PAPER

Re-examination of the Elliott–Yafet spin-relaxation mechanism

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Abstract

We analyze spin-dependent carrier dynamics due to *incoherent* electron–phonon scattering, which is commonly referred to as Elliott–Yafet (EY) spin-relaxation mechanism. For this mechanism one usually distinguishes two contributions: (1) from the spin–diagonal electrostatic interaction together with spin-mixing in the wave functions, which is often called the Elliott contribution, and (2) the phonon-modulated spin–orbit interaction, which is often called the Yafet or Overhauser contribution. By computing the reduced electronic density matrix, we improve Yafet’s original calculation, which neglects the spin-mixing in the single-particle states for the determination of the ensemble spin. The important novel quantity in our calculation is a torque operator that determines the spin dynamics due to incoherent scattering. The contribution (1) to this torque vanishes exactly. From this general result, we derive a modified expression for the EY spin relaxation time for Kramers degenerate bands.

1. Introduction

Spin relaxation plays a role in spin-dependent dynamics both on long and short timescales. While its contribution to (precessional) magnetization damping is usually ascribed to spin–lattice relaxation and treated phenomenologically, the analysis of ultrafast demagnetization dynamics has often been based on the microscopic concept of spin–flip processes due to electron–phonon interactions as developed for semiconductors in the 1950s [1]. Overhauser [2] was the first to identify the modulation of the spin–orbit interaction by lattice vibrations as the microscopic mechanism for spin relaxation due to incoherent electron–phonon scattering processes. Elliott [3] argued shortly thereafter that there is an additional contribution to the spin relaxation due to the momentum-dependent spin mixing in the wave functions and that, consequently, even incoherent scattering processes due to spin–diagonal interactions can contribute to spin relaxation. The subject was taken up again by Gerasimenko and Andreev [4], and Yafet [5]. The latter calculated the spin–flip matrix element due to electron–phonon interaction (as a function of electronic momentum transfer $q$) including both the Overhauser and the Elliott contributions and showed that the first few orders in $q$ vanish due to a cancellation of Overhauser and Elliott contributions. Nowadays, this combination of Overhauser and Elliott contributions is usually called Elliott–Yafet (EY) mechanism because Yafet derived a relatively simple result for the close-to-equilibrium spin relaxation time, which is suitable for evaluation from *ab initio* input and can be used to justify an approximate relation between the spin relaxation time and the momentum relaxation time.

The original Yafet result was derived for the case of Kramers degenerate bands, and the expression for the spin relaxation time derived as a special case was mainly used for semiconductors. Over the last decade, the EY result has also been used to describe ultrafast magnetization dynamics in itinerant ferromagnets after optical excitation. In optically excited ferromagnets, a macroscopic magnetization is quenched on an ultrafast timescale [6, 7] and some of the competing theories concerning the microscopic mechanism responsible for the magnetization dynamics on this short timescale [8] involve spin–lattice coupling. In particular, Koopmans *et al* [9] proposed spin–flip scattering due to spin mixing as the main mechanism, and it is in this sense that ‘EY mechanism’ is used in the ultrafast magnetism community [10–13]. Whereas the EY mechanism plays an
important role in a microscopic version of the three-temperature model [13], its role in the microscopic electronic dynamics is still debated [11, 12, 14–17]. In this context, no agreement has been reached as to the relative magnitude and cancellation effects between Elliott and Overhauser contributions to the electron–phonon interactions in ferromagnetic metals [10–12].

In this paper, we present a new analysis of the spin–relaxation problem due to incoherent electron–phonon scattering, as it was originally considered by Overhauser, Elliott, and Yafet. We derive the dynamical equation for the change of the reduced electronic spin–density matrix by expressing the spin dynamics in terms of phonon assisted density matrices. This approach achieves a correct description of the dynamics of the spin vector, as opposed to the Yafet derivation, which is inconsistent in its treatment of non-pure spin states, and thus cannot correctly account for the ‘amount of spin–flip’ in each scattering transition. If one correctly describes the spin vector for non-pure states, it becomes obvious that the important quantity for incoherent spin dynamics is a torque matrix element, which is not present in the conventional derivation [5]. Remarkably, there is no contribution to this torque matrix element from spin–diagonal scattering mechanisms. Put differently, incoherent spin–diagonal electron–phonon scattering and spin–orbit coupling alone, which is usually referred to as the Elliott spin–relaxation mechanism, yields no spin dynamics. This is a general result that applies to incoherent spin dynamics due to any spin diagonal interaction, regardless of the specific material. Based on this observation, we derive for the special case of Kramers degenerate bands, for which only incoherent dynamics play a role, a modified result for the EY spin–relaxation time.

