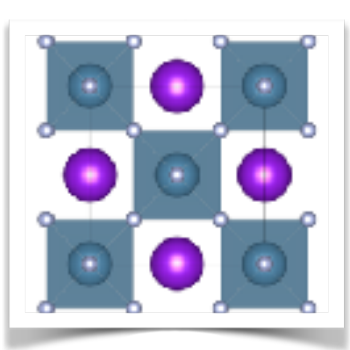




Harmonic Approximation breaks down completely!

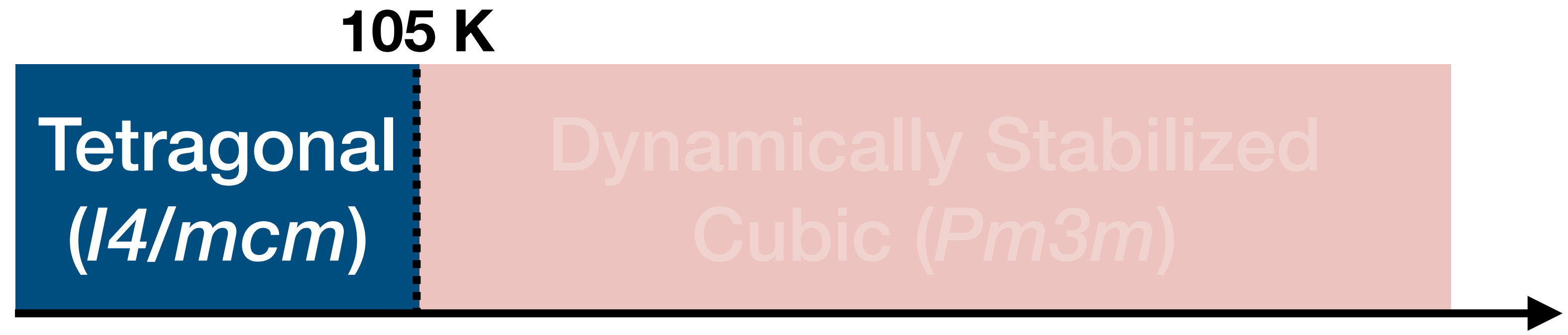
T < 105 K

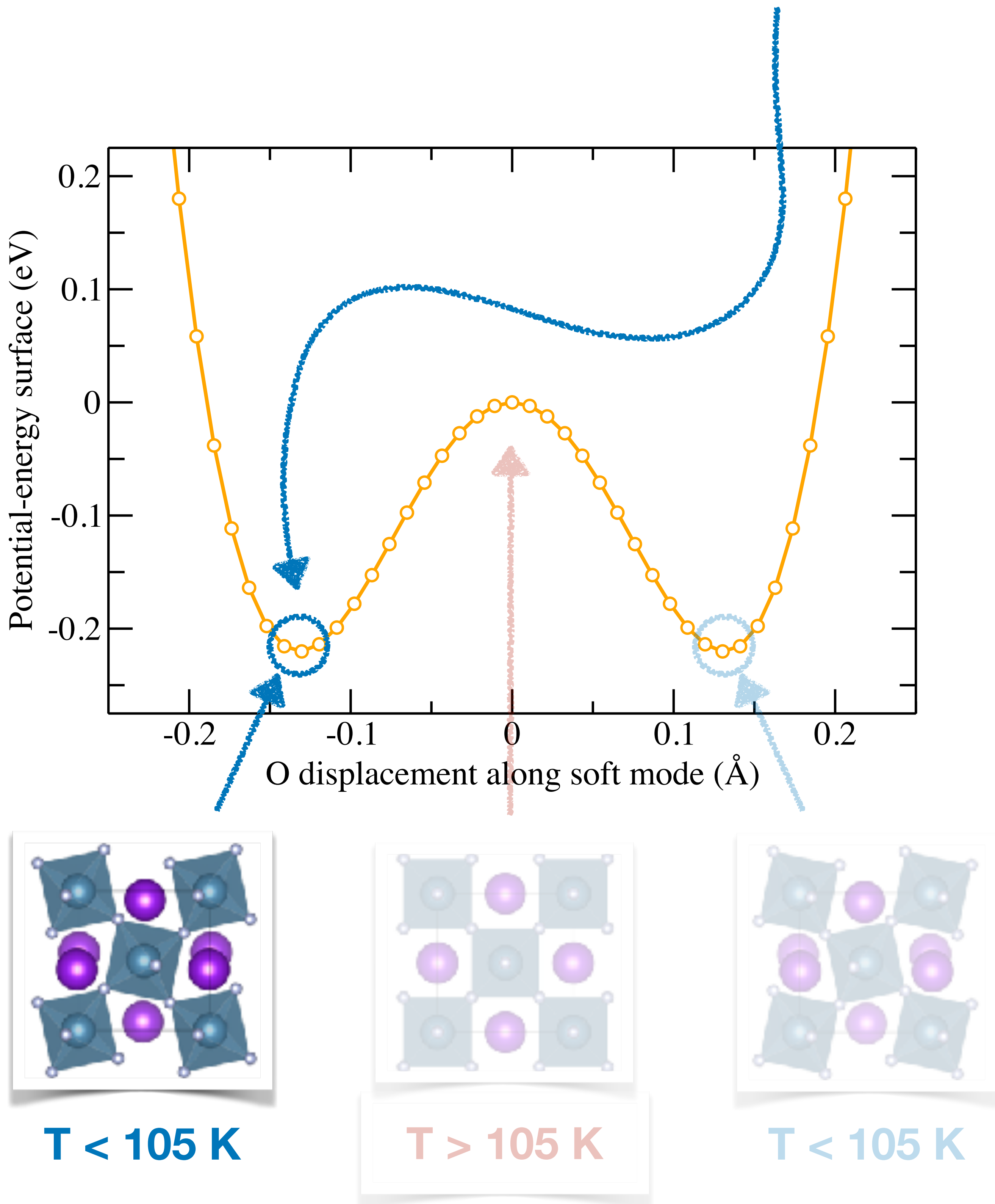


T > 105 K

T < 105 K

Cubic $SrTiO_3$: A Real Challenge





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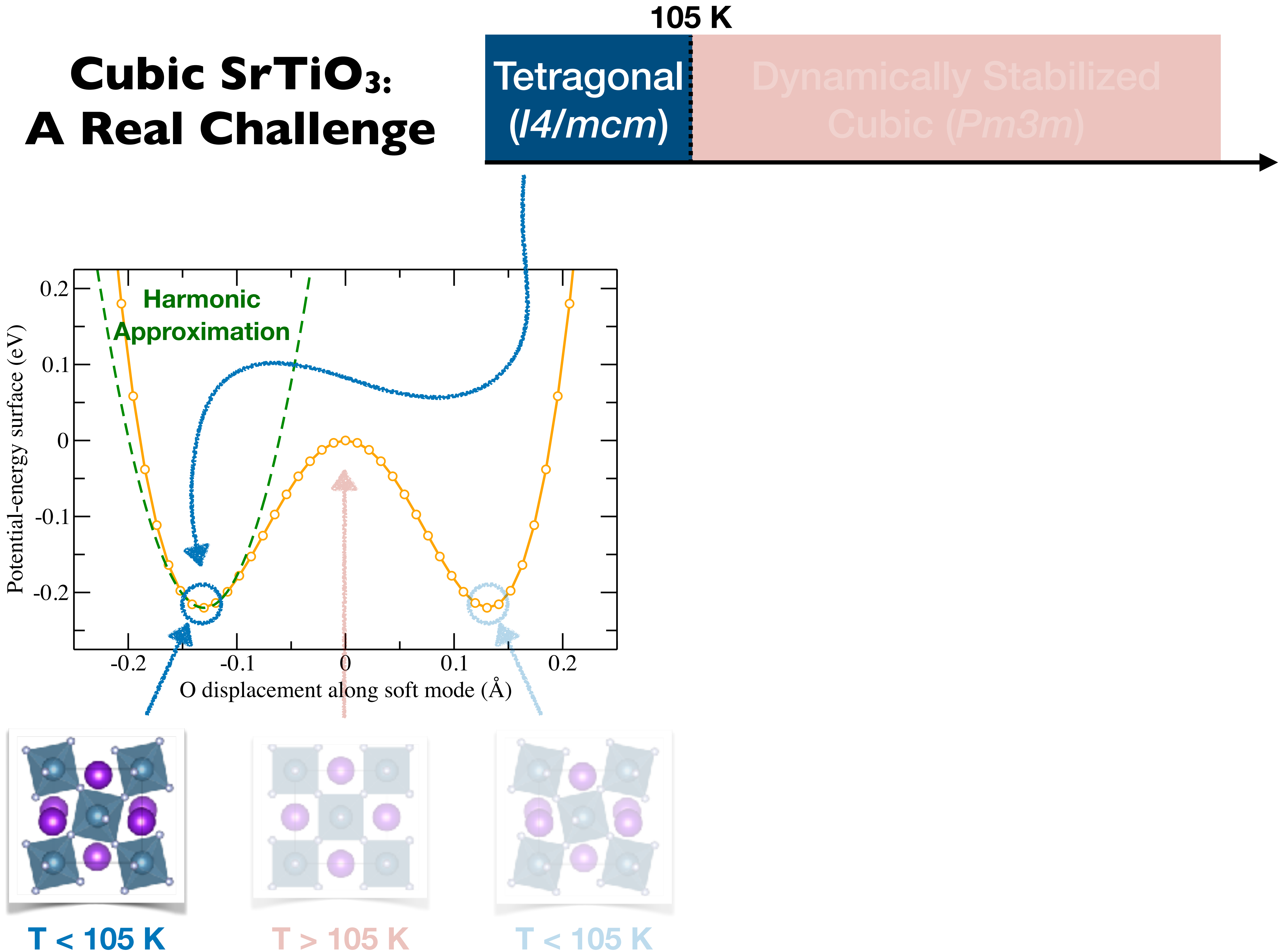

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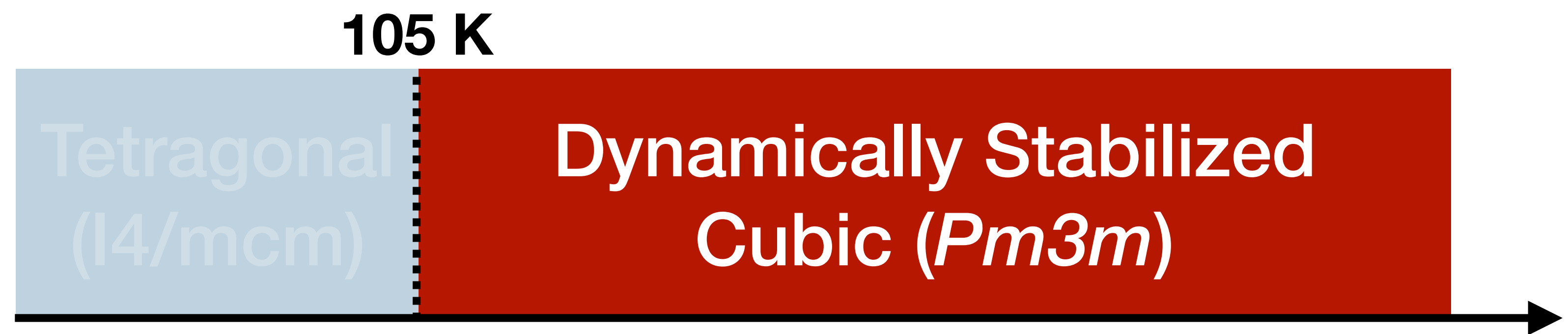

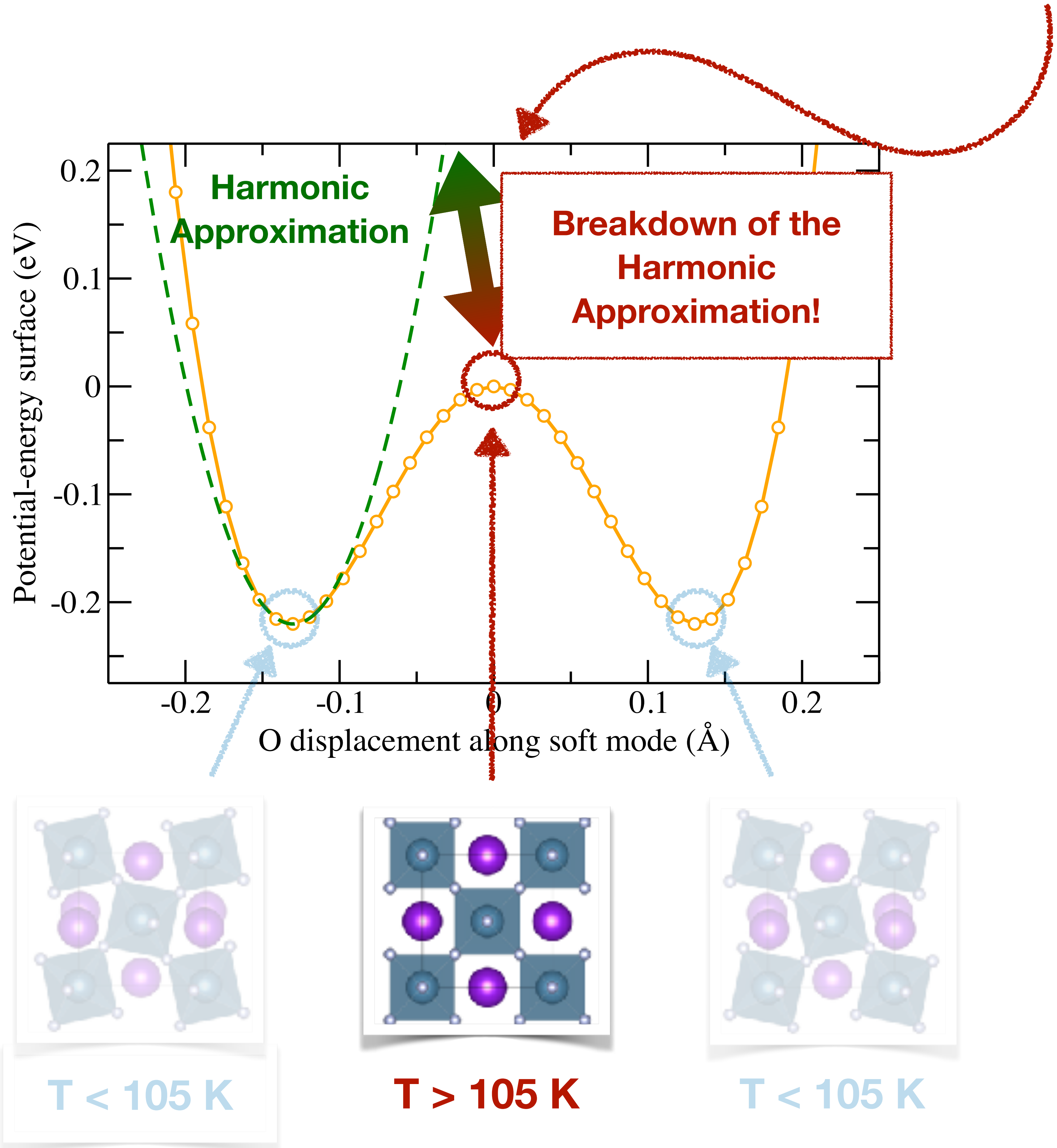

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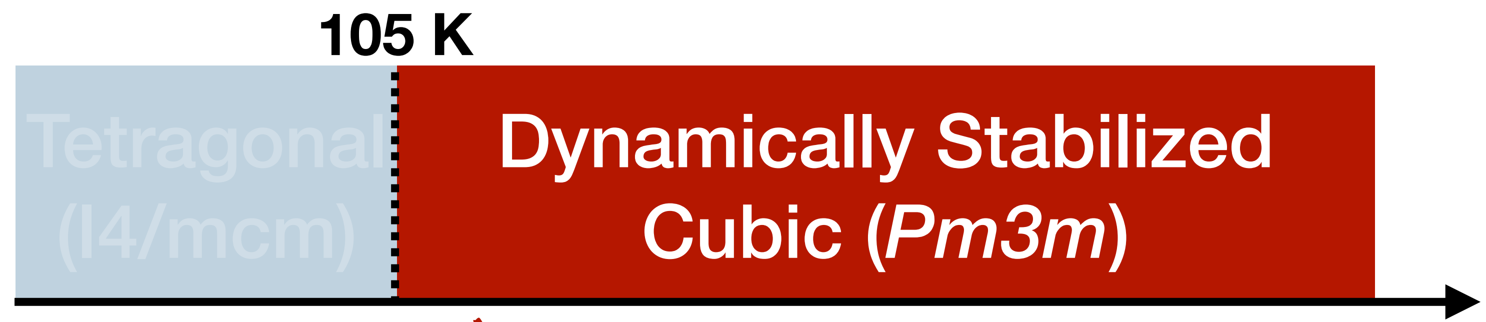

