Onsager Relations in Coupled Electric, Thermoelectric and Spin Transport: The Ten-Fold Way

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Onsager relations can be classified into ten classes, in terms of the presence or absence of time-reversal symmetry, particle-hole symmetry and sublattice/chiral symmetry. We construct a quantum coherent scattering theory of linear transport for coupled electric, heat and spin transport; including the effect of Andreev reflection from superconductors. We derive a complete list of the Onsager reciprocity relations between transport coefficients for coupled electric, spin, thermolectric and spin caloritronic effects. We apply these to all ten symmetry classes, paying special attention to specific additional relations that follow from the combination of symmetries, beyond microreversibility. We discuss these relations in several illustrative situations. We show the reciprocity between spin-Hall and inverse spin-Hall effects, and the reciprocity between spin-injection and magnetoelectric spin currents. We discuss the symmetry and reciprocity relations of Seebeck, Peltier, spin-Seebeck and spin-Peltier effects in systems with and without coupling to superconductors.

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I. INTRODUCTION

Onsager’s reciprocity relations are cornerstones of nonequilibrium statistical mechanics.12 They relate linear response coefficients between flux densities and thermodynamic forces to one another. They are based on the fundamental principle of microreversibility which, for systems with time-reversal symmetry (TRS), says that “if the velocities of all the particles present are reversed simultaneously the particles will retrace their former paths, reversing the entire succession of configurations”.1 When TRS is broken, microreversibility further requires to invert all TRS breaking fields, which, to fix ideas, one may take as magnetic fields, fluxes or exchange fields. Combining all of them into a single multi-component field \( \mathcal{H} \), the Onsager reciprocity relations read1,2

\[
\mathcal{L}_{ij}(\mathcal{H}) = \mathcal{L}_{ji}(-\mathcal{H}),
\]

where the linear coefficient \( \mathcal{L}_{ij} \) determines the response of the flux density \( \mathcal{A}_i \) – for instance the electric or heat current – to a weak thermodynamic force \( \mathcal{X}_j \) – for instance an electric field or a temperature gradient. Thus the precise form of the Onsager reciprocity relations depends on the symmetries of the system. Seminal works have classified noninteracting quantum mechanical systems into ten general symmetry classes,3,4 and it is the purpose of the present manuscript to derive Onsager’s relations for all these symmetry classes. Four of them, in particular, combine two different types of quasiparticles,3 with microscopic representations including, e.g. hybrid systems where quantum coherent normal metallic conductors are connected to superconductors. Since at sub-gap energies an interface between a normal metal and a superconductor blocks heat currents but not electric currents,5 it is natural to ask whether the Onsager reciprocity relation between, say, the Seebeck and Peltier thermoelectric coefficients survives in such systems. Onsager relations in the presence of superconductivity have been discussed rather incompletely until now,7–11 despite much experimental,12–14 and theoretical,15–17 interest in thermoelectric transport properties of hybrid normal-metallic/superconducting systems.

Further motivation is provided by fundamental aspects of spintronics18 and spin caloritronics (spin-Seebeck and spin-Peltier effects)19 where Onsager relations are of significant interest.20–25 As a matter of fact, reciprocity relations decisively helped in experimentally uncovering elusive spin effects, by suggesting to measure electric effects that are reciprocal to them. As but one example, we mention the inverse spin Hall effect,26–31 where a transverse electric current or voltage is generated by an injected spin current.32 Onsager relations also put constraints on the measurement of spin currents,33,34 that can be circumvented in the nonlinear regime only.35–37 Accordingly, we will incorporate spin currents and accumulations into our formalism. Several of the Onsager relations for spin transport we derive below appeared in one way or another in earlier publications, see in particular Refs. 21,26,32. Here, we summarize them in a unified way and extend them to all ten symmetry classes. We are unaware of earlier discussions of Onsager relations for spin transport in the presence of superconductivity.

The classification into ten different symmetry classes has recently received renewed attention, because the existence of topologically nontrivial phases depends on the system’s symmetries and its dimensionality.38 The Onsager relations we derive below depend only on fundamental symmetries and are equally valid in topologically trivial and nontrivial states. In several instances, how-
Table I: The ten-fold symmetry classification of Hamiltonians. The second column from the left refers to Cartan’s nomenclature for symmetric spaces, the three middle columns indicate whether the classes have broken (0) or unbroken (±1) time-reversal symmetry (TRS), particle-hole symmetry (PHS) and sublattice symmetry (SLS), while the rightmost column mentions microscopic realizations in each class, with SC indicating the presence of superconductivity. Aside from the indicated bipartite lattice models with preserved sublattice symmetry, the chiral classes are also realized in low-energy models for quantum chromodynamics. Spin rotational symmetry (SRS) is present in classes AI, BDI, C and CI, absent in classes AII, CII, D and DIII, and irrelevant in classes A and AIII.

II. THE TEN-FOLD WAY

Hamiltonian systems are classified according to the presence or absence of fundamental symmetries. The historical classification scheme is based on TRS and spin-rotational symmetry (SRS). Three Wigner-Dyson classes are defined in this way. Using the Cartan nomenclature for symmetric spaces, the class A has both symmetries broken, the class AI has both symmetries present, and the class AII has broken SRS but unbroken TRS. When TRS is broken, the presence or absence of SRS only affects the size of the Hamiltonian matrix — and not its symmetry — and there is thus no fourth class.

Chiral classes were next introduced, which capture the structure of the QCD Dirac operators. Besides relativistic fermions, they are also appropriate to describe bipartite lattice Hamiltonians with unbroken sublattice symmetry (SLS). Examples include two-dimensional square and hexagonal lattices, as well as three-dimensional cubic lattices without mass/on-site term, the latter generically breaking SLS. Here also, there are three classes, with (apart from their chiral symmetry) the same symmetries as the Wigner-Dyson classes.

Finally, four more classes of Bogoliubov-de Gennes (BdG) Hamiltonians appear - the Altland-Zirnbauer classes - when normal metals are brought into contact with superconductors: with SRS (C and CI) and without SRS (D and DIII), with TRS (CI and DIII) and without TRS (C and D). When dealing with such systems, we use a convention where the BdG Hamiltonian reads

\[
H = \begin{pmatrix}
\hbar - \mu_{sc} & \Delta \\
\Delta^* & \mu_{sc} - \sigma^{(y)} \sigma^{(y)}
\end{pmatrix},
\]

with the Pauli matrix \( \sigma^{(y)} \) acting on the spin degree
of freedom and the chemical potential $\mu_{sc}$ on the superconductor. With this convention, used for example in Refs. 39,40, the second-quantized Gogolinbov-de Gennes Hamiltonian is $\frac{1}{2}c^\dagger H c$, where 

$$c^\dagger = (c^\dagger_{ct}, c^\dagger_{cl}, c^\dagger_{hl}, -c^\dagger_{ht}).$$

with $c^\dagger_{ct}$ being the vector of creation operator for all $k$-states of spin-$\uparrow$ electrons, etc. This has the hole sector rotated by $i\sigma(y)$ with respect to the Hamiltonian in Refs. 5,37. The form of Eq. (2) has the advantage that upon assuming SRS (so $h^*$ commutes with $\sigma(y)$), it immediately reduces to that used in Refs. 7,41–43.

