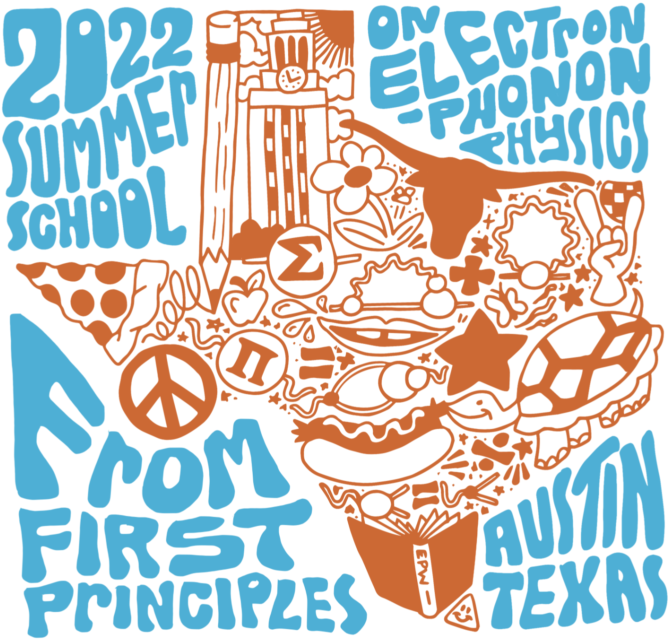


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LA LIBERTÉ DE CHERCHER

Lecture Wed.1

# Carrier transport

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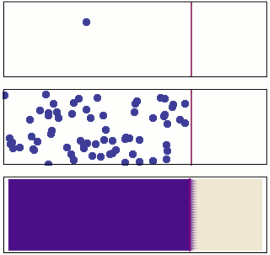
# Lecture Summary

- The transport of charge carriers
- Quantum theory of mobility
- Mobility in simple bulk semiconductors
- Hall mobility
- Resistivity in metals

Charges particles (electrons or holes) will move as a result of:

- a density gradient $\rightarrow$ **diffusion**

Fick's law (1855)
current density: $J = qD\nabla n$

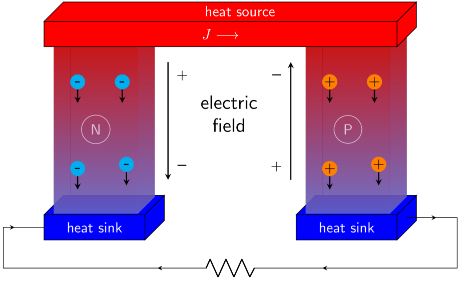


Wikipedia

Charges particles (electrons or holes) will move as a result of:

- a density gradient $\rightarrow$ **diffusion**
- a temperature gradient $\rightarrow$ **thermoelectricity**
  - Phonon-drag contribution - Gurevich (1945)

Seebeck effect (1821)
current density: $J \propto -\sigma S \nabla T$
S $\in$ [-100$\mu V/K$, 1000$\mu V/K$]

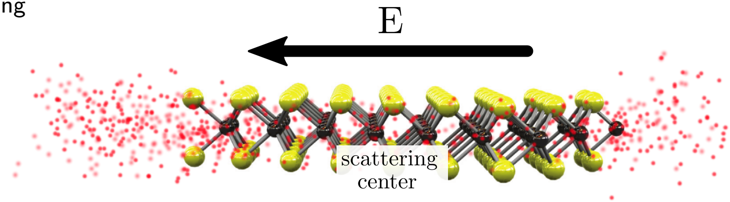


# Transport of charge carriers

Charges particles (electrons or holes) will move as a result of:

- a density gradient $\rightarrow$ **diffusion**
- a temperature gradient $\rightarrow$ **thermoelectricity**
  - Phonon-drag contribution - Gurevich (1945)
- an external electric field E $\rightarrow$ **drift**
  - lattice/phonon scattering
  - ionized impurity scattering
  - alloy scattering
  - defects scattering

Drude model (1900)
current density: $J = nq\mu E$




Mobility $\mu \propto \frac{\partial}{\partial E} \int d\mathbf{k} f_{\mathbf{k}} v_{\mathbf{k}}$

Current density

$$\mathbf{J}(\mathbf{r}_1, t_1) = \frac{-e\hbar^2}{2m} \lim_{\mathbf{r}_2 \to \mathbf{r}_1} (\nabla_2 - \nabla_1) G^<(\mathbf{r}_1, \mathbf{r}_2; t_1, t_1)$$

$$G^<(\mathbf{r}_1, \mathbf{r}_2; t_1, t_2) \equiv \frac{i}{\hbar} \left\langle \hat{\psi}^\dagger_{\mathrm{H}}(\mathbf{r}_2, t_2) \hat{\psi}_{\mathrm{H}}(\mathbf{r}_1, t_1) \right\rangle$$

Current density

$$\mathbf{J}(\mathbf{r}_1,t_1) = \frac{-e\hbar^2}{2m}\lim_{\mathbf{r}_2\to\mathbf{r}_1}(\nabla_2-\nabla_1)G^<(\mathbf{r}_1,\mathbf{r}_2;t_1,t_1)$$

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$$\hat{\psi}_{\mathrm{H}}(\mathbf{r},t) \equiv \overline{\mathcal{T}}\left[\mathrm{e}^{\frac{i}{\hbar}\int_{t_0}^{t}\mathrm{d}t'\,\hat{H}(t')}\right]\hat{\psi}(\mathbf{r})\mathcal{T}\left[\mathrm{e}^{\frac{-i}{\hbar}\int_{t_0}^{t}\mathrm{d}t'\,\hat{H}(t')}\right]$$

$$\left\langle\hat{O}\right\rangle \equiv \frac{1}{Z}\mathrm{tr}\left[\mathrm{e}^{-\beta\hat{H}(t_0)}\hat{O}\right]$$ ← thermodynamical average

$$Z \equiv \mathrm{tr}\left[\mathrm{e}^{-\beta\hat{H}(t_0)}\right]$$ ← partition function

Current density

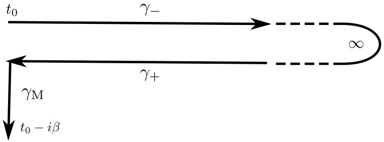
$$\mathbf{J}(\mathbf{r}_1,t_1) = \frac{-e\hbar^2}{2m} \lim_{\mathbf{r}_2\to\mathbf{r}_1} (\nabla_2 - \nabla_1) G^{<}(\mathbf{r}_1,\mathbf{r}_2;t_1,t_1)$$

$$G^{<}(\mathbf{r}_1,\mathbf{r}_2;t_1,t_2) \equiv \frac{i}{\hbar}\left\langle \hat{\psi}^{\dagger}_{\mathrm{H}}(\mathbf{r}_2,t_2)\hat{\psi}_{\mathrm{H}}(\mathbf{r}_1,t_1)\right\rangle$$

Keldysh-Schwinger contour formalism

$$G(\mathbf{r}_1,\mathbf{r}_2;z_1,z_2) = \frac{-i}{\hbar}\frac{1}{Z}\mathrm{tr}\Big\{\mathcal{T}_{\mathrm{C}}\Big[\mathrm{e}^{\frac{-i}{\hbar}\int_{\gamma}\mathrm{d}z\,\hat{H}(z)}[\hat{\psi}(\mathbf{r}_1)]_{z_1}[\hat{\psi}^{\dagger}(\mathbf{r}_2)]_{z_2}\Big]\Big\}$$

$$\hat{H}(z) = \hat{H}_0 + \hat{H}_{\mathrm{int}} + \hat{H}_{\mathrm{ext}}(z),$$



We can perform a perturbative expansion of the GF in powers of $\hat{H}_{\text{int}}$ and $\hat{H}_{\text{ext}}(z)$

$$G(\mathbf{r}_1,\mathbf{r}_2;z_1,z_2) = \boldsymbol{G_0(\mathbf{r}_1,\mathbf{r}_2;z_1,z_2)} + \sum_{n,m=1}^{\infty}\frac{(-i/\hbar)^{n+m}}{n!m!}\int_\gamma \mathrm{d}z'_1\ldots\int_\gamma \mathrm{d}z'_n\int_\gamma \mathrm{d}z''_1\ldots\int_\gamma \mathrm{d}z''_m$$

$$\times\frac{1}{Z}\mathrm{tr}\Big[\mathcal{T}_{\mathrm{C}}\mathrm{e}^{\frac{-i}{\hbar}\int_\gamma \mathrm{d}z\,[\hat{H}_0]_z}\big[\hat{H}_{\text{int}}\big]_{z'_1}\ldots\big[\hat{H}_{\text{int}}\big]_{z'_n}\hat{H}_{\text{ext}}(z''_1)\ldots\hat{H}_{\text{ext}}(z''_m)\big[\hat{\psi}(\mathbf{r}_1)\big]_{z_1}\big[\hat{\psi}^\dagger(\mathbf{r}_2)\big]_{z_2}\Big]$$

$$\boldsymbol{G_0(\mathbf{r}_1,\mathbf{r}_2;z_1,z_2)} = \frac{-i}{\hbar}\frac{1}{Z_0}\mathrm{tr}\Big[\mathcal{T}_{\mathrm{C}}\mathrm{e}^{\frac{-i}{\hbar}\int_\gamma \mathrm{d}z\,[\hat{H}_0]_z}\big[\hat{\psi}(\mathbf{r}_1)\big]_{z_1}\big[\hat{\psi}^\dagger(\mathbf{r}_2)\big]_{z_2}\Big]$$