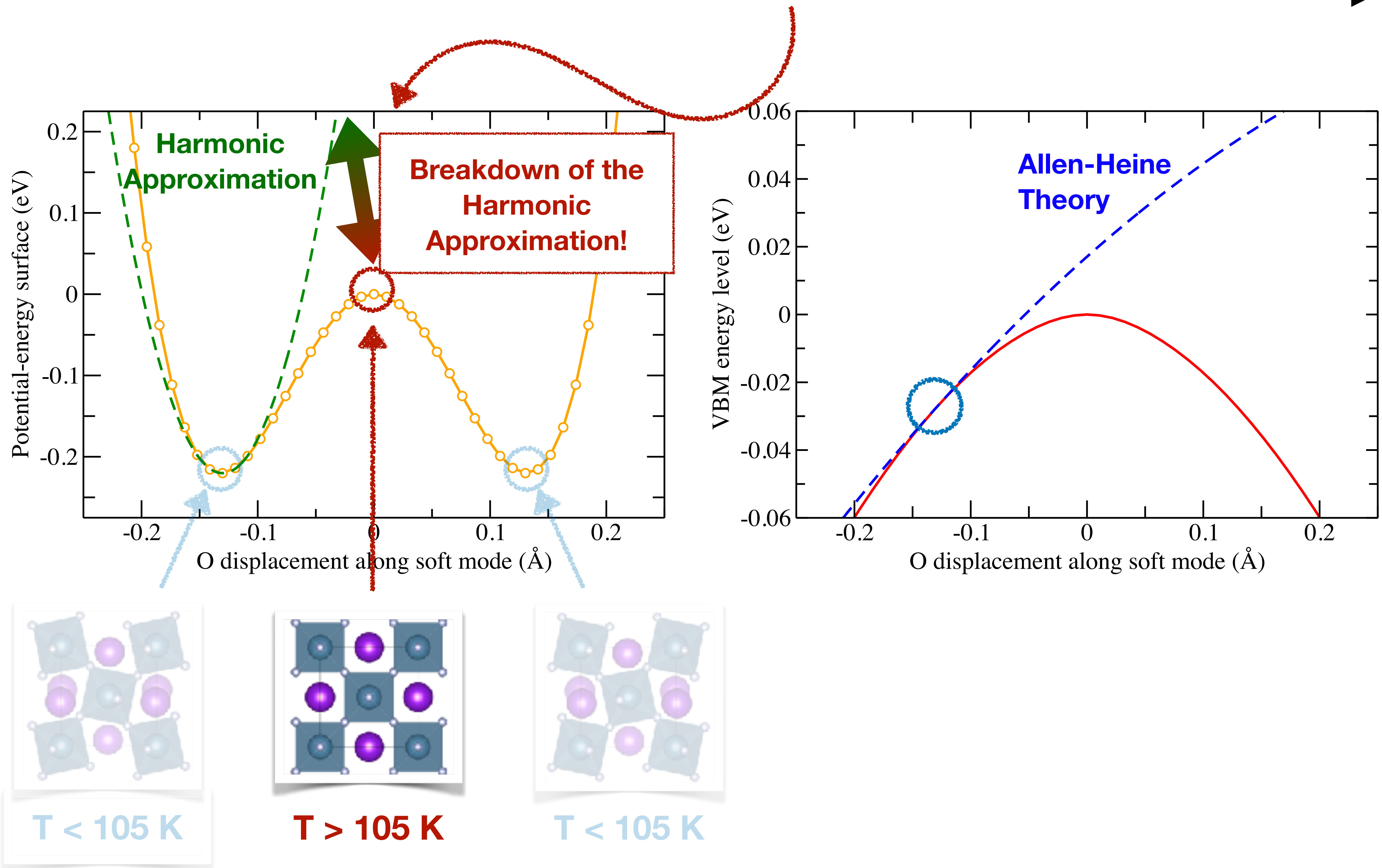

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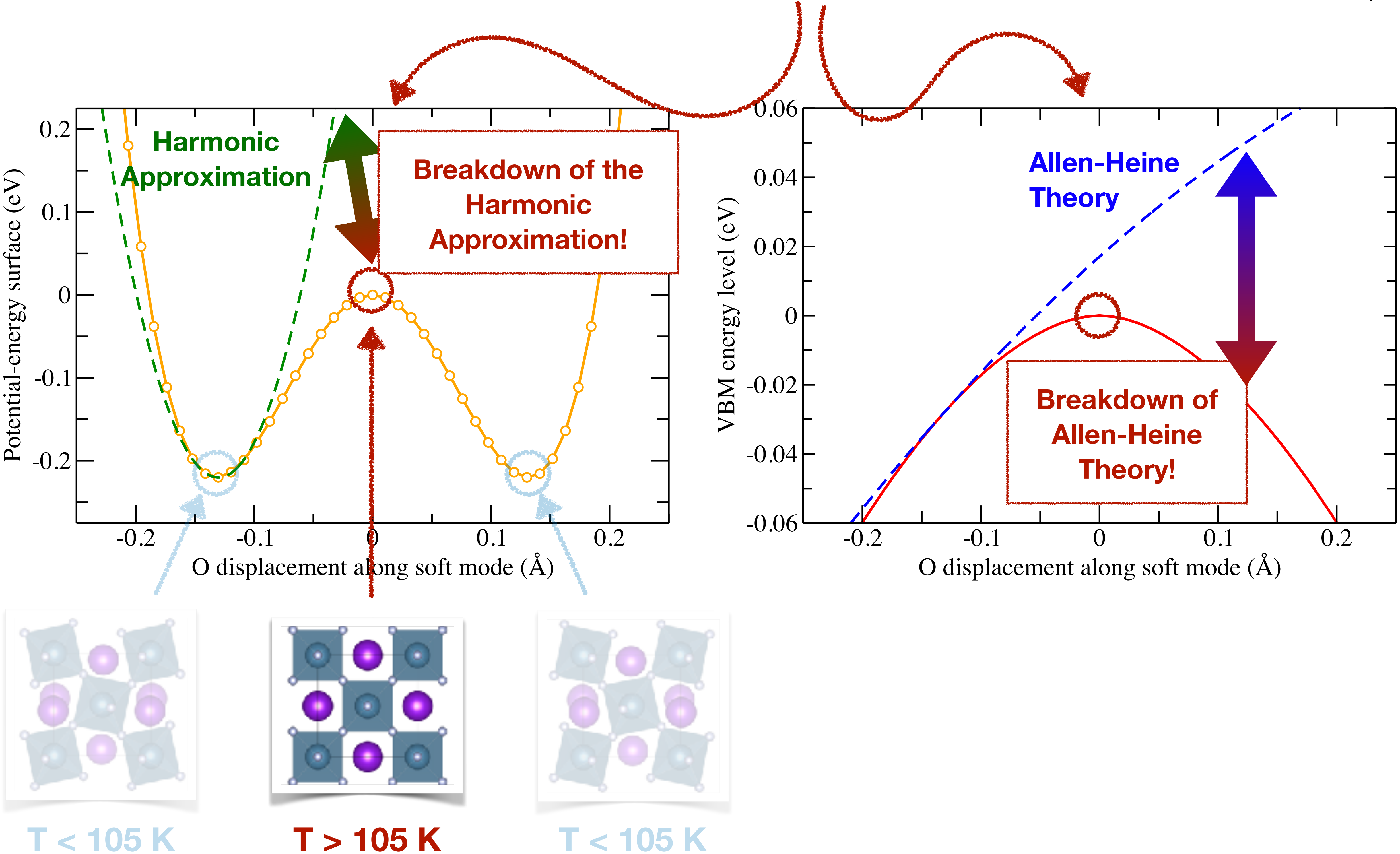

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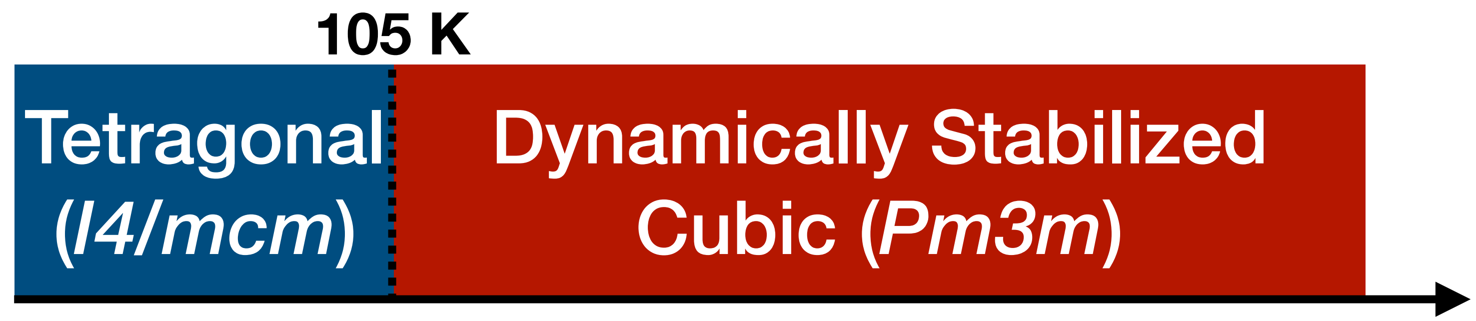

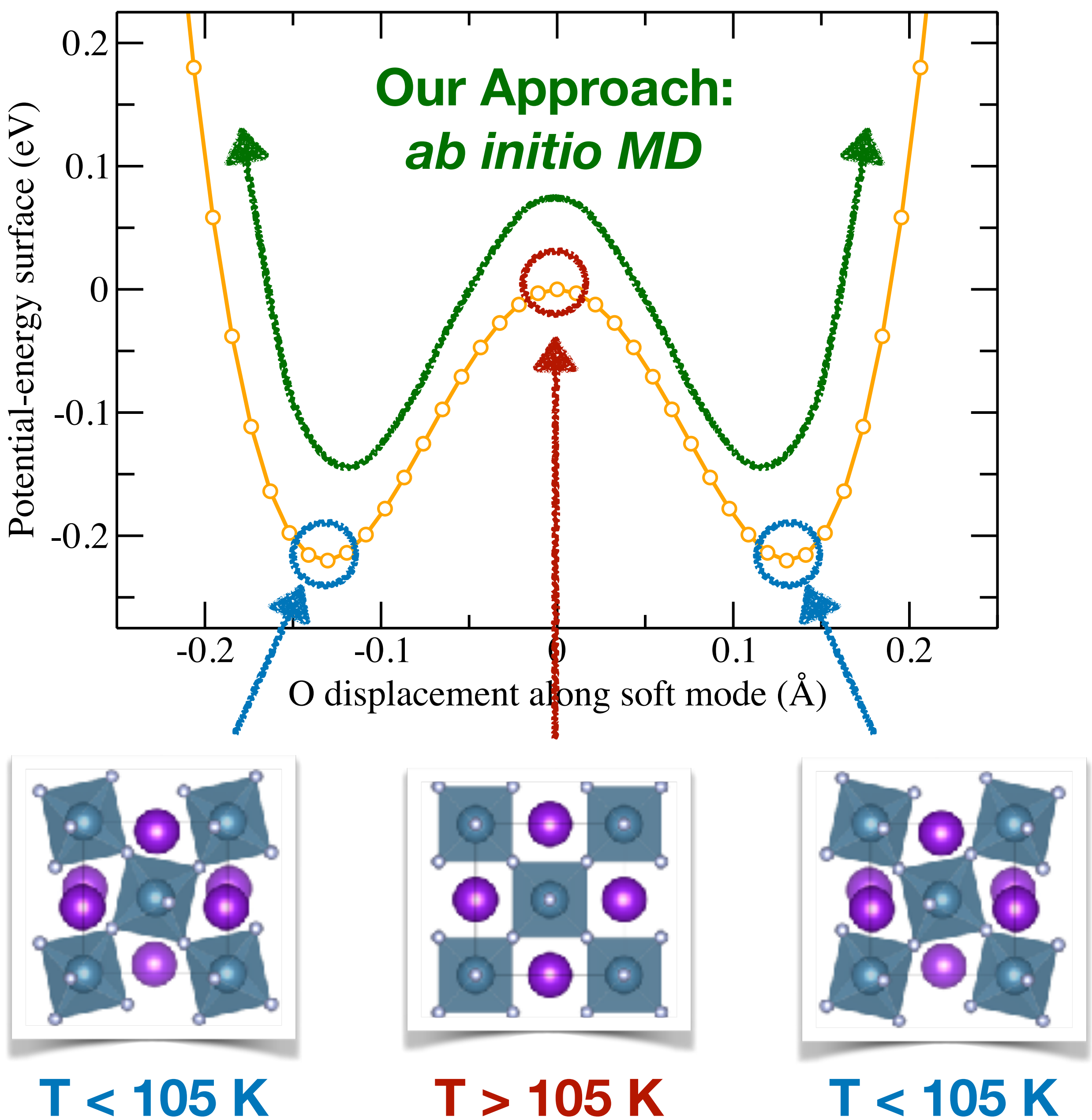

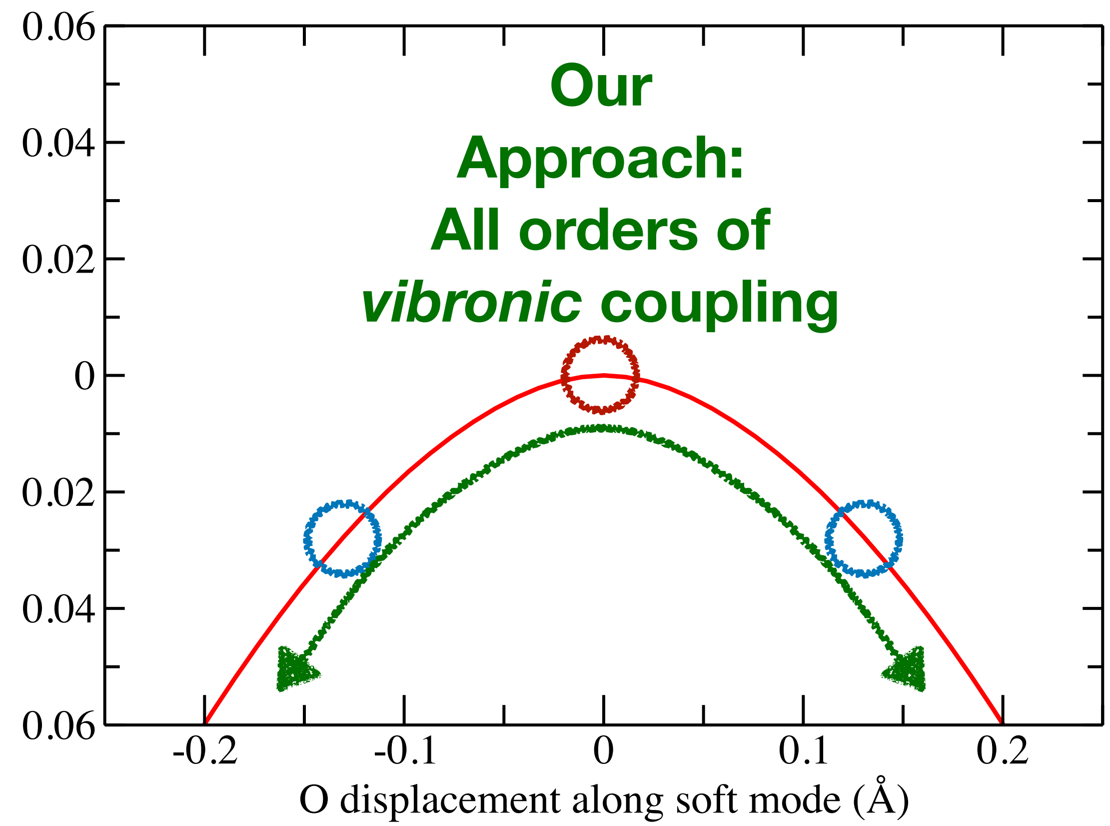

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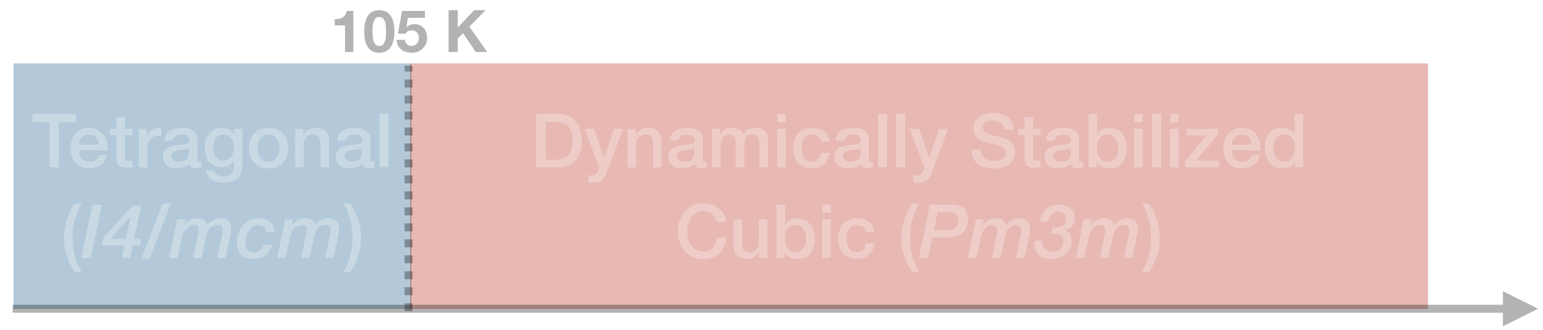
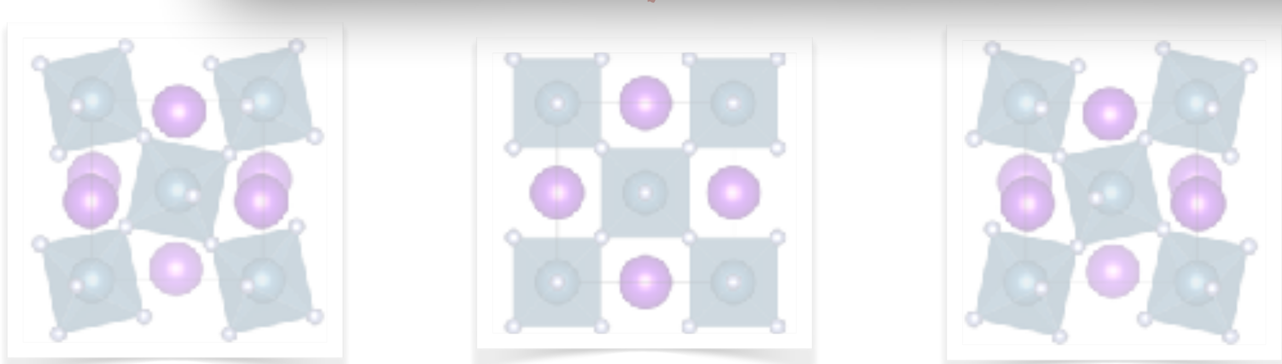


$SrTiO_3$ is tricky in DFT:

- **Significative** *Van der Waals* interactions:
  Tkatchenko-Scheffler (TS) method is used.
  A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009).

- **PBE-TS** used for *ab initio* MD and electronic-structure renormalization

- **Strong** *lattice expansion*: Non-perturbative *Ab initio MD* calculations



T < 105 K | T > 105 K | T < 105 K

Overcoming the Perturbational Limit

In our approach, we can systematically lift these approximations

(a) **Perturbative** description of **electronic structure**

(b) **Perturbative** description of **vibrational motion**

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$$\langle \varepsilon_l^{\mathrm{pt}}(\mathbf{k},t)\rangle_T^{\mathrm{ha}}$$

