

A Quality Factor B and Weighted Mobility μ_W

We begin from the definition of the thermoelectric quality factor,

$$B = \left(\frac{k_B}{e} \right)^2 \frac{\sigma_0}{\kappa_L} T, \quad (12)$$

where σ_0 (equivalently σ_{E_0} in the transport formulation) is the energy-independent conductivity prefactor. The term σ_0 can be explicitly written as

$$\sigma_0 = \frac{8\pi e^2}{3h^3} (2k_B T)^{3/2} (m_I^*)^{1/2} N_V \tau_0. \quad (13)$$

This form is particularly useful because it isolates the entire temperature dependence of σ_0 into the factor $(k_B T)^{3/2} \tau_0$.

To proceed, we determine τ_0 from the acoustic-deformation-potential scattering rate. Assuming that **intraband intravalley** scattering constitutes the sole operative scattering mechanism, as discussed in Sec. B.5, Eq. (52) gives

$$\tau^{-1}(E) = \tau_0^{-1} \left(\frac{E}{k_B T} \right)^{1/2} = \frac{\pi D_A^2 k_B T}{\hbar c_l} g(E). \quad (14)$$

Using the single-valley density of states and Eq. (9),

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2m_I^*}{\hbar^2} \right)^{3/2} E^{1/2}, \quad (15)$$

we obtain

$$\begin{aligned} \tau_0^{-1} \left(\frac{E}{k_B T} \right)^{1/2} &= \frac{\pi D_A^2 k_B T}{\hbar c_l} \cdot \frac{1}{2\pi^2} \left(\frac{2m_I^*}{\hbar^2} \right)^{3/2} E^{1/2} \\ &= \frac{D_A^2}{2\pi \hbar c_l} \left(\frac{2m_I^* k_B T}{\hbar^2} \right)^{3/2} \left(\frac{E}{k_B T} \right)^{1/2}. \end{aligned} \quad (16)$$

Since both sides are proportional to $E^{1/2}$, the energy dependence identically cancels, yielding

$$\tau_0^{-1} = \frac{D_A^2 (k_B T)^{3/2}}{2\pi \hbar c_l} \left(\frac{2m_I^*}{\hbar^2} \right)^{3/2}. \quad (17)$$

Therefore, the relaxation time prefactor is

$$\tau_0 = \frac{2\pi \hbar c_l}{D_A^2 (k_B T)^{3/2}} \left(\frac{\hbar^2}{2m_I^*} \right)^{3/2} = \frac{\pi \hbar^4 c_l}{\sqrt{2} D_A^2 (m_I^*)^{3/2} (k_B T)^{3/2}}. \quad (18)$$

Substituting Eq. (18) back into Eq. (13) yields

$$\begin{aligned} \sigma_0 &= \frac{8\pi e^2}{3h^3} (2k_B T)^{3/2} (m_I^*)^{1/2} N_V \left[\frac{\pi \hbar^4 c_l}{\sqrt{2} D_A^2 (m_I^*)^{3/2} (k_B T)^{3/2}} \right] \\ &= \frac{16\pi^2 e^2 \hbar^4}{3h^3} \frac{N_V c_l}{m_I^* D_A^2}. \end{aligned} \quad (19)$$

Using the relation $h = 2\pi\hbar$, this simplifies to

$$\sigma_0 = \frac{16\pi^2 e^2 \hbar^4}{3(2\pi\hbar)^3} \frac{N_V c_l}{m_I^* D_A^2} = \frac{2e^2 \hbar}{3\pi} \frac{N_V c_l}{m_I^* D_A^2}. \quad (20)$$

Finally, inserting this result into the definition of B gives

$$\begin{aligned} B &= \left(\frac{k_B}{e} \right)^2 \frac{1}{\kappa_L} \left(\frac{2e^2 \hbar}{3\pi} \frac{N_V c_l}{m_I^* D_A^2} \right) T \\ &= \frac{2k_B^2 \hbar}{3\pi} \frac{N_V c_l}{m_I^* D_A^2 \kappa_L} T. \end{aligned} \quad (21)$$

Similarly, the weighted mobility μ_W can be analytically expressed as

$$\begin{aligned}\mu_W &= \tau_0 N_V \frac{e}{m_I^*} \left(\frac{m_I^*}{m_e} \right)^{\frac{3}{2}} \\ &= \frac{e N_V}{m_I^*} \frac{\pi \hbar^4 c_l}{\sqrt{2} D_A^2 (m_e k_B T)^{\frac{3}{2}}}.\end{aligned}\quad (22)$$

Critically, this standard derivation explicitly demonstrates that the linear scaling of μ_W and B with N_V is mathematically contingent upon the assumption that the relaxation time τ_0 is dictated *exclusively* by the single-valley density of states, effectively ignoring the expanded phase space generated by intervalley scattering.

A.1 Valley-resolved conductivity relation with Scattering Rate

The current density contributed by valley with index ν can be expressed as

$$\mathbf{J}_\nu = -e \sum_{\mathbf{k} \in \nu} \mathbf{v}_\nu(\mathbf{k}) f_\nu(\mathbf{k}), \quad \nu = 1, 2, \quad (23)$$

where $\mathbf{v}_\nu(\mathbf{k}) = \hbar^{-1} \nabla_{\mathbf{k}} E_\nu(\mathbf{k})$ is the band velocity in valley ν .

At thermal equilibrium, the distribution in each valley is isotropic,

$$f_\nu(\mathbf{k}) = f_\nu^{(0)}(\mathbf{k}), \quad (24)$$

and the contributions from opposite states cancel, so that $\mathbf{J} = 0$. Under an external electric field $\mathbf{E}$, the carrier distribution is driven out of equilibrium,

$$f_\nu(\mathbf{k}) = f_\nu^{(0)}(\mathbf{k}) + \delta f_\nu(\mathbf{k}), \quad (25)$$

where $\delta f_\nu(\mathbf{k})$ denotes the non-equilibrium anisotropic part. This anisotropy is the origin of the drift current. The current is therefore controlled by the field-induced anisotropy δf_ν , rather than by the equilibrium part $f_\nu^{(0)}$. Scattering opposes this process by redistributing carriers in momentum space and pushing the distribution back toward a more isotropic form.

In the simplest relaxation-time approximation,

$$\left(\frac{\partial f_\nu}{\partial t} \right)_{\text{coll}} \simeq - \frac{f_\nu - f_\nu^{(0)}}{\tau_\nu}, \quad (26)$$

where τ_ν is interpreted as an effective relaxation time for valley ν rather than as an exact transport lifetime. Substituting $f_\nu = f_\nu^{(0)} + \delta f_\nu$ into the steady-state Boltzmann equation gives

$$-\frac{e\mathbf{E}}{\hbar} \cdot \nabla_{\mathbf{k}} f_\nu^{(0)} \simeq - \frac{\delta f_\nu}{\tau_\nu}, \quad (27)$$

or equivalently,

$$\delta f_\nu(\mathbf{k}) \simeq \tau_\nu \frac{e\mathbf{E}}{\hbar} \cdot \nabla_{\mathbf{k}} f_\nu^{(0)}. \quad (28)$$

Hence the nonequilibrium anisotropy satisfies

$$\delta f_\nu \propto \tau_\nu. \quad (29)$$

This relation shows directly that a longer relaxation time allows the electric field to build up a larger asymmetry in the distribution, and therefore a larger drift current. Conversely, a shorter relaxation time (higher scattering rate) destroys the field-induced anisotropy more rapidly, so the current is reduced. In the simplest one-valley form, this yields the familiar Drude-like result

$$\sigma = \frac{ne^2\tau}{m^*}, \quad (30)$$

which makes explicit that the conductivity is proportional to the relaxation time.

