Symmetry-based orbital overlap rules for scattering in band-degenerate valleys

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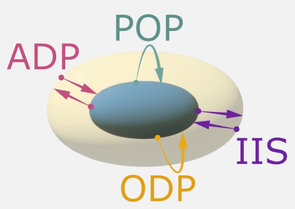
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The Fröhlich Hamiltonian

- The scattering rates of electrons can be obtained from Fermi's golden rule:

$$\frac{1}{\tau_{n\mathbf{k}}} = \frac{2\pi}{\hbar}\sum_{m\nu}\int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}}|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \times |(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}}-\hbar\omega_{\mathbf{q}\nu}-\varepsilon_{m\mathbf{k}+\mathbf{q}}) - f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}}+\hbar\omega_{\mathbf{q}\nu}-\varepsilon_{m\mathbf{k}+\mathbf{q}})|$$

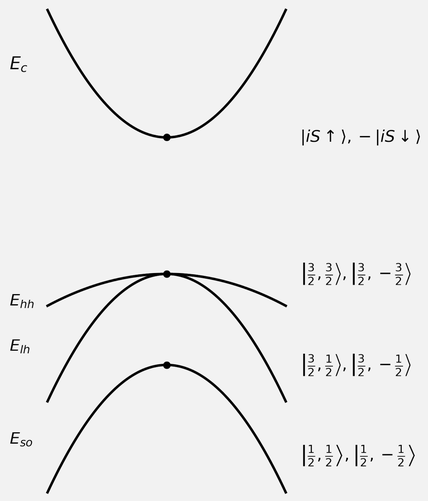
  where $g_{mn\nu}(\mathbf{k},\mathbf{q})$ is a coupling constant for electrons and phonons.
- We employ approximations to el-ph matrix elements by mechanisms: [1] (*e.g.* $|g_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \approx |S^{\mathrm{ADP/ODP}}_{\mathbf{k},\mathbf{k}'}| + |S^{\mathrm{POP}}_{\mathbf{k},\mathbf{k}'}|$)



  - Acoustic deformation potential $|S^{\mathrm{ADP}}_{\mathbf{k},\mathbf{k}'}| = \frac{2\pi}{\hbar}D^2_{\mathrm{ADP}}\frac{k_BT}{\rho v_S^2}g_{\mathbf{k}'}|I^{\mathbf{k}\mathbf{k}'}_{nm}|^2$
  - Optical deformation potential $|S^{\mathrm{ODP}}_{\mathbf{k},\mathbf{k}'}| = \frac{\pi D^2_{\mathrm{ODP}}}{\rho\omega}\left(N_\omega+\frac{1}{2}\mp\frac{1}{2}\right)g_{\mathbf{k}'}|I^{\mathbf{k}\mathbf{k}'}_{nm}|^2$
  - Polar optical phonon $|S^{\mathrm{POP}}_{\mathbf{k},\mathbf{k}'}| = \frac{\pi q_0^2\omega}{|\mathbf{k}-\mathbf{k}'|^2\epsilon_0^2}\left(\frac{1}{\kappa_\infty}-\frac{1}{\kappa_s}\right)\left(N_\omega+\frac{1}{2}\mp\frac{1}{2}\right)g_{\mathbf{k}'}|I^{\mathbf{k}\mathbf{k}'}_{nm}|^2$
  - Ionised impurity scattering $|S^{\mathrm{IIS}}_{\mathbf{k},\mathbf{k}'}| = \frac{2\pi}{\hbar}\frac{Z^2q_0^4}{\kappa_s^2\epsilon_0^2}\frac{N_{\mathrm{imp}}}{(|\mathbf{k}-\mathbf{k}'|^2+1/L_D^2)^2}g_{\mathbf{k}'}|I^{\mathbf{k}\mathbf{k}'}_{nm}|^2$
- In essence, they can be considered as the Born approximations, with the overlap integral factor defined as $|I^{\mathbf{k}\mathbf{k}'}_{nm}|^2 = |\langle u_{n\mathbf{k}}|u_{m\mathbf{k}'}\rangle|^2$.
- In a non-degenerate valley, $|I^{\mathbf{k}\mathbf{k}+\mathbf{q}}_{nn}|^2 = 1$ in the limit $\mathbf{q}\to 0$.

Heuristic model: Spherical Luttinger-Kohn Hamiltonian

- Analytical expressions for overlap factors are required for estimating matrix elements for bands in degenerate valleys.



- The Hamiltonian for holes in typical semiconductors can be given as:

$$H_{LK} = \frac{\hbar}{2m}\left[\left(\gamma_1+\frac{5}{2}\gamma_2\right)k^2 - 2\gamma_2(\mathbf{k}\cdot\mathbf{J})^2\right]$$

  with eigenstates: $\{|j=\pm\frac{3}{2}\rangle_{\mathbf{k}}, |j=\pm\frac{1}{2}\rangle_{\mathbf{k}}\}$.