Expressing the $\hat{H}$ in terms of $\hat{\psi}$ we can use Wick's theorem to write the perturbation series of $G$ in terms of products of $G_0$ and then solve the expansion with Feynman diagram to obtain Dyson's equation

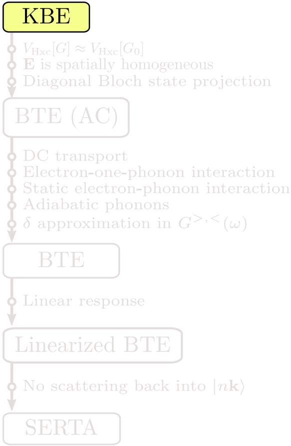
$$G(1,2) = G_0(1,2) + \int_\gamma \mathrm{d}3\int_\gamma \mathrm{d}4\, G_0(1,3)\Sigma[G](3,4)G(4,2)$$

$$1 \equiv (\mathbf{r}_1, z_1)$$

Using Langreth rules, $G_0^{-1}$, explicit $\hat{H}_0$ and evaluating Dyson at equal time, we obtain the Kadanoff-Baym equation for $G^<$ in the limit $t_0 \to -\infty$:

$$i\hbar\frac{\partial}{\partial t}G^<(\mathbf{r}_1,\mathbf{r}_2;t,t) = \left[h_0(\mathbf{r}_1,-i\hbar\nabla_1) - h_0(\mathbf{r}_2,+i\hbar\nabla_2)\right]G^<(\mathbf{r}_1,\mathbf{r}_2;t,t)$$
$$+\int \mathrm{d}^3r_3\left[\Sigma^\delta(\mathbf{r}_1,\mathbf{r}_3;t)G^<(\mathbf{r}_3,\mathbf{r}_2;t,t) - G^<(\mathbf{r}_1,\mathbf{r}_3;t,t)\Sigma^\delta(\mathbf{r}_3,\mathbf{r}_2;t)\right]$$
$$+\int_{-\infty}^{t}\mathrm{d}t'\int \mathrm{d}^3r_3\Big[\Sigma^>(\mathbf{r}_1,\mathbf{r}_3;t,t')G^<(\mathbf{r}_3,\mathbf{r}_2;t',t)$$
$$+G^<(\mathbf{r}_1,\mathbf{r}_3;t,t')\Sigma^>(\mathbf{r}_3,\mathbf{r}_2;t',t)$$
$$-\Sigma^<(\mathbf{r}_1,\mathbf{r}_3;t,t')G^>(\mathbf{r}_3,\mathbf{r}_2;t',t) - G^>(\mathbf{r}_1,\mathbf{r}_3;t,t')\Sigma^<(\mathbf{r}_3,\mathbf{r}_2;t',t)\Big]$$

- Unperturbed time-evolution of $G^<$ in static $V(\mathbf{r})$
- Local time self-energy
- Internal dynamical correlations (collisions, scattering)




Nonequilibrium Many-Body Theory of Quantum Systems, Cambridge Uni. Press (2013)

SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)

# Boltzmann transport equation

Approximation:

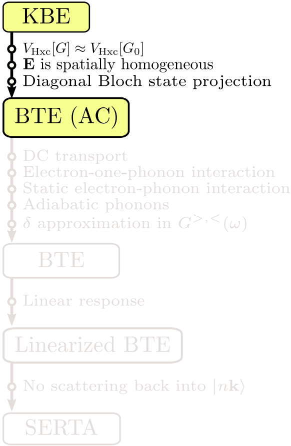
- $V_{\mathsf{Hxc}}[G] \approx V_{\mathsf{Hxc}}[G_0]$

$$\Sigma^{\delta}(\mathbf{r}_1, \mathbf{r}_2; t) \approx -e\phi_{\text{ext}}(\mathbf{r}_1, t)\delta^{(3)}(\mathbf{r}_1 - \mathbf{r}_2)$$

- **E** is spatially homogeneous

$$\phi_{\text{ext}}(\mathbf{r}_1, t) - \phi_{\text{ext}}(\mathbf{r}_2, t) = -\mathbf{E}(t) \cdot (\mathbf{r}_1 - \mathbf{r}_2)$$

$$\int \mathrm{d}^3 r_3 \left[\Sigma^{\delta}(\mathbf{r}_1, \mathbf{r}_3; t) G^{<}(\mathbf{r}_3, \mathbf{r}_2; t, t) - G^{<}(\mathbf{r}_1, \mathbf{r}_3; t, t)\Sigma^{\delta}(\mathbf{r}_3, \mathbf{r}_2; t)\right]$$
$$\approx e\mathbf{E}(t) \cdot (\mathbf{r}_1 - \mathbf{r}_2) G^{<}(\mathbf{r}_1, \mathbf{r}_2; t, t)$$

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# Boltzmann transport equation

We consider electrons in a solid and project the KBE in the $\{\varphi_{n\mathbf{k}}(\mathbf{r})\}$ basis.

Approximation:

- diagonal matrix elements of G and $\Sigma$ (ok if no strong band mixing)

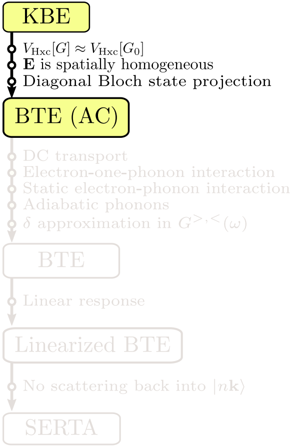
By expanding the Bloch WF in plane waves and taking the diagonal elements we have:

$$\int d^3 r_1 \int d^3 r_2 \, \varphi^*_{n\mathbf{k}}(\mathbf{r}_1) e\mathbf{E}(t) \cdot (\mathbf{r}_1 - \mathbf{r}_2) G^{<}(\mathbf{r}_1, \mathbf{r}_2; t, t) \varphi_{n\mathbf{k}}(\mathbf{r}_2)$$

$$= -e\mathbf{E}(t) \cdot \frac{1}{\hbar} \frac{\partial f^{<}_{n\mathbf{k}}}{\partial \mathbf{k}}(t,t)$$

where

$$\mp \frac{i}{\hbar} f^{>,<}_{n\mathbf{k}}(t,t') \equiv \int d^3 r_1 \int d^3 r_2 \, \varphi^*_{n\mathbf{k}}(\mathbf{r}_1) G^{>,<}(\mathbf{r}_1, \mathbf{r}_2; t, t') \varphi_{n\mathbf{k}}(\mathbf{r}_2)$$

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# Boltzmann transport equation

The quantum BTE is:

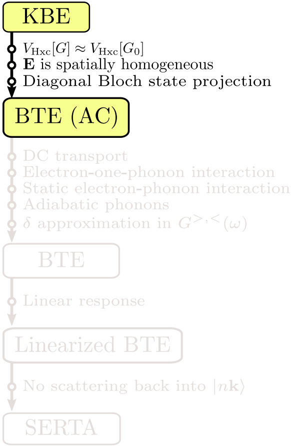
$$\frac{\partial f^{<}_{n\mathbf{k}}}{\partial t}(t,t) - e\mathbf{E}(t)\cdot\frac{1}{\hbar}\frac{\partial f^{<}_{n\mathbf{k}}}{\partial \mathbf{k}}(t,t) = -\Gamma^{(\mathrm{co})}_{n\mathbf{k}}(t)$$

where the *collision rate* is defined as:

$$\Gamma^{(\mathrm{co})}_{n\mathbf{k}}(t) \equiv \int_{-\infty}^{t} \mathrm{d}t' \Big[ \Gamma^{>}_{n\mathbf{k}}(t,t')\, f^{<}_{n\mathbf{k}}(t',t) + f^{<}_{n\mathbf{k}}(t,t')\, \Gamma^{>}_{n\mathbf{k}}(t',t) - \Gamma^{<}_{n\mathbf{k}}(t,t')\, f^{>}_{n\mathbf{k}}(t',t) - f^{>}_{n\mathbf{k}}(t,t')\, \Gamma^{<}_{n\mathbf{k}}(t',t) \Big]$$

and

$$\mp i\hbar\, \Gamma^{>,<}_{n\mathbf{k}}(t,t') \equiv \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2\, \varphi^{*}_{n\mathbf{k}}(\mathbf{r}_1)\Sigma^{>,<}(\mathbf{r}_1,\mathbf{r}_2;t,t')\varphi_{n\mathbf{k}}(\mathbf{r}_2)$$




SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)

# Boltzmann transport equation

For time-independent $\mathbf{E}$ (DC) we can do a FT:

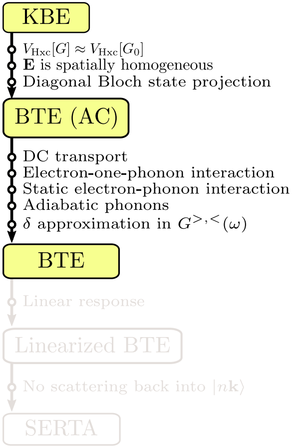
$$-e\mathbf{E}\cdot\frac{1}{\hbar}\frac{\partial f_{n\mathbf{k}}}{\partial\mathbf{k}} = -\int\frac{d\omega}{2\pi}\left[f^{<}_{n\mathbf{k}}(\omega)\Gamma^{>}_{n\mathbf{k}}(\omega) - f^{>}_{n\mathbf{k}}(\omega)\Gamma^{<}_{n\mathbf{k}}(\omega)\right]$$

where the $\mathbf{E}$-field dependent occupation number is

$$f_{n\mathbf{k}} \equiv \int\frac{d\omega}{2\pi}f^{<}_{n\mathbf{k}}(\omega).$$

Approximations:

- Only scattering by lattice vibrations
- Neglect phonon-phonon interactions
- Frequency-independent el-ph matrix elements
- Phonon Green's function in the adiabatic approximation
- $f^{>,<}(\omega)$ is approximated at the level of $\hat{H}_0$ $[f^{<}_{n\mathbf{k}}(\omega) \approx 2\pi f_{n\mathbf{k}}\delta(\omega-\varepsilon_{n\mathbf{k}}/\hbar)]$

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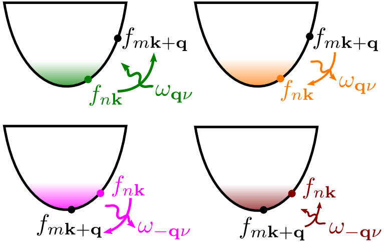
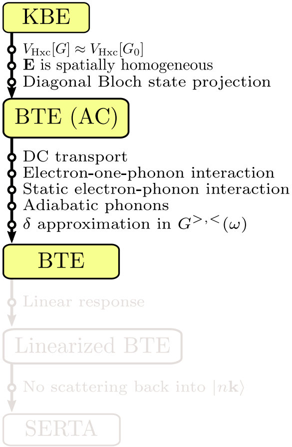
$$
\begin{aligned}
-e\mathbf{E}\cdot\frac{1}{\hbar}\frac{\partial f_{n\mathbf{k}}}{\partial \mathbf{k}} = \frac{2\pi}{\hbar}\sum_{m,\nu}\int\frac{\mathrm{d}^3q}{\Omega_{\mathrm{BZ}}}\,|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \\
\times \big[ f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}+\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu} \\
+ f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{m\mathbf{k}+\mathbf{q}}-\hbar\omega_{\mathbf{q}\nu})(n_{\mathbf{q}\nu}+1) \\
-(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}+\hbar\omega_{\mathbf{q}\nu})n_{\mathbf{q}\nu} \\
-(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{n\mathbf{k}}-\hbar\omega_{\mathbf{q}\nu})(n_{\mathbf{q}\nu}+1)\big]
\end{aligned}
$$

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# Linearized Boltzmann transport equation

Macroscopic average of the current density is

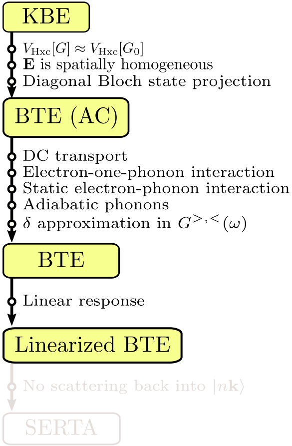
$$\mathbf{J}_{\mathrm{M}}(\mathbf{E}) = \frac{-e\hbar^2}{2m}\frac{1}{V}\int \mathrm{d}^3 r \lim_{\mathbf{r}_2\to\mathbf{r}_1}(\nabla_2 - \nabla_1)G^{<}(\mathbf{r}_1,\mathbf{r}_2;t,t;\mathbf{E})$$
$$= \frac{-e}{V_{\mathrm{uc}}}\sum_n \int \frac{\mathrm{d}^3 k}{\Omega_{\mathrm{BZ}}}\mathbf{v}_{n\mathbf{k}} f_{n\mathbf{k}}(\mathbf{E})$$

For weak $\mathbf{E}$, we can use the *linear response* of the current density to define the *conductivity*:

$$\sigma_{\alpha\beta} \equiv \frac{\partial J_{\mathrm{M},\alpha}}{\partial E_\beta}\bigg|_{\mathbf{E}=\mathbf{0}} = \frac{-e}{V_{\mathrm{uc}}}\sum_n \int \frac{\mathrm{d}^3 k}{\Omega_{\mathrm{BZ}}} v^{\alpha}_{n\mathbf{k}}\partial_{E_\beta} f_{n\mathbf{k}}$$

where $\partial_{E_\beta} f_{n\mathbf{k}} = (\partial f_{n\mathbf{k}}/\partial E_\beta)|_{\mathbf{E}=\mathbf{0}}$.
The *carrier drift mobility* is

$$\mu^{\mathrm{d}}_{\alpha\beta} \equiv \frac{\sigma_{\alpha\beta}}{e n_{\mathrm{c}}}$$

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$$= \frac{-e}{V_{\rm uc}}\sum_n\int\frac{\mathrm{d}^3k}{\Omega_{\rm BZ}}\,\mathbf{v}_{n\mathbf{k}}f_{n\mathbf{k}}(\mathbf{E})$$

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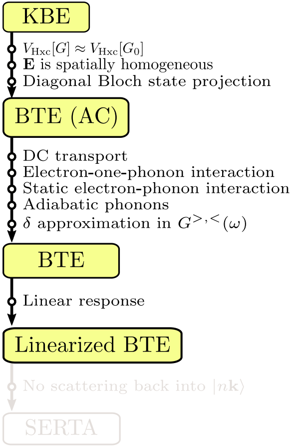


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## Side note

Berryology [TM Ivo Souza]:

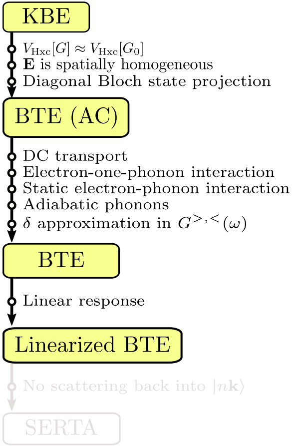
$$j_\alpha = -e \int_{\mathbf{k}} \dot{r}_a f(\varepsilon)$$

$$= -e \int_{\mathbf{k}} [\underbrace{v_a}_{\text{band}} + \underbrace{(e/\hbar)\Omega_{ab} E_b}_{\text{anomalous}} + \dots][f_0 + \tau e v_c E_c f_0' + \dots]$$

$$= C + \sigma_{ab} E_b + \sigma_{abc} E_b E_c + \dots$$

$$\sigma_{ab} = -e^2\tau \int_{\mathbf{k}} v_a v_b f_0' - \frac{e^2}{\hbar} \int_{\mathbf{k}} \Omega_{ab} f_0$$ Linear Ohmic + Hall