A.2 Quality Factor B for Multiband Carriers

We consider two valleys, labeled 1 and 2, with distribution functions $f_1(\mathbf{k})$ and $f_2(\mathbf{k})$. The total current is written as the sum of the current contributed by each valley,

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2. \quad (31)$$

Within the two-valley picture, intervalley scattering has two simultaneous effects. First, it removes carriers from the source valley and therefore reduces the anisotropic, current-carrying part of that valley's distribution. Second, it injects carriers into the target valley with a distribution that generally differs from the one that valley would have developed under the electric field alone. Therefore, intervalley scattering modifies both valley-resolved currents, $\mathbf{J}_1$ and $\mathbf{J}_2$, even though it is only one physical scattering channel.

In this case, we can adopt the bipolar zT equation to get a Quality Factor B for multivalley carrier transport with different inertial effective masses,

$$zT = \frac{\left(\frac{S_p + S_n}{\sigma}\right)^2 (\sigma_p + \sigma_n)}{L_p \sigma_p T + L_n \sigma_n T + \kappa_L + \kappa_B} T \quad (32)$$

$$= \frac{(\sigma'_p S'_p + \sigma'_n S'_n)^2}{\frac{1}{B_p F_0(\eta_p) + B_n F_0(\eta_n)} + \sigma'_p L'_p + \sigma'_n L'_n + \sigma'_p \sigma'_n (S'_p - S'_n)^2},$$

where the conductivity, Seebeck coefficient, and Lorenz number are denoted by $\sigma = \sigma_n + \sigma_p$, S , L respectively for positive and negative carrier type, and their dimensionless form $\sigma'_i = \sigma_i/\sigma$, $S' = S/(k_B/e)$, and $L' = L/(k_B/e)^2$. Since the chemical potential is the same for the degenerate valleys, the quality factor can be decomposed linearly as

$$B = \left(\frac{k_B}{e}\right)^2 \frac{\sum_i \sigma_{0,i} T}{\kappa_L} \quad (33)$$

$$\propto \sum_i \frac{\sqrt{m_{I,i}^*}}{(\tau_{0,intra,i}^{-1} + \sum_{j \neq i} \tau_{0,i \rightarrow j}^{-1})}. \quad (34)$$

B Derivation From Fermi's Golden Rule

When analyzing electronic transitions from an initial to a final state in a crystal lattice, one must account for both the continuous momentum vector $|\mathbf{k}\rangle$ and the cell-periodic Bloch state vector $|\mathbf{c}\rangle$. Thus, the complete state vector is represented as a direct product:

$$|i\rangle = |\mathbf{k}, \mathbf{c}\rangle = |\mathbf{k}\rangle |\mathbf{c}\rangle, \quad (35)$$

where the final state follows analogously as $|f\rangle = |\mathbf{k}', \mathbf{c}'\rangle$.

B.1 Deformation Hamiltonian Matrix Element Derivation

When an electron interacts with a phonon due to lattice deformation, the perturbing Hamiltonian H' is defined by the deformation potential scaled by the macroscopic lattice dilation $\nabla \cdot \mathbf{u}(\mathbf{r})$. This can be expressed through a Fourier expansion of the phonon-induced displacements:

$$H' = D \nabla \cdot \mathbf{u}(\mathbf{q}, \mathbf{r})$$

$$= \sum_{\mathbf{q}} \left[\frac{\hbar}{2\rho\Omega\omega_q} \right]^{\frac{1}{2}} (a_{\mathbf{q}} + a_{-\mathbf{q}}) \exp(i\mathbf{q} \cdot \mathbf{r}) iD_{lj} q_l \lambda_j.$$

With the above formulation, the transition matrix element can be expanded as:

$$\langle \mathbf{k}', \mathbf{c}' | H' | \mathbf{k}, \mathbf{c} \rangle = \sum_{\mathbf{q}} \langle \mathbf{c}' | \mathcal{H}'(\mathbf{q}, \mathbf{u}) | \mathbf{c} \rangle$$

$$\times \int d\mathbf{r} \psi_{\mathbf{k}'}^\dagger(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}), \quad (36)$$

where the Fourier coefficient of the perturbation is isolated as:

$$\mathcal{H}'(\mathbf{q}, \mathbf{u}) = \left[\frac{\hbar}{2\rho\Omega\omega_q} \right]^{\frac{1}{2}} (a_{\mathbf{q}} + a_{-\mathbf{q}}) iD_{lj} q_l \lambda_j. \quad (37)$$

B.2 Bloch-State Overlap and $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory

According to Bloch's theorem, an electron in a periodic crystal lattice (comprising N unit cells) can be described by a wavefunction:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (38)$$

which is the product of a plane wave and the cell-periodic Bloch function $u_{\mathbf{k}}(\mathbf{r})$.

The spatial integral in Eq. 36 governs the fundamental momentum and orbital selection rules. We define the isolated Bloch overlap integral within a single unit cell as $\mathcal{I}$. In an intervalley scattering scenario, $\mathcal{I}$ can be evaluated as:

$$\mathcal{I} = \int_{cell} d\mathbf{r}'' u_{\mathbf{k}'}^\dagger(\mathbf{r}'') \exp(i(\mathbf{k} - \mathbf{k}' + \mathbf{q}) \cdot \mathbf{r}'') u_{\mathbf{k}}(\mathbf{r}'')$$

$$= \int_{cell} d\mathbf{r}'' u_{\mathbf{k}'+\mathbf{k}_0}^\dagger(\mathbf{r}'') u_{\mathbf{k}}(\mathbf{r}''). \quad (39)$$

Consequently, the full matrix element from Eq. 36 simplifies to:

$$\begin{aligned} \langle \mathbf{k}', \mathbf{c}' | H' | \mathbf{k}, \mathbf{c} \rangle &= \mathcal{I} \sum_{\mathbf{q}} \langle \mathbf{c}' | a_{\mathbf{q}} + a_{-\mathbf{q}} | \mathbf{c} \rangle \\ &\times \left[\frac{\hbar}{2\rho\Omega\omega_q} \right]^{\frac{1}{2}} iD_{lj}q_l\lambda_j. \end{aligned} \quad (40)$$

Expanding the integral over the entire crystal volume reveals the momentum conservation constraint:

$$\begin{aligned} \int d\mathbf{r} \psi_{\mathbf{k}'}^\dagger(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}) \\ = \sum_{\mathbf{R}} \exp(i(\mathbf{k} - \mathbf{k}'' + \mathbf{q}) \cdot \mathbf{R}) \frac{1}{N} \mathcal{I} \\ = \begin{cases} \mathcal{I}, & \text{if } \mathbf{k} - \mathbf{k}'' + \mathbf{q} = \mathbf{G}, \\ 0, & \text{if } \mathbf{k} - \mathbf{k}'' + \mathbf{q} \neq \mathbf{G}, \end{cases} \end{aligned} \quad (41)$$

where $\mathbf{G}$ is a reciprocal lattice vector. The crystal sum, and hence the corresponding transition matrix element, vanishes when this momentum-conservation condition is not satisfied. Note that $\mathbf{k}' = \mathbf{k}'' - \mathbf{k}_0$ represents the final electron momentum state mapped relative to the valley separation vector $\mathbf{k}_0$, reducing to $\mathbf{k}' = \mathbf{k}''$ for pure intravalley scattering.