Ref. 37 introduced a unifying ten-fold classification scheme for all the above Hamiltonians. They considered TRS and particle-hole symmetry (PHS), which can both be represented by antiunitary operators, and accordingly, these two symmetries can be either broken, or unbroken. In the former case, we represent this by a 0, while in the latter case, the antiunitary operator squares to either +1 or −1. A squared TRS of +1 corresponds to spinless or integer-spin particles, while a squared TRS of −1 corresponds to half-integer-spin particles. A squared PHS of +1 corresponds to triplet pairing, while a squared PHS of −1 corresponds to singlet pairing in a Bogoliubov-de Gennes Hamiltonian. Naively one would think that this leads to $3 \times 3 = 9$ classes, however there are two distinct possibilities when both TRS and PHS are broken. In this case, the symmetry represented by the product of the two antiunitary operators gives either 0 (when the corresponding symmetry is broken) or +1. This finally gives $3 \times 3 - 1 = 10$ symmetry classes again. Using the just defined three indices, we summarize the ten symmetry classes in Table I, where we additionally mention relevant physical realizations for each of them.

In this classification, the possible symmetries that the Hamiltonian $H$ satisfies are (i) TRS : $H = THT^{-1}$, with $T = -iK$, with the complex conjugation operator $K$ in the spinless case, and $T = -i\sigma(y)K$ for spin-1/2 fermions, with the Pauli matrix $\sigma(y)$ acting in spin space; (ii) PHS : $H = -PHP^{-1}$, with $P = -i\sigma(y)\tau(y)K$, with the Pauli matrix $\tau(y)$ acting in Nambu space; (iii) SLS : $H = -H^T H^\dagger$, with the Pauli matrix $\tau^\dagger$ acting on sublattice space (bipartite lattices are assumed here).

TRS, SRS and SLS can be broken by an orbital magnetic field, spin-orbit interaction and mass/on-site terms respectively. The Altland-Zirnbauer classes assume PHS, which strictly speaking forces thermolectric effects to vanish identically. PHS can be broken, for instance, by moving away in energy from the special $\epsilon = 0$ symmetry point – the superconductor’s chemical potential. This occurs upon increasing the temperature, when the latter exceeds a Thouless energy scale, $E_T \sim \tau^{-1}_{Andr}$. This finally breaks PHS is to make $\tau_{Andr}$ not negligible, where $\tau_{Andr}$ is a timescale associated with impinging on or returning to the superconducting contacts.

### Table II: Crossovers from the Altland-Zirnbauer to the Wigner-Dyson classes.

| Crossovers | TRS | PHS | SLS | Physical example |
|------------|-----|-----|-----|------------------|
| D → A      | 0   | +1  | 0   | as $D$ but $\tau_{Alt}$ is not small |
| for Andreev| C   | +1  | 0   | as $C$ but $\tau_{Alt}$ is not small |
| interfe.   | DIII | +1  | 0   | as DIII but $\tau_{Alt}$ is not small |
|            | CI  | +1  | 0   | as CI but $\tau_{Alt}$ is not small |

Increasing the temperature breaks PHS so that the quasiparticle excitation energy $\epsilon$ cannot be treated as small. One way to break PHS is to make $(k_B T_0)\tau_{Andr}$ not negligible, where $\tau_{Andr}$ is a timescale associated with impinging on or returning to the superconducting contacts.

### III. SYMMETRIES AND RECIPROCITIES OF THE $S$-MATRIX

Our investigations are based on the scattering theory of quantum transport, which allows to straightforwardly derive Onsager reciprocity relations solely from the symmetries of the system’s scattering matrix $S$.

Reciprocity relations for $S$ follow directly from microreversibility. They read

$$S(\mathcal{H}) = \sigma(y) S^T (-\mathcal{H}) \sigma(y),$$

where $\sigma(y)$ is a Pauli matrix acting in spin space, and $\sigma(y)$ indicates the matrix transpose of spin, transport channel and (with superconductivity) quasiparticle indices. Included in Eq. (4) is the relation $S(\mathcal{H}) = S^T (-\mathcal{H})$ valid when the antiunitary TRS operator squares to 1 and SRS is not broken. Eq. (4) can be derived by constructing $S$ first with scattering states $\phi_{n\sigma}(\mathcal{H})$, then with their time-reversed $-i\sigma(y)K\phi_{n\sigma}(\mathcal{H})$, with the complex conjugation operator $K$, and equating the two results. Eq. (4) is intimately related to Kramers degeneracy, which in the presence of TRS ($\mathcal{H} = 0$) follows from the symmetry property $H = \sigma(y) H^\dagger \sigma(y)$ of the Hamiltonian $H$. Specifying to half-integer-spin particles, it can equivalently be
rewritten in a form that renders its connection to microreversibility more evident
\[
S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}) = \sigma\sigma' S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}),
\]
where \(i, j\) are transport channel indices, \(\mu, \nu = e, h\) are quasiparticle indices and \(\bar{\sigma} = -\sigma\) are spin indices.

Further relations can be constructed by combining Eqs. (4) and (5) with additional symmetries of the \(S\)-matrix. The latter are obtained by translating PHS and SLS of the Hamiltonian into symmetries of the \(S\)-matrix. For this purpose, we use the relation (9)
\[
S(\epsilon) = 1 + 2\pi i W^\dagger (H - \epsilon - i\pi W W^\dagger)^{-1} W,
\]
between \(S\) and \(H\), with a rectangular matrix \(W\) that couples the scatterer to external leads. We consider first PHS. The presence of superconductivity requires to introduce electron and hole quasiparticles, and when PHS is present, the energy spectrum is symmetric about zero energy (taken as the chemical potential of the superconductor). With the convention of Eq. (2), PHS reads \(H = -\sigma^{(y)}(\mathcal{H})H^*\sigma^{(y)}(\mathcal{H})\) with the minus-sign indicating how the symmetry of the energy spectrum differs from Kramers degeneracy. From this we obtain
\[
S(\mathcal{H}) = \sigma^{(y)}(\mathcal{H}) S^*(\mathcal{H}) \sigma^{(y)}(\mathcal{H}).
\]
Combining Eqs. (4) and (7) and paying attention to the ordering of spin-indices given in Eq. (5), one obtains,
\[
S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}) = (S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}))^* = \sigma\sigma' S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}) = \sigma\sigma' S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}^*),
\]
where quasiparticle indices \(\mu, \nu = +1(e), -1(h)\) when they appear as prefactors.

The reciprocity relations (4) and (7) for the \(S\)-matrix are illustrated in Fig. 1. We defined the \(S\)-matrix via the relation \(S a = b\) between vectors \(a\) and \(b\) of components for incoming and outgoing quasiparticle flux amplitudes, respectively. Each component of these vectors corresponds to a given terminal, a transverse transport channel in that terminal, a spin orientation and, in the presence of superconductivity, a quasiparticle index. Complex conjugation in Fig. 1 and Eq. (4) occurs because TRS and PHS are represented by antiunitary operators, i.e., products of a unitary operator with complex conjugation.