This paper is organized as follows. In section 2 we briefly review the original EY treatment, and some more recent contributions. In section 3 we set up the electron–phonon interaction hamiltonian, discuss long and short-range contributions, and derive the equations of motion for the spin–density matrix and the spin expectation value. Section 4 is devoted to the derivation of a spin relaxation time for the special case of Kramers degenerate bands. An important ingredient for this derivation is the form of the quasi-equilibrium spin–density matrix in the presence of spin–orbit coupling, which is discussed in some detail. The conclusions are presented in section 5. Appendix A contains a short demonstration concerning the form of the spinor wavefunctions for Kramers degenerate bands, and appendix B details the derivation of the equation of motion of the spin–density matrix at the scattering level.

2. EY approach

The EY approach has been reviewed often [1, 18, 19]. Only for comparison with our calculations, we repeat here some of the main points of Yafet’s derivation in [5] using his notation. The objective of Yafet is to calculate the rate of a spin–flip transition for two Kramers degenerate bands including spin–orbit coupling. The Kramers degeneracy implies that for a band index \( b \) we have two wave functions

\[
\psi_{b\uparrow}(x) = \phi_{b\uparrow,k}(x) | \uparrow \rangle + \phi_{b\downarrow,k}(x) | \downarrow \rangle,
\]

\[
\psi_{b\downarrow}(x) = \hat{K} \psi_{b\uparrow}(x),
\]

with the same energy \( E_{bk} \), where \( \hat{K} \) is the time-reversal operator. Focusing on one band and dropping the corresponding \( b \) index, he then calculates the Golden-Rule transition probability \( W_{\uparrow\downarrow,k,k'} \) for a spin–flip transition \( \psi_{\uparrow,k} \rightarrow \psi_{\downarrow,k'} \) due to the electron–phonon interaction. More precisely, Yafet calculates the dynamics of the spin polarization, which is defined as

\[
D_{\text{spin}} = \frac{1}{V} \sum_{k} [n_{\uparrow,k} - n_{\downarrow,k}],
\]

where \( n_{\lambda,k} \) denote the carrier distributions with momentum \( k \) and \( \lambda = \uparrow, \downarrow \) labels the Kramers degenerate bands. It is clear that \( D_{\text{spin}} \) cannot be a good approximation to the spin polarization for pronounced spin mixing. Then (including a factor of 2 as in Yafet’s derivation) one obtains

\[
\frac{d}{dt} D_{\text{spin}} = 2(W_{\uparrow\downarrow} - W_{\downarrow\uparrow}) = 4W_{\uparrow\downarrow}.
\]

Thus the change of spin polarization is determined essentially by the number of transitions (per unit time), which is obtained by adding the in-scattering and out-scattering Golden-Rule probabilities

\[
W_{\lambda\lambda'} = \frac{1}{V^{2}} \sum_{kk'} [W_{\lambda,k,k'} n_{\lambda,k} [1 - n_{\lambda',k'}] - W_{\lambda',k,k'} n_{\lambda',k} [1 - n_{\lambda,k}]],
\]
where

\[
W_{\epsilon, k} = \frac{2\pi}{\hbar} |M^{(\lambda)}_{\epsilon, k}|^2 \frac{f_\epsilon}{2MN\omega_q} \times [\delta(E_k - E'_k) + \hbar\omega_q]N_q + \delta(E_k - E'_k) - \hbar\omega_q)(N_q - 1)]
\]

and \( q = |k' - k| \). The other symbols have an obvious meaning and are defined below. To obtain a relaxation time valid for a small spin polarization, the distribution functions \( n_{\epsilon, k} \) are assumed to be of the quasi-equilibrium form \( f(\epsilon_{\epsilon, k} = \mu_{\epsilon, k}) \) with \( \mu_{\epsilon, k, \lambda} \), the chemical potentials that depend on the band index, and the distributions are expanded for small \( \mu_{\epsilon, k, \lambda} \)'s. This treatment has recently been extended to ferromagnets \([20]\). Finally, Yafet shows from a symmetry argument that, in the long-wavelength limit, there is a cancellation between the contributions to the electron–phonon (e–pn) coupling matrix element due to the electrostatic electron–ion interaction and the phonon-modulated spin–orbit coupling. In this paper, we refer to these two contributions as the Elliott and Overhauser contributions, which we explain in detail below.