The analytic overlap integrals expressions:

- $P_{HH} = P_{LL} = \sum_{\eta,\eta'=\pm1}|_{\mathbf{k}'}\langle j=\eta\frac{3}{2}|j=\eta\frac{3}{2}\rangle_{\mathbf{k}}|^2 = 1-\frac{3}{4}\sin^2\theta_{\mathbf{k}'\mathbf{k}}$
- $P_{HL} = P_{LH} = \sum_{\eta,\eta'=\pm1}|_{\mathbf{k}'}\langle j=\eta\frac{1}{2}|j=\eta\frac{3}{2}\rangle_{\mathbf{k}}|^2 = \frac{3}{4}\sin^2\theta_{\mathbf{k}'\mathbf{k}}$

  where $\theta_{\mathbf{k}'\mathbf{k}} = \cos^{-1}(\mathbf{k}'\cdot\mathbf{k}/k'k)$.

- *However, this is only applicable to cubic crystals in the strong SOC limit.*
- Here we show expressions for the overlap factors in a two-fold orbitally degenerate valley, rationalised with group theory.

Two-fold degenerate bands in crystalline symmetry [2, 3]

- Spinless $k\cdot p$ Hamiltonian for band E at TRIM k_0 in symmorphic crystal:

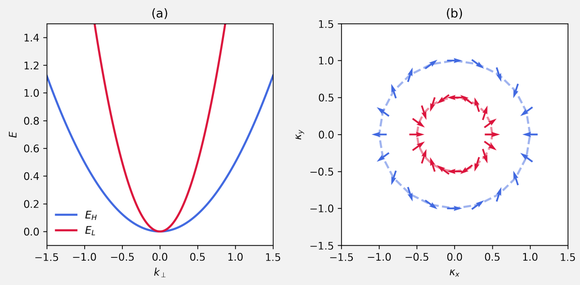
$$H_{\mathbf{k}\cdot\mathbf{p}} = L(\kappa_x^2+\kappa_y^2)\sigma_0 + M\left[(\kappa_x^2-\kappa_y^2)\sigma_x + 2\kappa_x\kappa_y\sigma_y\right]$$

in the basis $\{|1,1\rangle, |1,\bar{1}\rangle\}$.

Analytic overlap factor expressions:

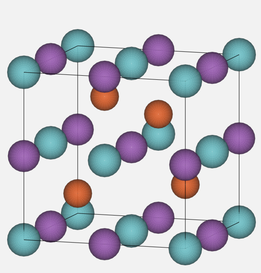
- $P_{HH} = P_{LL} = \cos^2\theta_{\kappa'\kappa}$
- $P_{HL} = P_{LH} = \sin^2\theta_{\kappa'\kappa}$

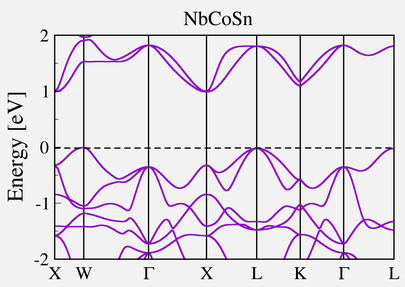
where $\theta_{\kappa'\kappa} = \tan^{-1}(\kappa'_y/\kappa'_x) - \tan^{-1}(\kappa_y/\kappa_x)$.

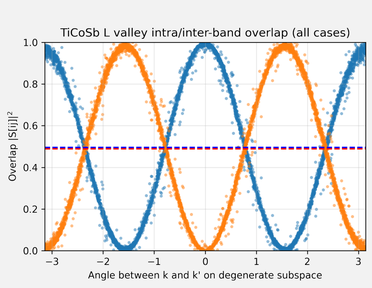


We define the coordinate κ in symmetry-adapted axis of little co-group $\bar{G}_{\mathbf{k}}$. *i.e.* κ_z is parallel to k_0.

- Example: L valley in half-Heuslers (cubic, $F\bar{4}3m$, spg. 216)







- As predicted by the spinless degenerate Hamiltonian, DFT w/o SOC results show the sinuous overlap relations between LH and HH bands.
- *DFT w/o SOC always predicts non-negligible transitions between the two.*