To evaluate the analytical dependence of the overlap magnitude $\mathcal{I}$ on the momentum shift $\Delta\mathbf{k}$, we employ $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. In a periodic lattice, the cell-periodic function $u_{n\mathbf{k}}(\mathbf{r})$ satisfies:

$$E_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}) = \left(\frac{p^2}{2m} + \frac{\hbar\mathbf{k} \cdot \mathbf{p}}{m} + V(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}).$$

The $\mathbf{k} \cdot \mathbf{p}$ method allows us to estimate the wave-function evolution at a shifted momentum $\mathbf{k}_0 + \Delta\mathbf{k}$. While degenerate perturbation theory is traditionally required at highly symmetric, fully degenerate band extrema (like the valence band maximum in zinc-blende structures), scattering events involving large momentum transfers typically shift the carrier to a general finite $\mathbf{k}_0$ where these exact degeneracies are broken. We can therefore reasonably apply the standard non-degenerate perturbation expansion for the Bloch periodic function up to the second order:

$$\begin{aligned} u_{n,\mathbf{k}_0+\Delta\mathbf{k}} &= u_{n\mathbf{k}_0} + \frac{\hbar}{m} \sum_{n' \neq n} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n'\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{n',\mathbf{k}_0}} u_{n'\mathbf{k}_0} \\ &+ \frac{\hbar^2}{m^2} \sum_{n' \neq n} \sum_{n'' \neq n} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n''\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{n'',\mathbf{k}_0}} \frac{\langle u_{n''\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n'\mathbf{k}_0} \rangle}{E_{n'',\mathbf{k}_0} - E_{n',\mathbf{k}_0}} u_{n'\mathbf{k}_0} \\ &- \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{n',\mathbf{k}_0}} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n'\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{n',\mathbf{k}_0}} u_{n'\mathbf{k}_0} \\ &- \frac{1}{2} \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n'\mathbf{k}_0} \rangle|^2}{(E_{n,\mathbf{k}_0} - E_{n',\mathbf{k}_0})^2} u_{n\mathbf{k}_0}. \end{aligned} \quad (42)$$

For the **intraband** case ($\Delta N = 0$), evaluating the inner product yields:

$$\begin{aligned} \langle u_{n,\mathbf{k}_0+\Delta\mathbf{k}} | u_{n\mathbf{k}_0} \rangle &= 1 - \frac{1}{2} \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n'\mathbf{k}_0} \rangle|^2}{(E_{n,\mathbf{k}_0} - E_{n',\mathbf{k}_0})^2} \\ &\leq 1. \end{aligned} \quad (43)$$

Consistent with the wavefunction normalization, the first-order correction vanishes due to orthogonality, ensuring that the intraband overlap decays quadratically ($\mathcal{O}(\Delta\mathbf{k}^2)$) from a maximum of exactly 1 at $\Delta\mathbf{k} = 0$.

Conversely, the exact magnitude trend for the **interband** case ($\Delta N \neq 0$) is fundamentally different:

$$\begin{aligned}
& \langle u_{n,\mathbf{k}_0+\Delta\mathbf{k}} | u_{m\mathbf{k}_0} \rangle \\
&= \frac{\hbar}{m} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{m\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{m,\mathbf{k}_0}} \\
&+ \frac{\hbar^2}{m^2} \sum_{n'' \neq n} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n''\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{n'',\mathbf{k}_0}} \\
&\quad \times \frac{\langle u_{n''\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{m\mathbf{k}_0} \rangle}{E_{n'',\mathbf{k}_0} - E_{m,\mathbf{k}_0}} \\
&- \frac{\hbar^2}{m^2} \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{n\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{m,\mathbf{k}_0}} \\
&\quad \times \frac{\langle u_{n\mathbf{k}_0} | \Delta\mathbf{k} \cdot \mathbf{p} | u_{m\mathbf{k}_0} \rangle}{E_{n,\mathbf{k}_0} - E_{m,\mathbf{k}_0}}.
\end{aligned} \tag{44}$$

Because the initial wavefunctions $|u_{n\mathbf{k}_0}\rangle$ and $|u_{m\mathbf{k}_0}\rangle$ are strictly orthogonal, the zeroth-order term is zero. Therefore, to leading order, the interband overlap amplitude increases linearly with the momentum shift $\Delta\mathbf{k}$, while its squared magnitude increases quadratically:

$$|\mathcal{I}_{n,m,\Delta\mathbf{k}}|^2 = \begin{cases} 1 - \mathcal{O}(|\Delta\mathbf{k}|^2), & (n = m), \\ \mathcal{O}(|\Delta\mathbf{k}|^2), & (n \neq m). \end{cases} \tag{45}$$

The nondegenerate $k \cdot p$ expansion above is used only to establish the limiting powers of $|\Delta k|$ away from exact degeneracies. At an exactly degenerate band edge, the electronic basis should formally be obtained using degenerate perturbation theory; accordingly, Eq. 45 is used here as a qualitative limiting constraint on the pseudo-overlap descriptor rather than as a universal finite- Δk expression.

Although higher-order summation terms modulate this behavior across the Brillouin zone, this gives the limiting behavior in which the interband overlap vanishes at zero momentum separation ($|\mathbf{k}_0| = 0$) and increases at finite separations, corroborating the contrasting topological behaviors observed in Eq. 10 in the main text.

B.3 Numerical Approach of the Model

Equation 8 is evaluated numerically by representing each isotropic parabolic band constant-energy surface with a Fibonacci sphere. The Fibonacci construction provides an approximately uniform angular distribution of points on the sphere. Each sampled state is stored as a four-component array,

$$\left[k_x, k_y, k_z, \frac{1}{|\nabla_{\mathbf{k}} E|} \right]. \tag{46}$$

The first three components specify the reciprocal-space position, whereas the fourth component is the Jacobian weight that appears when the energy-conserving delta function is converted into an integral over the final-state constant-energy surface. Energy conservation determines the radius of the final-state surface directly. For elastic scattering, at each initial state $\mathbf{k}_i$, we do the algebra to find the set of $\{q\}$ to all the final states $\mathbf{k}_f$ directly. For inelastic scattering, the final state radius and momentum transfer are coupled through energy conservation. The allowed $\mathbf{k}_f$ and $\mathbf{q}$ are therefore solved self-consistently for each final state direction.