In our view this method has three problems.

1. The spin polarization \( D_{\text{spin}} \), defined in (3), is computed as the difference of occupation numbers as if the electrons were in pure spin states for all \( k \) values. Here, the Yafet derivation ignores spin mixing, which leads to a \( k \) dependent expectation value of \( \hat{z}_\epsilon \). Importantly, the modulus of this spin expectation value in a mixed state may be significantly smaller than \( \hbar/2 \). This particular shortcoming is avoided in some modern treatments, see, e.g., \([21, 22]\).

2. The calculation of spin dynamics is based on transition probabilities between mixed spin states. Such a treatment neglects coherences between the mixed-spin states, which are the off-diagonal elements of the spin–density matrix

\[
\rho(k) = \begin{pmatrix}
\rho_{\epsilon, k} & \rho_{\epsilon, k, \lambda, \lambda'} \\
\rho_{\lambda', \lambda, k} & n_{\epsilon, k}
\end{pmatrix}
\]

3. Yafet proves the cancellation between the Elliott and Overhauser contributions to the spin–flip matrix element \( M^{(\lambda)}_{\epsilon, k, k'} \) for the short range part of the electron–phonon coupling matrix element. As shown by Grimaldi and Fulde \([23]\) there is also a long-range contribution, for which this cancellation does not hold, and which is larger than the short-range contribution in the long-wavelength limit.

The Yafet method is so widely accepted that it may be worthwhile to mention that ours is not the first paper to point to these problems. For instance \([20]\), already pointed out that the magnetic moment of state \( \lambda, k \) is different for different \( k \)-vectors, and that neglecting this dependence in the Yafet derivation is certainly problematic in systems with spin ‘hot spots’, i.e., with regions in the Brillouin zone where the spin mixing is very large. Also, for semiconductors, Yu et al \([21]\) have used spin projection operators to avoid the first problem in their calculation of the EY spin–relaxation time, but missed the Overhauser contribution, as they only include spin–diagonal scattering processes.

Going beyond spin-relaxation times, there are microscopic approaches to spin-dependent carrier dynamics that compute the reduced density matrix \([24–27]\), see \([28]\) for a review. Numerically solving for the full dynamical spin–density matrix also yields Dyakonov–Perel and Bir–Abramov–Pikus contributions to spin relaxation, but is very CPU-time intensive and difficult because the microscopic carrier dynamics have to be computed to obtain spin relaxation times, which are often orders of magnitude longer than typical scattering times. Numerically calculating the spin–density matrix does not yield explicit expressions for spin relaxation times, which is one of the goals of our paper. Further, our calculation gives a more transparent description of the ensemble spin dynamics due to incoherent scattering processes in terms of the torque matrix element than is possible by ‘brute-force’ calculation of the dynamical spin–density matrix.

As mentioned in the Introduction, the EY mechanism has also been applied to the demagnetization dynamics in ferromagnets \([9–14]\). While \([9]\) introduced the name of EY spin dynamics as a mechanism for demagnetization, it assumed incoherent spin–flip scattering where the angular momentum is transferred to the phonons. In \([10–14]\), the assumptions of Yafet for semiconductors have essentially been taken over. While we are mainly concerned with a reexamination of the original EY mechanism, we hope that our results will also help to clarify some questions in magnetization dynamics.
3. Spin-dependent electron–phonon scattering dynamics

In this section we present a derivation of spin-dependent carrier dynamics due to electron–phonon interaction that avoids the three problems listed above. We first derive the interaction hamiltonian between electrons and phonons including the long-range contribution of the Coulomb potential, and specialize to the long-wavelength limit. With this interaction we derive the equation of motion for the spin–density matrix including phonon-assisted correlation functions. We identify the torque matrix element that determines the incoherent dynamics of the average spin. Finally, we derive the scattering limit of the dynamical equation. Note that the development in this section applies to systems with and without spin splitting, we only specialize to the case of Kramers degenerate bands in section 4.