In system with TR symmetry: $\int_{\mathbf{k}} \Omega_{ab} f_0 = 0$

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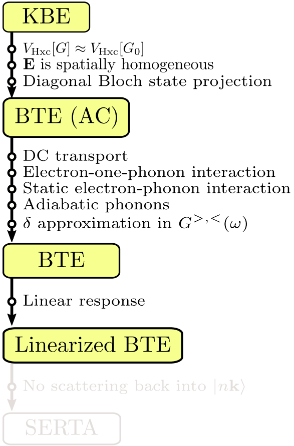
# Linearized Boltzmann transport equation

$$\mu^{\mathrm{d}}_{\alpha\beta} = \frac{-1}{V_{\mathrm{uc}} n_{\mathrm{c}}} \sum_n \int \frac{\mathrm{d}^3 k}{\Omega_{\mathrm{BZ}}} v^{\alpha}_{n\mathbf{k}} \partial_{E_\beta} f_{n\mathbf{k}}$$

$$\partial_{E_\beta} f_{n\mathbf{k}} = e v^{\beta}_{n\mathbf{k}} \frac{\partial f^0_{n\mathbf{k}}}{\partial \varepsilon_{n\mathbf{k}}} \tau_{n\mathbf{k}} + \frac{2\pi \tau_{n\mathbf{k}}}{\hbar} \sum_{m\nu} \int \frac{\mathrm{d}^3 q}{\Omega_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \times \Big[(n_{\mathbf{q}\nu} + 1 - f^0_{n\mathbf{k}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu}) + (n_{\mathbf{q}\nu} + f^0_{n\mathbf{k}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu})\Big] \partial_{E_\beta} f_{m\mathbf{k}+\mathbf{q}}$$

where

$$\tau^{-1}_{n\mathbf{k}} \equiv \frac{2\pi}{\hbar} \sum_{m\nu} \int \frac{d^3 q}{\Omega_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \big[(n_{\mathbf{q}\nu} + 1 - f^0_{m\mathbf{k}+\mathbf{q}}) \times \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu}) + (n_{\mathbf{q}\nu} + f^0_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu})\big]$$

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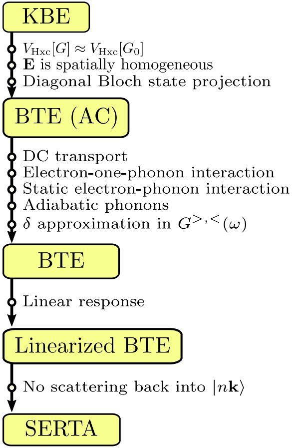
# Self-energy relaxation time approximation

$$\mu^{\mathrm{d,SERTA}}_{\alpha\beta} = \frac{-1}{V_{\mathrm{uc}} n_{\mathrm{c}}} \sum_n \int \frac{d^3k}{\Omega_{\mathrm{BZ}}} v^{\alpha}_{n\mathbf{k}} \, \partial_{E_\beta} f_{n\mathbf{k}}$$

$$\partial_{E_\beta} f_{n\mathbf{k}} = e v^{\beta}_{n\mathbf{k}} \frac{\partial f^0_{n\mathbf{k}}}{\partial \varepsilon_{n\mathbf{k}}} \tau_{n\mathbf{k}}$$

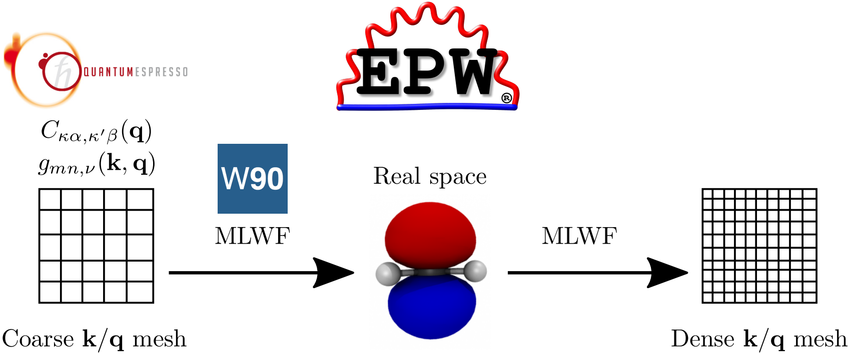
where

$$\tau^{-1}_{n\mathbf{k}} \equiv \frac{2\pi}{\hbar} \sum_{m\nu} \int \frac{d^3q}{\Omega_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \big[(n_{\mathbf{q}\nu} + 1 - f^0_{m\mathbf{k}+\mathbf{q}}) \times \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu}) + (n_{\mathbf{q}\nu} + f^0_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu})\big]$$




SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)

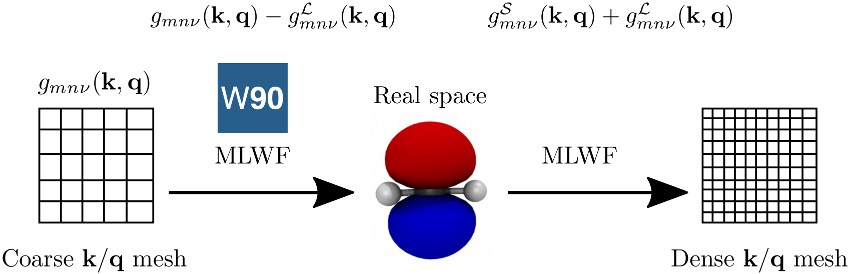
EPW relies on MLWF to interpolate electron-phonon matrix elements.




SP *et al.*, Comput. Phys. Commun. **209**, 116 (2016)

# Long range electrostatics

EPW relies on MLWF to interpolate electron-phonon matrix elements.




SP *et al.*, Comput. Phys. Commun. **209**, 116 (2016)

# Dipoles & quadrupoles

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\mathcal{S}}_{mn\nu}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\mathcal{L},\mathrm{D}}_{mn\nu}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L},\mathrm{Q}}_{mn\nu}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L},\mathrm{O}}_{mn\nu}(\mathbf{k},\mathbf{q}) + \cdots$$

$$g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q}) = \sum_{\kappa\alpha}\left[\frac{\hbar}{2NM_\kappa\omega_\nu(\mathbf{q})}\right]^{\frac{1}{2}} \frac{4\pi e^2 e^{-\frac{|\mathbf{q}|^2}{4\Lambda^2}}}{\Omega\sum_{\delta\delta'} q_\delta \epsilon^\infty_{\delta\delta'} q_{\delta'}}$$

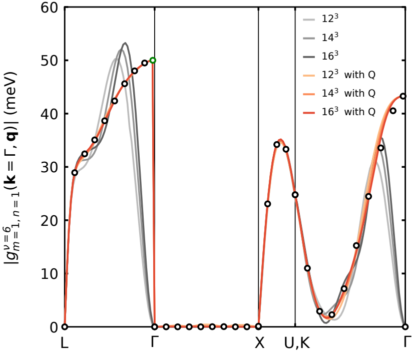
$$\times\, e^{-i\mathbf{q}\cdot\boldsymbol{\tau}_\kappa}\Big[\sum_\beta iq_\beta Z_{\kappa\alpha\beta} + \sum_\gamma \frac{q_\beta q_\gamma}{2} Q_{\kappa\alpha\beta\gamma}\Big] e_{\kappa\alpha\nu}(\mathbf{q})\langle\Psi_{m\mathbf{k}+\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}[1 + iq_\alpha v^{\mathrm{Hxc},\mathcal{E}_\alpha}(\mathbf{r})]\rangle\Psi_{n\mathbf{k}}.$$