The factors $\mathcal{I}(\mathbf{q})$ and M_q^2 are evaluated separately for each final state, where M_q^2 contains the mechanism-specific q -dependence listed in Table. 1. The integrand $M_q^2 \mathcal{I}(\mathbf{q}) / |\nabla_{\mathbf{k}} E_f|$ is multiplied by the area dS of each triangular surface element and summed over the constant-energy surface. The sampled final state surface is triangulated using `scipy.spatial.ConvexHull`. Because the distribution of momentum-transfer magnitudes depends on the orientation of $\mathbf{k}_i$, the calculation is repeated over symmetry-inequivalent initial states and the resulting integrals are averaged with the appropriate weights. Finally, the result is multiplied by the physical prefactors $n_s M_0^2$ to obtain the scattering rate.

The computational cost can be reduced by exploiting the symmetry of the isotropic surfaces. For zone-center scattering, symmetry equivalent orientations of $\mathbf{k}_i$ generate identical momentum transfer distributions, so only one representative initial state is required. For intervalley scattering, the valley separation vector $\mathbf{k}_0$ breaks the full spherical symmetry. It is nevertheless sufficient to sample only the symmetry nonequivalent arc in the plane containing $\mathbf{k}_0$, rather than the complete initial-state sphere.

B.4 Transition Rate and Phonon Occupation

To evaluate the transition rate, strict momentum conservation dictates the allowable phonon wavevectors $\mathbf{q}$ that facilitate an electronic transition across a valley separation vector $\mathbf{k}_0$. For phonon absorption and emission, this requirement yields

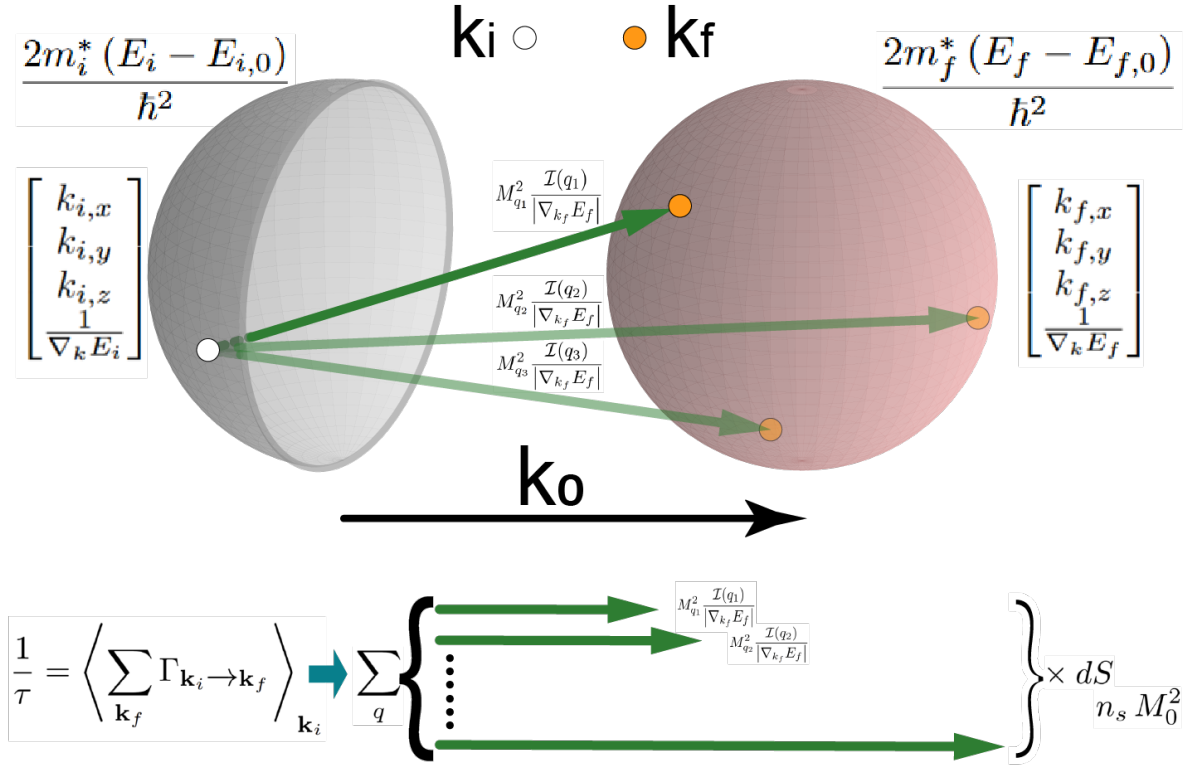


Fig. 5 Numerical evaluation of the final-state surface integral. For each initial state $\mathbf{k}_i$, the allowed final states $\mathbf{k}_f$ are sampled on a constant-energy surface. Each final-state point carries the weight $M_q^2 \mathcal{I}(q) / |\nabla_{\mathbf{k}_f} E_f|$. The weighted surface is triangulated and summed, averaged over the symmetry-nonequivalent initial states, and multiplied by the physical prefactors $n_s M_0^2$.

the following equalities, respectively:

$$\mathbf{q} = \begin{cases} \mathbf{k}_f - \mathbf{k}_i + \mathbf{k}_0, & (\text{absorption}), \\ \mathbf{k}_i - \mathbf{k}_f - \mathbf{k}_0, & (\text{emission}), \end{cases} \quad (47)$$

Here $\mathbf{k}_0$ is the minimum reciprocal-lattice-equivalent valley separation defined in Sec. 1.

The transition probabilities are heavily governed by the phonon occupation numbers, which arise from the phononic operators acting on the system's Fock states:

$$\begin{aligned} \langle \mathbf{c}' | a_{-\mathbf{q}} | \mathbf{c} \rangle &= \sqrt{N_q + 1} \\ \langle \mathbf{c}' | a_{\mathbf{q}} | \mathbf{c} \rangle &= \sqrt{N_q} \end{aligned}$$

Because phonon absorption and emission are mutually exclusive events, their transition probabilities sum independently. By incorporating the allowable $\mathbf{q}$ values and assuming a highly symmetric lattice where the deformation potential tensor effectively reduces to an isotropic scalar ($|D_{lj} q_l \lambda_j|^2 \approx D^2 q^2$), the transition rate from Eq. 4 becomes:

$$\begin{aligned} \Gamma_{i \rightarrow f} &= \delta(E_f - E_i - \Delta E) \left[\frac{\pi}{\rho \Omega \omega_q} \right] \mathcal{I}^2 D^2 q^2 \\ &\times \begin{cases} N_q, & (\text{absorption}), \\ N_q + 1, & (\text{emission}). \end{cases} \end{aligned} \quad (48)$$

B.5 Lundstrom Phonon Integration Approach

Due to momentum conservation, the final electronic state $\mathbf{k}'$ can be uniquely mapped to the phonon wavevector $\mathbf{q}$. Consequently, the discrete scattering rate summation over $\mathbf{q}$ (Eq. 48) can be transformed into a continuous integral over

spherical coordinates:

$$\begin{aligned} \frac{1}{\tau} &= \sum_{\mathbf{q}} \Gamma_{\mathbf{k} \rightarrow \mathbf{k}'} \\ &= \frac{\Omega}{(2\pi)^3} \int_0^{2\pi} \int_0^\infty \left(N_q + \frac{1}{2} \mp \frac{1}{2} \right) C_q q^2 \int \delta(q, \theta) d\theta dq d\phi, \end{aligned} \quad (49)$$

where $\frac{\Omega}{(2\pi)^3}$ is the density of states in $\mathbf{q}$ -space (with Ω representing the crystal volume), N_q is the phonon occupation number following the Bose-Einstein distribution, and the upper and lower signs correspond to phonon absorption and emission, respectively. This integration encompasses all available phonons across varying magnitudes q and scattering angles (θ, ϕ) . The Dirac delta function $\delta(q, \theta)$ strictly enforces energy conservation, which geometrically dictates the allowable upper and lower integration bounds for the wavenumber q .