We finally comment on SLS. The chiral Hamiltonian symmetry reads \(H_{\mathcal{H}} = -H_{\mathcal{H}}^*\eta(\mathcal{H})\), with the Pauli matrix \(\eta(\mathcal{H})\) acting in sublattice space. For the scattering matrix, this translates into
\[
S_{\mathcal{H}} = \eta(\mathcal{H}) S_{\mathcal{H}}^*(\mathcal{H}),
\]
where in contrast to earlier symmetry relations, we explicitly had to write the energy-dependence of the \(S\)-matrix. Combining Eqs. (4) and (9), one obtains,
\[
S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}, \epsilon) = m n S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}, -\epsilon)^* = \sigma\sigma' S_{\mu,\nu}^{\mu,\nu}(\mathcal{H}, \epsilon),
\]
where we introduced sublattice indices \(m, n = A(+1), B(-1)\).
IV. SCATTERING APPROACH TO TRANSPORT AND FORMULATION OF THE PROBLEM

We consider a multiterminal device connected to \( i, j = 1, 2, \ldots, N \) electrodes. The linear response relation is

\[
\begin{pmatrix}
J_i \\
I_i^{(0)} \\
I_i^*(x) \\
I_i^*(y) \\
I_i^*(z)
\end{pmatrix} = \sum_j \begin{pmatrix}
\Xi_{ij}^{(0)} & \Gamma_{ij}^{(0x)} & \Gamma_{ij}^{(0y)} & \Gamma_{ij}^{(0z)} \\
B_{ij}^{(0x)} & G_{ij}^{(0x)} & G_{ij}^{(0y)} & G_{ij}^{(0z)} \\
B_{ij}^{(2x)} & G_{ij}^{(2x)} & G_{ij}^{(2y)} & G_{ij}^{(2z)} \\
B_{ij}^{(4y)} & G_{ij}^{(4y)} & G_{ij}^{(4y)} & G_{ij}^{(4y)} \\
B_{ij}^{(6z)} & G_{ij}^{(6z)} & G_{ij}^{(6z)} & G_{ij}^{(6z)}
\end{pmatrix} \begin{pmatrix}
T_j - T_0 \\
V_j - V_0
\end{pmatrix},
\]

(11)

between heat, \( J_i \), electric, \( I_i^{(0)} \) and spin, \( I_i^{(\alpha)} \) currents on the one hand, and temperatures, \( T_j \), voltages, \( V_j \) and spin accumulations, \( \mu_j^{(\alpha)} \) on the other.

The coefficients with superindices \( ^{(0)} \) are the usual thermoelectric coefficients, while the coefficients \( G^{(\alpha\beta)} \) are conductances and spin-dependent conductances, relating electric and spin currents to electric voltages and spin accumulations.\(^{55,56}\) Finally, one has spin-Peltier matrix elements \( \Gamma^{(0\beta)} \) connecting heat currents to spin accumulations and spin-Seebeck matrix elements \( B^{(0\alpha)} \) connecting spin currents to temperature differences.\(^{55} \) The resulting spin caloritronic (spin-Seebeck and spin-Peltier) effects have been investigated theoretically and experimentally.\(^{57,58} \) As usual, we assume that there is no spin relaxation in the terminals where spin currents are measured, so that the latter are well defined. Our goal is to determine reciprocity relations between the elements of the Onsager matrix defined on the right-hand side of Eq. (11) in the ten symmetry classes discussed in Section II.3.

We will express the matrix elements of the Onsager matrix in Eq. (11) in terms of the \( \hat{S} \)-matrix. We discuss separately purely metallic systems and hybrid systems consisting of normal metallic components connected to superconductors.

A. Purely metallic systems

Purely metallic systems fall in either one of the Wigner-Dyson or in one of the chiral classes. We start from the expression for electric current in Ref. 17, extending it to account for heat and spin currents, e.g. along the lines of Refs. 14,53. This gives us the following linear relations between electric, heat and spin currents, on one hand, and voltages, temperatures and spin accumulations, on the other hand,

\[
J_i = \frac{1}{\hbar} \int_{-\infty}^{\infty} d\epsilon \left( -\frac{\partial f}{\partial \epsilon} \right) \epsilon \sum_{j,\beta} \left[ 2N_s \delta_{\alpha\beta} \delta_{ij} - \mathcal{T}_{ij}^{(\alpha\beta)}(\epsilon) \right] \times \left[ \mu_j^{(\beta)} + \delta_{\alpha\beta} \epsilon (T_j - T_0)/T_0 \right],
\]

(12a)

\[
I_i^{(\alpha)} = \frac{e}{\hbar} \int_{-\infty}^{\infty} d\epsilon \left( -\frac{\partial f}{\partial \epsilon} \right) \sum_{j,\beta} \left[ 2N_s \delta_{\alpha\beta} \delta_{ij} - \mathcal{T}_{ij}^{(\alpha\beta)}(\epsilon) \right] \times \left[ \mu_j^{(\beta)} + \delta_{\alpha\beta} \epsilon (T_j - T_0)/T_0 \right],
\]

(12b)

where the sums run over all terminal indices \( i, j \) and all charge-spin indices \( \alpha, \beta = 0, x, y, z \). The electrochemical potential in terminal \( j \) is \( \mu_j^{(0)} = \mu_j + eV_j \) with the applied voltage \( V_j \) and \( T_0 \) is the base temperature about which the Fermi function \( f = (\exp[\epsilon/T]+1)^{-1} \) is expanded. The spin accumulations \( \mu_j^{(\beta)} \), \( \beta \neq 0 \), are one half times the \( \beta \)-components of the spin accumulation vector \( \boldsymbol{\mu}_j \), giving the difference in chemical potential between the two spin species along the \( \beta \) axis, e.g. \( \mu_j^{(z)} = (\mu_j^{(1)} - \mu_j^{(0)})/2 \). They are nonequilibrium spin accumulations whose origin is of little importance here.

In Eqs. (12), we introduced the spin-dependent transmission and reflection coefficients

\[
\mathcal{T}_{ij}^{(\alpha\beta)} = \text{Tr}[\hat{S}_{ij}] \sigma^{(\alpha)}_{ij} \sigma^{(\beta)}_j,
\]

(13)

where \( \sigma^{(\alpha)}_j, \alpha = 0, x, y, z \) are Pauli matrices \( (\sigma^{(0)}_j \) is the identity matrix) and the trace is taken over both spin and transmission channel indices. Note the position of the Pauli matrices, where \( \sigma_j^{(\alpha)} \) measures the spin in direction \( \alpha \) as the electron exits the system, while \( \sigma_j^{(\beta)} \) measures it along \( \beta \) as the electron enters the system.\(^{59,61} \) These coefficients depend on the energy \( \epsilon \) of the injected electrons, which we explicitly wrote in Eq. (12). Reciprocity relations for the Onsager matrix elements in purely metallic systems directly follow from combining Eqs. (12) with the transformation rules for the \( \mathcal{T}_{ij}^{(\alpha\beta)} \) under microreversibility. Pauli matrices satisfy \( \sigma_{ij}^{(\alpha)} = (-1)^{n_x n_y n_z} \sigma_j^{(\alpha)} \sigma_i^{(\alpha)} \) with \( n_x, y, z = 1 \) and \( n_0 = 0 \). Using this and Eq. (5) we obtain

\[
\mathcal{T}_{ij}^{(\alpha\beta)}(\mathcal{H}, \epsilon) = (-1)^{n_\alpha + n_\beta} \mathcal{T}_{ji}^{(\beta\alpha)}(-\mathcal{H}, \epsilon).
\]

(14)

Thus the reciprocity relation between spin-dependent transmission coefficients in Eq. (14) picks up a minus sign if the spin is resolved upon entering the system, and another if it is resolved upon leaving the system.
B. Metallic systems with chiral symmetry

The chiral classes correspond to systems with a bipartite lattice, however currently no experiments are capable of measuring sublattice-resolved currents. Thus the charge and spin-transport is given by Eqs. [12][13], with the trace over channels supplemented by a trace over the sublattice indices (A and B sites). If one could measure sublattice isospin current, then one would have to add further Pauli matrices acting in sublattice space into the trace over channels supplemented by a trace over the charge and spin-transport is given by Eqs. (12,13), with 

$$I_{in}/T, \rho_{in}/T = \frac{1}{i} \sum_{i,j} T_{ij}(\epsilon) \delta_{\epsilon, T_{ij}} \sum_{\alpha \beta} \left\{ \begin{array}{c} \text{counted from the chemical potential of the superconductor} \\
\text{due to}\end{array} \right\}$$

$$T_{ij}(H, \epsilon) = T_{ji}(\epsilon, -H)$$

$$= (-1)^{n_{\alpha} + n_{\beta}} T_{ij}(\epsilon)$$

These relations are strictly valid only insofar as leads are preserving SLS, meaning that they connect equally to both sublattice sites of each unit cell.