- **Perturbative** Electrons
- **Harmonic** Nuclei

Standard Perturbation Theory Approach from Literature

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

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⇩

Comparison of Quantum vs. Classical Nuclei in an analytic fashion

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⇩

Comparison of Quantum vs. Classical Nuclei in an analytic fashion

$$\langle \varepsilon_l(\mathbf{k},t)\rangle_T^{\mathrm{MD}}$$

- **Full** Electronic Structure
- **Anharmonic** Nuclei

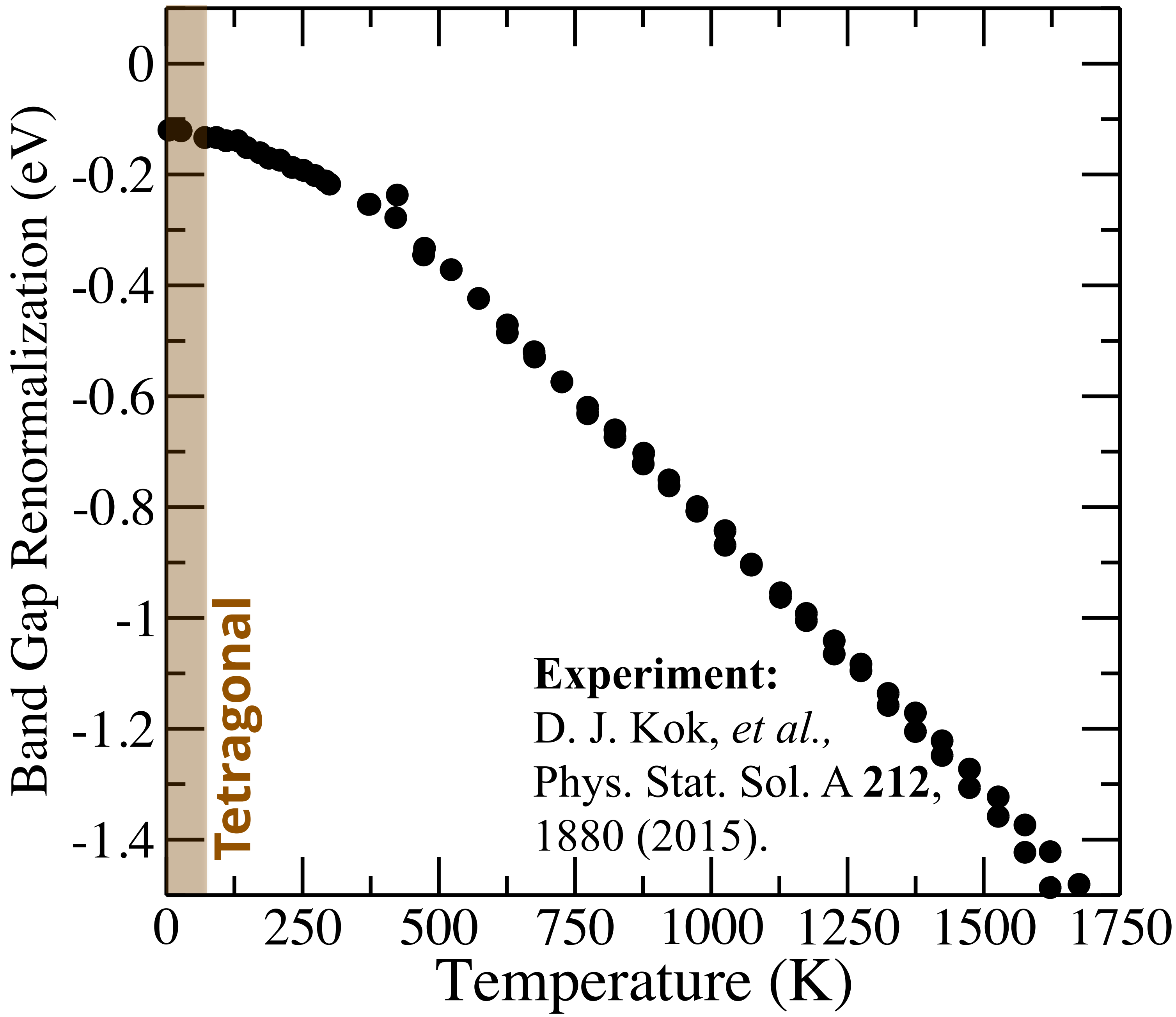
⇩

Classical Nuclei

⇩

***Exact** solution at **elevated** temperatures*

Cubic $SrTiO_3$ – A Real Challenge



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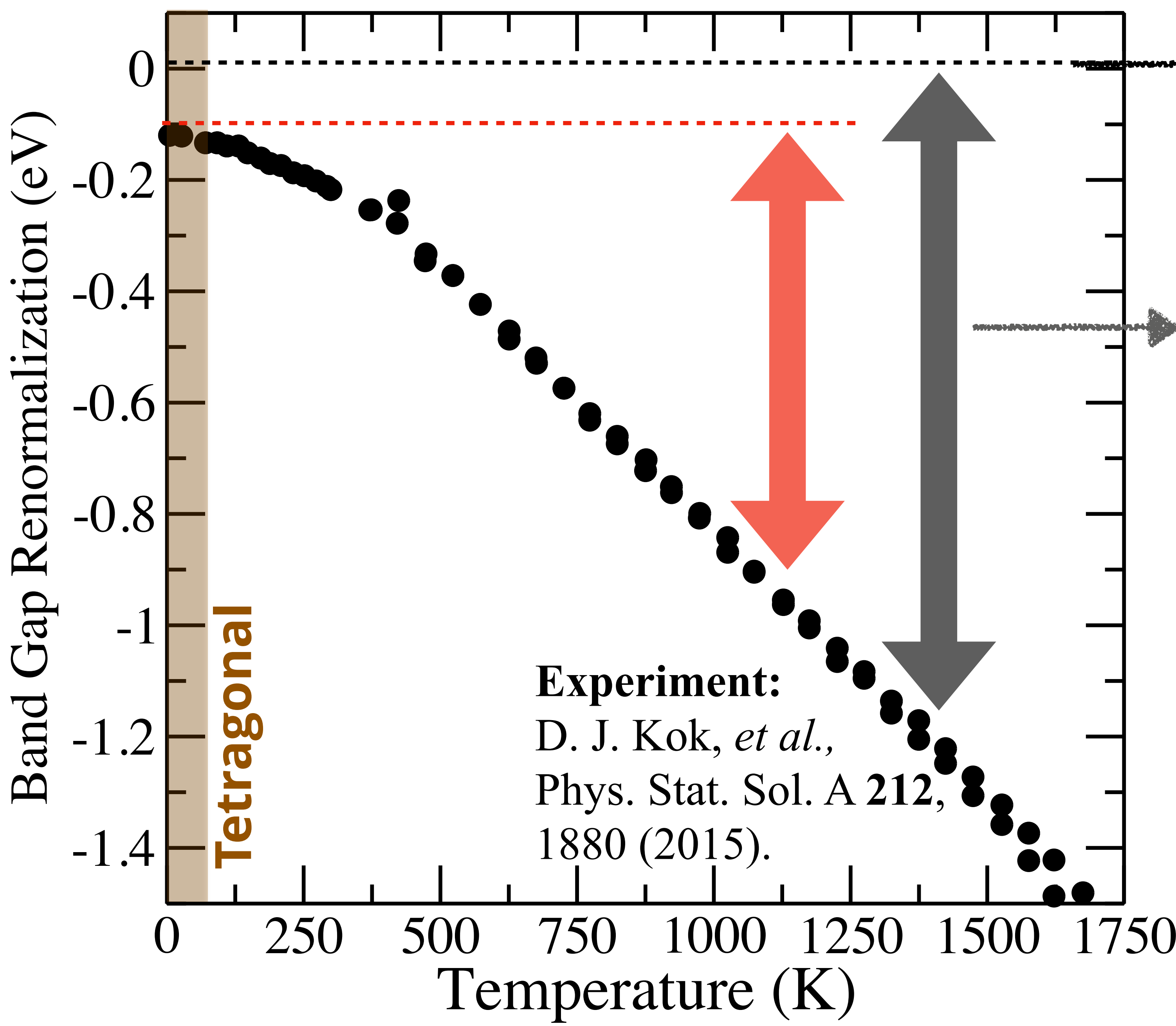
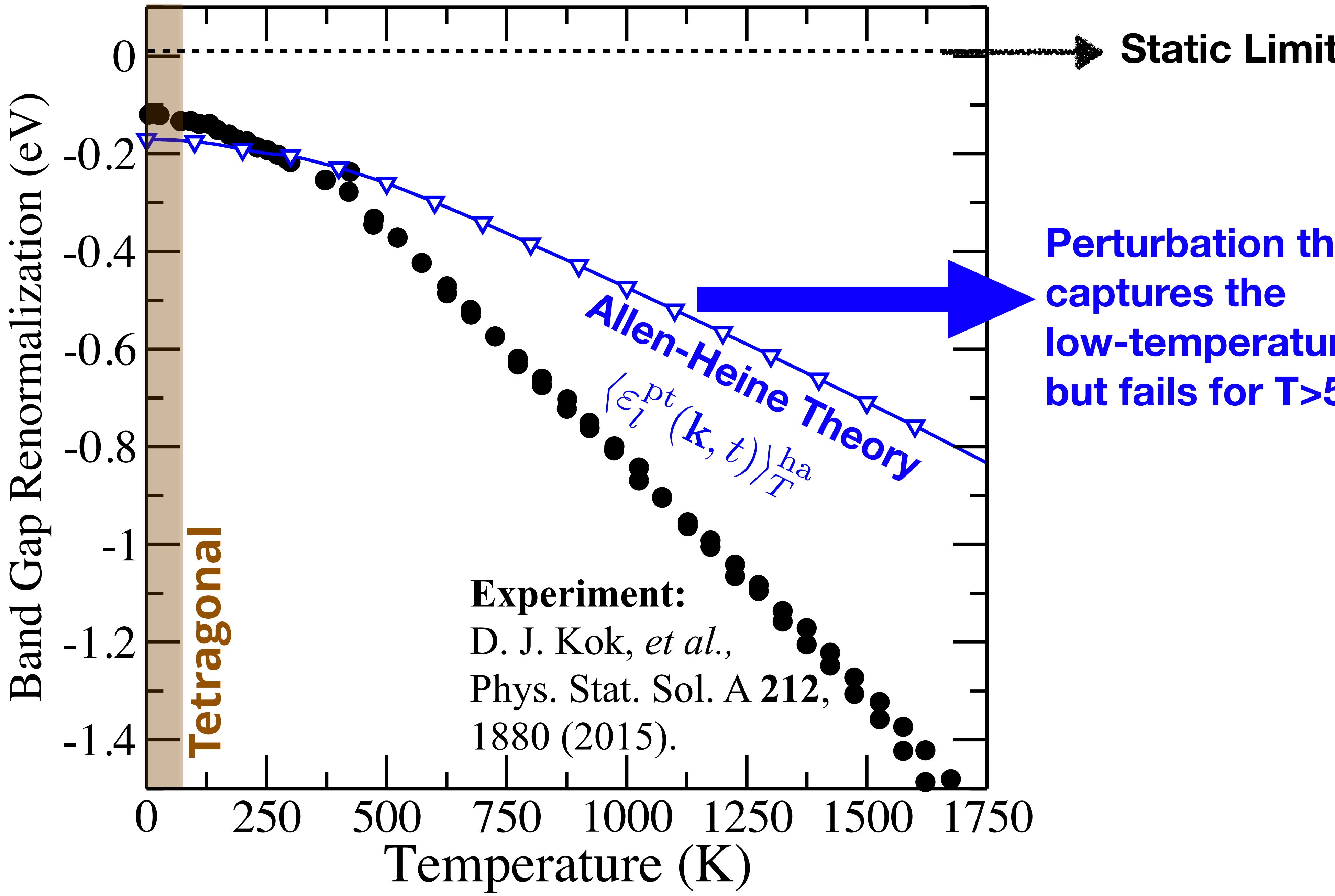


Static Limit
HSE06: 3.45 eV
PBE: 2.30 eV

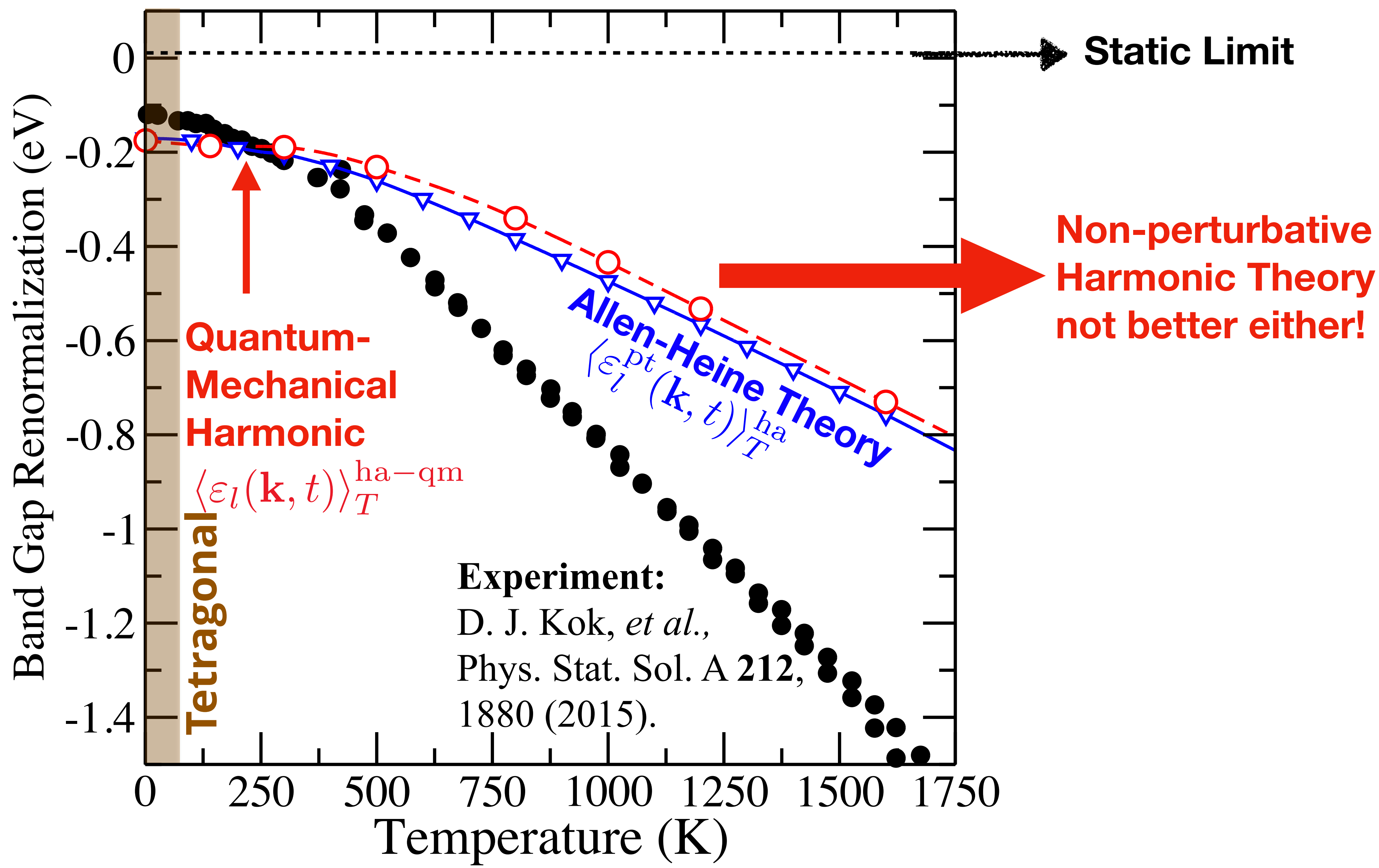
Massive Band-Gap Renormalization with Temperature!

Cubic $SrTiO_3$ – A Real Challenge



Perturbation theory captures the low-temperature limit, but fails for T>500K.

Cubic $SrTiO_3$ – A Real Challenge



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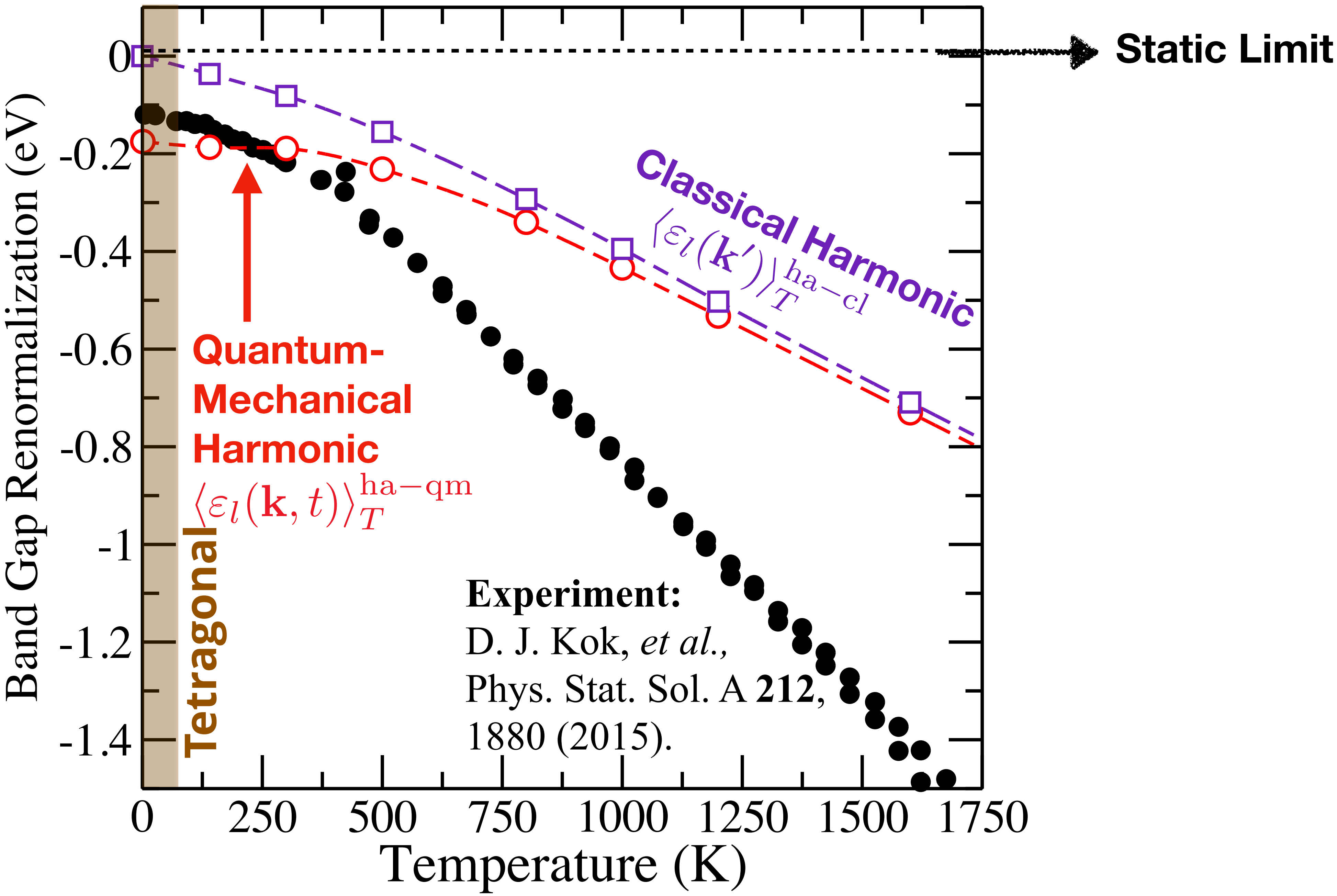

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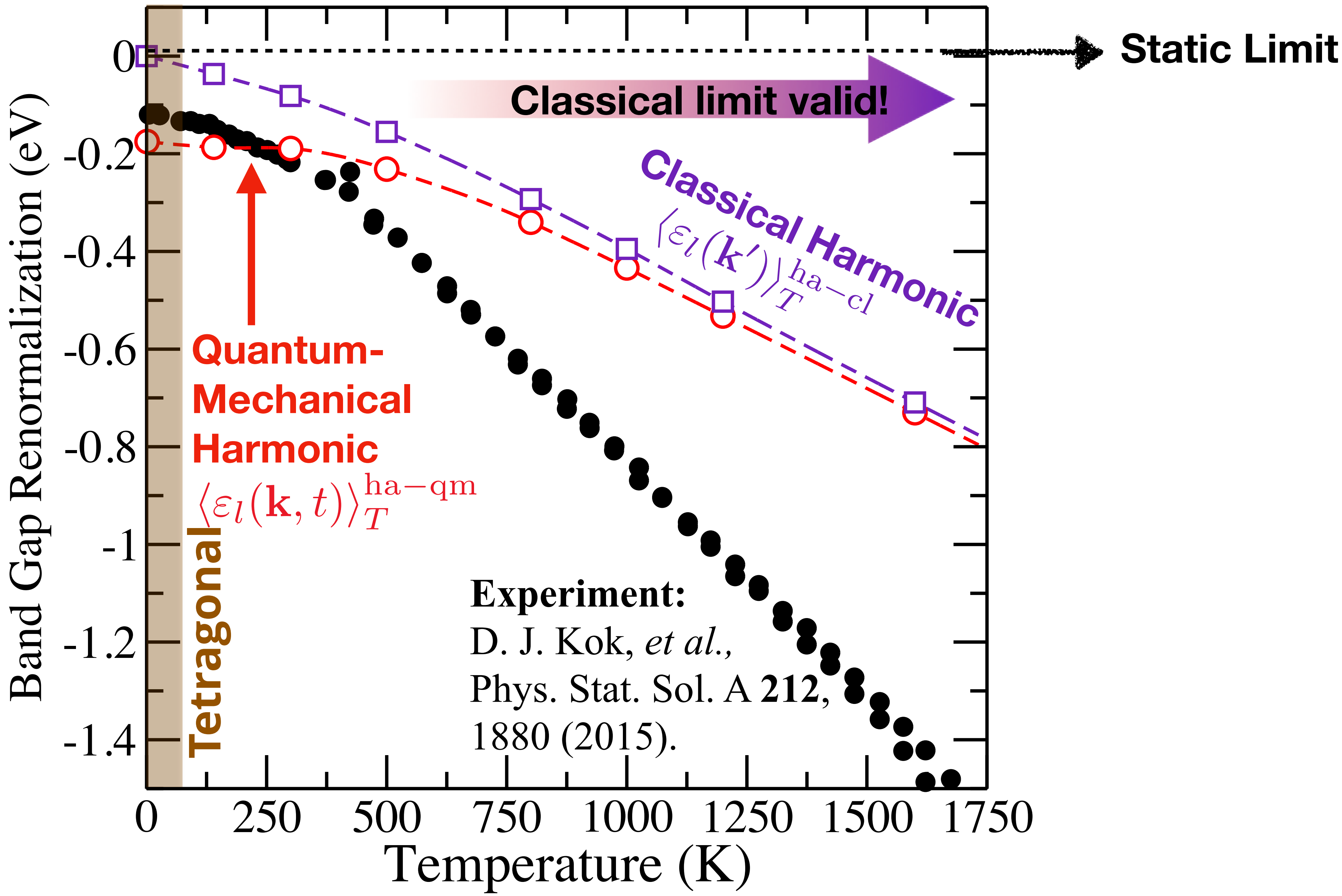