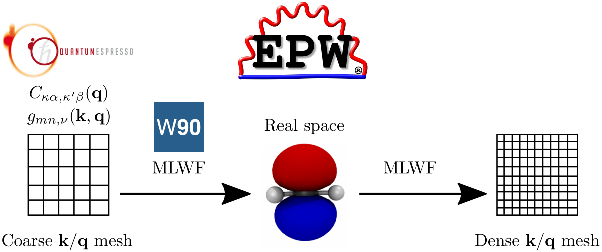
C. Verdi and F. Giustino, Phys. Rev. Lett. **119**, 176401 (2015)
G. Brunin *et al.*, Phys. Rev. Lett. **125**, 136601 (2020)

# Dynamical quadrupoles: Si

$$g_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\mathcal{S}}_{mn\nu}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q})$$

$$g^{\mathcal{L}}_{mn\nu}(\mathbf{k},\mathbf{q}) = g^{\mathcal{L},\mathrm{D}}_{mn\nu}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L},\mathrm{Q}}_{mn\nu}(\mathbf{k},\mathbf{q}) + g^{\mathcal{L},\mathrm{O}}_{mn\nu}(\mathbf{k},\mathbf{q}) + \cdots$$




G. Brunin *et al.*, PRL **125**, 136601 (2020)
V. A. Jhalani *et al.*, PRL **125**, 136602 (2020)

$$\mu^{\mathrm{d}}_{\alpha\beta} = \frac{-1}{V_{\mathrm{uc}} n_{\mathrm{c}}} \sum_n \int \frac{\mathrm{d}^3 k}{\Omega_{\mathrm{BZ}}} v^{\alpha}_{n\mathbf{k}} \partial_{E_\beta} f_{n\mathbf{k}}$$

Obtained from the commutator:

$$\hat{\mathbf{v}} = (i/\hbar)[\hat{H}, \hat{\mathbf{r}}]$$
$$\mathbf{v}_{nm\mathbf{k}} = \langle \psi_{m\mathbf{k}} | \hat{\mathbf{p}}/m_e + (i/\hbar)[\hat{V}_{\mathrm{NL}}, \hat{\mathbf{r}}] | \psi_{n\mathbf{k}} \rangle,$$

where $\hat{\mathbf{p}} = -i\hbar\partial/\partial\mathbf{r}$ is the momentum operator.
$P_{\mathrm{c}} r_\alpha |\psi_{n\mathbf{k}}\rangle$ are the solution of the linear system:

$$[H - \varepsilon_{n\mathbf{k}} S] P_{\mathrm{c}} r_\alpha |\psi_{n\mathbf{k}}\rangle = P^{\dagger}_{\mathrm{c}} [H - \varepsilon_{n\mathbf{k}} S, r_\alpha] |\psi_{n\mathbf{k}}\rangle,$$

where $S$ is the overlap matrix and $P_{\mathrm{c}}$ the projector over the empty states.

In the local approximation (neglecting $\hat{V}_{\mathrm{NL}}$):

$$v_{mn\mathbf{k}\mathbf{k}'\alpha} \approx \langle \psi_{m\mathbf{k}'} | \hat{p}_\alpha | \psi_{n\mathbf{k}} \rangle = \delta(\mathbf{k} - \mathbf{k}') \left( k_\alpha \delta_{mn} - i \int d\mathbf{r} u^{*}_{m\mathbf{k}'}(\mathbf{r}) \nabla_\alpha u_{n\mathbf{k}}(\mathbf{r}) \right)$$

J. Tóbik and A. D. Corso, J. Chem. Phys. **120**, 9934 (2004)

# Electronic velocities

$$\mu^{\mathrm{d}}_{\alpha\beta} = \frac{-1}{V_{\mathrm{uc}} n_{\mathrm{c}}} \sum_n \int \frac{\mathrm{d}^3 k}{\Omega_{\mathrm{BZ}}} v^{\alpha}_{n\mathbf{k}} \partial_{E_\beta} f_{n\mathbf{k}}$$

Wannier interpolated velocities:

$$v_{nm\mathbf{k}',\alpha} = \frac{1}{\hbar} H_{nm\mathbf{k}',\alpha} - \frac{i}{\hbar}(\varepsilon_{m\mathbf{k}'} - \varepsilon_{n\mathbf{k}'}) A_{mn\mathbf{k}',\alpha}$$

$$A_{mn\mathbf{k}',\alpha} = \sum_{m'n'} U^{\dagger}_{mm'\mathbf{k}'} A^{(\mathrm{W})}_{m'n'\mathbf{k}',\alpha} U_{n'n\mathbf{k}'}$$

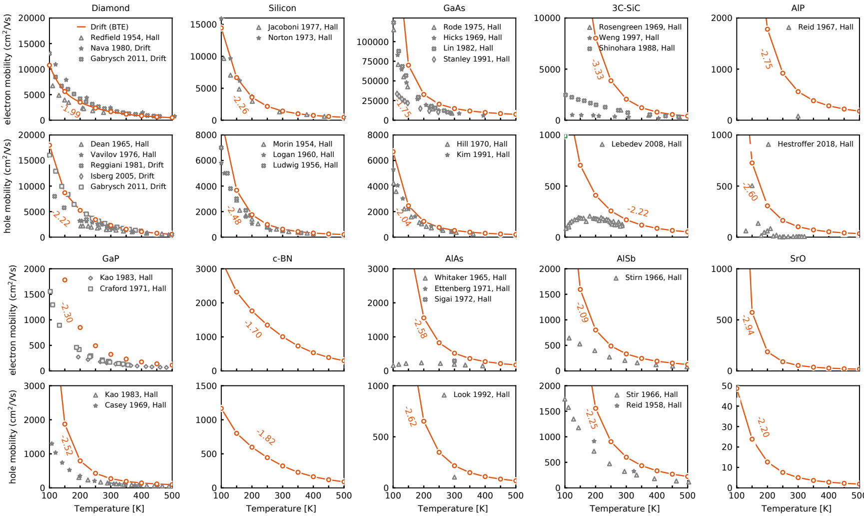
$$A^{(\mathrm{W})}_{nm\mathbf{k},\alpha} = i \sum_{\mathbf{b}} w_b b_\alpha \left( \langle u^{(\mathrm{W})}_{n\mathbf{k}} | u^{(\mathrm{W})}_{m\mathbf{k}+\mathbf{b}} \rangle - \delta_{nm} \right),$$

$\mathbf{b}$ are the vectors connecting $\mathbf{k}$ to its nearest neighbor and overlap matrices are:

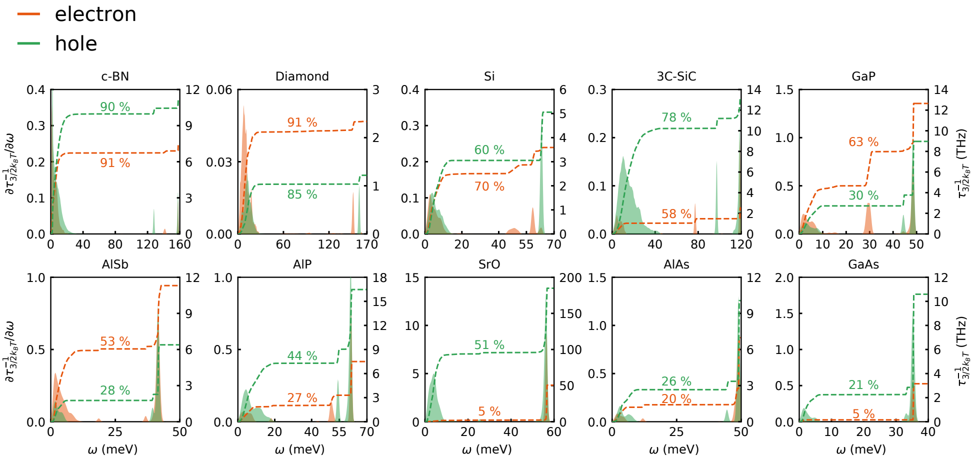
$$\langle u^{(\mathrm{W})}_{n\mathbf{k}} | u^{(\mathrm{W})}_{m\mathbf{k}+\mathbf{b}} \rangle = \sum_{n'm'} U^{\dagger}_{mm'\mathbf{k}} M_{mn\mathbf{k}} U_{nn'\mathbf{k}+\mathbf{b}},$$

$M_{mn\mathbf{k}} = \langle u_{n\mathbf{k}} | u_{m\mathbf{k}+\mathbf{b}} \rangle$ is the phase relation between neighboring Bloch orbitals.