C. Hybrid superconducting-normal metallic systems

Hybrid normal-metallic/superconducting systems have Andreev electron-hole scattering. This scattering may induce PHS, in which case the system falls in one of the four Altland-Zirnbauer symmetry classes in Table [14].

To include Andreev scattering, one has to consider two kinds of quasiparticles (electrons and holes), which carry excitation energy $\pm \epsilon$ counted from the chemical potential of the superconductor $\mu_{sc}$. These quasiparticles are counted into one another when they hit the superconductor. Ref. [17] constructed a scattering theory of thermoelectric transport which include these effects. We need to include spin currents and accumulations.

To do this, we go back to the derivation of the scattering theory in terms of creation and annihilation operators acting on scattering states in the lead (see e.g. Ref. [11]). We write hole creation operators at energy $\epsilon$, in terms of electron annihilation operators at energy $-\epsilon$ as $c_{i;n}^{(h)in/out}(\epsilon) = c_{i;n}^{(e)in/out}(\epsilon)$ with

$$c_{i;n}^{(h)in/out}(\epsilon) = \left( \begin{array}{c} c_{i;n}^{(h)in/out}(\epsilon) \\
\epsilon^{(h)in/out} \\
\epsilon^{(h)in/out} \\
\epsilon^{(h)in/out} \end{array} \right)$$

$$c_{i;n}^{(e)in/out}(\epsilon) = \left( \begin{array}{c} c_{i;n}^{(e)in/out}(\epsilon) \\
\epsilon^{(e)in/out} \\
\epsilon^{(e)in/out} \\
\epsilon^{(e)in/out} \end{array} \right).$$

Here, $i$ gives the index of a transverse mode in the nth lead, while “in” and “out” indicate whether the wave in that mode is ingoing or outgoing. As these operators obey fermionic commutation relations, one has

$$c_{i;n}^{(e)in}(\epsilon) c_{j;n}^{(e)in}(\epsilon) = \sigma_{i,j}^{\alpha, \alpha} c_{i;n}^{(e)in}(\epsilon) c_{j;n}^{(e)in}(\epsilon) = \sigma_{i,j}^{\alpha, \alpha} T_{i;j}^{\alpha, \alpha}(\epsilon)$$

with a similar relation for outgoing waves. The transpose in the second term is due to the fact that we commuted the hole operators to ensure normal ordering. We then use the scattering matrix to write outgoing operators in terms of incoming ones. Contributions coming from the first term in Eq. (16) cancel each other. We find that the operator which gives the spin-current along axis $\alpha$ in the electron sector is $\sigma_{\alpha}$ [as in Eq. (13)], while it is $-\sigma_{\alpha}^T$ in the hole sector. Recalling that we use the convention in Eqs. (2,3), we must also rotate the spin-current operator in the hole sector. It becomes $-\sigma_{\alpha}^T \sigma_{\alpha}^T = (1)^{n_{\alpha} + 1} \sigma_{\alpha}^T$. Thus in this convention, we can write this spin-current operator compactly as $\mu_{\alpha}^\nu T_{\alpha, \beta}^{\mu, \nu} c_{\alpha}^{(\nu)T} c_{\alpha}^{(\nu)}$, which works for both electrons ($\mu = 1$) and holes ($\mu = -1$). From here on, quasiparticle indices $\mu, \nu = +1(\epsilon), -1(\tilde{h})$ when they appear as prefactors.

This calculation in terms of creation and annihilation operators for electrons and holes gives us the scattering matrix formula that we desire. Assuming that the number of transport channels $N_i$ is the same for each quasiparticle species, Eqs. (12) is replaced by

$$J_i = \frac{1}{\hbar} \int_0^\infty d\epsilon \sum_{j,\beta} \left\{ 4N_i \delta_{ij} - \sum_{\mu,\nu} \alpha_{ij}^{(\mu,\nu)}(\epsilon) \delta_{0\beta} \epsilon(T_j - T_0)/T_0 - \sum_{\mu,\nu} \mu \bar{T}_{ij}^{\alpha, \alpha}(\epsilon) \mu_j^{(\beta)} \right\}, \quad (17a)$$

$$I_i^{(\alpha)} = \frac{\epsilon}{\hbar} \int_0^\infty d\epsilon \sum_{j,\beta} \left\{ 4N_i \delta_{0\beta} \delta_{ij} - \sum_{\mu,\nu} \mu \bar{T}_{ij}^{\mu, \alpha}(\epsilon) \mu_j^{(\beta)} - \sum_{\mu,\nu} \mu \bar{T}_{ij}^{\mu, \alpha}(\epsilon) \delta_{0\beta} \epsilon(T_j - T_0)/T_0 \right\}, \quad (17b)$$

where the integrals now go over a range of positive excitation energies and we defined $\mu_0(0) = e(V_j - V_{sc})$, i.e. voltages are measured from the superconducting voltage $V_{sc} = \mu_{sc}/e$. We also introduced the spin-dependent, quasi-particle resolved transmission coefficients

$$\bar{T}_{ij}^{\mu, \nu} = \mu^{\alpha, \nu} T_{ij}^{\alpha, \beta} \left[ S_{ij}^{(\alpha)} S_{ij}^{(\nu)} S_{ij}^{(\beta)} \right] \quad (18)$$
where $S_{ij}^{\mu\nu}$ is the block of the $S$-matrix corresponding to the transmission of a quasiparticle of type $\nu = e, h$ in lead $j$ to a $\mu$-quasiparticle in lead $i$.

The main novelty brought about by superconductivity is that the elements of the Onsager matrix now depend on Andreev processes via hybrid transmission coefficients $\gamma_{ij}^{(e, h; \alpha, \beta)}$ and $\gamma_{ij}^{(h, e; \alpha, \beta)}$, which contribute differently to heat versus electric and spin currents — see in particular the last terms in Eqs. (17a) and (17b). From Eq. (3) one obtains

$$\mathcal{G}_{ij}^{(\mu; \nu; \alpha; \beta)}(\mathcal{H}, \epsilon) = (-1)^{n_\alpha + n_\beta} \mathcal{G}_{ji}^{(\nu; \mu; \alpha; \beta)}(-\mathcal{H}, \epsilon),$$

which extends Eq. (14) to include superconductivity.