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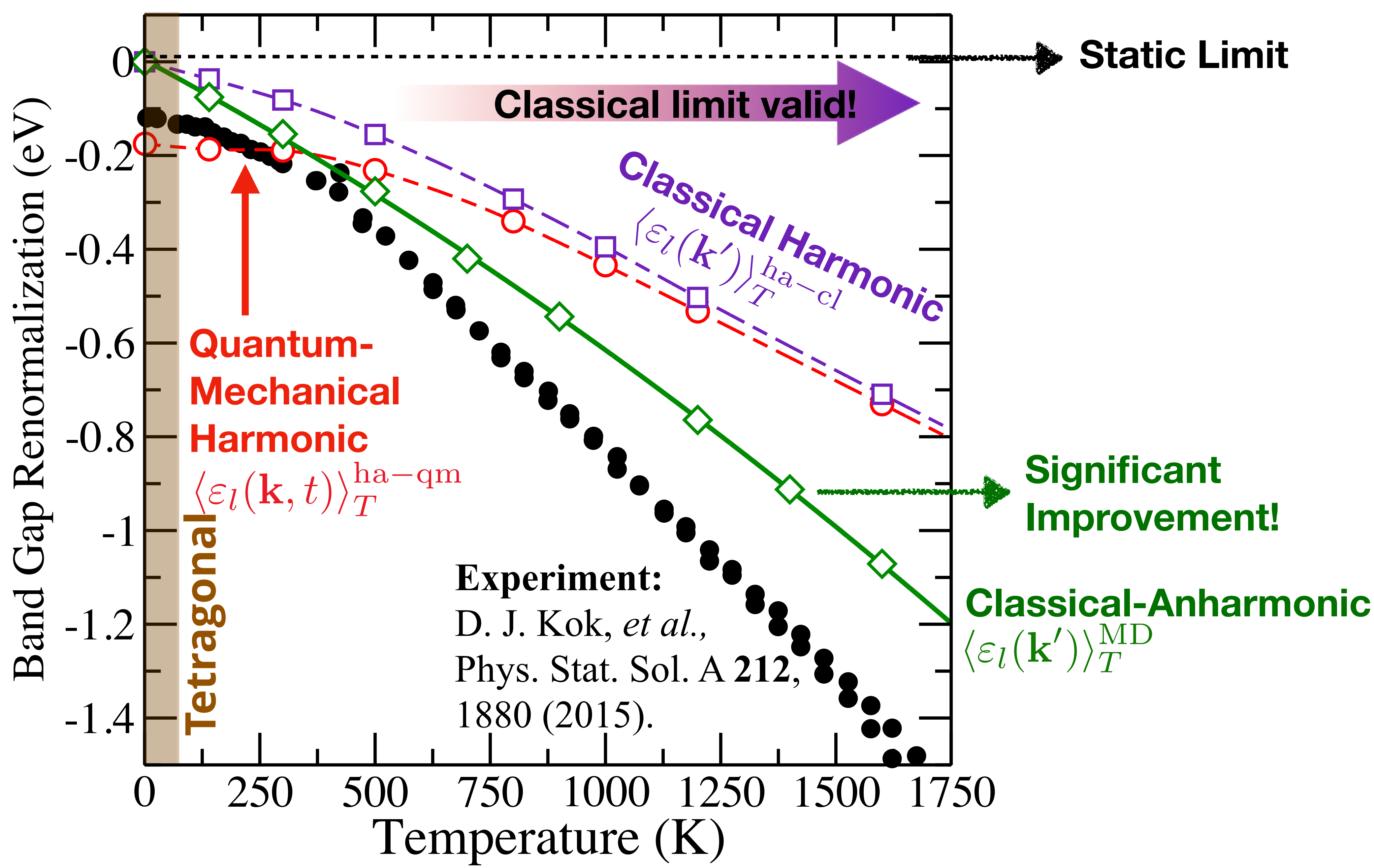
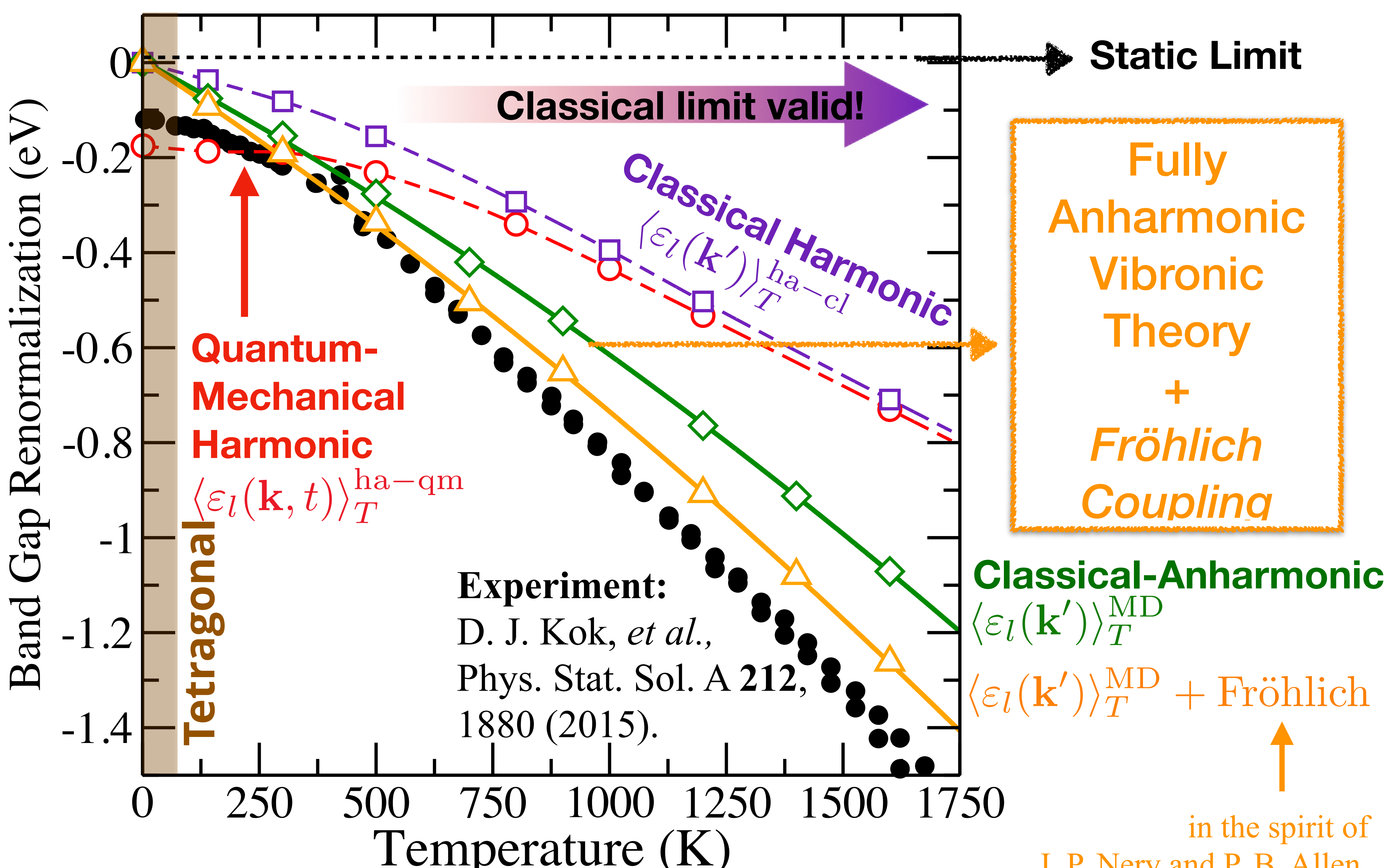
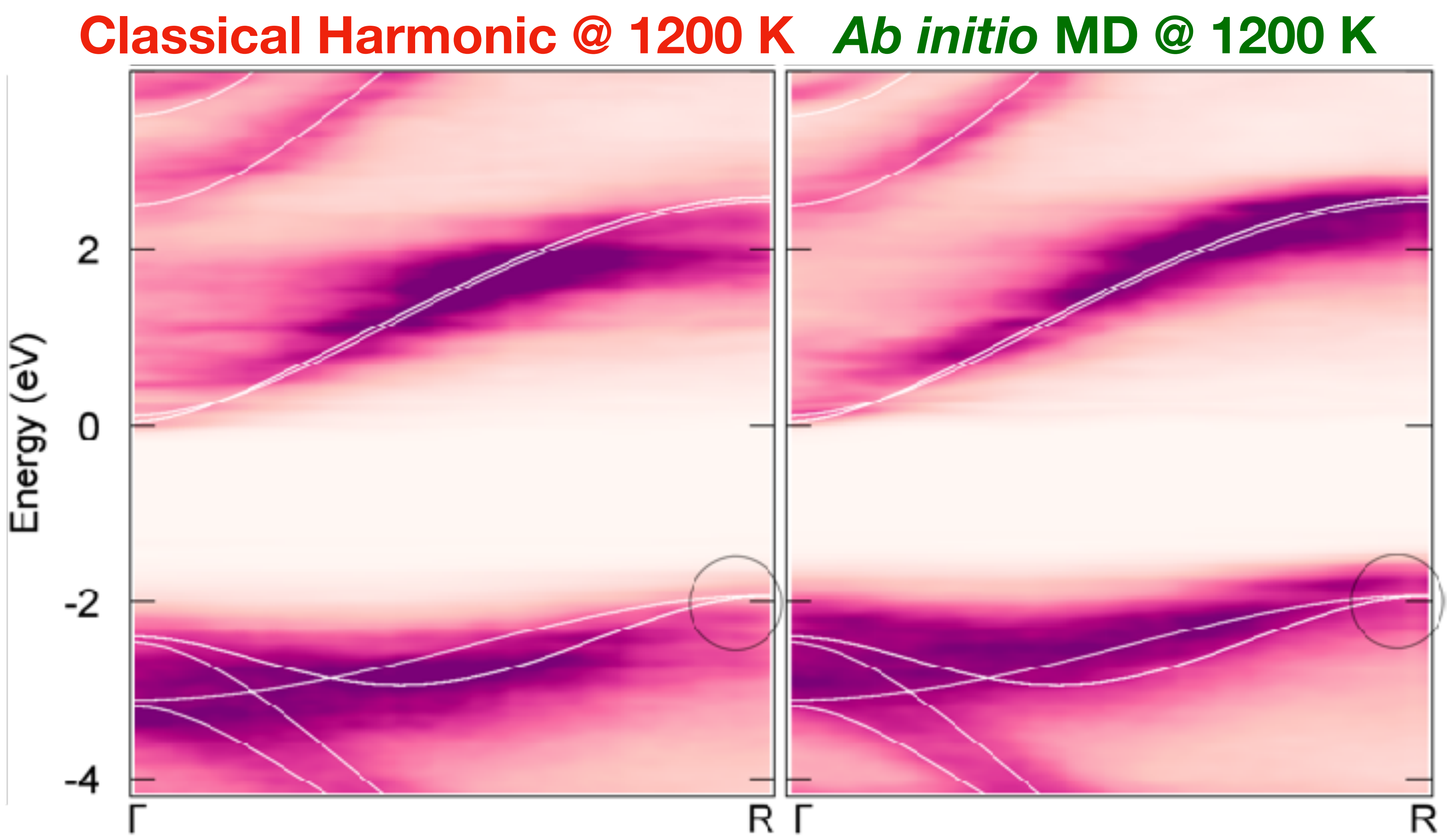


Cubic $SrTiO_3$ – A Real Challenge



in the spirit of
J. P. Nery and P. B. Allen,
Phys. Rev. B **94**, 115135 (2016).

Spectral Functions



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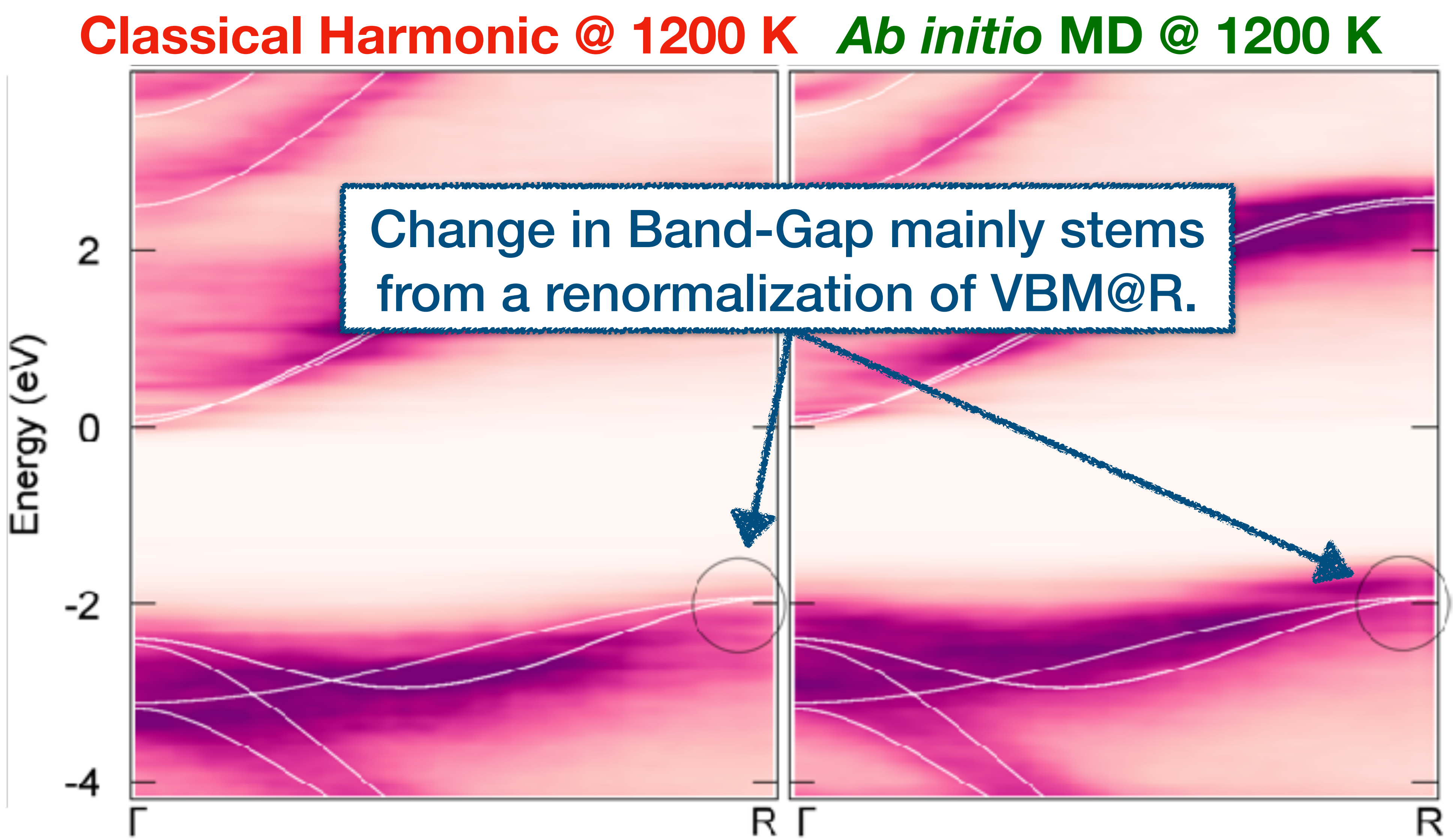

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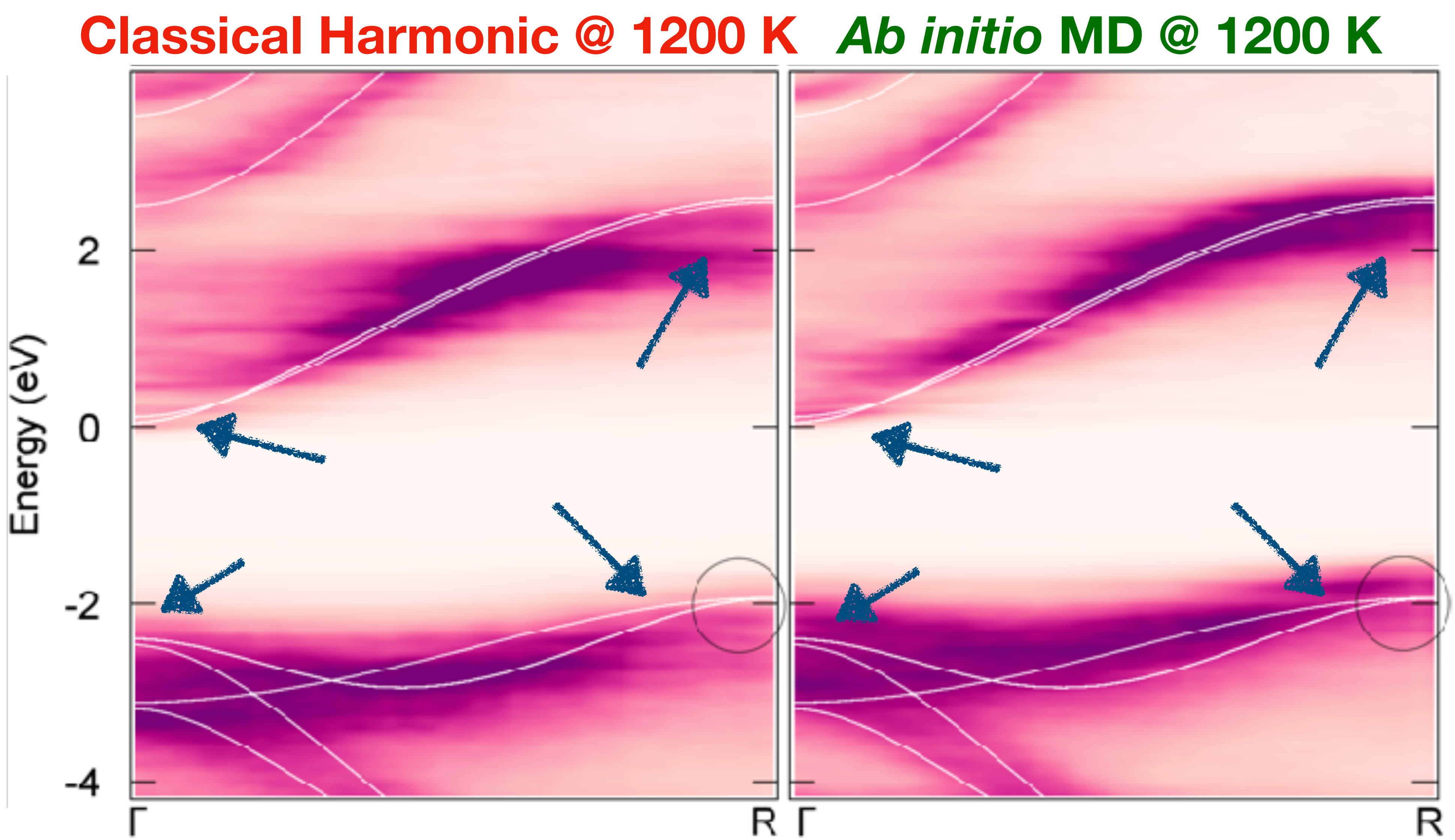
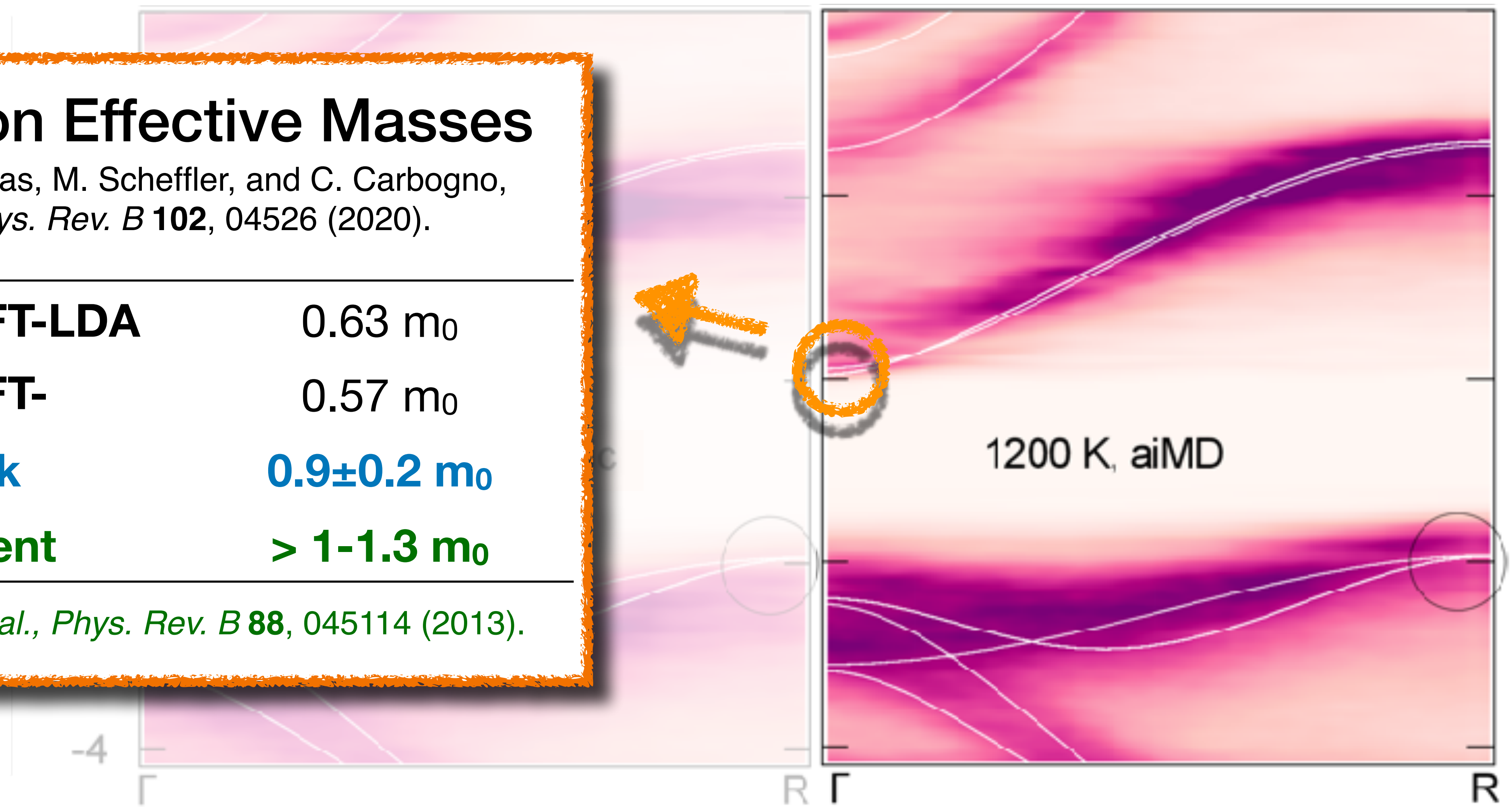


Much more properties and physics affected by vibronic/anharmonic couplings: absorption spectra, effective masses, line widths viz. lifetimes,…