The effect of spin-orbit textures on overlap integral factors

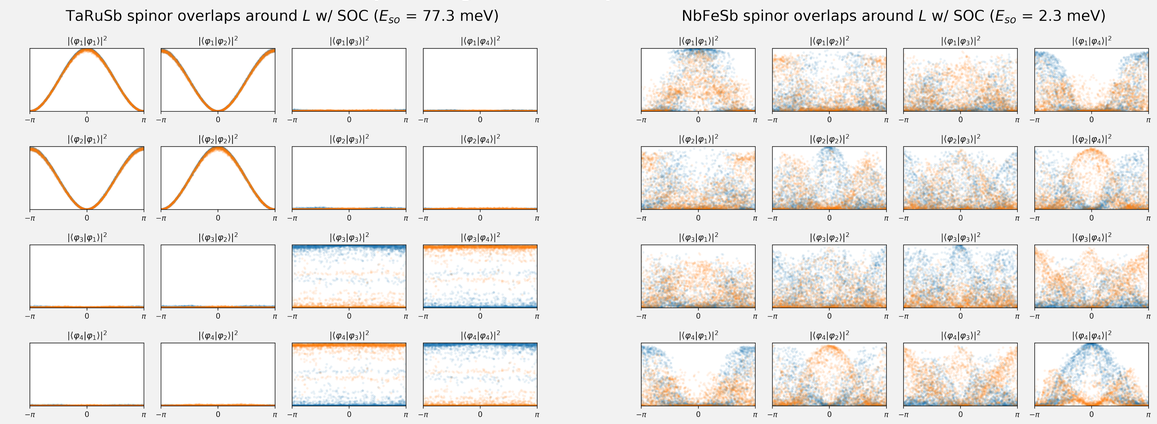
- The form of $H_{\mathbf{k}\cdot\mathbf{p}}$ with SOC depends on the band representation. *e.g.* bands with 2D representation E at valley L whose $G_{\mathbf{k}}\cong C_{3v}$ split as:

$$E\otimes D_{1/2} = E_{1/2}\oplus {}^1E_{3/2}\oplus {}^2E_{3/2}$$

- The corresponding Hamiltonian is tractable only in the strong SOC limit:

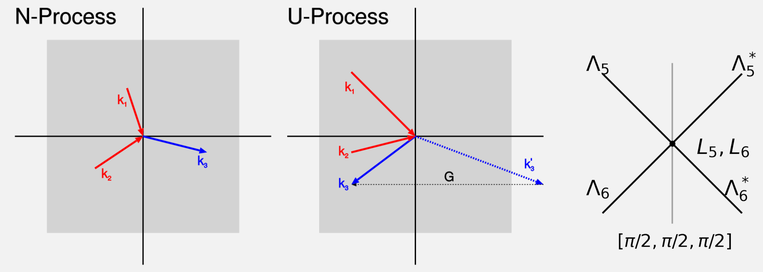
$$H_L \approx H_{1/2}\oplus {}^1H_{3/2}\oplus {}^1H^*_{3/2}$$

  which is first order in κ as the crystal lacks inversion symmetry.
- DFT results of overlap integrals for spinors w/ SOC for TaRuSb & NbFeSb:



- With the strong SOC (left), the overlap integrals for HL and LH vanish, while with the weak SOC (right), they average to 0.5 in all transitions.
- Different overlap relations for normal (blue) and Umpklapp (orange) process as the time-reversed Hamiltonian is not equivalent, *i.e.* $H_{-L} = \bar{H}_L$.
- *The simple sinuous relations from the spinless model can not be recovered from DFT with SOC in either case.*

Normal *versus* Umklapp process



- Time-reversal symmetry may result in two different overlap relations for two bands in normal and Umklapp processes.
- To determine the representations Γ of the band is equivalent under time-reversal Γ^*, Frobenius-Schur indicator reads:

$$\frac{1}{|G|}\sum_{g\in G}\chi(g^2) = \begin{cases}1 & \text{(a) } \Gamma \text{ is real}\\ -1 & \text{(b) } \Gamma \text{ is pseudo-real}\\ 0 & \text{(c) } \Gamma \text{ is not equivalent to } \Gamma^*\end{cases}.$$

- The representations of bands $L_5({}^1E_{3/2})$ and $L_6({}^2E_{3/2})$ in HHs are type (c), hence the corresponding $H_{\mathbf{k}\cdot\mathbf{p}}$ is not equivalent between L and $-L$.

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Implications for transport properties

- We solve the semi-classical Boltzmann equation with ElecTra [1] to calculate transport properties of p-type NbFeSb with two overlap relations for bands at L: (1) vanishing, and (2) equal overlaps (average to 0.5) between light and heavy holes.
- Calculated maximum power factor is up to 10 percent higher in case (1) compared to (2). However, the relationship between overlap factors and scattering mechanism is complex and further investigation is required.

References

[1] Patrizio Graziosi, Zhen Li, and Neophytos Neophytou. *ElecTra* code: Full-band electronic transport properties of materials. 287:108670.

[2] Rajeev Dutt, Bhawna Sahni, Yao Zhao, Yuji Go, Saff E. Awal Akhtar, Ankit Kumar, Sumit Kukreti, Patrizio Graziosi, Zhen Li, and Neophytos Neophytou. Carrier scattering considerations and thermoelectric power factors of half-heuslers. 14(17):10332–10345.

[3] Bhawna Sahni, Yao Zhao, Zhen Li, Rajeev Dutt, Patrizio Graziosi, and Neophytos Neophytou. Thermoelectric transport and the role of different scattering processes in the half-heusler NbFeSb. 12(23):10255–10269.

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