Eq. (19) applies to any hybrid system, regardless of whether PHS is present or not. If additionally, the system has unbroken PHS, then the scattering matrix obeys Eq. (7), i.e. $S_{ij}^{\mu\nu}(\mathcal{H}) = \mu\nu \sigma(\nu) S_{ij}^{\mu\nu}(\mathcal{H}) \sigma(\mu)$, where, as before, $\mu, \nu = \pm 1(e), -1(h)$. (Ref. 2) has this formula for SRS, where $S_{ij}^{\mu\nu}$ commutes with $\sigma(\mu)$. We substitute this into Eq. (19), then substitute $\sigma(\nu) \sigma(\mu) = (-1)^{n_\mu + n_\nu} \mathcal{S}^{(\mu; \nu)}$. Observing that the trace is invariant under the transpose of its argument, we find that PHS gives

$$\mathcal{G}_{ij}^{(\mu; \nu; \alpha; \beta)}(\mathcal{H}, \epsilon) = \mathcal{G}_{ji}^{(\nu; \mu; \alpha; \beta)}(\mathcal{H}, \epsilon) = (-1)^{n_\alpha + n_\beta} \mathcal{G}_{ji}^{(\nu; \mu; \alpha; \beta)}(-\mathcal{H}, \epsilon) = (-1)^{n_\alpha + n_\beta} \mathcal{G}_{ji}^{(\mu; \nu; \alpha; \beta)}(-\mathcal{H}, \epsilon).$$

V. ONSAGER RELATIONS

Eqs. (12), (14), (17), (19) and (20) are all we need to derive reciprocity relations between the coefficients of the Onsager matrix in Eq. (11). Tables III, IV and V provide a complete list of all Onsager reciprocity relations for coupled electric, thermoelectric and spin transport in single-particle Hamiltonian systems. The Onsager relations which can be derived from microreversibility are divided into two sets. Firstly, Table III gives the Peltier/Seebeck relations, between coefficients $\Gamma_{ij}^{(0; 0)}$ and $B_{ij}^{(0; 0)}$. Secondly Table IV gives the reciprocity relations for conductances $G_{ij}^{(0; 0)}$, $\Xi_{ij}^{(0; 0)}$. As an example, we note that for both the Wigner-Dyson and chiral orthogonal classes, the presence of SRS imposes $\Gamma_{ij}^{(0; 0)} = \Gamma_{ij}^{(0; 0)} \delta_{\alpha\beta}$, while TRS gives $\Xi_{ij}^{(0; 0)} = \Xi_{ij}^{(0; 0)} \delta_{\alpha\beta}$. Therefore, when both symmetries are present in those classes, $X_{ij}^{(0; 0)} = X_{ji}^{(0; 0)}$, for $X = \Xi, \Gamma, B$ and $G$. In addition there are those Onsager relations which can be derived from either the conservation of quasiparticle species (absence of Andreev processes turning $e$ into $h$, and vice-versa), or from the presence of PHS or SLS. They are listed in Table V.

Some important features are that (i) in multiterminal devices one needs to consider conductance, Seebeck and Peltier matrices, and the reciprocity relations require to take their transpose, the latter operation being tantamount to momentum inversion as required by microreversibility; (ii) spin transport introduces additional minus signs everyday a spin is measured, (iii) exact PHS leads to the disappearance of thermoelectric and spin caloritronic effects, (iv) at half-filling, exact SLS leads to the disappearance of thermoelectric but not spin caloritronic effects.

That thermoelectric and spin caloritronic effects vanish in the presence of PHS directly follows from Eq. (18) that transmission coefficients satisfy $\gamma_{ij}^{(\mu; \nu; \alpha; \beta)} = \gamma_{ji}^{(\nu; \mu; \alpha; \beta)}$ when PHS is strictly enforced. This gives in particular $\sum_{\mu} \mu \gamma_{ij}^{(\mu; \nu; \alpha; \beta)} = 0$ which, together with Eq. (17), directly gives $B_{ij}^{(0; 0)}(\mathcal{H}) = \Gamma_{ij}^{(0; 0)}(\mathcal{H}) = 0$.

The vanishing of thermoelectric effects with PHS is reminiscent of Mott’s relation, giving that the Seebeck coefficient is proportional to the derivative of the conductance at the Fermi energy — the latter vanishes in PHS systems. Still, hybrid normal metallic/superconducting systems often exhibit larger thermoelectric effects than their purely metallic counterpart, which typically happens in the crossover regime between Altland-Zirnbauer and Wigner-Dyson symmetry classes. For the crossover systems described in Table VI, thermoelectric effects can be quite large.

We close this section with two comments on SLS at half-filling, when the chemical potential is at zero energy. Systems in the chiral symmetry classes have transmission coefficients with extra symmetries given in Eq. (15). The latter have important consequences for the symmetry of transport, if the trace over the sublattice index in Eq. (13) involves only pairs of sublattice sites, i.e. when SLS is not broken by the terminals. When this is the case, the first and second equalities in Eq. (15), together with Eqs. (12), give $G_{ij}^{(\alpha; \beta)}(\mathcal{H}) = G_{ji}^{(\beta; \alpha)}(\mathcal{H})$ and $G_{ij}^{(0; 0)}(\mathcal{H}) = (-1)^{n_\alpha + n_\beta} G_{ji}^{(0; 0)}(-\mathcal{H})$ respectively, where we recall that $n_0 = 0$ and $n_{x,y,z} = 1$. We obtain identical results for $\Xi_{ij}^{(0; 0)}$, and thus conclude that

$$G_{ij}^{(\alpha; \beta)}(\mathcal{H}) = (-1)^{n_\alpha + n_\beta} G_{ji}^{(\beta; \alpha)}(-\mathcal{H}),$$

$$\Xi_{ij}^{(0; 0)}(\mathcal{H}) = \Xi_{ij}^{(0; 0)}(-\mathcal{H}).$$

We see that charge-conductance, spin-conductances and thermal conductance are even in external fields, $\mathcal{H}$, irrespective of how many terminals the device has. This is in contrast to normal-metallic systems without SLS, where only two-terminal devices have conductances even in $\mathcal{H}$. In contrast, spin-to-charge and charge-to-spin conversion are strictly odd in $\mathcal{H}$, irrespective of how many terminals the device has.

Turning to thermoelectric and spin caloritronic effects, the first equality in Eq. (15) gives $B_{ij}^{(0; 0)}(\mathcal{H}) T_0 = -\Gamma_{ij}^{(0; 0)}(\mathcal{H})$, while the second equality in Eq. (15) gives us the usual relation $B_{ij}^{(0; 0)}(\mathcal{H}) T_0 = (-1)^{n_\alpha} \Gamma_{ji}^{(0; 0)}(-\mathcal{H})$. Thus we can conclude that

$$B_{ij}^{(0; 0)}(\mathcal{H}) = B_{ij}^{(0; 0)}(-\mathcal{H}) \text{ for } \beta \in \{x, y, z\},$$

$$B_{ij}^{(0; 0)}(\mathcal{H}) = 0.$$
Table III: The Onsager reciprocity relations arising from microreversibility and which involve the Peltier and spin-Peltier matrix elements, $\Gamma^{(03)}$, and the Seebeck and spin-Seebeck matrix elements, $B^{(03)}$. These relations, combined with those due to PHS or SLS in Table V, give the complete set of Onsager relations for each symmetry class.

| Symmetry class      | Seebeck-Peltier Onsager relations from microreversibility |
|---------------------|----------------------------------------------------------|
| Wigner-Dyson        | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha} + n_{\beta}} \Gamma^{(03)}_{ji}(\mathcal{F})$ |
|                     | $B^{(03)}_{ij}(\mathcal{F}) T_0 = \Gamma^{(03)}_{ji}$ |
| AI (unitary)        | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\beta}} \Gamma^{(03)}_{ji}$ |
| AII (sympl.)        | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha}} \Gamma^{(03)}_{ji}$ |
| Chiral              | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha} + n_{\beta}} \Gamma^{(03)}_{ji}(\mathcal{F})$ |
| AIII (unitary)      | $B^{(03)}_{ij}(\mathcal{F}) T_0 = \Gamma^{(03)}_{ji}$ |
| BDI (orthog.)       | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\beta}} \Gamma^{(03)}_{ji}$ |
| CI (sympl.)         | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha}} \Gamma^{(03)}_{ji}$ |
| Altland-Zirnbauer   | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha} + n_{\beta}} \Gamma^{(03)}_{ji}(\mathcal{F})$ |
| D                   | $B^{(03)}_{ij}(\mathcal{F}) T_0 = \Gamma^{(03)}_{ji}$ |
| C                   | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\beta}} \Gamma^{(03)}_{ji}$ |
| DIII                | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha}} \Gamma^{(03)}_{ji}$ |
| CI                  | $B^{(03)}_{ij}(\mathcal{F}) T_0 = (-1)^{n_{\alpha} + n_{\beta}} \Gamma^{(03)}_{ji}(\mathcal{F})$ |