For deformation potential scattering, the coupling coefficients C_q are defined as:

$$C_q = \frac{\pi m^* D_{ac}^2}{\hbar \rho v_s \Omega (\hbar k)} \quad (\text{Acoustic Phonons}) \quad (50)$$

$$C_q = \frac{\pi m^* D_{op}^2}{\hbar \rho \omega_O q \Omega (\hbar k)} \quad (\text{Optical Phonons}) \quad (51)$$

where D_{ac} is the acoustic deformation potential (in Joules), D_{op} is the optical deformation potential (in J/m), ρ is the mass density, v_s is the acoustic sound velocity, and ω_O is the optical phonon frequency.

For acoustic deformation potential scattering, the quasi-elastic approximation restricts the allowable phonon wavenumber to the range $q \in [0, 2k]$, determined by both geometric constraints and the δ -function argument. Evaluating the integral yields:

$$\begin{aligned} \frac{1}{\tau} &= \frac{m^* D_{ac}^2 k_B T}{4\pi \hbar^3 c_l k} (q_{max}^2 - q_{min}^2) \\ &= \frac{m^* D_{ac}^2 k_B T k}{\pi \hbar^3 c_l} = \frac{\pi D_{ac}^2 k_B T}{\hbar c_l} g_C(E), \end{aligned} \quad (52)$$

where $g_C(E) = \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} E^{1/2}$ is the single-valley electronic density of states, and $c_l = \rho v_s^2$ represents the longitudinal elastic constant.

Conversely, for optical deformation phonon scattering, the assumption of a relatively constant ω_O modifies the energy conservation relation. The acceptable phonon wavenumbers are bounded by a maximum $q_{max} = k \left[1 + \sqrt{1 \pm \frac{\hbar \omega_O}{E_k}} \right]$, while the minimum bounds diverge for absorption and emission: $q_{min,abs} = k \left[-1 + \sqrt{1 + \frac{\hbar \omega_O}{E_k}} \right]$ and $q_{min,emi} = k \left[1 - \sqrt{1 - \frac{\hbar \omega_O}{E_k}} \right]$.

Integrating over these specific bounds yields the optical intravalley scattering rate:

$$\frac{1}{\tau} = \frac{m^* D_{op}^2 k}{2\pi \rho \hbar (\hbar \omega_O)} \left(N_O + \frac{1}{2} \mp \frac{1}{2} \right) \sqrt{1 \pm \frac{\hbar \omega_O}{E_k}}. \quad (53)$$

While the optical deformation potential (ODP) treated above relies on a momentum-independent matrix element D_{op} , polar semiconductors are heavily influenced by the long-range Fröhlich interaction. For polar optical phonon (POP) scattering, the perturbation matrix element is strongly dependent on the momentum exchange q :

$$|\mathcal{M}_{pop}|^2 \propto \frac{1}{q^2}. \quad (54)$$

In the context of multivalley band topologies, intravalley transitions involve small momentum transfer (where q is bounded by the Fermi surface diameter), leading to an intensely strong scattering response. Conversely, intervalley transitions necessitate a large momentum transfer $q \approx |\mathbf{k}_0|$. Because of the $1/q^2$ scaling, the Fröhlich contribution to intervalley scattering is severely suppressed relative to the intravalley channel. Therefore, while our simplified analytical model focuses on acoustic phonons to isolate the pure Bloch overlap ($\mathcal{I}_{n,m,\Delta\mathbf{k}}$) effects, the inclusion of POP scattering in our explicit DFT frameworks naturally leads to an even more pronounced divergence between intravalley and intervalley scattering rates, strictly reinforcing the primary conclusions of this work.

B.6 Linear Acoustic Phonon Dispersion

In our derivations, we assume acoustic deformation phonons have a linear dispersion relationship for which $\omega_q = v_s q$. With this relationship, the explicit q -dependence of the acoustic deformation-potential coupling cancels that of the equipartition phonon occupation N_q , leaving no residual q -dependence outside the overlap factor $\mathcal{I}$. However, acoustic phonon dispersion is generally linear only in the small- q regime and becomes sublinear toward larger q . For large- $\mathbf{k}_0$ intervalley processes, this sublinear relation can increase the predicted intervalley scattering rate relative to the linear-dispersion approximation.

Here, we simply test the scattering rate with an Einstein-like large- q limiting dispersion, for which $\omega_q \approx \omega_0$ in NbFeSb. In this limiting case, the cancellation of the explicit q -dependence is no longer complete, and the residual coupling factor acquires an approximately $M_q^2 \propto q^2$ dependence. We find that the ratios, $\tau_{inter}^{-1}/\tau_{intra}^{-1}$, shown below remain smaller than

one.	$\frac{I_{pseudo}}{I_{DFT}}$	$m_{heavy} \rightarrow m_{light}$	$m_{light} \rightarrow m_{heavy}$
		0.191	0.281
		0.004	0.014

C First-Principles Calculations

First-principles electronic and phonon band structures were computed within the frameworks of density functional theory (DFT) and density functional perturbation theory (DFPT), as implemented in the Quantum ESPRESSO package [43]. Exchange-correlation interactions were described using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [44], in conjunction with norm-conserving Martins-Troullier pseudopotentials [45]. Spin-orbit coupling and van der Waals interactions were not included in the present calculations. To simulate p -type doping across the investigated material systems (including PbTe, ZnSe, and NbFeSb), the rigid band approximation was employed. Electron-phonon coupling (EPC) matrix elements and subsequent scattering rates were evaluated using the EPW code [36]. To achieve rigorous convergence of the electron-phonon scattering rates at $T = 300$ K, the electronic and phononic states were interpolated onto an ultra-dense $200 \times 200 \times 200$ Brillouin-zone $\mathbf{k}$ - and $\mathbf{q}$ -point mesh for PbTe and $40 \times 40 \times 40$ for NbFeSb and ZnSe using maximally localized Wannier functions (MLWFs) [46]. Furthermore, the long-range screened polar (Fröhlich) interaction was explicitly included to accurately capture the scattering contributions from longitudinal optical phonons.