3.1. Electron–phonon interaction hamiltonian

We start our derivation by writing down the interaction potential of a single electron in a lattice in terms of lattice site coordinates \( \mathbf{R}_n \) as \( \hat{v}_{\text{io}}(\mathbf{x}, |\mathbf{R}_n|) = \sum_n \hat{v}_{\text{io}}(\mathbf{x} - \mathbf{R}_n) \), where

\[
\hat{v}_{\text{io}}(\mathbf{x}) = v_{\text{eff}}(\mathbf{x}) + \xi [\nabla v_{\text{eff}}(\mathbf{x}) \times \mathbf{p}] \cdot \hat{\sigma}.
\]  

(8)

Here, \( v_{\text{eff}} \) is the effective electrostatic Coulomb interaction between the electron and the ionic core and \( \xi = e^2/(4 \pi \varepsilon^2) \). We have made here the rigid-ion approximation, that is, we assume that the core electrons and the nuclei form ions, which set up a potential for the valence electrons \( \hat{v}_{\text{io}}(\mathbf{x}) \), which follows rigidly the motion of the ions. This is, in general, a good approximation for semiconductors [29] and simple metals [30].

We stress that this approximation places no fundamental restriction on the following development, but the equations of motion become more complicated without it. We denote single-particle operators acting on the electronic space and spin variables by small letters and a hat; for instance, \( \hat{\psi}_n \) is an operator in spin space.

For ferromagnets, the electron–ion interaction is sometimes written as

\[
\hat{v}_{\text{io}}(\mathbf{x}) = \hat{v}(\mathbf{x}) + \xi [\nabla \hat{v}(\mathbf{x}) \times \mathbf{p}] \cdot \hat{\sigma},
\]  

(9)

with \( \hat{v} = v_{\text{eff}}(\mathbf{x}) \hat{1} + \Delta \hat{v}(\mathbf{x}) \hat{\sigma}_z \),

(10)

where \( v_{\text{eff}} = (v_1 + v_f)/2 \), \( \Delta v = (v_1 - v_f)/2 \), \( \hat{\sigma}_z \) is a Pauli matrix, and \( \hat{1} \) the identity in spin space. In both cases, the electron–ion interaction has a spin–vectorial and an explicitly spin-dependent contribution. We will use the electron–ion interaction hamiltonian in the form (8) as it applies to semiconductors, but distinguish in the following only between spin–vectorial and explicitly spin-dependent contributions, which also applies to (9). In semiconductors, these two contributions could be called, respectively, Elliott and Overhauser (or Yafet) contributions. However if it is not clearly stated to which one of the interaction hamiltonians (8) and (9) one refers, this terminology can be ambiguous.

We follow the usual treatment of the electron–phonon coupling [30] by considering small deviations \( \mathbf{R}_n = \mathbf{R}_n^{(0)} + \mathbf{Q}_n \) around the equilibrium configuration \( \mathbf{R}_n^{(0)} \) and expand \( v_{\text{eff}}(\mathbf{r} - \mathbf{R}_n) \) with respect to \( \mathbf{R}_n \). The resulting electron–phonon hamiltonian in second quantization is

\[
H_{\text{e–pn}} = \sum_n \int \Psi_\uparrow(\mathbf{r}) \left[ \mathbf{Q}_n \cdot \frac{\partial \hat{v}_{\text{io}}(\mathbf{r} - \mathbf{R}_n)}{\partial \mathbf{R}_n} \right] \Psi_\downarrow(\mathbf{r}) \mathrm{d}^3r,
\]  

(11)

where \( \Psi \equiv (\Psi_\uparrow, \Psi_\downarrow) \) denotes a spinor field operator. Note that \( \partial \hat{v}_{\text{io}}/\partial \mathbf{R}_n \) is an operator in spin space.