Spectral Functions

Classical Harmonic @ 1200 K   *Ab initio* MD @ 1200 K



Electron Effective Masses

M. Zacharias, M. Scheffler, and C. Carbogno,
Phys. Rev. B **102**, 04526 (2020).

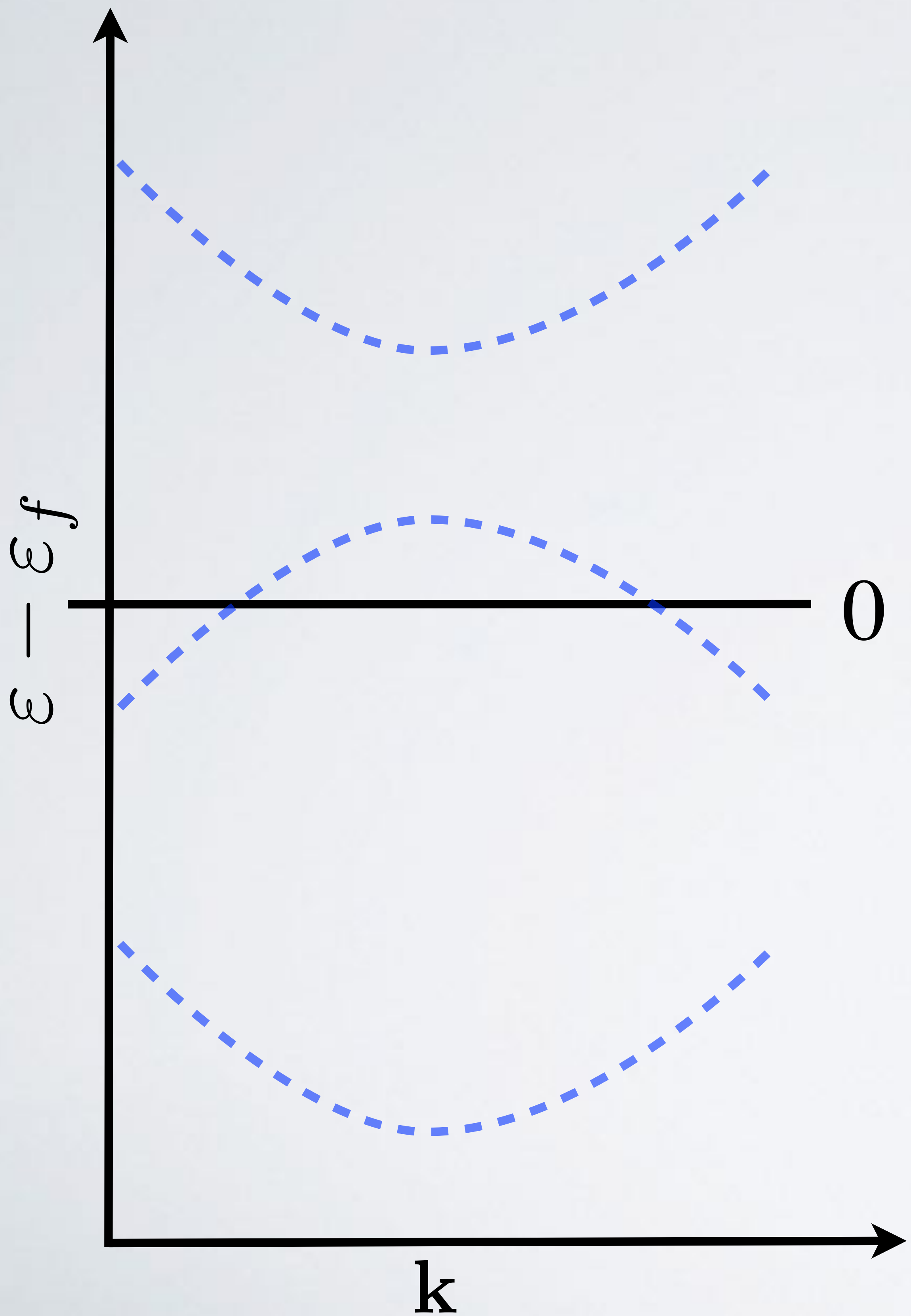
Static DFT-LDA	0.63 m_0
Static DFT-	0.57 m_0
This work	**0.9±0.2 m_0**
Experiment	**> 1-1.3 m_0**

S. J. Allen *et al., Phys. Rev. B* **88**, 045114 (2013).

Much more properties and physics affected by vibronic/anharmonic couplings: absorption spectra, effective masses, line widths viz. lifetimes,…

III. CHARGE TRANSPORT

ELECTRONS IN A PERIODIC POTENTIAL

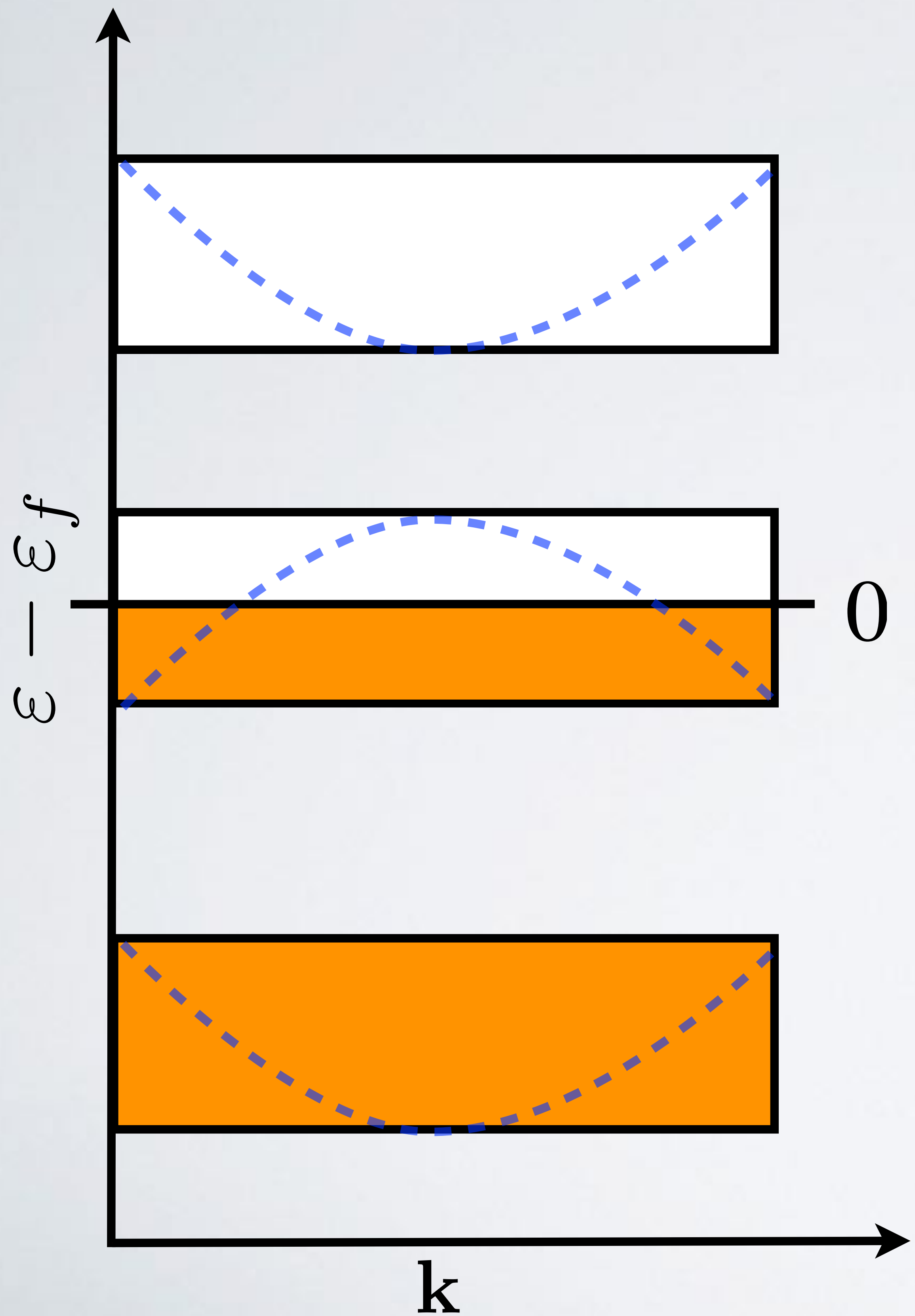


The Bloch Theorem:

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

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

ELECTRONS IN A PERIODIC POTENTIAL



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Fermi-Dirac Statistics:

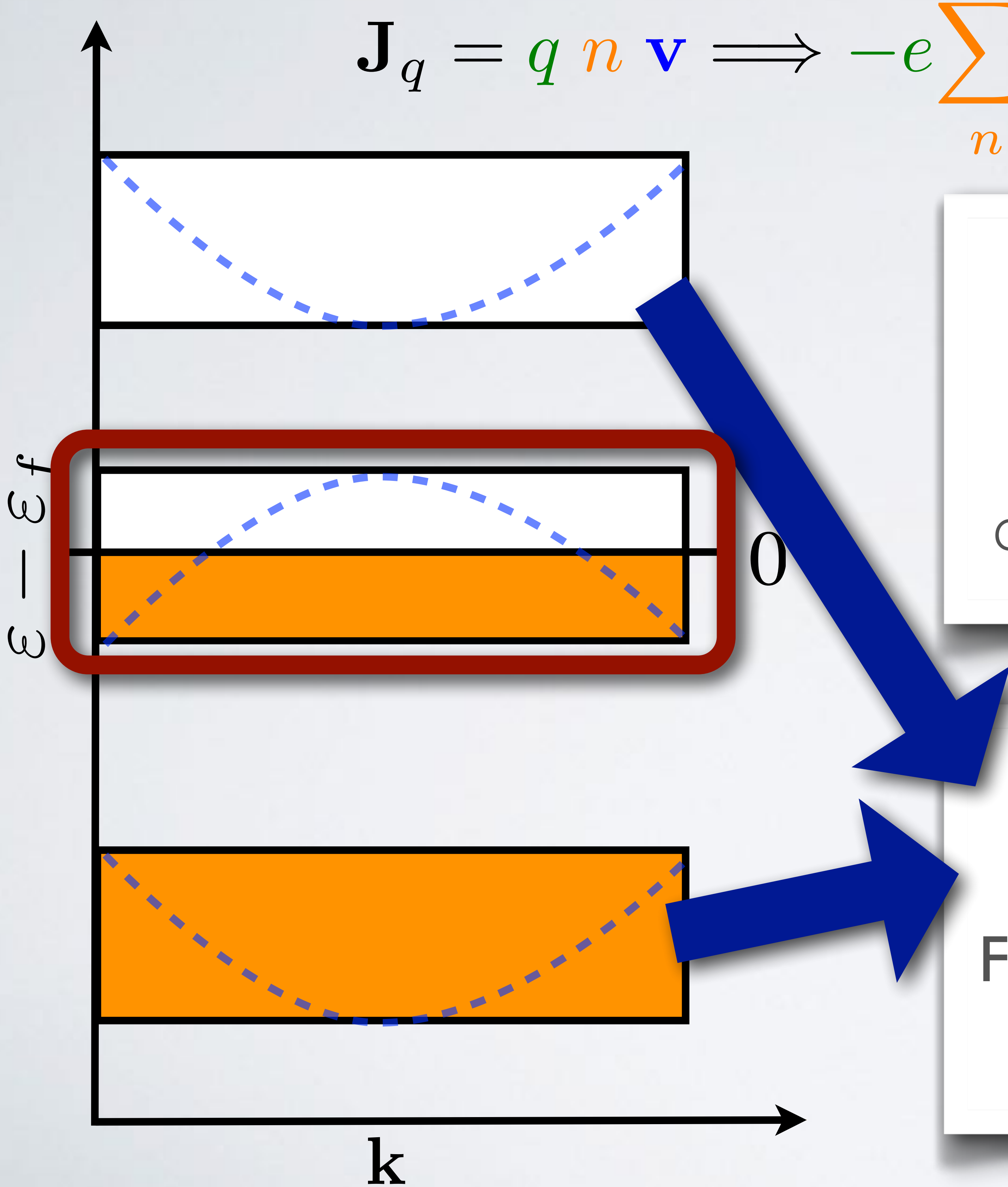
E. Fermi, *Z. Physik* **36**, 902 (1926).

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

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



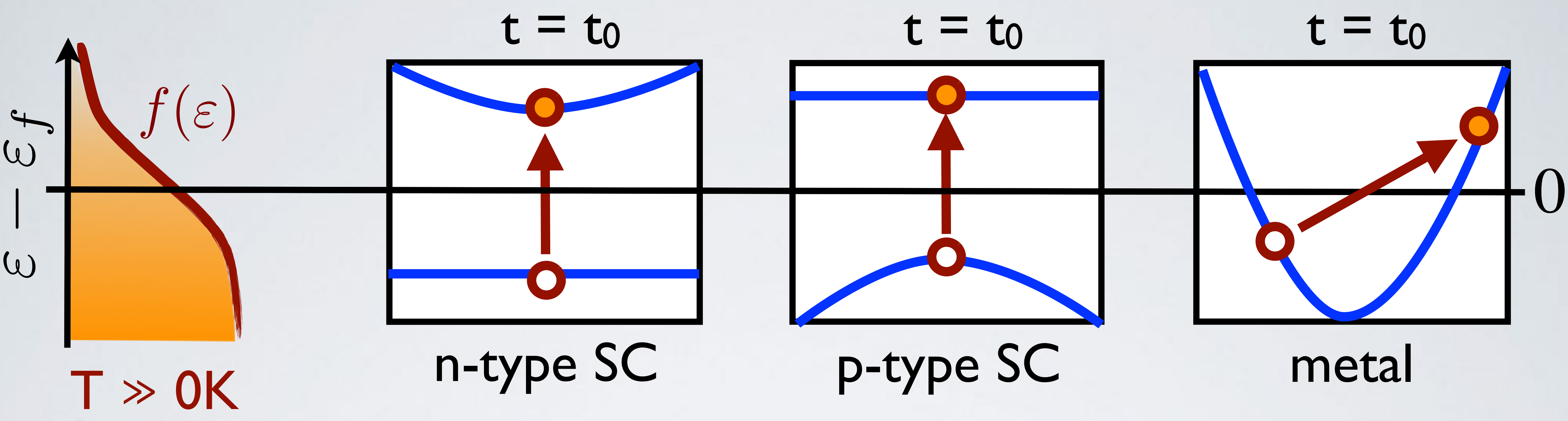
$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$$

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

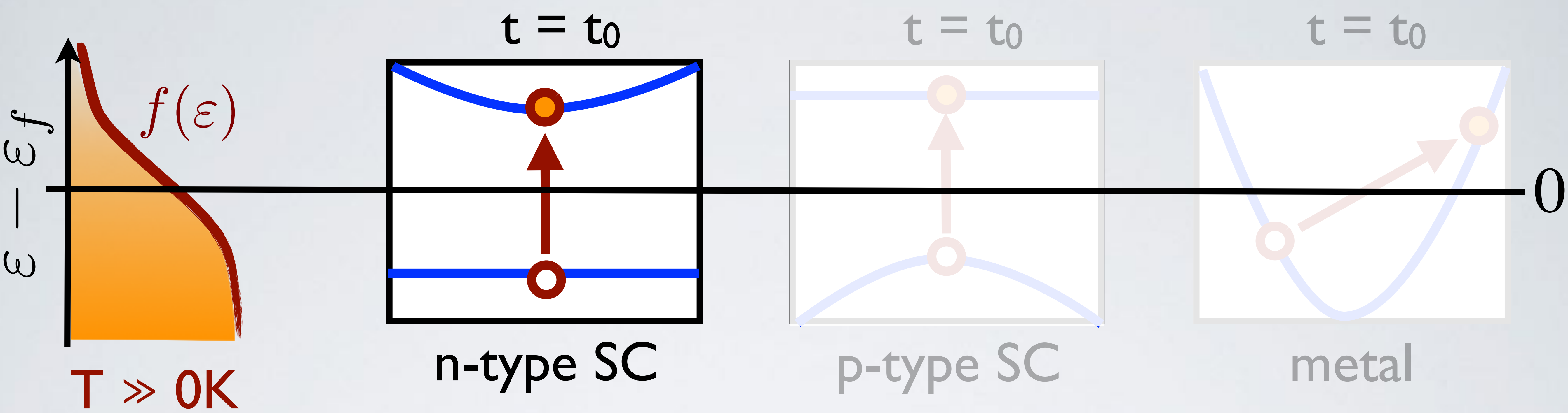
$$\int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k}) = 0$$

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

INSTANTANEOUS NON-EQUILIBRIUM



INSTANTANEOUS NON-EQUILIBRIUM

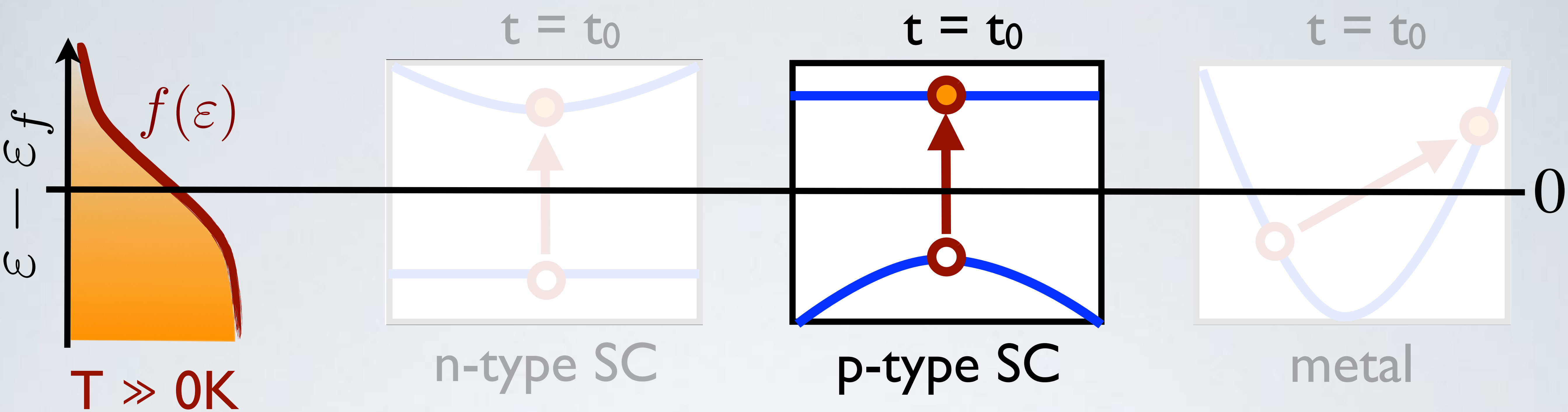


$$\mathbf{J}_q^{nk} = -e\,\mathbf{v}_n(\mathbf{k})$$

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

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

INSTANTANEOUS NON-EQUILIBRIUM

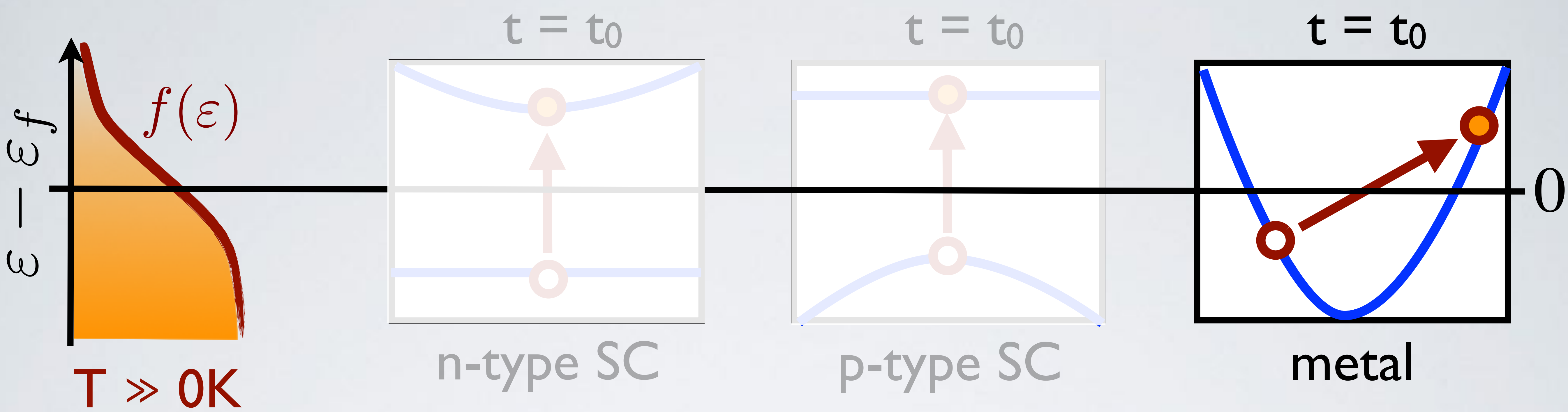


$$\mathbf{J}_q^{nk} = -e\,\mathbf{v}_n(\mathbf{k})$$

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

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

INSTANTANEOUS NON-EQUILIBRIUM



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

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).