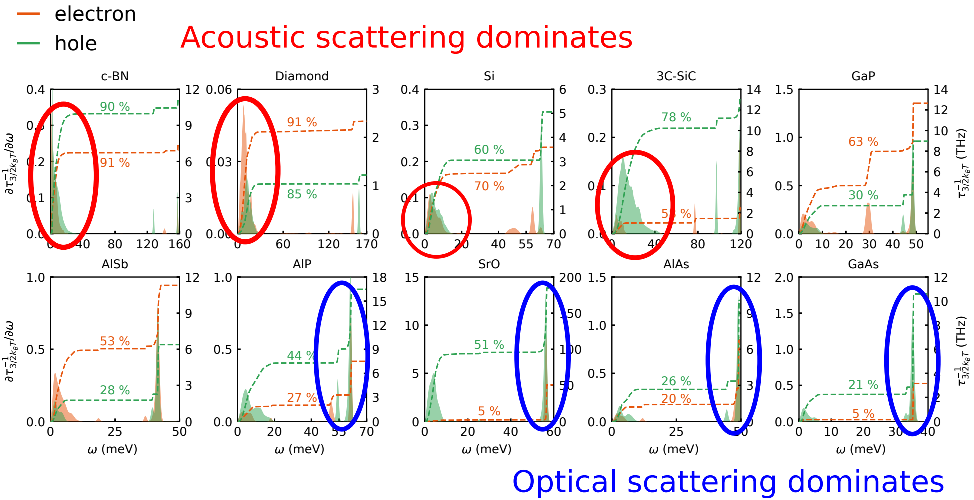
X. Wang, J. R. Yates, I. Souza, and D. Vanderbilt, Phys. Rev. B **74**, 195118 (2006)




SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

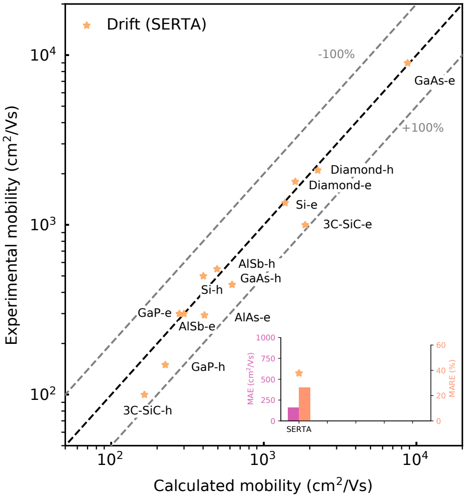



SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)



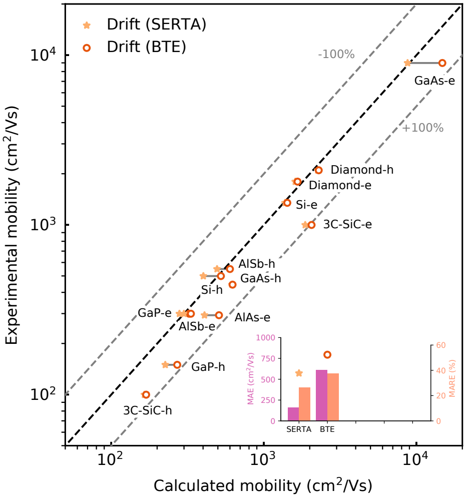

SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

# Experimental comparison




SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

# Experimental comparison



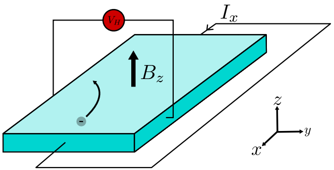

SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

$$\mu^{\rm Hall}_{\alpha\beta}(\hat{\mathbf{B}}) = \sum_{\gamma} \mu^{\rm drift}_{\alpha\gamma}\, r_{\gamma\beta}(\hat{\mathbf{B}})$$

$$r_{\alpha\beta}(\hat{\mathbf{B}}) \equiv \lim_{\mathbf{B}\to 0} \sum_{\delta\epsilon} \frac{[\,\mu^{\rm drift}_{\alpha\delta}\,]^{-1}\, \mu_{\delta\epsilon}(\mathbf{B})\, [\,\mu^{\rm drift}_{\epsilon\beta}\,]^{-1}}{|\mathbf{B}|}$$

$$\mu_{\alpha\beta}(B_\gamma) = \frac{-1}{S_{\rm uc} n_{\rm c}} \sum_n \int \frac{{\rm d}^3k}{S_{\rm BZ}} v_{n\mathbf{k}\alpha} \left[\, \partial_{E_\beta} f_{n\mathbf{k}}(B_\gamma) - \partial_{E_\beta} f_{n\mathbf{k}} \,\right]$$

$$\mu^{\rm drift}_{\alpha\beta} = \frac{-1}{S_{\rm uc} n_{\rm c}} \sum_n \int \frac{{\rm d}^3k}{S_{\rm BZ}} v_{n\mathbf{k}\alpha}\, \partial_{E_\beta} f_{n\mathbf{k}}$$




F. Macheda and N. Bonini, Phys. Rev. B **98**, 201201R (2018)
SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)
SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

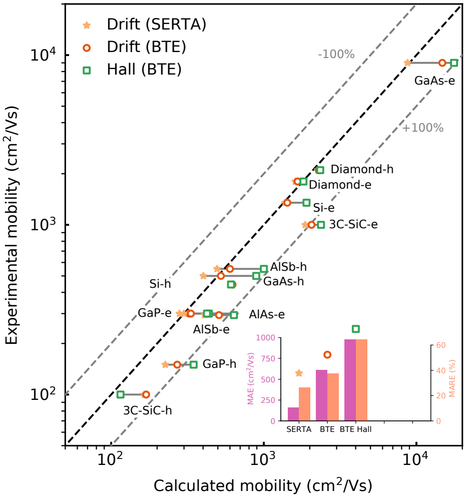
# Hall mobility

$$\left[1 - \frac{e}{\hbar}\tau_{n\mathbf{k}}(\mathbf{v}_{n\mathbf{k}} \times \mathbf{B}) \cdot \nabla_{\mathbf{k}}\right] \partial_{E_\beta} f_{n\mathbf{k}}(\mathbf{B}) = e v_{n\mathbf{k}\beta} \frac{\partial f^0_{n\mathbf{k}}}{\partial \varepsilon_{n\mathbf{k}}} \tau_{n\mathbf{k}}$$
$$+ \frac{2\pi \tau_{n\mathbf{k}}}{\hbar} \sum_{m\nu} \int \frac{\mathrm{d}^3 q}{S_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \Big[(n_{\mathbf{q}\nu} + 1 - f^0_{n\mathbf{k}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu})$$
$$+ (n_{\mathbf{q}\nu} + f^0_{n\mathbf{k}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu})\Big] \partial_{E_\beta} f_{m\mathbf{k}+\mathbf{q}}(\mathbf{B}),$$

where the scattering rate is

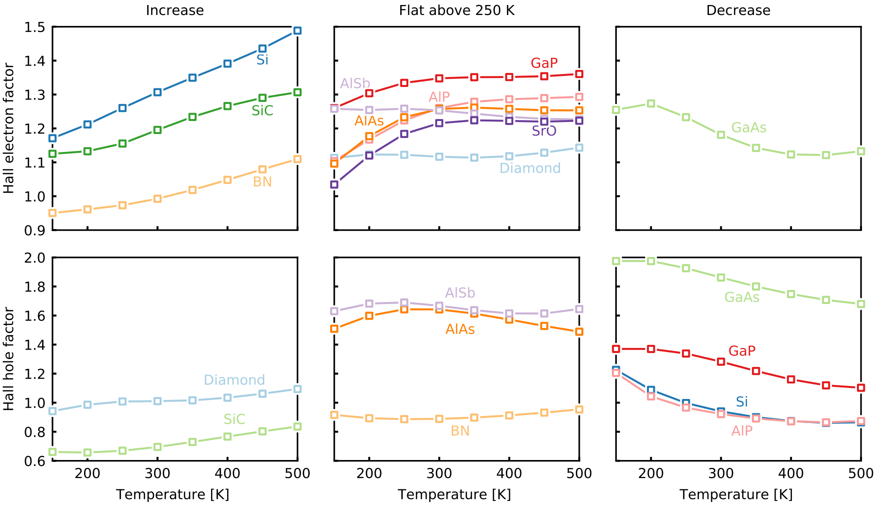
$$\tau^{-1}_{n\mathbf{k}} \equiv \frac{2\pi}{\hbar} \sum_{m\nu} \int \frac{d^3 q}{\Omega_{\mathrm{BZ}}} |g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \big[(n_{\mathbf{q}\nu} + 1 - f^0_{m\mathbf{k}+\mathbf{q}})$$
$$\times \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu}) + (n_{\mathbf{q}\nu} + f^0_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu})\big]$$