Table IV: The Onsager reciprocity relations arising from microreversibility and which involve the electrical and spin-dependent conductances $G^{(03)}_{ij}$ and the heat conductance $\Xi^{(00)}$, These relations, combined with those due to PHS or SLS in Table V give the complete set of Onsager relations for each symmetry class.

| Symmetry class      | Onsager relations between conductances, $X = G, \Xi$ from microreversibility |
|---------------------|--------------------------------------------------------------------------------|
| Wigner-Dyson        | $X_{ij}^{(03)}(\mathcal{F}) = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}(\mathcal{F})$ |
| AI (unitary)        | $X_{ij}^{(03)} = X_{ji}^{(03)} \propto \delta_{\alpha,\beta}$ |
| AII (sympl.)        | $X_{ij}^{(03)} = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}$ |
| Chiral              | $X_{ij}^{(03)}(\mathcal{F}) = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}(\mathcal{F})$ |
| AIII (unitary)      | $X_{ij}^{(03)} = X_{ji}^{(03)} \propto \delta_{\alpha,\beta}$ |
| BDI (orthog.)       | $X_{ij}^{(03)} = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}$ |
| CI (sympl.)         | $X_{ij}^{(03)} = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}$ |
| Altland-Zirnbauer   | $X_{ij}^{(03)}(\mathcal{F}) = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}(\mathcal{F})$ |
| D                   | $X_{ij}^{(03)} = X_{ji}^{(03)} \propto \delta_{\alpha,\beta}$ |
| C                   | $X_{ij}^{(03)} = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}$ |
| DIII                | $X_{ij}^{(03)} = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}$ |
| CI                  | $X_{ij}^{(03)} = (-1)^{n_{\alpha} + n_{\beta}} X_{ji}^{(03)}$ |

VI. EXAMPLES OF RECIPROCITY RELATIONS IN SPINTRONICS AND SPIN CALORITRONICS

A. Spin Hall and inverse spin Hall effects

As a first example of the reciprocities we derived, we discuss the spin Hall effect and the inverse spin Hall effect. The two effects are sketched in Fig. 2. In the spin Hall effect, Fig. 2a, one passes an electric current between terminals 1 and 2 and measures the spin current between terminals 3 and 4. The voltages at terminals 3 and 4 are set such that no current flows through them on time average. In the limit of large and identical number of channels in each terminal, $N \gg 1$, the voltages $V_3$ and $V_4$ lie almost exactly in the middle between $V_1$ and $V_2$, $V_{3,4} \simeq (V_1 + V_2)/2$ for ballistic systems. We assume that this is the case here, and set

We stress, however, that the analysis leading to Eqs. 21 and 22 holds only at half-filling, when the Fermi function in Eq. 12 is symmetric around $\epsilon = 0$, and, perhaps physically more important, when the terminals do not break SLS. This requires leads to be connected with equal strength to both sublattice sites in each unit cell.
Together with Eq. (14), Eq. (25a) gives \( G_{\text{He}} = G_{\text{He}} \). The reciprocity between direct and inverse spin Hall conductances is exact and does not require sample averaging, as sometimes claimed[25].

### B. Reciprocity between spin injection and magnetoelectric spin currents

For a spin index \( \beta = 0 \), Eqs. (14) and (19) establish the reciprocity between magnetoelectric effects generating spin currents from electric voltage biases and spin injection from spin accumulations in the terminals, a special case of which is the above-discussed spin Hall effect/inverse spin Hall effect reciprocity. In the presence of TRS, it has already been observed that one consequence of Eq. (5) is that no spin current can be magnetoelectrically generated in a two-terminal device if the exit lead carries a single (spin-degenerate) transport channel. The reciprocity relations of Eqs. (14) and (19) further impose that a spin injection from such a terminal is incapable of generating an electric current, unless one goes to the nonlinear regime[23]. This seems not to have been noted so far.

### C. Spin Seebeck and spin Peltier coefficients in two-terminal geometries

In two-terminal geometries, the electric conductance is symmetric in TRS breaking fields, which follows from current conservation or gauge invariance, together with the symmetry of electric reflection coefficients, \( G_{ii}^{(00)}(\mathcal{H}) = G_{ii}^{(00)}(-\mathcal{H}) \) (see e.g. Ref. [47]). Including spin-transport, the unitarity of the scattering matrix fur-
ther results in spin-current conservation and generalized gauge invariance,
\[ \sum_i (2N_i \delta_{\alpha\beta} \delta_{ij} - T_{\alpha \beta}) = 0, \]
\[ \sum_j (2N_j \delta_{\alpha\beta} \delta_{ij} - T_{\alpha \beta}) = 0, \quad (26) \]
under the assumption that the number of transport channels coupling the system to external reservoirs is spin-independent. In two-terminal geometries this gives
\[ B_{11}^{(20)} + B_{12}^{(20)} = B_{21}^{(30)} + B_{22}^{(30)} = 0, \]
\[ \Gamma_{11}^{(20)} + \Gamma_{21}^{(20)} = \Gamma_{12}^{(02)} + \Gamma_{22}^{(02)} = 0. \quad (27) \]
However, unlike for the charge conductance, the thermoelectric reflection coefficients can have both a symmetric and an antisymmetric component. This is directly seen from the expression
\[ B_{ii}^{(20)}(\mathcal{H}) = -\frac{e}{h} \int d\epsilon \left( -\frac{\partial f}{\partial \epsilon} \right) \frac{\epsilon}{i_0} \mathcal{T}_{ii}^{(20)}(\mathcal{H}, \epsilon), \quad (28) \]
for the spin Seebeck reflection coefficient. For example for $\beta = z$, the spin-dependent transmission coefficient in the integrand reads
\[ \mathcal{T}_{zz}^{(20)} = \mathcal{T}_{zz}^{(20)} - \mathcal{T}_{zz}^{(20)}, \quad (29a) \]
\[ \mathcal{T}_{xz}^{(20)} = T_{xz}^{(\uparrow,\uparrow)} - T_{xz}^{(\uparrow,\downarrow)}, \quad (29b) \]
\[ \mathcal{T}_{xz}^{(20)} = T_{xz}^{(\downarrow,\uparrow)} - T_{xz}^{(\downarrow,\downarrow)}, \quad (29c) \]
which, from Eq. \[5\] has both symmetric, $\mathcal{T}_{zz}^{(20)}(\mathcal{H}) = \mathcal{T}_{zz}^{(20)}(-\mathcal{H})$, and antisymmetric, $\mathcal{T}_{xz}^{(20)}(\mathcal{H}) = -\mathcal{T}_{xz}^{(20)}(-\mathcal{H})$ components.