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

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

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

~~Electron-electron scattering~~

Electron-nuclei scattering

defects

phonons

SINGLE RELAXATION TIME APPROXIMATION

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

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

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

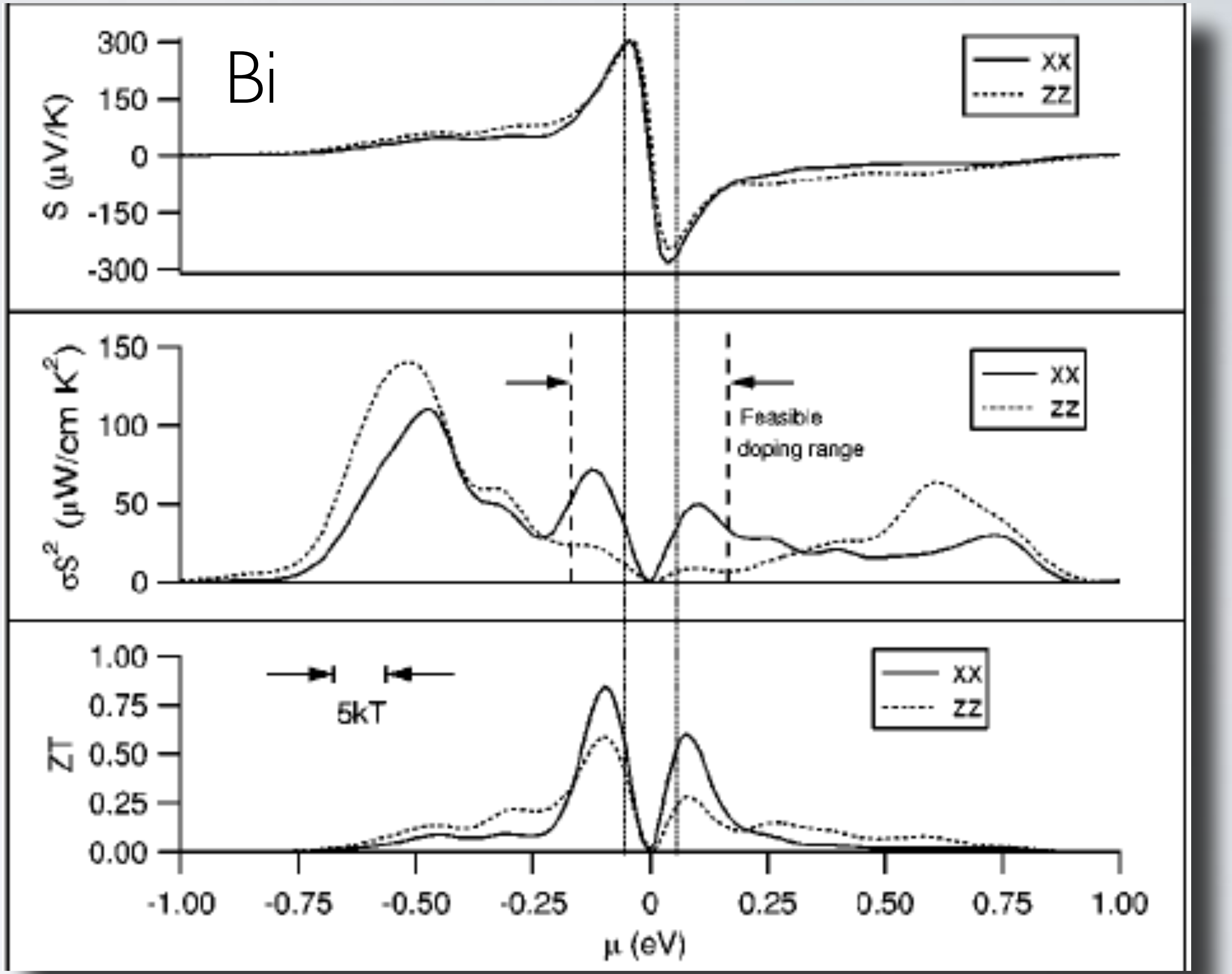
$$\kappa_{el} = -k_B^2\,\tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3}\, \mathbf{v}_n(\mathbf{k})\, \mathbf{v}_n(\mathbf{k}) \left(\frac{\partial f(\varepsilon_n)}{\partial \varepsilon_n} \right) \left(\frac{\varepsilon_n - \varepsilon_F}{k_B T} \right)^2$$

Energy and Crystal Momentum
independent scattering time:
SRTA

SINGLE RELAXATION TIME APPROXIMATION

- Accurate **band structure**
- *"Reasonable" relaxation time*

Electronic Transport Coefficients



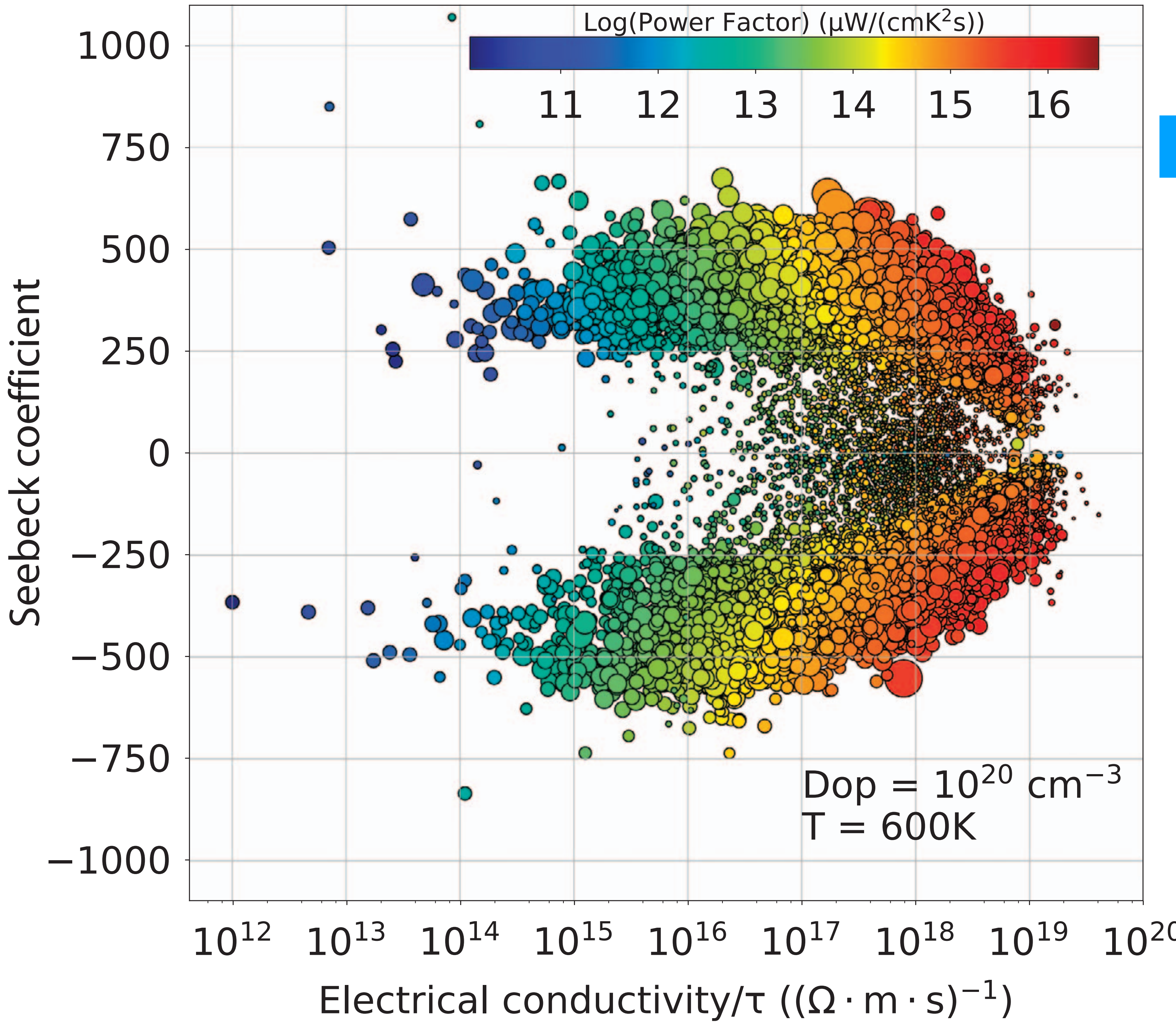
T. Thonhauser, T. J. Scheidemantel, and J. O. Sofo, *Appl. Phys. Lett.* **85**, 588 (2004).

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

Ab initio electronic transport database

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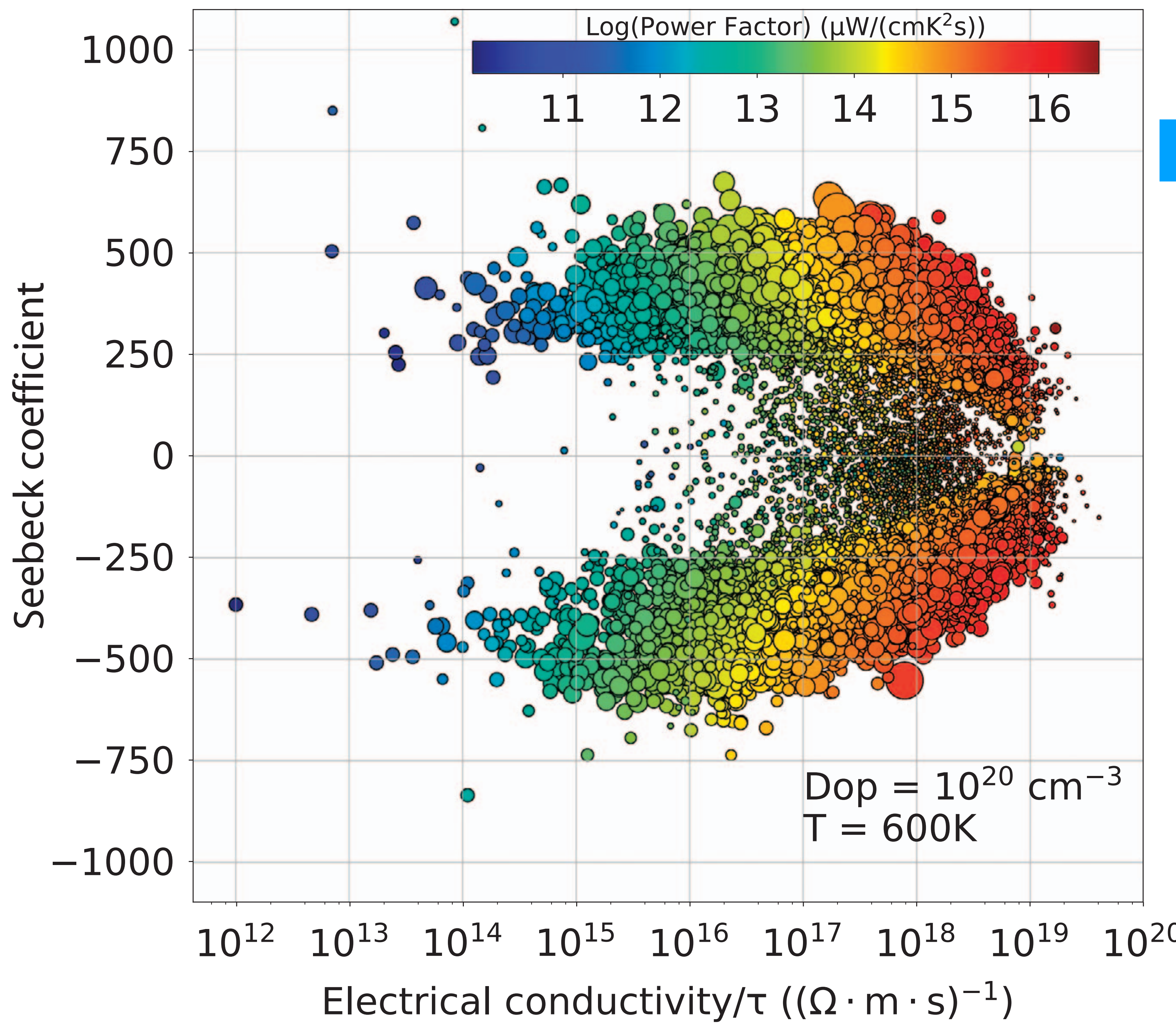
F. Ricci, *et al.*, *Scientific Data* 4,170085 (2017).



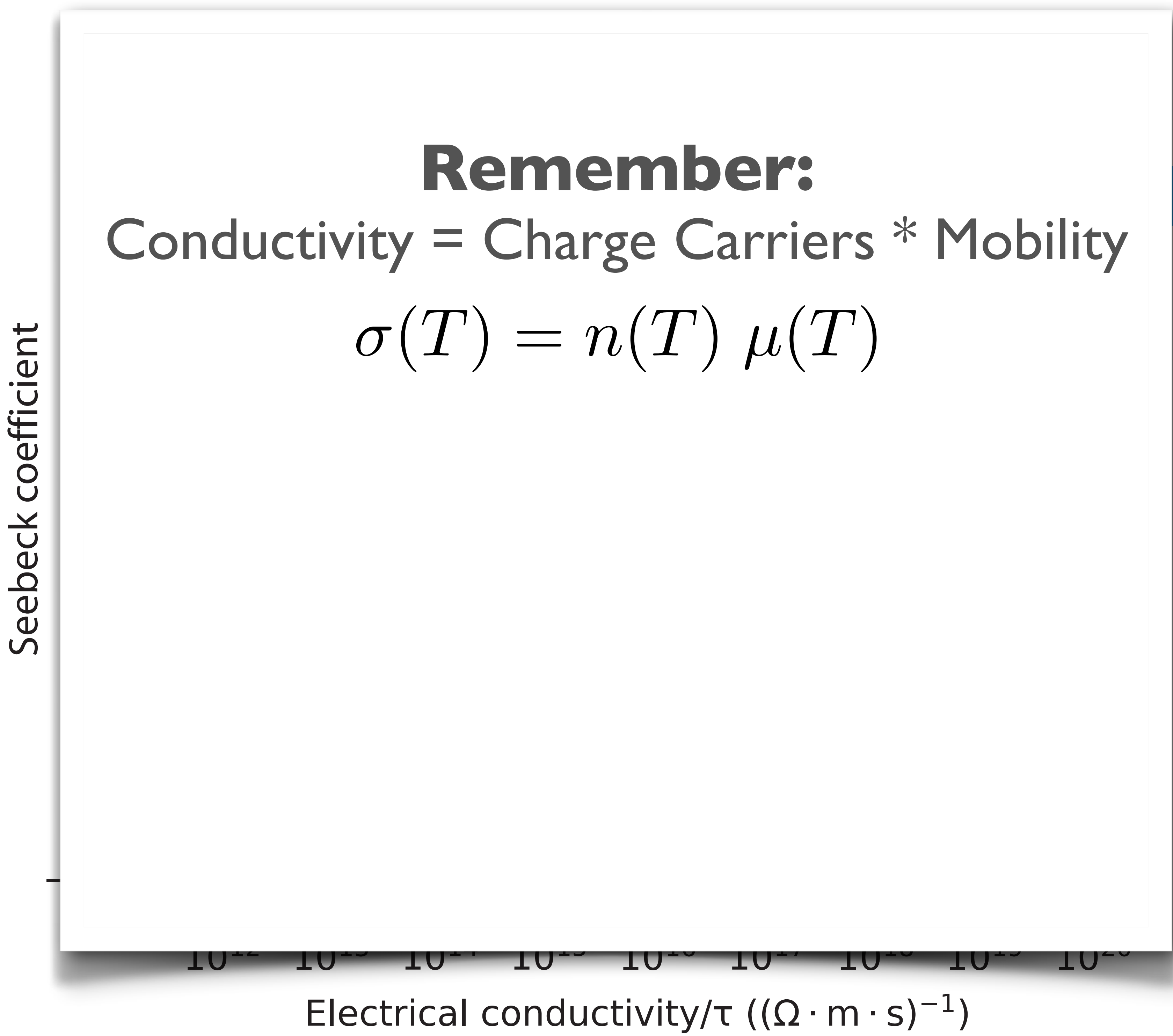
~48,000 materials

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).

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



Remember:

Conductivity = Charge Carriers * Mobility

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

~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).

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

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 ((Ω · m · s)$^{-1}$)

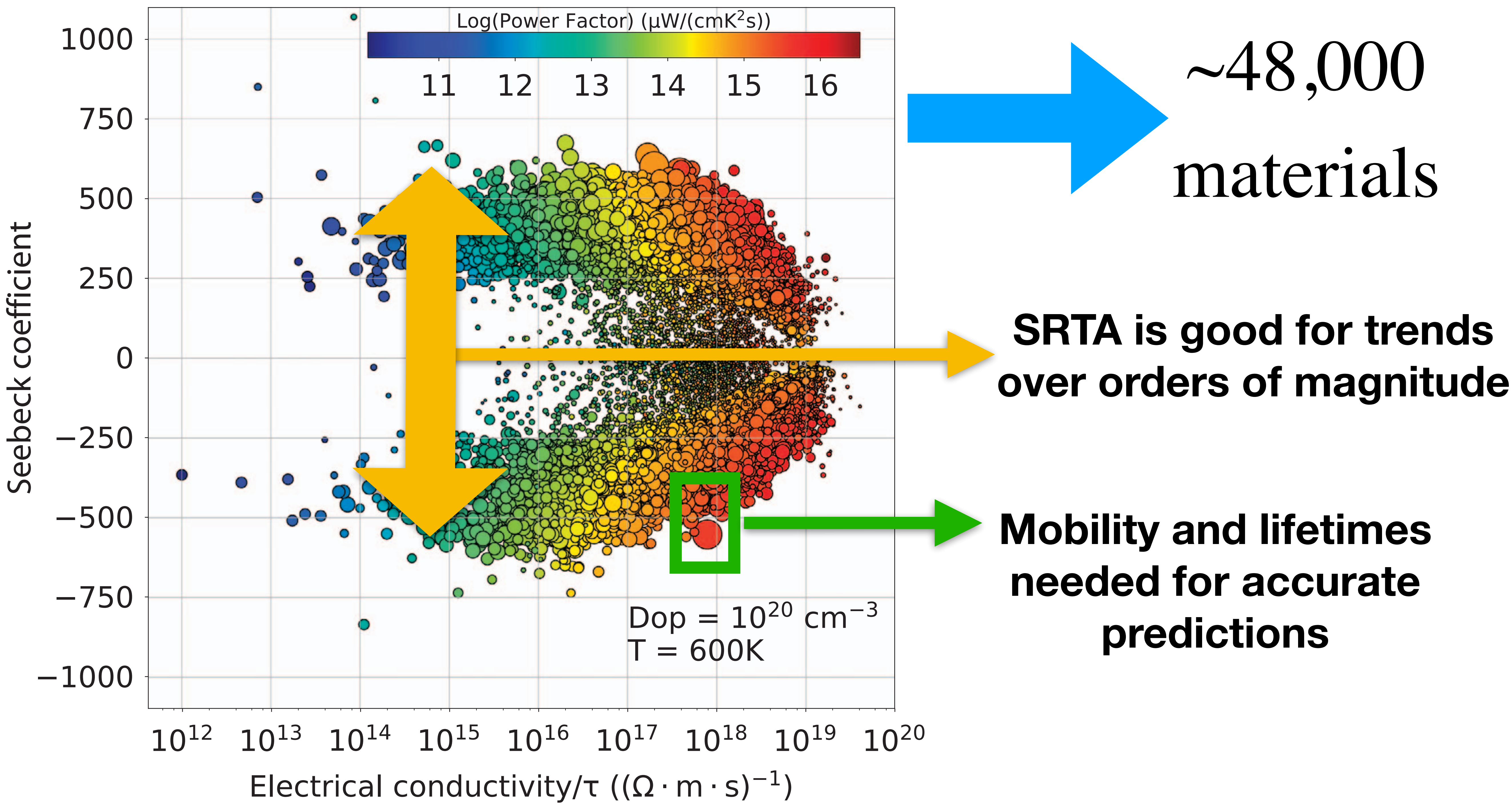
~48,000 materials

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).