D Acoustic-Phonon-Mediated Intervalley Scattering and Literature Comparison

Assuming a highly populated acoustic phonon regime (the high-temperature classical limit) and a linear phonon dispersion relation, the overall scattering rate is obtained by summing Eq. 48 over all possible final states $\mathbf{k}'$:

$$\begin{aligned}
 \frac{1}{\tau} &= \sum_{\mathbf{k}'} \Gamma_{\mathbf{k} \rightarrow \mathbf{k}'} \\
 &= \sum_{\mathbf{k}'} \left[\frac{\pi \mathcal{I}^2 D^2 q^2}{\rho \Omega v_s q} \right] \frac{k_B T}{\hbar v_s q} \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \\
 &\approx \frac{\mathcal{I}_{\mathbf{k}_0}^2 D^2 k_B T}{8\pi^2 \rho \hbar v_s^2} \int d^3 \mathbf{k}' \delta \left(\frac{\hbar^2}{2m} (k'^2 - k^2) \right).
 \end{aligned} \tag{55}$$

Assuming that the final state $\mathbf{k}'$ spans a full sphere of available states—a geometrically valid approximation for both intravalley scattering and intervalley scattering when the momentum transfer satisfies $|\mathbf{k}_0| \geq 2|\mathbf{k}| \approx 2|\mathbf{k}'|$ —the volume integral over $\mathbf{k}'$ -space can be rigorously evaluated as a surface integral by exploiting the energy-conserving Dirac delta function:

$$\begin{aligned}
 \int d^3 \mathbf{k}' \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) &= \int k'^2 dk' d\Omega \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \\
 &= \int \frac{k'^2 d\Omega dE}{|dE/dk|} \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) \\
 &= \int \frac{k'^2 d\Omega}{|dE/dk|} = \frac{4\pi m k}{\hbar^2}.
 \end{aligned} \tag{56}$$

Substituting this phase-space integral back into the rate equation resolves the explicit intravalley scattering rate. For the intervalley case, where an electron scatters between valleys separated by the vector $\mathbf{k}_0$, the momentum conservation constraint ($\pm \mathbf{q} = \mathbf{k}' - \mathbf{k} + \mathbf{k}_0$) must be strictly enforced. Provided there is a sufficient phonon population to satisfy this momentum matching, the integration yields an identical functional form, assuming $|\mathbf{k}| \approx |\mathbf{k}'|$. However, the intervalley

scattering magnitude is fundamentally modulated by the squared overlap integral $\mathcal{I}_{\mathbf{k}_0}^2$, which decays as the valley separation $\mathbf{k}_0$ increases:

$$\frac{1}{\tau} = \frac{\mathcal{I}_{\mathbf{k}_0}^2 D^2 k_B T m}{2\pi \hbar^3 c_l} k, \quad (57)$$

where the analytical overlap function defined in Eq. 10 dictates the ultimate suppression behavior.

The analytical expressions for intravalley and intervalley scattering mechanisms derived from Eq. 49 have been extensively discussed in standard transport literature and textbooks [19, 21–24]. In conventional treatments, the Bloch overlap factor is typically approximated as $|\mathcal{I}_{n,m,\Delta\mathbf{k}}|^2 \approx 1$ for intravalley scattering. Conversely, for intervalley scattering, the intricate overlap effects and interaction potentials are frequently absorbed into a phenomenological intervalley deformation potential, D_{if} [24, 32].

The standard literature expression for intervalley scattering generally takes a form similar to Eq. 53:

$$\frac{1}{\tau} = \frac{m^* D_{if}^2 Z_f k}{2\pi \rho \hbar (\hbar \omega_{if})} \left(N_i + \frac{1}{2} \mp \frac{1}{2} \right) \sqrt{1 + \frac{\pm \hbar \omega_{if} - \Delta E_{if}}{E_k}}, \quad (58)$$

where $\hbar \omega_{if}$ is the characteristic intervalley phonon energy, ΔE_{if} is the energy offset between the initial and final valley extrema, and Z_f represents the degeneracy of the final receiving valleys. While alternative methods exist—such as empirically fitting scattering matrix elements [47], which generally aligns well only with optical deformation results—these approaches remain heavily parameterized.

Crucially, subsuming all intervalley scattering complexities into a single empirical parameter D_{if} heavily obscures the underlying physical insights. Although diverse experimental and numerical methods attempt to accurately quantify D_{if} to evaluate the intervalley scattering rate [48], this phenomenological approach limits predictive capability, particularly in advanced material engineering where band topologies are deliberately modified via alloying or strain. Therefore, in this paper, we explicitly formulate an acoustic-phonon-mediated intervalley scattering model that parallels the analytical transparency of the intravalley framework, effectively unpacking the "black box" of D_{if} to isolate the topological $\mathbf{k}_0$ -dependence.

E Supplemental Model Prediction and EPW Calculations

Fig. 7 compares the energy-dependent scattering rates predicted by the analytical model with the EPW results over the relevant chemical potential ranges of PbTe and NbFeSb. The overlap integral used for the NbFeSb model prediction is shown in Fig. 6.

The model parameters are listed in Table 2.

Table 2 Parameters related to acoustic phonon scattering used in the model to predict the scattering rates in PbTe and NbFeSb.

Material	PbTe	NbFeSb
Lattice Constant ($\text{\AA}$)	6.46[49]	5.95[50]
Density ρ ($\times 10^3 \text{ kg/m}^3$)	8.24[51]	8.45[52, 53]
Longitudinal v_s ($\times 10^3 \text{ m/s}$)	3.62[51]	5.60[54]
Transverse v_s ($\times 10^3 \text{ m/s}$)	1.85[55]	3.10[54]
Effective Mass m_I^*/m_e	0.34(Σ)[56]	1.65(L)[50]
Acoustic Deformation D_a (eV)	1.87[57]	2.5[42]
Polar D_a (eV)		2.5[42]

F Other Transition Mechanisms

For optical deformation potential (ODP) scattering, the foundational assumptions differ significantly. Unlike the linear dispersion characteristic of acoustic modes, optical phonon energies are nearly independent of the phonon wavevector; thus, the optical phonon frequency ω_O can be treated as a constant. Because optical phonon energies are typically much higher than acoustic ones, their equilibrium occupation numbers are substantially lower. Consequently, the electron energy change during scattering is strictly non-negligible when determining the integration boundaries in momentum space. Notably, phonon emission is physically forbidden if the initial electron energy is less than the optical phonon quantum ($\hbar \omega_O$).