While the properties of the electron–phonon interaction can be discussed without specifying a model for the single-particle band structure, we also need the electronic single-particle contribution to the hamiltonian for the derivation of the equations of motion. We thus consider the model hamiltonian \( H = H_e + H_{\text{e–pn}} \) with

\[
H_e = \int \Psi_\uparrow(\mathbf{r}) \left[ \frac{\mathbf{p}^2}{2m_0} + \sum_n \hat{v}_{\text{io}}(\mathbf{r} - \mathbf{R}_n^{(0)}) \right] \Psi(\mathbf{r}) \mathrm{d}^3r.
\]  

(12)

We follow the standard approach [31] and expand the field operators according to

\[
\Psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mu} \sum_k \phi_{\mu k}(\mathbf{r}) c_{\mu k},
\]  

(13)

where \( \phi_{\mu k}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} u_{\mu k}(\mathbf{r}) \) are Bloch spinor wavefunctions with band and crystal momentum labels \( (\mu k) \). The destruction operator corresponding to \( \phi_{\mu k} \) is \( c_{\mu k} \), and \( V \) is the normalization volume of the crystal. A Greek index labels the bands including spin–orbit coupling. In the case of Kramers degenerate bands, to which we...
specialize below, it includes a band index \( b \) and an additional label \( \lambda \) to distinguish the degenerate states, which is sometimes called a pseudospin index, i.e., \( \mu = (b, \lambda) \).

Instead of the Bloch wavefunctions, which are orthogonal on the whole crystal volume \( V \), we will mainly deal with the lattice periodic \( u_{\mathbf{k}} \)'s, which are defined and orthogonal on the unit cell \( \Omega \), because we intend to derive matrix elements on the unit cell \( \Omega \). Matrix elements of any single-electron operator \( \hat{a} \) that occur in the present paper have the meaning

\[
\langle u_{\mathbf{k} BZ} | \hat{a} | u_{\mathbf{k}' BZ} \rangle_{\Omega} := \frac{1}{\Omega} \int_{\Omega} [\hat{a} u_{\mathbf{k}}(\mathbf{r})]_B [\hat{a} u_{\mathbf{k}'}(\mathbf{r})]_{BZ} \, d^3r.
\]

(14)

By virtue of equation (8), the electron–phonon interaction Hamiltonian (11) can be split into two parts \( H_{e-\text{pn}} = H_{e-\text{pn}}^{(1)} + H_{e-\text{pn}}^{(2)} \), one of which

\[
H_{e-\text{pn}}^{(1)} = \sum_{n} \sum_{\mathbf{k}k'\mu\mu'} \xi_{\mathbf{q}k\mu} \phi_{\mathbf{q}k\mu}(\mathbf{r}) \frac{\nabla v_{\text{eff}}(\mathbf{r} - \mathbf{R}_n^{(0)})}{\sqrt{V}} \phi_{\mathbf{q}k'\mu'}(\mathbf{r}).
\]

(15)

is spin–diagonal, whereas the other one explicitly depends on the electronic spin \( \mathbf{\hat s} \)

\[
H_{e-\text{pn}}^{(2)} = -\sum_{n} \sum_{\mathbf{k}k'\mu\mu'} \xi_{\mathbf{q}k\mu} \phi_{\mathbf{q}k\mu}(\mathbf{r}) \frac{\nabla v_{\text{eff}}(\mathbf{r} - \mathbf{R}_n^{(0)})}{\sqrt{V}} \phi_{\mathbf{q}k'\mu'}(\mathbf{r})
\]

\[
\int d^3r \frac{\nabla v_{\text{eff}}(\mathbf{r} - \mathbf{R}_n^{(0)})}{\sqrt{V}} \phi_{\mathbf{q}k\mu}(\mathbf{r}) \left[ \nabla (\mathbf{Q}_n \cdot \nabla v_{\text{eff}}(\mathbf{r} - \mathbf{R}_n^{(0)})) \times \mathbf{\hat p} \right] \cdot \mathbf{\hat s} \phi_{\mathbf{q}k'\mu'}(\mathbf{r}).
\]

(16)

We next expand the phonon displacement operators according to [31]

\[
\mathbf{\hat Q}_n(t) = i \sum_{\mathbf{q},\lambda} \mathbf{\hat Q}_n^{(0)} B_{\mathbf{q},\lambda} e^{i\mathbf{q} \cdot \mathbf{R}_n^{(0)}} \mathbf{\hat e}_{\mathbf{q},\lambda},
\]