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



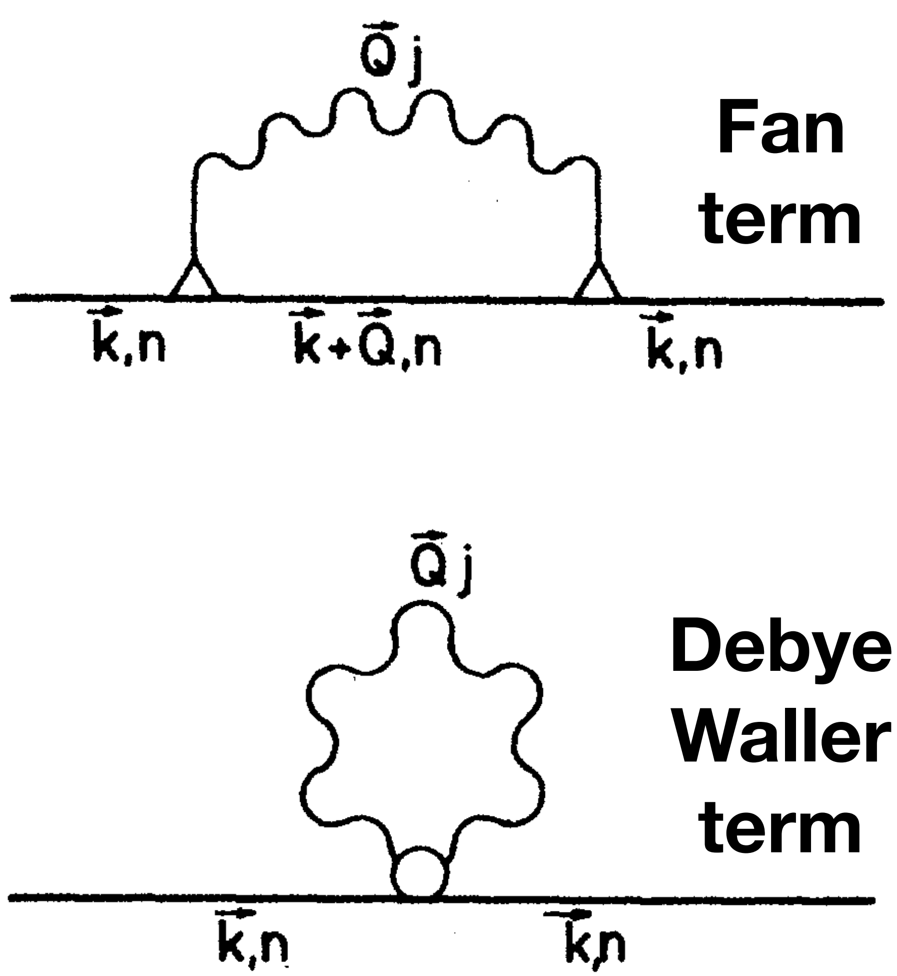
Heine-Allen-Cardona Theory

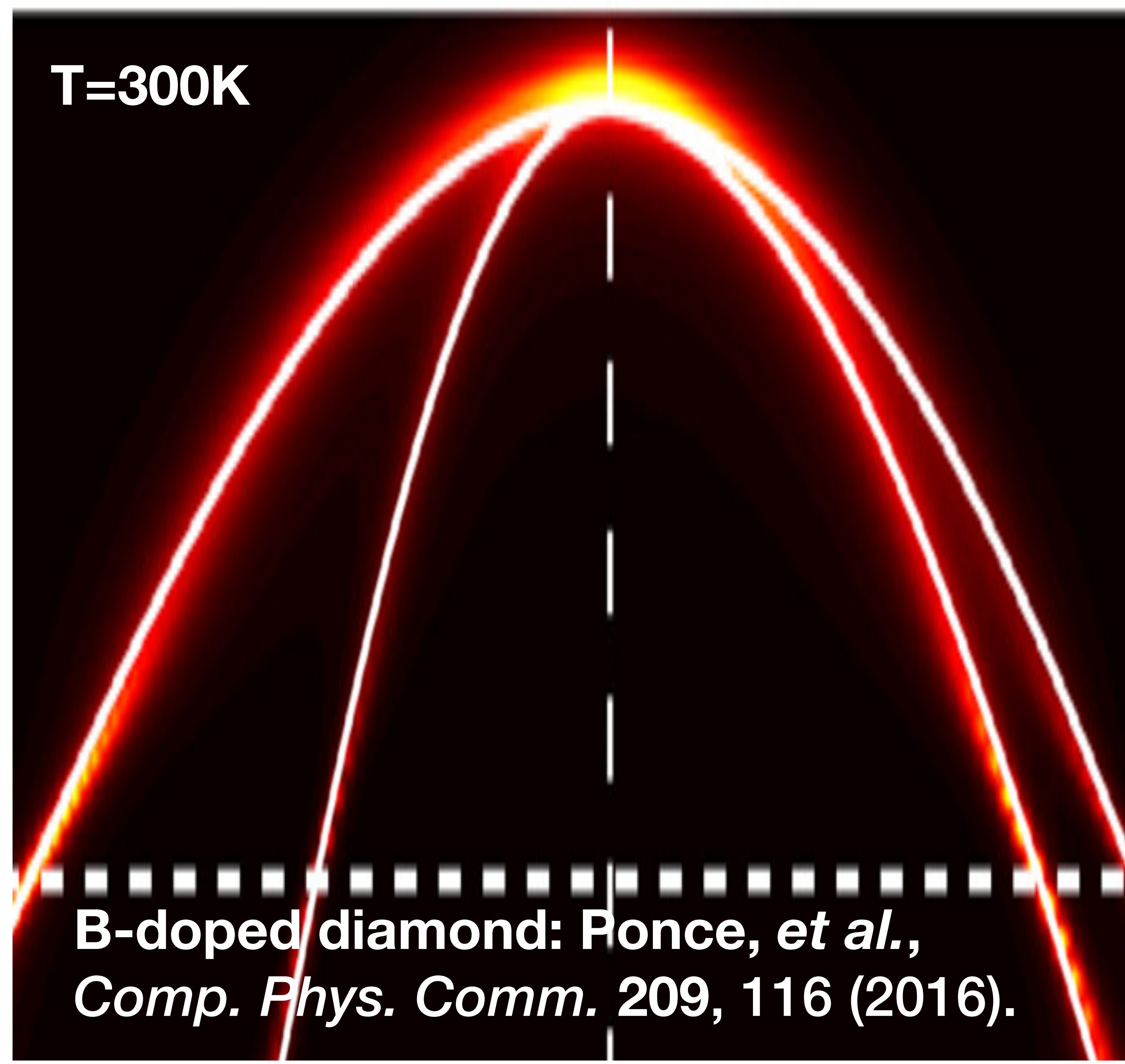
P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).

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

Imaginary Electronic Self-energies

Many-Body Perturbation Theory

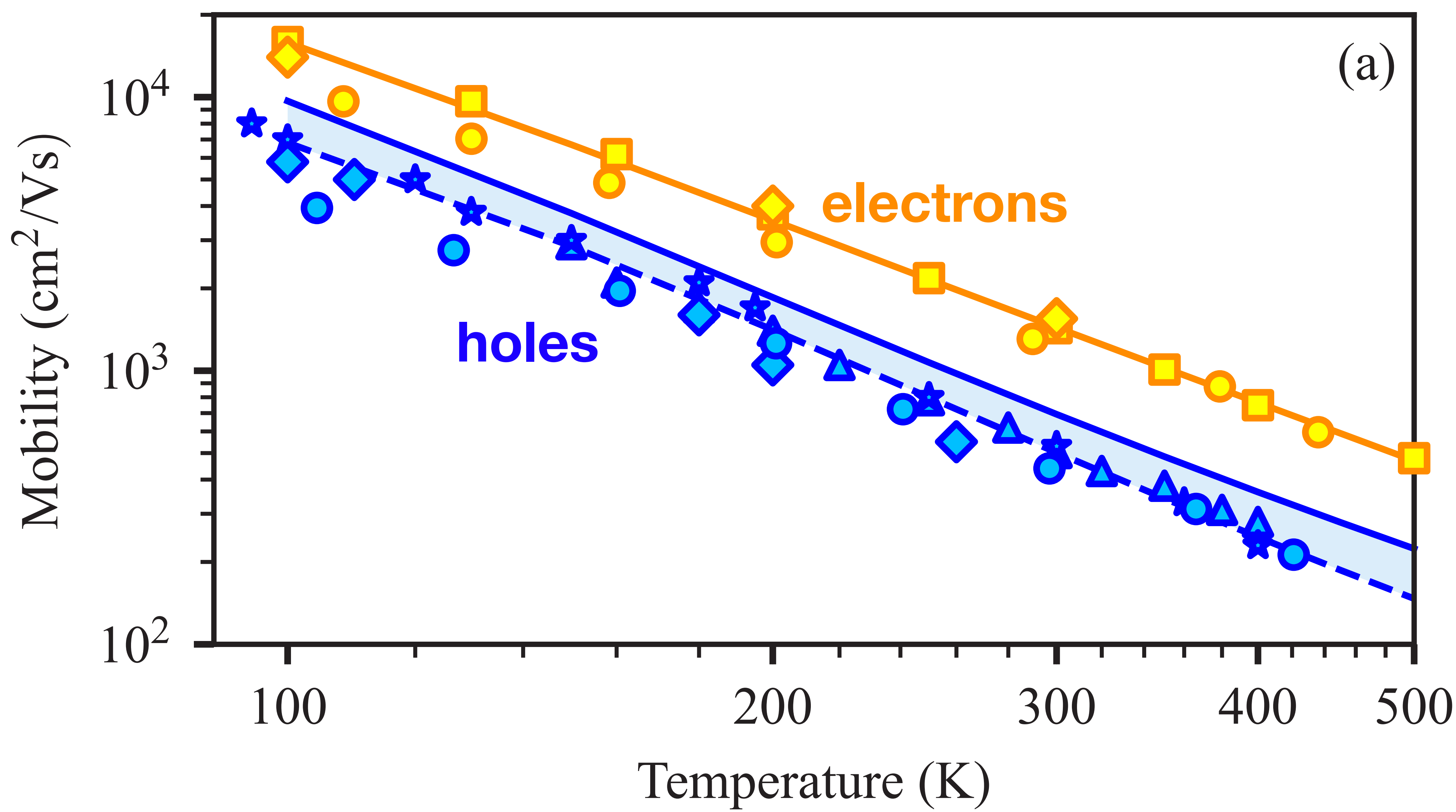




B-doped diamond: Ponce, *et al.*, *Comp. Phys. Comm.* 209, 116 (2016).

Heine-Allen-Cardona Theory

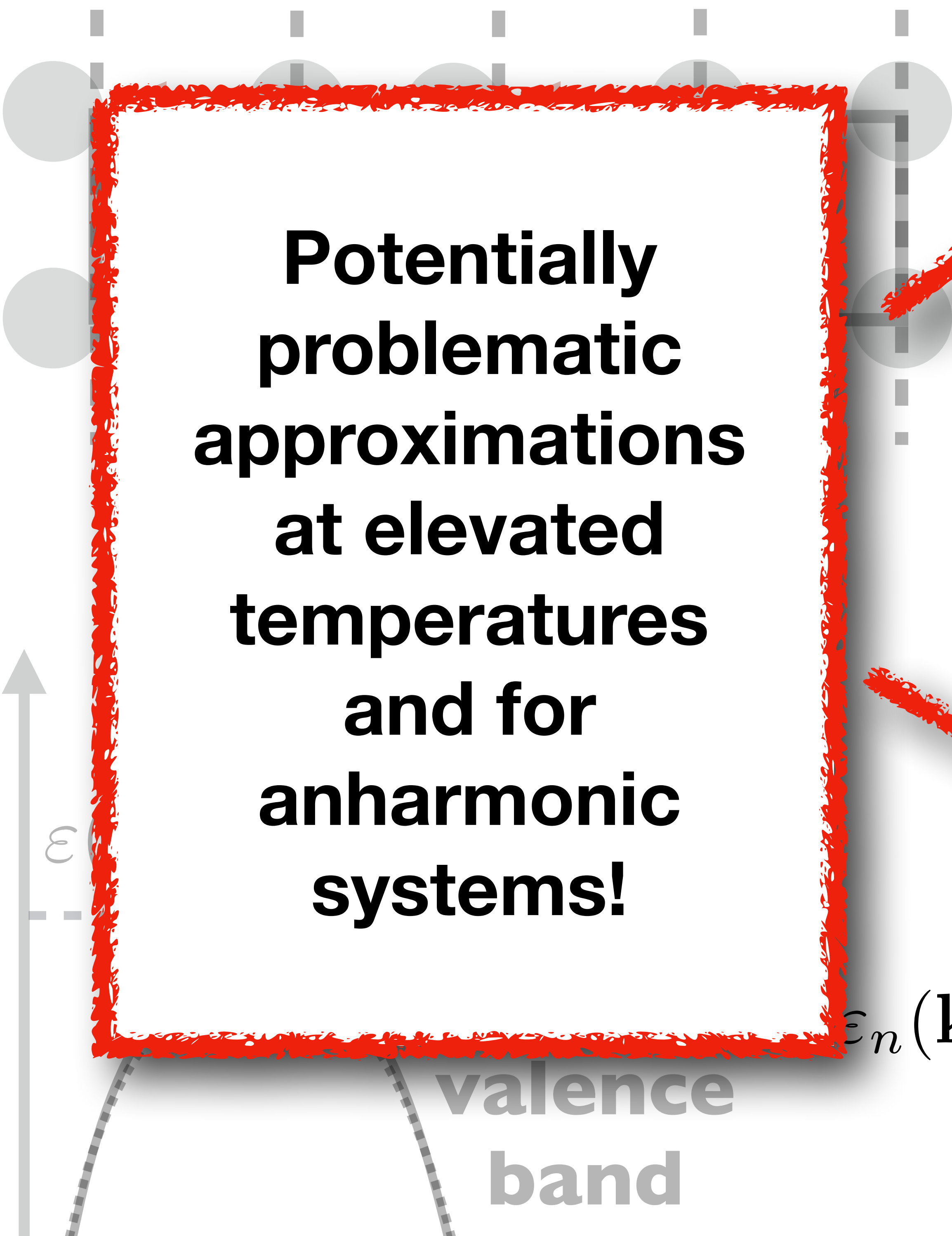
P. B. Allen and M. Cardona, *Phys. Rev. B* **23**, 1495 (1981).



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 ωτ ≫ 1

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

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

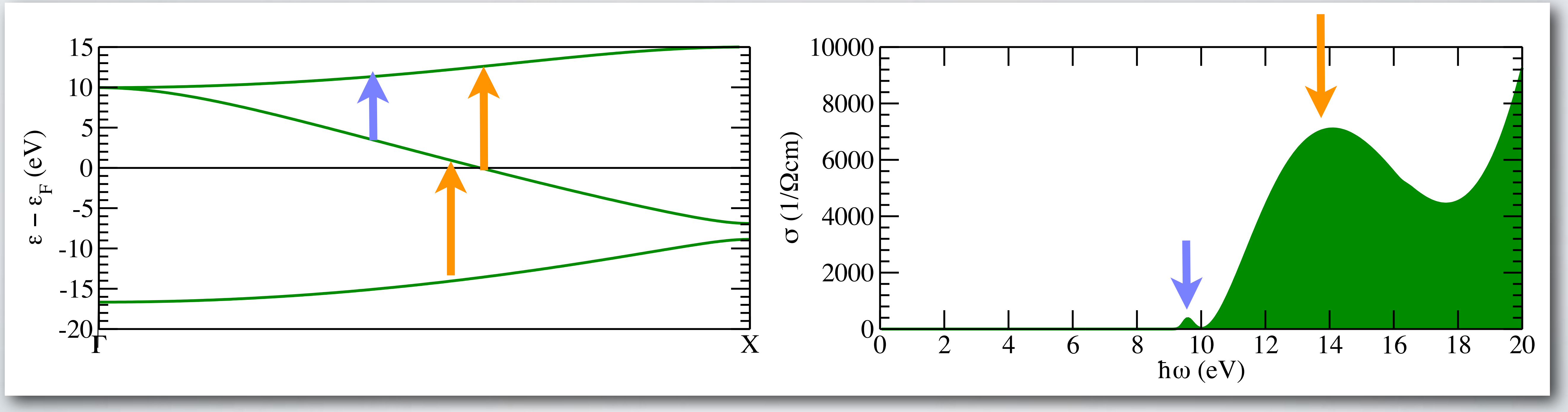
OPTICAL CONDUCTIVITY

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:

$$\sigma(\omega) = \frac{1}{V} \left\langle \lim_{\varepsilon \to 0} \int_0^\infty dt\, e^{i(\omega + i\varepsilon)t} \int\limits_0^{(k_B T)^{-1}} d\tau\, \mathbf{Tr} \left[\hat{\rho}_0\, \mathbf{j}_c(t - i\hbar\tau) \cdot \mathbf{j}_c(t) \right] \right\rangle_T$$

Independent Particle Picture:

$$\mathbf{j}_c = -\frac{e}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$$

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

GREENWOOD-KUBO FORMALISM

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

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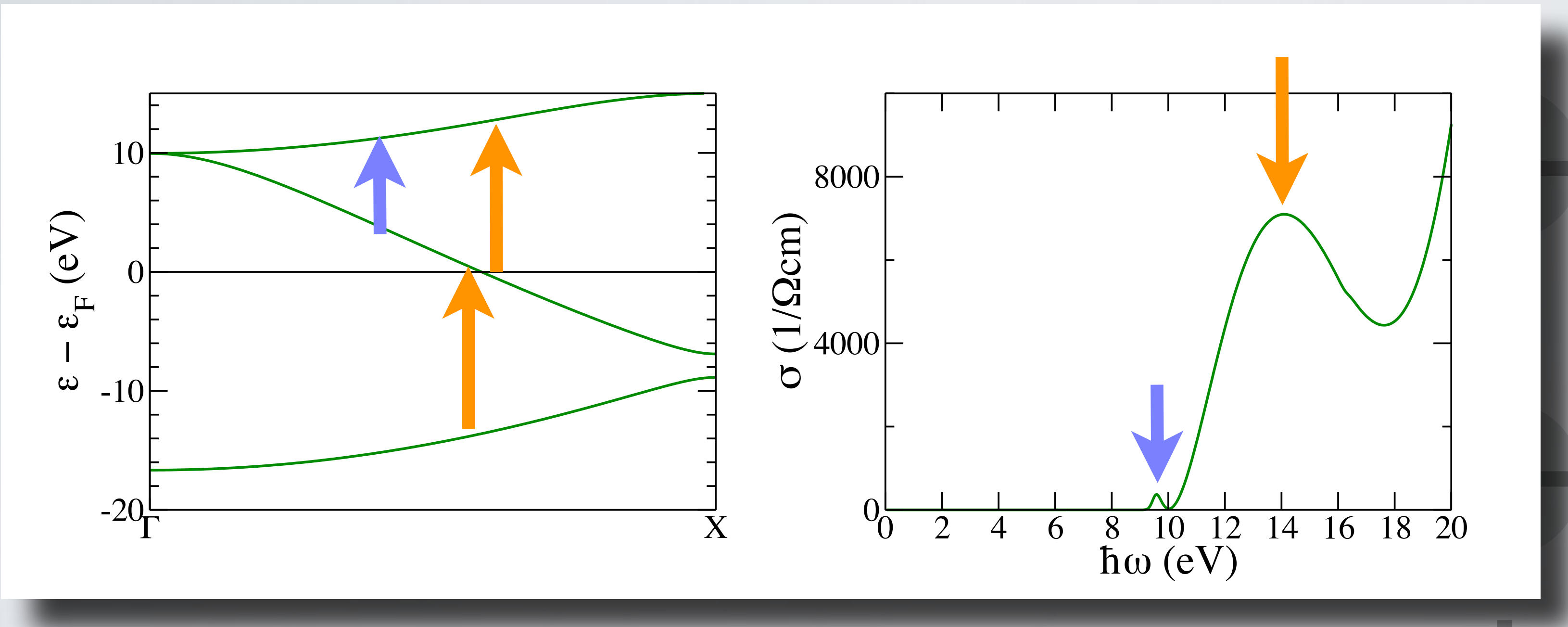
$$\sigma(\omega) = \frac{e^2\hbar^2}{m_e^2\omega}\frac{2\pi}{V}\left\langle \sum_{n,n\neq m}\sum_{\mathbf{k}} w_k \left[f(\varepsilon_n) - f(\varepsilon_m)\right] \left|\langle n\mathbf{k}|\nabla|m\mathbf{k}\rangle\right|^2 \delta\left(\varepsilon_n - \varepsilon_m - \hbar\omega\right)\right\rangle_T$$

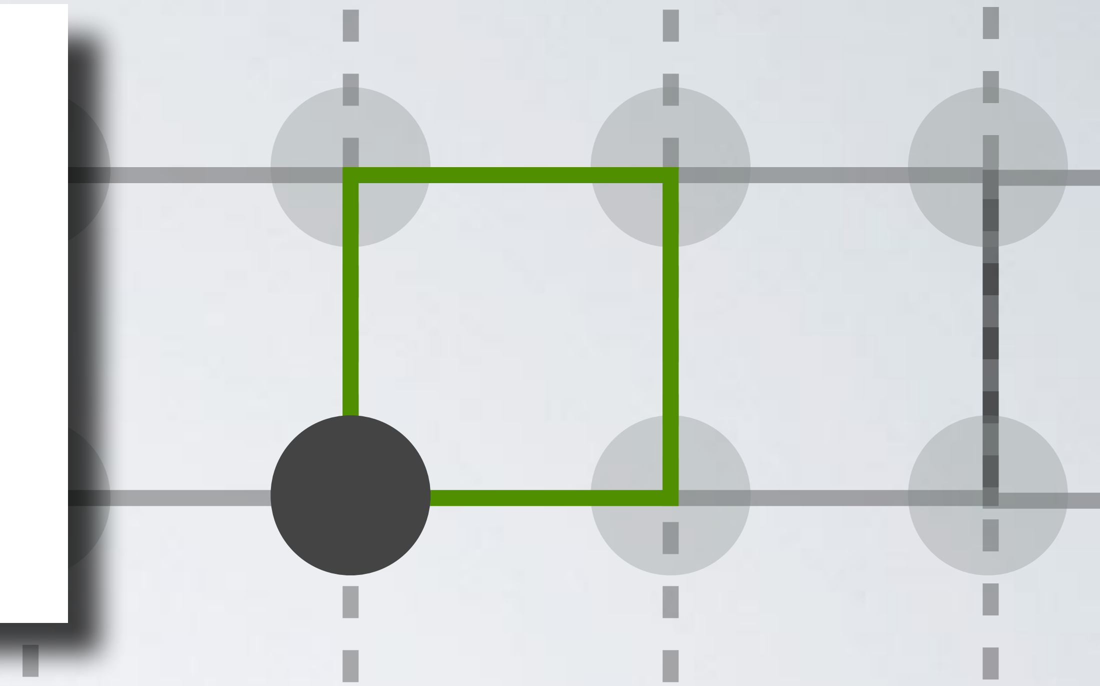
Compare: Optical conductivity in **SRT approximation**

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

GREENWOOD-KUBO FORMALISM

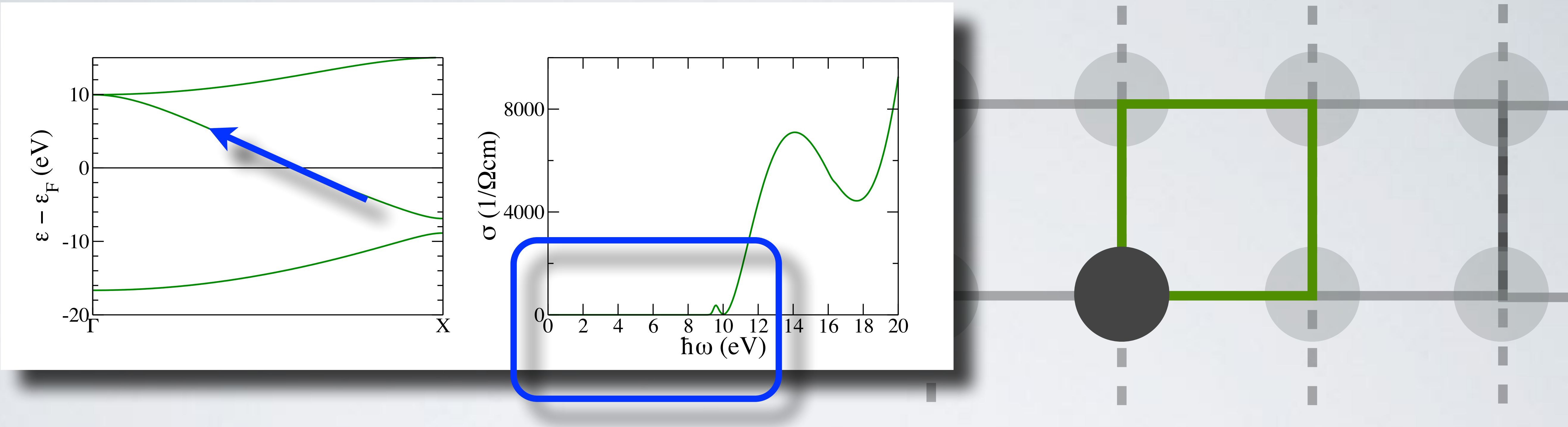
D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).