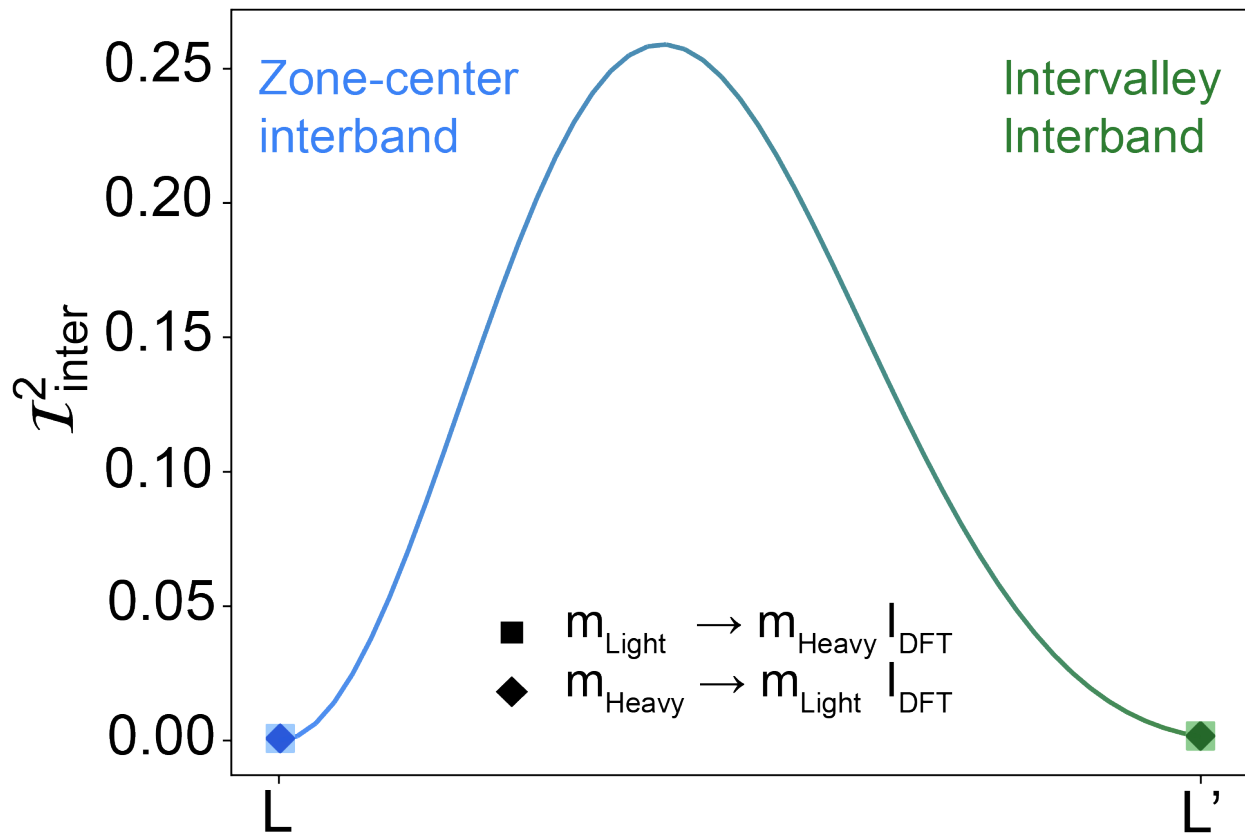


Fig. 6 $\mathcal{I}_{\text{pseudo}}^2$ in NbFeSb used to evaluate interband scattering results shown in Fig. 7d, g and Fig. 3b

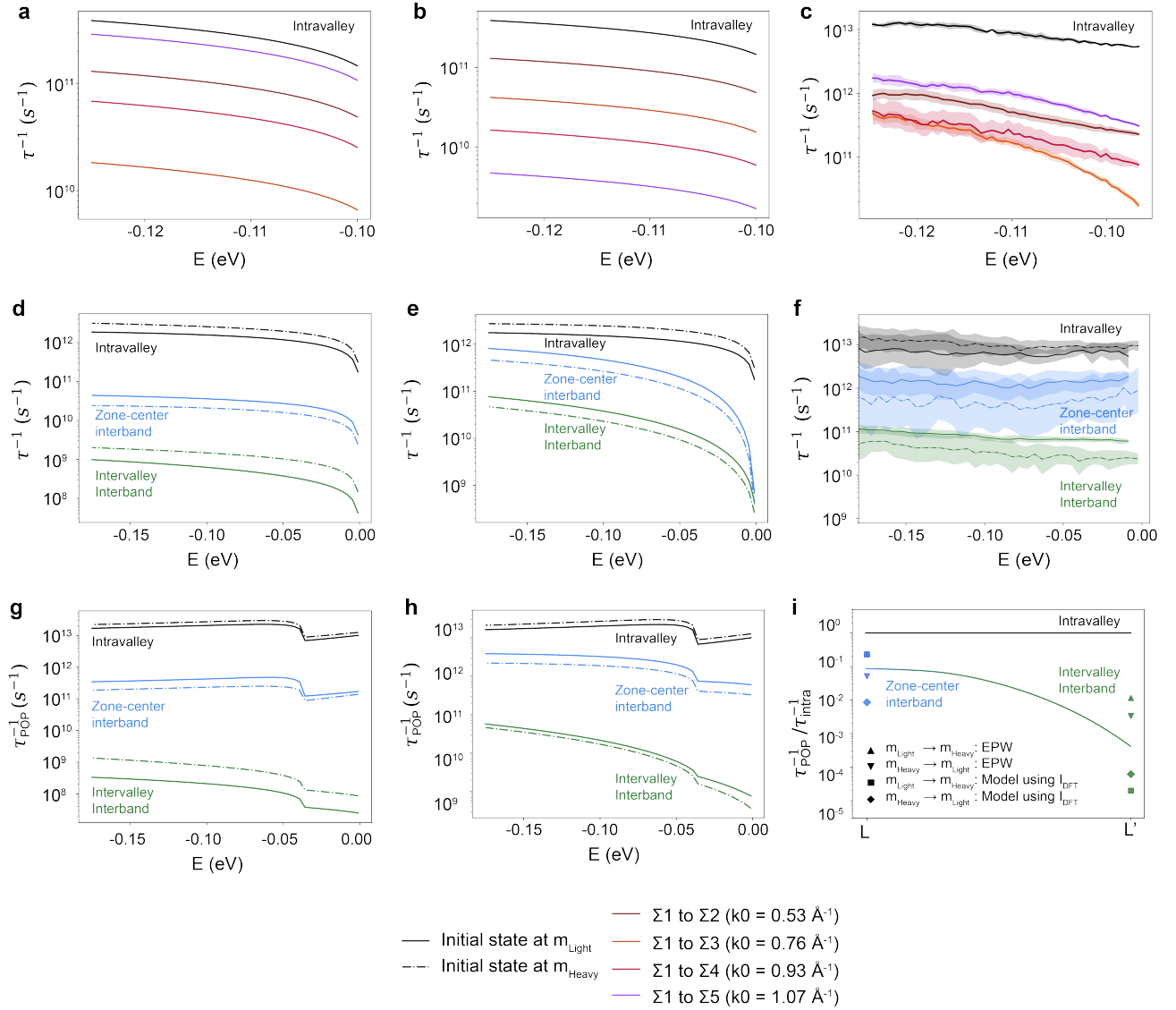


Fig. 7 Energy-dependent carrier scattering rates as a function of carrier energy relative to the Fermi level for (a)–(c) PbTe and (d)–(f) NbFeSb, obtained from (a,d) the model using $\mathcal{I}_{\text{DFT}}$, (b,e) the model using $\mathcal{I}_{\text{Pseudo}}$, and (c,f) first-principles EPW calculations; the error bars represent one standard deviation. Polar-optical-phonon scattering in NbFeSb, discussed in Appendix F.0.2 is shown in (g)–(i) and exhibits the same qualitative trend as the acoustic-phonon results.