(17)

with \( B_{\mathbf{q},\lambda} \equiv b_{-\mathbf{q},\lambda}^+ + b_{\mathbf{q},\lambda} \), where \( b_{\mathbf{q},\lambda}^{\dagger} \) annihilates (creates) phonons with momentum \( \mathbf{q} \) in the first Brillouin zone and mode index \( \lambda \). We use the abbreviation of \( \mathbf{Q}_n^{(0)} = \sqrt{\hbar/(2\rho \omega_{\mathbf{q},\lambda})} \), which has the unit of length, where \( \rho \) is the density. The phonon dispersion is denoted by \( \omega_{\mathbf{q},\lambda} \). Further, \( \mathbf{\hat e}_{\mathbf{q},\lambda} \) is the polarization vector of the phonon mode with the property \( (\mathbf{\hat e}_{\mathbf{q},\lambda})^* = -\mathbf{\hat e}_{-\mathbf{q},\lambda} \). We introduce the Fourier transformation of the interaction potential in the form [31]

\[
v_{\text{eff}}(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{q} \in \text{BZ}} \sum_{\mathbf{G}} v_{\text{eff}}(\mathbf{q} + \mathbf{G}) e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}},
\]

which has a long-range part \( (\mathbf{G} = 0) \) and short-range part \( (\mathbf{G} \neq 0) \).

Now we split the integral over the crystal volume \( V \) according to

\[
\frac{1}{V} \int_{V} f(\mathbf{r}) d^3r = \frac{1}{N\Omega} \sum_{n} \int_{\Omega} f(\mathbf{r} + \mathbf{R}_n^{(0)}) d^3r,
\]

(19)

use the periodicity \( u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n^{(0)}) = u_{\mathbf{k}}(\mathbf{r}) \) and the relation \( \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{k}} = N \delta_{\mathbf{k} - \mathbf{k}'} \). We thus obtain for the e–pn coupling Hamiltonian (11)

\[
H_{e-\text{pn}} = \sum_{\mathbf{k}k'\mu\mu'} \xi_{\mathbf{q}k\mu} \phi_{\mathbf{q}k\mu}(\mathbf{r}) B_{\mathbf{q},\lambda} \phi_{\mathbf{q}k'\mu'}(\mathbf{r})
\]

(20)

with the matrix element

\[
\delta_{\mathbf{q},\lambda}^{(\mathbf{k} \rightarrow \mathbf{k}')} = \langle u_{\mathbf{k} BZ} | \phi_{\mathbf{q}k\mu}^{(\mathbf{k} \rightarrow \mathbf{k}' BZ)} \rangle_{\Omega}
\]

(21)

in terms of the e–pn interaction operator

\[
\phi_{\mathbf{q}k\mu}^{(\mathbf{k} \rightarrow \mathbf{k}')}(\mathbf{r}) = \mathbf{\hat Q}_n^{(0)} B_{\mathbf{q},\lambda} \phi_{\mathbf{q}k\mu}(\mathbf{r}) \frac{\nabla v_{\text{eff}}(\mathbf{r} + \mathbf{G})}{\sqrt{V}}
\]

\[
\left[ (\mathbf{q} + \mathbf{G}) \cdot \mathbf{\hat e}_{\mathbf{q},\lambda} \right] \left[ \frac{1}{i} + i \lambda \left[ (\mathbf{q} + \mathbf{G}) \times (\mathbf{\hat p} + \hbar \mathbf{k}) \right] \cdot \mathbf{\hat s} \right].
\]

(22)

The first term in the curly braces in the above expression comes from the spin diagonal term (15) and the rest from the explicitly spin-dependent term (16). The \( \mathbf{q} \) and \( \mathbf{k} \) vectors are restricted to the first Brillouin zone, and we have already neglected Umklapp processes, which contribute if \( \mathbf{k} + \mathbf{q} \) lies outside the first BZ. This is a common approximation for optically excited electron dynamics when one is not interested in transport processes. The long-range part of this expression results from the \( \mathbf{G} = 0 \) contribution to the sum, whereas the sum over the \( \mathbf{G} = 0 \) defines the short-range part of the matrix elements. Grimaldi and Fulde [23] demonstrate that the long-range part of the matrix element is most important in the long-wavelength limit, so that we explicitly isolate the long-range part in the following.