An interesting example is provided by a two-terminal system with a well-defined spin quantization axis. This is the case, for example, for a system without spin-orbit coupling in a uniform Zeeman field, for two-dimensional systems with both Rashba and Dresselhaus spin-orbit interactions of equal strength, or for a system with pure $\vec{I} \cdot \vec{s}$ spin-orbit coupling. Without loss of generality we define the spin quantization axis as the $z$-axis. Then $\mathcal{S}$ commutes with $\sigma^{(z)}$, i.e. it is diagonal in spin space. From Eq. \[13\], we find that $\mathcal{T}_{ij}^{(20)}(\mathcal{H}) = \mathcal{T}_{ij}^{(02)}(\mathcal{H})$ and $\mathcal{T}_{ij}^{(a0)}(\mathcal{H}) = 0$ when $\alpha = x, y$. Combining this with Eqs. \[26\], we have $\mathcal{T}_{12}^{(20)}(\mathcal{H}) = \mathcal{T}_{12}^{(02)}(\mathcal{H}) = \mathcal{T}_{21}^{(02)}(\mathcal{H}) = \mathcal{T}_{21}^{(a0)}(\mathcal{H})$. Thus
\[ B_{12}^{(a0)}(\mathcal{H})T_0 = \Gamma_{12}^{(02)}(\mathcal{H}), \quad (30) \]
with $\Gamma_{12}^{(02)}(\mathcal{H}) = 0$ when $\alpha = x, y$. Next we recall that the Seebeck-Peltier Onsager relations contain an extra minus sign for spin caloritronic effects compared to usual thermoelectric effects (see Table \[III\]). This extra minus sign means that $B_{12}^{(20)}$ and $\Gamma_{12}^{(02)}$ are odd in $\mathcal{H}$, while $B_{12}^{(00)}$ and $\Gamma_{12}^{(00)}$ are even in $\mathcal{H}$. Thus any two-terminal system with a spin-quantization axis will have spin-Seebeck and spin-Peltier effects which are odd functions of TRS breaking fields, while the normal Seebeck and Peltier effects are even function of those fields.

**VII. EXAMPLES OF RECIPROCITY RELATIONS IN THERMOELECTRICITY WITH HYBRID SYSTEMS**

Thermoelectric effects in the presence of superconductivity, in particular the thermopower $S = -B^{(00)}/G^{(00)}$ and thermal conductance $\Xi^{(00)}$, have attracted quite some experiments and theoretical interest. However, the exact form that the Seebeck-Peltier Onsager reciprocity relation takes has never been clarified, despite the fact that two-terminal devices with superconductors usually exhibit odd Seebeck coefficients $S(\mathcal{H}) = -S(-\mathcal{H})$, in stark contrast with Mott’s relation. Mott’s relation between the thermopower of metallic systems at low temperature and the energy
the form. as depicted in Fig. 3, Eq. (17) can be rewritten in when PHS is broken. Focusing on a two-terminal geome-
tical systems, one has both $\Gamma_{ij}^{(00)}(\mathcal{H})T_0 = \Gamma_{ji}^{(00)}(\mathcal{H})$; however, with supercond-
cuity, only $B_{ij}^{(00)}(\mathcal{H})T_0 = B_{ji}^{(00)}(-\mathcal{H})$ holds.

When PHS strictly holds, however, $\sum_{i\alpha}\nu\Gamma^{(\mu\nu;\alpha\beta)} = \sum_{i\alpha}\nu\Gamma^{(\mu\nu;\alpha\beta)} = 0$ and both $\Gamma$- and $B$-coefficients vanish identically, regardless of the temperature. However, interesting thermoelectric effects appear in hybrid systems when PHS is broken. Focusing on a two-terminal geometry, as depicted in Fig. 3, Eq. (17) can be rewritten in the form

$$\begin{pmatrix} J \\ I \end{pmatrix} = \begin{pmatrix} \Xi & \Gamma \\ B & G \end{pmatrix} \begin{pmatrix} \Delta T \\ \Delta V \end{pmatrix},$$

which depends only on the voltage and temperature differences between the two normal reservoirs. The two-terminal thermoelectric coefficients are given by

$$G = G_{11}^{(00)} - \frac{1}{2} \left( G_{11}^{(00)} + G_{22}^{(00)} \right) \left( G_{12}^{(00)} + G_{21}^{(00)} \right),$$

$$\Xi = \Xi_{11}^{(00)} - \frac{1}{2} \left( \Gamma_{11}^{(00)} + \Gamma_{12}^{(00)} \right) \left( B_{11}^{(00)} + B_{21}^{(00)} \right),$$

$$B = B_{11}^{(00)} - \frac{1}{2} \left( G_{11}^{(00)} + G_{22}^{(00)} \right) \left( B_{11}^{(00)} + B_{21}^{(00)} \right),$$

$$\Gamma = \Gamma_{11}^{(00)} - \frac{1}{2} \left( \Gamma_{11}^{(00)} + \Gamma_{12}^{(00)} \right) \left( G_{11}^{(00)} + G_{21}^{(00)} \right),$$

in terms of the coefficients $X_{ij}^{(00)} (X = G, B, \Xi, \Gamma)$ defined by Eqs. (11) and (17).

It is then straightforward to see that the reciprocity relations read specifically

$$G(\mathcal{H}) = G(-\mathcal{H}),$$

$$\Xi(\mathcal{H}) = \Xi(-\mathcal{H}),$$

$$B(\mathcal{H}) T_0 = \Gamma(-\mathcal{H}).$$

In particular the presence of superconductivity forces one to invert the sign of the TRS breaking field in the relation of Eq. (34c) between Seebeck and Peltier coefficients.

B. Symmetry of the thermopower

The symmetry of the two-terminal thermopower, $S = -B_{ij}^{(00)}/G_{ij}^{(00)}$ is not specified in the presence of supercond-
cuity. The Seebeck coefficients read

$$B_{ij}^{(00)}(\mathcal{H}) = \frac{2e}{hT_0} \int_0^\infty d\varepsilon \left( -\partial_\varepsilon f \right) \varepsilon \times \left[ \tau_{ij}^{(\epsilon\epsilon;00)}(\varepsilon,\mathcal{H}) + \tau_{ij}^{(\epsilon\chi;00)}(\varepsilon,\mathcal{H}) \right],$$

From this expression we see that thermoelectric effects vanish, $B_{ij}^{(00)} = 0$, if PHS is enforced; we thus consider this equation in the absence of PHS. From Eq. (9) we know that $\tau_{ij}^{(\mu\nu;00)}(\varepsilon,\mathcal{H}) = \tau_{ii}^{(\epsilon\mu;00)}(\varepsilon,\mathcal{H})$, while $\tau_{ij}^{(\epsilon\chi;00)}(\varepsilon,\mathcal{H}) = \tau_{ij}^{(\epsilon\chi;00)}(\varepsilon,\mathcal{H})$. Together with unitarity, $\sum_{ij}\tau_{ij}(\varepsilon,\mathcal{H}) = N^v_0$ and assuming that the number $N^v_0$ of transport channels depends neither on the quasi-
particle type nor on the magnetic field, we readily obtain that $B_{ij}^{(00)}(\mathcal{H}) = B_{ij}^{(00)\text{even}}(\mathcal{H}) + B_{ij}^{(00)\text{odd}}(\mathcal{H})$ is the sum of an even and an odd component,

$$B_{ij}^{(00)\text{even}}(\mathcal{H}) = \frac{2e}{hT_0} \int_0^\infty d\varepsilon \left( -\partial_\varepsilon f \right) \varepsilon \times \left[ \tau_{ij}^{(\epsilon\epsilon;00)}(\varepsilon,\mathcal{H}) - \tau_{ij}^{(\epsilon\chi;00)}(\varepsilon,\mathcal{H}) \right],$$