F. Macheda and N. Bonini, Phys. Rev. B **98**, 201201R (2018)
SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)
SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)




SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

# Hall factor is not unity




SP *et al.*, Phys. Rev. Research **3**, 043022 (2021)

Can be obtained from the solution of the BTE:

$$\rho_{\alpha\beta} = \sigma_{\alpha\beta}^{-1}$$

$$\sigma_{\alpha\beta} = \frac{-e}{V_{\mathrm{uc}}} \sum_n \int \frac{\mathrm{d}^3 k}{\Omega_{\mathrm{BZ}}} \, v_{n\mathbf{k}}^{\alpha} \, \partial_{E_\beta} f_{n\mathbf{k}}$$

Further approximation:

- constant $g_{mn\nu}(\mathbf{k},\mathbf{q})$ close to the Fermi level
- $-\frac{\partial f^0_{n\mathbf{k}}}{\partial \varepsilon_{n\mathbf{k}}} \approx \delta(\varepsilon^{\mathrm{F}} - \varepsilon_{n\mathbf{k}})$

Lowest-order variational approximation (LOVA) / Ziman formula:

$$\rho(T) = \frac{4\pi m_e}{ne^2 k_B T} \int_0^\infty d\omega \, \hbar\omega \, \alpha^2_{\mathrm{tr}} F(\omega) \, n(\omega,T) \big[1 + n(\omega,T)\big],$$

SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)

Lowest-order variational approximation (LOVA) / Ziman formula:

$$\rho(T) = \frac{4\pi m_e}{ne^2 k_B T}\int_0^\infty d\omega\, \hbar\omega\, \alpha^2_{\text{tr}}F(\omega)\, n(\omega,T)\big[1+n(\omega,T)\big],$$

Isotropic Eliashberg transport spectral function:

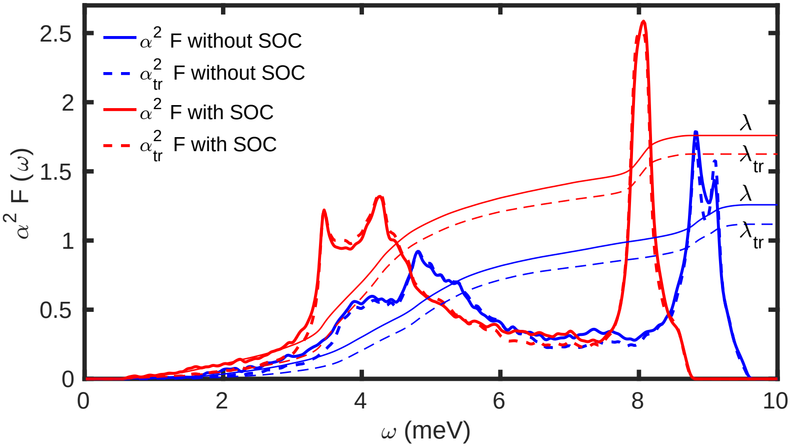
$$\alpha^2_{\text{tr}}F(\omega) = \frac{1}{2}\sum_{\nu}\int_{\text{BZ}}\frac{d\mathbf{q}}{\Omega_{\text{BZ}}}\omega_{\mathbf{q}\nu}\,\lambda_{\text{tr},\mathbf{q}\nu}\,\delta(\omega-\omega_{\mathbf{q}\nu}),$$

Mode-resolved transport coupling strength is defined by:

$$\lambda_{\text{tr},\mathbf{q}\nu} = \frac{1}{N(\varepsilon_F)\omega_{\mathbf{q}\nu}}\sum_{nm}\int_{\text{BZ}}\frac{d\mathbf{k}}{\Omega_{\text{BZ}}}|g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2\delta(\varepsilon_{n\mathbf{k}}-\varepsilon_{\text{F}})\delta(\varepsilon_{m\mathbf{k}+\mathbf{q}}-\varepsilon_{\text{F}})\Big(1-\frac{v_{n\mathbf{k}}\cdot v_{m\mathbf{k}+\mathbf{q}}}{|v_{n\mathbf{k}}|^2}\Big).$$

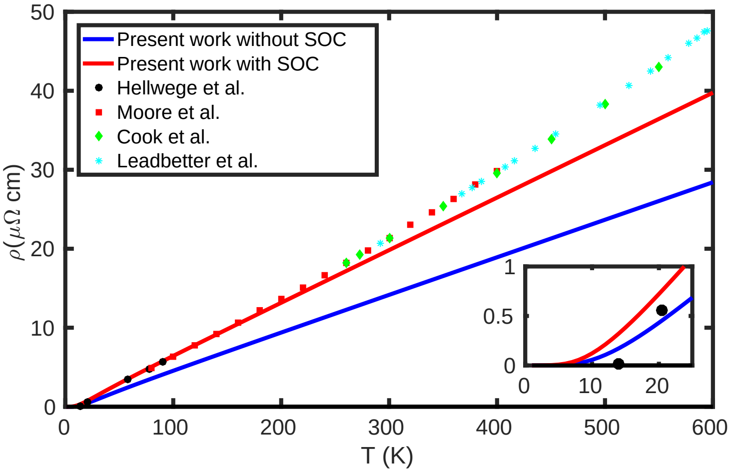
SP *et al.*, Rep. Prog. Phys. **83**, 036501 (2020)

# Eliashberg spectral function




SP *et al.*, Comput. Phys. Commun. **209**, 116 (2016)

# Ziman's formula




SP *et al.*, Comput. Phys. Commun. **209**, 116 (2016)

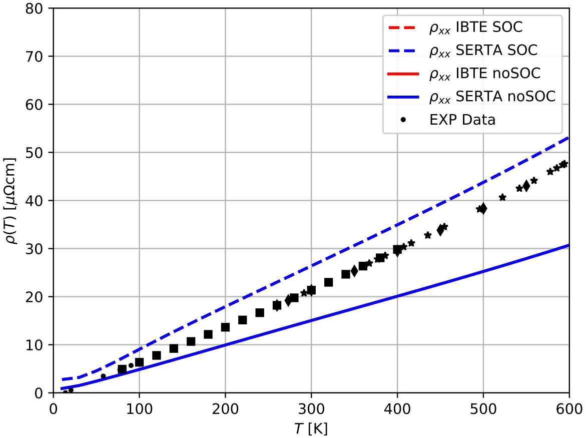
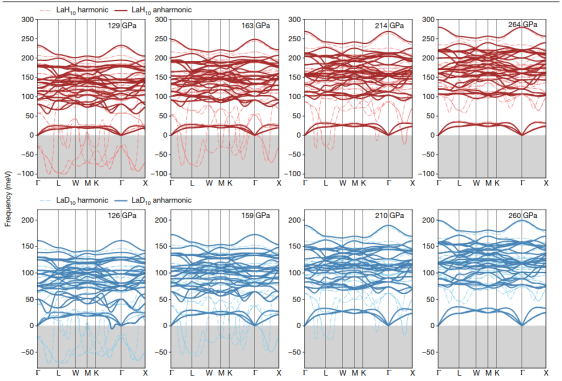



Figure courtesy of Félix Goudreault

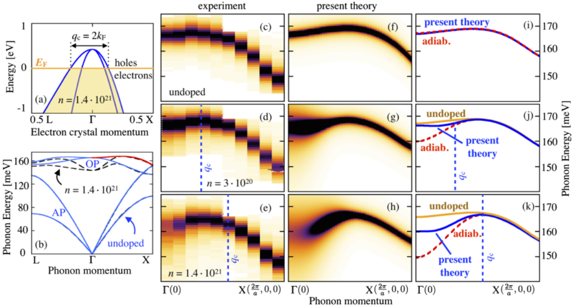
# Flavor of what lies beyond

- Anharmonicities and non-adiabatic phonons
- Transport with renormalized bandstructure / spectral functions
- Coupled transport of phonons and carriers
  N. H. Protik and D. A. Broido, Phys. Rev. B **101**, 075202 (2020)
- Electron-two-phonon scattering
  N.-E. Lee, J.J. Zhou, H.-Y. Chen, and M. Bernardi, Nature Commun. **11**, 1607 (2020)
- High field / warm electrons
  A. Y. Choi, P. S. Cheng, B. Hatanpää, and A. J. Minnich, Phys. Rev. Materials **5**, 044603 (2021)
- Electron-defect scattering
  I.-T. Lu, J. Park, J.-J. Zhou, and M. Bernardi, npj Comput. Mater. **6**, 17 (2020)