Based on Fermi's Golden Rule, the intervalley scattering rate mediated by optical phonons can be formally expressed as:

$$\begin{aligned} \frac{1}{\tau_{op}} &= \frac{\Omega}{4\pi^2\hbar} \int \frac{\pi D_{op}^2 N_q}{2\rho\Omega\omega_O} \delta(E_{\mathbf{k}'} - E_{\mathbf{k}} - \hbar\omega_O) d^3\mathbf{k}' \\ &\quad + \frac{\Omega}{4\pi^2\hbar} \int \frac{\pi D_{op}^2 (N_q + 1)}{2\rho\Omega\omega_O} \delta(E_{\mathbf{k}'} - E_{\mathbf{k}} + \hbar\omega_O) d^3\mathbf{k}' \\ &= \frac{\pi D_{op}^2}{2\rho\omega_O} \begin{cases} g(E_{\mathbf{k}} + \hbar\omega_O) N_q, & \text{(absorption),} \\ g(E_{\mathbf{k}} - \hbar\omega_O) (N_q + 1), & \text{(emission).} \end{cases} \end{aligned} \quad (59)$$

While the optical deformation potential (ODP) treated above relies on a momentum-independent matrix element D_{op} , polar semiconductors are heavily influenced by the long-range Fröhlich interaction. For polar optical phonon (POP) scattering, the perturbation matrix element is strongly dependent on the momentum exchange q :

$$|\mathcal{M}_{pop}|^2 \propto \frac{1}{q^2}. \quad (60)$$

In the context of multivalley band topologies, intravalley transitions involve small momentum transfer (where q is bounded by the Fermi surface diameter), leading to an intensely strong scattering response. Conversely, intervalley transitions necessitate a large momentum transfer $q \approx |\mathbf{k}_0|$. Because of the $1/q^2$ scaling, the Fröhlich contribution to intervalley scattering is severely suppressed relative to the intravalley channel. Therefore, while our simplified analytical model focuses on acoustic phonons to isolate the pure Bloch overlap ($\mathcal{I}_{n,m,\Delta\mathbf{k}}$) effects, the inclusion of POP scattering in our explicit DFT frameworks naturally leads to an even more pronounced divergence between intravalley and intervalley scattering rates, strictly reinforcing the primary conclusions of this work.

F.0.1 Piezoelectric acoustic-phonon scattering

For acoustic piezoelectric scattering, the squared matrix element for one phonon process is

$$|M_{PE}(q)|^2 = \frac{\hbar e_0^2 p^2}{2\rho\Omega v_s q}, \quad (61)$$

where p is the effective piezoelectric coefficient. In the acoustic equi-partition limit, $N_q \approx \frac{k_B T}{\hbar v_s q}$.

Since absorption and emission contribute approximately equally, $N_q + 1 \approx N_q$, their combined squared matrix element, including both absorption and emission, is

$$2|M_{PE}(q)|^2 N_q = \frac{e_0^2 p^2 k_B T}{\rho v_s^2 \Omega \varkappa q^2} \propto q^{-2}, \quad (62)$$

where $c_l = \rho v_s^2$.

The momentum relaxation rate is

$$\frac{1}{\tau_{PE}(k)} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}'} |M_{PE}^{eq}(q)|^2 (1 - \cos\theta) \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}). \quad (63)$$

Replacing the sum by an integral,

$$\sum_{\mathbf{k}'} \rightarrow \frac{\Omega}{(2\pi)^3} \int d^3\mathbf{k}'. \quad (64)$$

For elastic scattering, $k' = k$, and

$$q^2 = |\mathbf{k}' - \mathbf{k}|^2 = 2k^2(1 - \cos\theta). \quad (65)$$

Substituting $\frac{1 - \cos\theta}{q^2} = \frac{1}{2k^2}$ gives

$$\begin{aligned} \frac{1}{\tau_{PE}(k)} &= \frac{2\pi}{\hbar} \frac{\Omega}{(2\pi)^3} \int \frac{e_0^2 p^2 k_B T}{c_l \Omega \varkappa q^2} (1 - \cos\theta) \\ &\quad \delta(E_{\mathbf{k}'} - E_{\mathbf{k}}) d^3\mathbf{k}'. \end{aligned} \quad (66)$$

Using

$$\begin{aligned} \int_0^\infty k'^2 \delta\left(\frac{\hbar^2 k'^2}{2m^*} - E_k\right) dk' &= \frac{m^* k}{\hbar^2} \\ \int d\Omega_{\mathbf{k}'} &= 4\pi, \end{aligned}$$

the momentum relaxation rate becomes

$$\frac{1}{\tau_{\text{PE}}(k)} = \frac{e_0^2 p^2 k_B T m^*}{2\pi \hbar^3 c_l \kappa} \frac{1}{k}. \quad (67)$$

Therefore,

$$\frac{1}{\tau_{\text{PE}}(E)} = \frac{e_0^2 p^2 k_B T}{2\pi \hbar^2 c_l \kappa} \sqrt{\frac{m^*}{2E}}. \quad (68)$$

, with parabolic band $k = \frac{\sqrt{2m^*E}}{\hbar}$.

Defining the effective piezoelectric coupling $\Pi_0^2 = \frac{p^2}{c_l}$, we obtain:

$$\frac{1}{\tau_{\text{PE}}(E)} = \frac{e_0^2 \Pi_0^2}{2\pi \hbar^2 \kappa} \left(\frac{m^* k_B T}{2} \right)^{1/2} \left(\frac{E}{k_B T} \right)^{-1/2}. \quad (69)$$

F.0.2 Polar optical-phonon scattering

For NbFeSb, we also evaluate the polar optical phonon (POP) scattering with its Thomas–Fermi screening. Using the previously reported material parameters $\hbar\omega_o = 36\text{meV}$, $m_{I^*} = 0.92m_e$, $\epsilon_s = 42.83$, and $\epsilon_\infty = 23.91$ [58, 59], we obtain the Thomas–Fermi screening wavevector magnitude:

$$\begin{aligned} n &= 2N_V \left(\frac{k_B T m_I^*}{2\pi \hbar^2} \right)^{\frac{3}{2}} F_{1/2}(\eta) \\ \frac{\partial n_i}{\partial \mu} &= 2N_{V,i} \left(\frac{k_B T m_{I,i}^*}{2\pi \hbar^2} \right)^{\frac{3}{2}} F_{-1/2}(\eta) \frac{1}{k_B T} \\ q_s^2 &= \frac{e^2}{\epsilon_0 \epsilon_\infty} \left(\frac{\partial n_1}{\partial \mu} + \frac{\partial n_2}{\partial \mu} \right) \\ &= \frac{e^2}{\epsilon_0 \epsilon_\infty k_B T} \left(\frac{k_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} \sum_i N_{V,i} m_{I,i}^{\frac{3}{2}} F_{-1/2}(\eta_i) \end{aligned}$$

The results are shown in Fig. 7(g)-(i). The results exhibit the same qualitative trend as the acoustic-phonon scattering rates, demonstrating that the framework can also be applied to other scattering mechanisms.