We will use the e–pn interaction matrix element in the long-wavelength limit as customary in semiconductor spintronics [28]. Grimaldi and Fulde [23] also demonstrate how the long-range contribution is
screened so that \( v_{\text{eff}}(q) \) has a well defined \( q \to 0 \) (long-wavelength) limit. In this limit, the long-range interaction operator is

\[
\hat{g}^{(\Lambda)}_{k,q\cdot k} = \epsilon^{(0)}_{q\cdot k,\Lambda} v_{\text{eff}}(q \to 0)(q\cdot \epsilon_{q\cdot k,\Lambda}) \left( \frac{1}{\hbar} - \frac{i\hbar}{\hbar} [q \times (\hat{p} + \hbar \hat{\mathbf{k}})] \cdot \hat{s} \right). \tag{23}
\]

Note that for small \( q \) the electrons couple exclusively to longitudinal phonons, where the polarization vector \( \epsilon_{q\cdot k,\Lambda} \) points in the same direction as the wave-vector \( q \).

### 3.2. Equation of motion for spin–density-matrix

In this section we derive the equation of motion for the reduced spin–density matrix

\[
\rho^{\mu\nu}_k(t) \equiv \langle \hat{c}^\dagger_{k\mu} \hat{c}_{k\nu} \rangle \tag{24}
\]

which determines all single-particle properties of the electronic ensemble.

We will for definiteness also include coherent terms and eventually take the scattering limit. Therefore we need the single-particle Hamiltonian (12) in diagonal form

\[
H_k = \sum_{\mu} \epsilon_{\mu k} c^\dagger_{k\mu} c_{k\mu}.
\tag{25}
\]

Here, we \( \mathbf{k} \cdot \mathbf{p} \) theory [32, 33], i.e., the \( u_{\mathbf{k} \mathbf{\Lambda}}'s \) and energy dispersions \( \epsilon_{\mu k} \) are determined as the solution of the eigenvalue problem of the self-adjoint \( \mathbf{k} \cdot \mathbf{p} \) operator \( \hat{H}_{\text{eff}}(\mathbf{k}) \)

\[
\hat{H}_{\text{eff}}(\mathbf{k}) u_{\mathbf{k} \mathbf{\Lambda}} = \epsilon_{\mu k} u_{\mathbf{k} \mathbf{\Lambda}}
\tag{26}
\]

for lattice-periodic \( u_{\mathbf{k} \mathbf{\Lambda}}'s \) on \( \Omega \). This guarantees that, for each \( \mathbf{k} \), the eigenvalue spectrum \( \epsilon_{\mu k} \) is discrete and the \( u_{\mathbf{k} \mathbf{\Lambda}} \) form a complete set, i.e.

\[
\sum_{\mu} \langle u_{\mathbf{k} \mu} \rangle (u_{\mathbf{k} \mu}) = 1.
\tag{27}
\]

Further, the \( u_{\mathbf{k} \mu} \)’s for each \( \mathbf{k} \) are orthogonal with regard to the scalar product (14). In semiconductors, the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian operator can be approximated on a subset of bands by an effective Hamiltonian, such as the Luttinger Hamiltonian [33]. The number of bands included in (25) determines the dimension of the reduced density matrix \( \rho_k \).

The equation of motion for the electronic spin–density–matrix \( \rho^{\mu\nu}_k \) due to (20) and (25) is

\[
\frac{\partial}{\partial t} \rho^{\mu\nu}_k = \frac{i}{\hbar} (\epsilon_{\mu k} - \epsilon_{\mu k}) \rho^{\mu\nu}_k + \frac{\partial}{\partial t} \rho^{\mu\nu}_k \bigg|_{e-pn},
\tag{28}
\]

with

\[
\frac{\partial}{\partial t} \rho^{\mu\nu}_k \bigg|_{e-pn} = \frac{i}{\hbar} \sum_{\mathbf{k}} \sum_{\mathbf{k}^\prime} \left\{ \langle u_{\mathbf{k} \mu + q} \hat{c}^\dagger_{\mathbf{k}^\prime + q \mu} u_{\mathbf{k} \mu} \rangle \langle B_{q \Lambda \mu} \hat{c}^\dagger_{\mathbf{k}^\prime + q \Lambda} \hat{c}_{\mathbf{k} \Lambda} \rangle
\right.