# Anharmonicities and non-adiabatic phonons



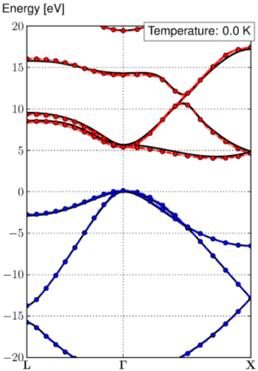

SSCHA



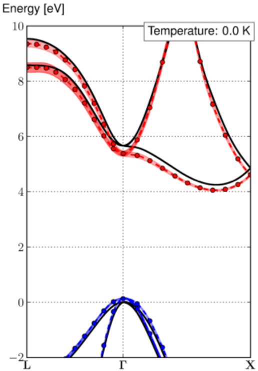

$$\hbar\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega) = 2\sum_{mn}\int \frac{d\mathbf{k}}{\Omega_{\mathrm{BZ}}} g^{b}_{mn,\nu}(\mathbf{k},\mathbf{q}) g^{*}_{mn,\nu}(\mathbf{k},\mathbf{q}) \times \left( \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}} - \hbar(\omega + i\eta)} - \frac{f_{n\mathbf{k}} - f_{m\mathbf{k}+\mathbf{q}}}{\epsilon_{m\mathbf{k}+\mathbf{q}} - \epsilon_{n\mathbf{k}}} \right)$$

I. Errea *et al.*, Nature **578**, 66 (2020)

F. Caruso *et al.*, Phys. Rev. Lett. **119**, 017001 (2017)

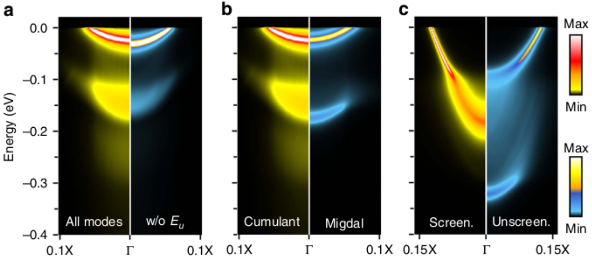



(a) Diamond band structure at 0K.



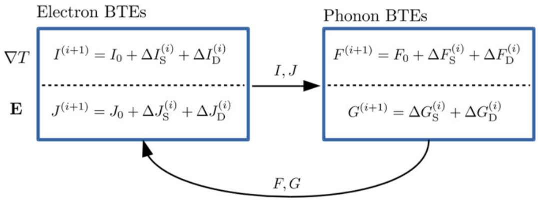

(b) Zoom of the left-hand side figure.

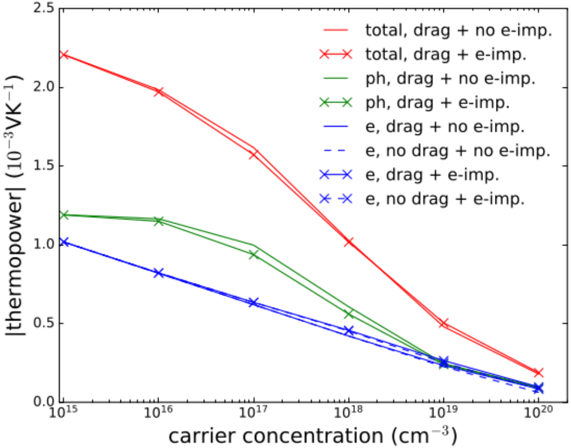
ZPR - AHC




S. Poncé *et al.*, J. Chem. Phys. **143**, 102813 (2015)

C. Verdi *et al.*, Nature Commun. **8**, 15769 (2017)




N. H. Protik and D. A. Broido, Phys. Rev. B **101**, 075202 (2020)

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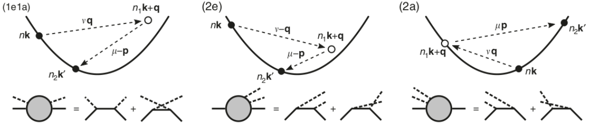
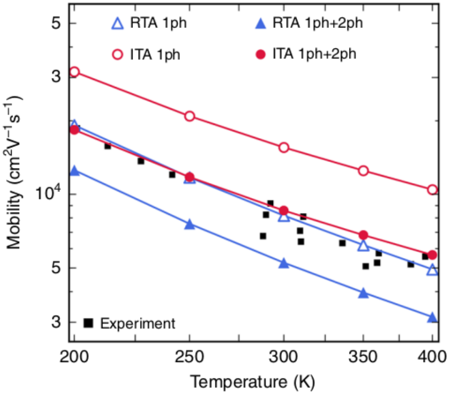
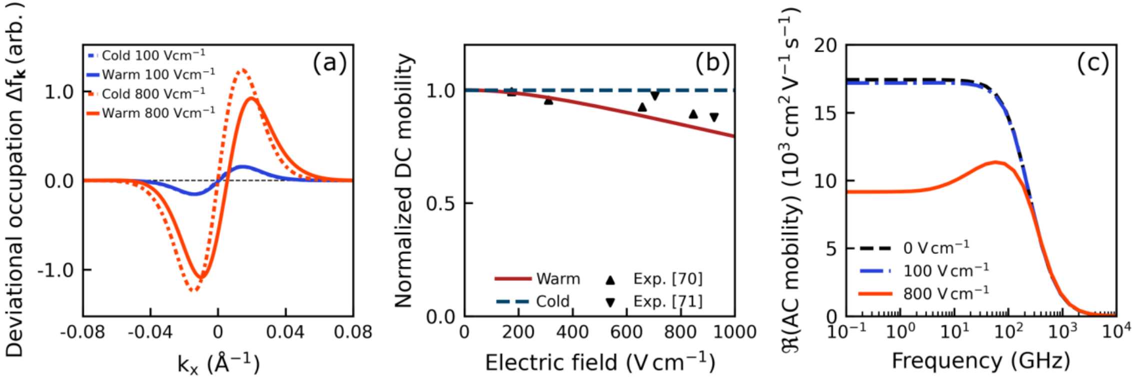


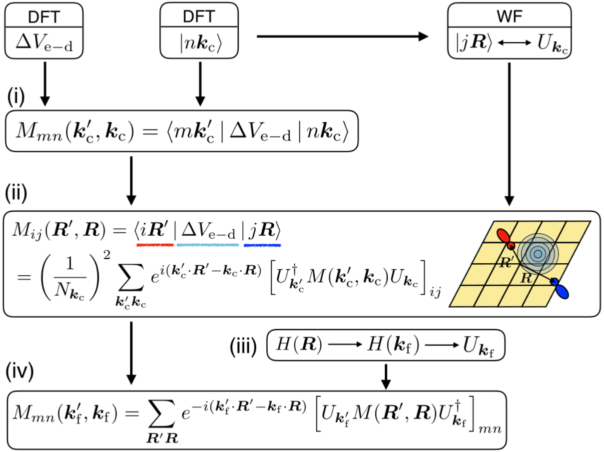

GaAs

N.-E. Lee, J.J. Zhou, H.-Y. Chen, and M. Bernardi, Nature Commun. **11**, 1607 (2020)




GaAs

A. Y. Choi, P. S. Cheng, B. Hatanpää, and A. J. Minnich, Phys. Rev. Materials **5**, 044603 (2021)




I.-T. Lu, J. Park, J.-J. Zhou, and M. Bernardi, npj Comput. Mater. **6**, 17 (2020)

# Conclusion

- The Boltzmann transport equation can be obtained from a rigorous many-body framework
- Long-range electrostatics is important for accurate interpolation
- The Hall factor is temperature dependent and can deviate from unity
- BTE mobilities overestimates experiment

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# Supplemental Slides

- Local velocity approximation
- Neglect of quadrupoles
- SOC for hole mobility
- Self energy relaxation time approximation