$$B_{ij}^{(00)\text{odd}}(\mathcal{H}) = \frac{2e}{hT_0} \int_0^\infty d\varepsilon \left( -\partial_\varepsilon f \right) \varepsilon \times \left[ \tau_{ij}^{(\epsilon\chi;00)}(\varepsilon,\mathcal{H}) - \tau_{ij}^{(\epsilon\chi;00)}(\varepsilon,\mathcal{H}) \right].$$
where \( B^{(00)}_{\text{even}}(\mathcal{H}) = B^{(00)}_{\text{even}}(\mathcal{H}) \) and \( B^{(00)}_{\text{odd}}(\mathcal{H}) = -B^{(00)}_{\text{even}}(\mathcal{H}) \). In the absence of Andreev scattering, \( B^{(00)}(\mathcal{H}) = B^{(00)}_{\text{even}}(\mathcal{H}) \) is strictly even in two-terminal geometries, however Andreev scattering gives rise to an odd component. The asymmetric Andreev interferometers considered in Ref. [10] were devised to render \( B^{(00)}_{\text{odd}}(\mathcal{H}) \) finite on mesoscopic average, which led to an antisymmetric thermopower in such systems. There are currently no known hybrid systems which have a finite-average \( B^{(00)}_{\text{even}}(\mathcal{H}) \). Recent theoretical works pointed out asymmetries in the thermopower of metallic systems in the presence of inelastic scattering, which is of interest because asymmetric thermopower may lead to more efficient thermal engines.\(^{[11,21]}\) Hybrid systems are examples of systems with purely elastic scattering and antisymmetric thermopower.

C. Onset of thermoelectric effects upon breaking of PHS

Thermoelectric effects vanish identically in all Altland-Zirnbauer symmetry classes because of PHS. However in physical systems PHS is often at least partially broken, leading to finite thermoelectric effects. Here we show that the symmetry of such thermoelectric effects is subtly dependent on how PHS symmetry is broken.

To that end we consider the Andreev interferometer shown in Fig. 3. A two-terminal chaotic ballistic or disordered diffusive quantum dot is connected to a superconducting loop via two contacts. The superconducting phase difference at the two contacts can be tuned by a magnetic flux piercing the loop. There are two important time scales in the system, (i) the typical time \( \tau_{\text{Andr}} \) between two consecutive Andreev reflections at the superconducting contact, and (ii) the escape time \( \tau_{\text{esc}} \) to one of the normal leads. We additionally choose a special geometry where the average time to reach one of the two superconducting contacts from one of the normal leads is longer — this is achieved by an extra ballistic “neck” of length \( \ell \) between the cavity and the superconducting contact (see Fig. 3). Because of the neck, quasiparticles need an additional time delay \( \delta \tau = \ell/\nu_p \) to reach the left superconducting contact from a normal lead. Together with this time delay, a magnetic flux piercing the superconducting loop and making the superconducting phase difference \( \phi_{\text{sc}} \) finite also breaks PHS, thereby turning thermoelectric effects on.\(^{[10,11]}\)

Formally, PHS requires that \( \tau_{\text{Andr}} \to 0 \), which practically means that \( \tau_{\text{Andr}} \) has to be smaller than any other time scale and any other inverse energy scale. When this is not the case, transport processes without any Andreev reflection exist, giving contributions to the conductance that fluctuate randomly in energy around the Fermi energy. This breaks PHS and leads for instance to finite, albeit relatively weak, thermopower.\(^{[10,11]}\) More generally, breaking PHS can be achieved in three different ways,

(i) rendering escape into the normal leads faster (for instance by widening the normal leads), until \( \tau_{\text{esc}} \sim \tau_{\text{Andr}} \).

(ii) raising the temperature until \( (k_B T)^{-1} \sim \tau_{\text{Andr}} \), or

(iii) changing the flux through the superconducting loop so that \( \phi_{\text{sc}} \neq 0, \pi \), when the neck length \( \ell \) is finite.

In case (i), a significant proportion of quasiparticles go out from one normal lead to another without Andreev reflection. Then contributions to \( T^{ij}_{\mu\nu,\alpha\beta}(\mathcal{H}) \) which arise from processes without Andreev reflection will start to dominate thermoelectric transport, meaning \( B^{(00)}_{\text{even}} \gg B^{(00)}_{\text{odd}} \) [as defined in Eq. (36)]. Thus, thermoelectric effects acquire the same symmetry as systems without SC contacts, i.e. they become predominantly even.

The situation is more complicated in case (ii), where both \( T^{ij}_{\mu\nu,\alpha\beta}(\mathcal{H}) \) and \( T^{\pi ij}_{\mu\nu,\alpha\beta}(\mathcal{H}) \) have similar magnitude. In the absence of a neck, \( \ell = 0 \), thermoelectric effects vanish on average and are dominated by mesoscopic fluctuations.\(^{[10,11]}\) An analysis of these mesoscopic fluctuations analogous to that in Ref. [10] shows that there is no correlation between \( B^{(00)}_{ij}(\mathcal{H}) \) and \( B^{(00)}_{ji}(-\mathcal{H}) \), so that the thermoelectric effects have no particular symmetry beyond the generic Onsager reciprocities given in Table III. In particular, for a two terminal device \( B^{(00)}_{\text{even}} \) and \( B^{(00)}_{\text{odd}} \) are independent random variables with the same variance. Thus for a given Andreev interferometer (given disorder or cavity shape) either quantity could be positive or negative, and either could have a larger magnitude than the other.

Finally in case (iii), the physics changes completely. Due to the presence of a finite-sized neck, \( \ell \neq 0 \), and superconducting phase difference \( \phi_{\text{sc}} \neq 0, \pi \), the system develops a large average thermopower which is an odd function of the flux \( \phi_{\text{sc}} \),\(^{[10,11]}\) with a much smaller even component coming from mesoscopic fluctuations.\(^{[10]}\)

In summary depending on how particle-hole symmetry is broken, one gets a thermopower which is predominantly even in \( \mathcal{H} \) [case (i)], predominantly odd in \( \mathcal{H} \) [case (iii)], or which has no particular symmetry [case (ii)].

VIII. CONCLUSIONS

We have derived a complete list of reciprocity relations for coupled electric, spin, thermoelectric and spin caloritronic transport effects in all ten symmetry classes for single-particle Hamiltonian systems. Several of these relations appeared in one way or another in earlier works, and the main novelties we found are (i) reciprocities in spintronics and spin caloritronics pick a number of additional minus signs reflecting spin current injection and measurement, (ii) a number of special relations have been listed in Table [V] which exist only in specific symmetry classes, (iii) we clarified the exact form of Onsager relations in the presence of superconductivity, and (iv) we derived all Onsager relations for transport in spintronics.
and spin caloritronics in the presence of superconductivity. We present a pictorial summary of the Onsager reciprocity relations we derived in Fig. 4.

Generally speaking, our investigations of the specific reciprocity shown in Table V allowed us to clarify the form that the Seebeck-Peltier relations take in the presence of superconductivity. While the two relations, $B_{ij}^{(00)} (3\mathcal{H}) T_0 = \Gamma_{ij}^{(00)} (3\mathcal{H})$ and $B_{ij}^{(00)} (3\mathcal{H}) T_0 = \Gamma_{ji}^{(00)} (3\mathcal{H})$, exist in purely metallic systems, only one of these two Onsager relations survives in the presence of superconductivity, that being $B_{ij}^{(00)} (3\mathcal{H}) T_0 = \Gamma_{ji}^{(00)} (3\mathcal{H})$.

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