GREENWOOD-KUBO FORMALISM

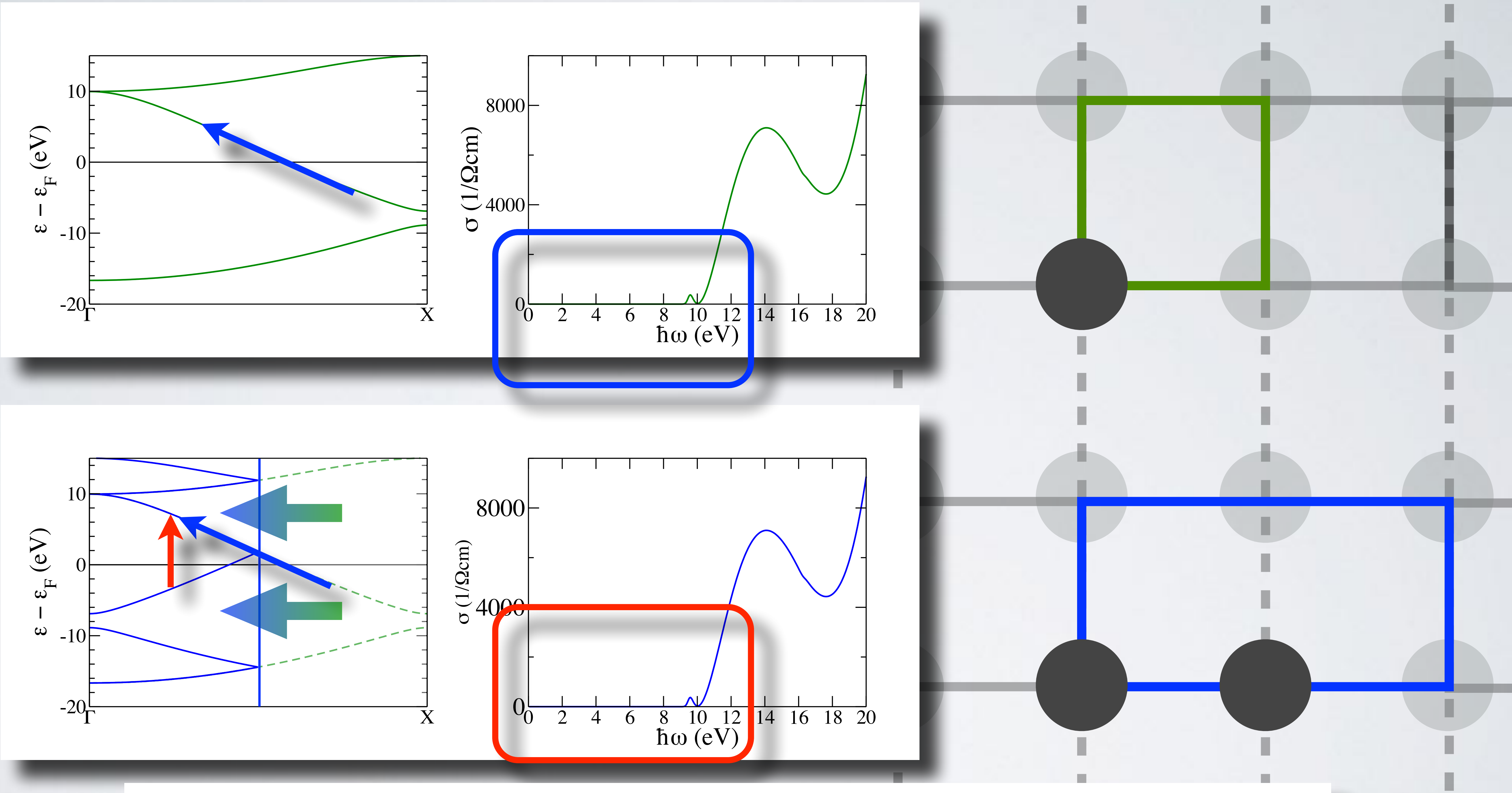
D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).



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

GREENWOOD-KUBO FORMALISM

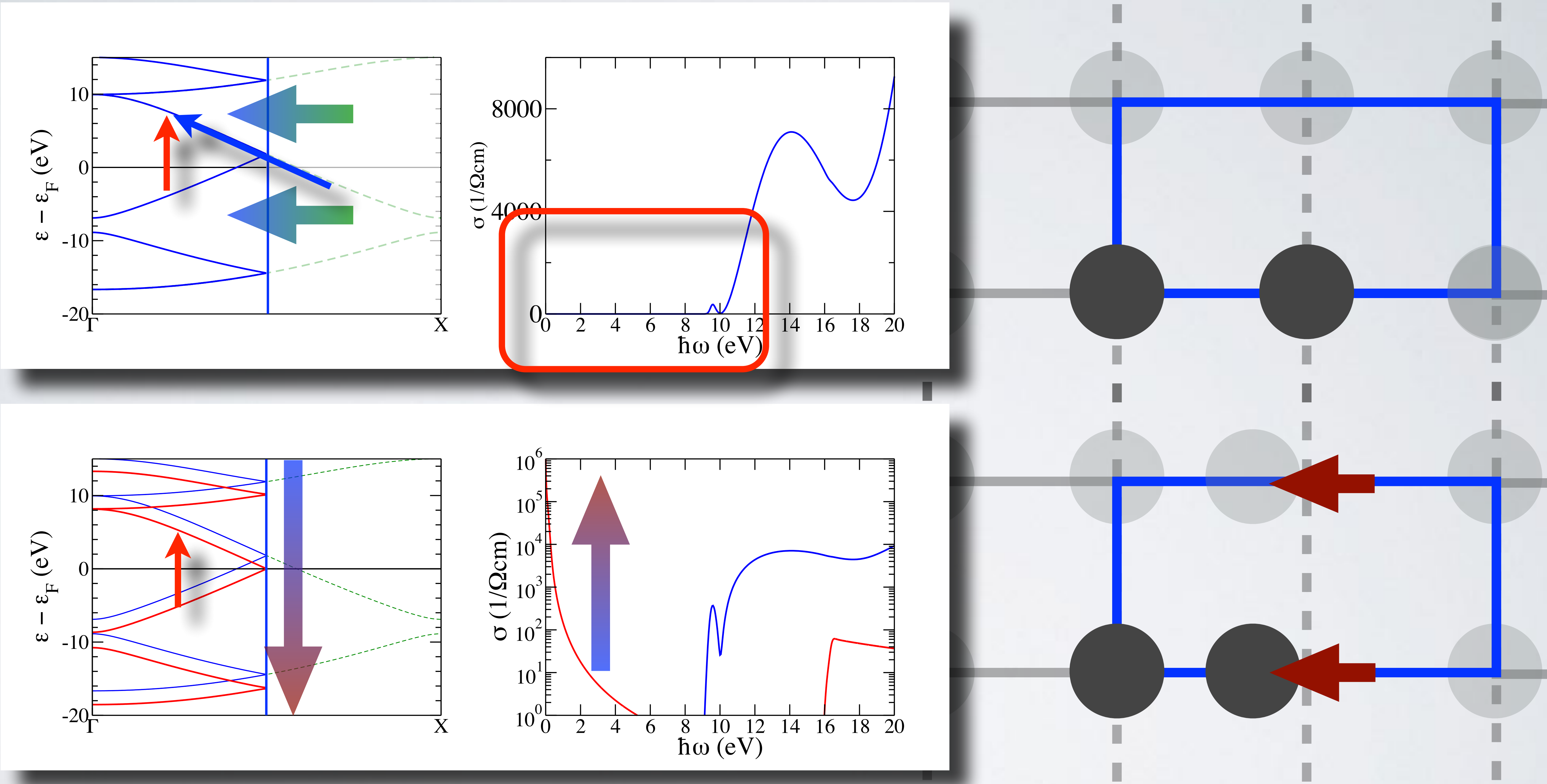
D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).



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).

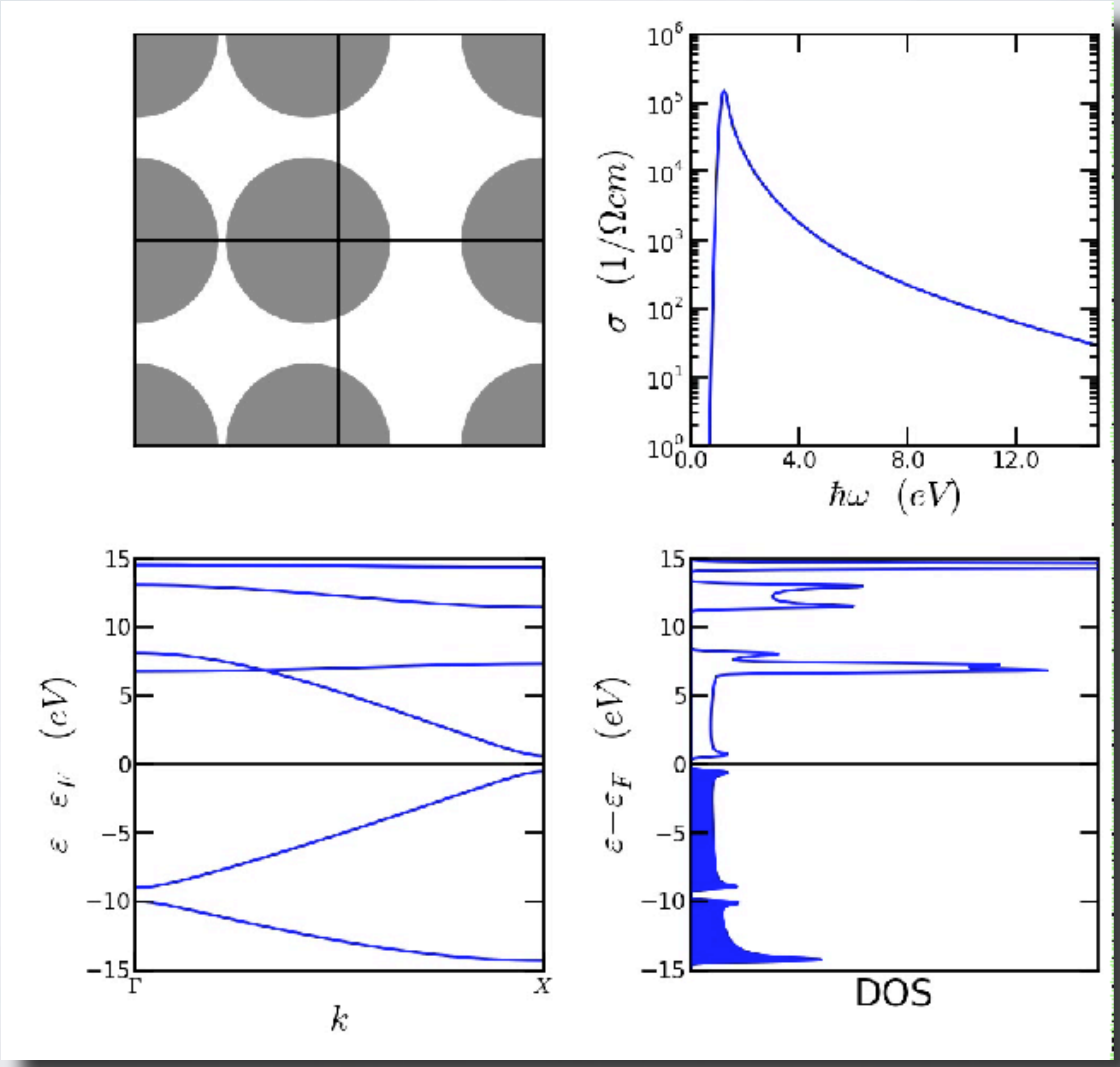


Thermal Motion of the nuclei:

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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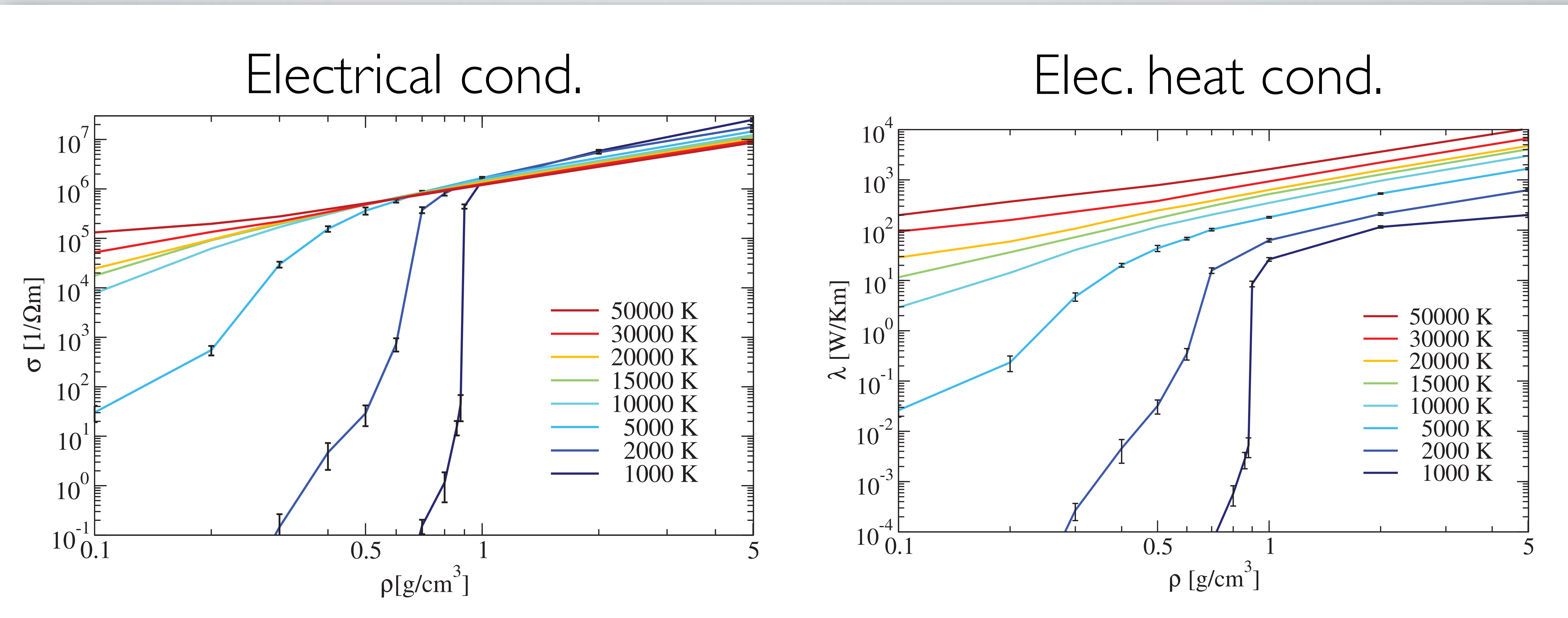

Non-metal to metal transition in dense liquid hydrogen

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

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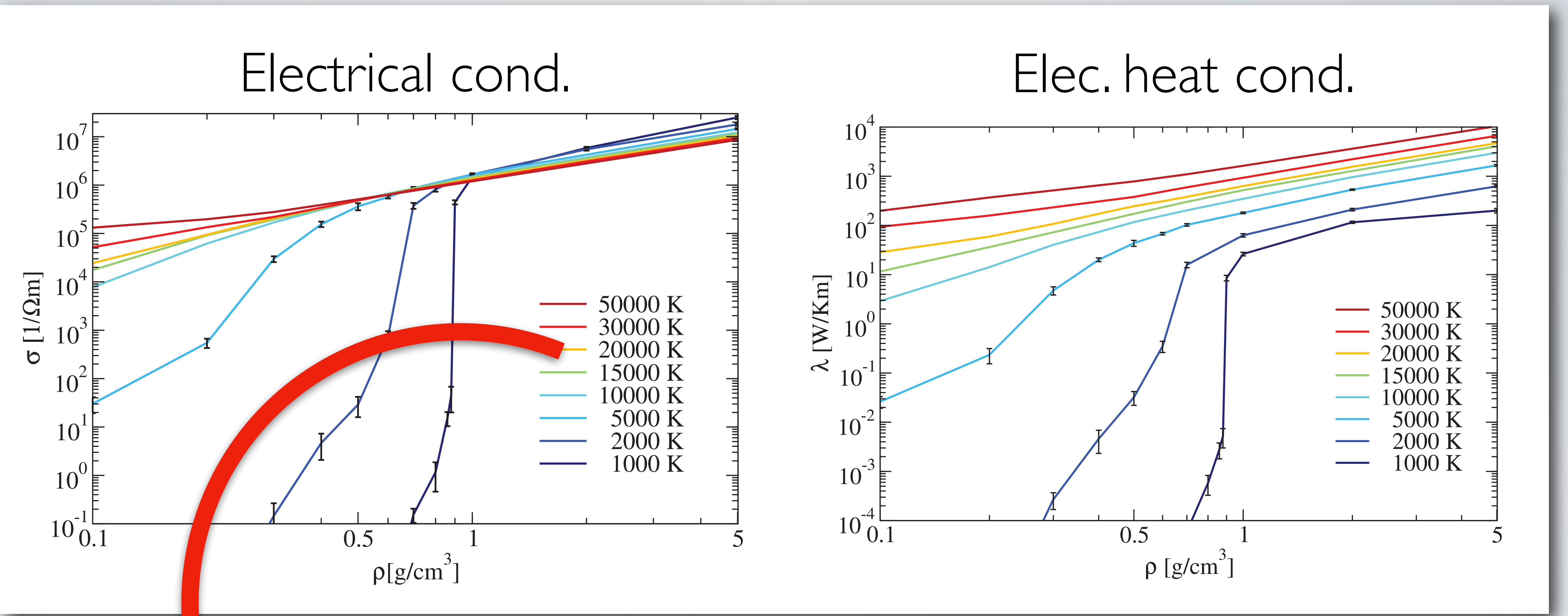
D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).



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.