\left. - \langle u_{\mathbf{k} \mu} \hat{c}^\dagger_{\mathbf{k}^\prime + q \Lambda} u_{\mathbf{k} \mu} \rangle \langle B_{-q \Lambda \mu} \hat{c}^\dagger_{\mathbf{k}^\prime + q \Lambda} \hat{c}_{\mathbf{k} \Lambda} \rangle \right\}.
\tag{29}
\]

Equation (28) is the full equation of motion that contains the coherent contribution, which includes a rotation of the off-diagonal elements of the spin–density matrix with energy difference \( \epsilon_{\mu k} - \epsilon_{\mu k} \), and the e–pn interaction contribution (29), in which the phonon-assisted electronic density matrix \( \langle \hat{b}_{q \Lambda \mu} \hat{c}^\dagger_{\mathbf{k}^\prime + q \Lambda} \hat{c}_{\mathbf{k} \Lambda} \rangle \) appears [33, 34]. Equation (28) also describes spin relaxation due to the coherent rotation of \( \rho \) because the single-particle Hamiltonian (26) includes spin–orbit coupling and thus may lead to spin–split bands. For the case of hole bands in GaAs, the influence of coherent rotation times has been studied, e.g., [27, 35, 36]. In the context of ferromagnets, the importance of the off–diagonal elements of the spin–density matrix has been also investigated in the framework of a quantum kinetic calculation recently [37]. In accordance with [27] we obtain the pure EY mechanism by neglecting the spin splitting, i.e., coherent contributions in (28), in the basis in which the single-particle Hamiltonian (26) is diagonal. For the case of a pair of Kramers degenerate bands, to which we specialize in section 4 below, the coherent contributions vanish exactly.

### 3.3. Dynamics of the average spin due to incoherent e–pn interaction

Before we make approximations to the phonon-assisted density matrix, we compute the dynamics of the vector of the average spin

\[
\mathbf{S} = \left\langle \int_V |\Psi(t)\rangle \hat{\mathbf{s}} |\Psi(t)\rangle d^3r \right\rangle = \sum_{k \mu \nu} \langle u_{\mu k} |\hat{\mathbf{s}} |u_{\nu k}\rangle \rho^{\mu\nu}_k.
\tag{30}
\]
By combining (29) and (30) we obtain for the $\alpha = x, y, z$ components
\[
\frac{\partial}{\partial t} S_{\alpha} \bigg|_{e-pn} = \frac{i}{\hbar} \sum_{kqj}\sum_{\mu
u'}\sum_{\lambda}\langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | kq j \rangle \Omega \{ \langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | kq j \rangle \Omega \times \langle B_{q, \lambda}^{\alpha} \mu, \nu'| \lambda \rangle \Omega, \langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | kq j \rangle \Omega \times \langle B_{-q, \lambda}^{\alpha} \mu, \nu'| \lambda \rangle \Omega \} \bigg|_{e-pn}.
\]
We can employ the completeness property (27) of the $u_{j\mu}$’s to show that this has the form
\[
\frac{\partial}{\partial t} S_{\alpha} \bigg|_{e-pn} = \sum_{kqj} \sum_{\mu
u'} \frac{1}{2} \frac{1}{\hbar^2} \langle B_{q, \lambda}^{\alpha} \mu, \nu'| \lambda \rangle \Omega, \langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | kq j \rangle \Omega, \langle B_{-q, \lambda}^{\alpha} \mu, \nu'| \lambda \rangle \Omega \bigg|_{e-pn},
\]
with the torque vector operator due to the e–pn interaction
\[
\hat{\tau}_{k+q}^{(\lambda)} \equiv \frac{1}{\hbar} \langle \lambda | \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | k+q \lambda \rangle \bigg|_{e-pn}.
\]
This matrix element completely determines the spin change that occurs in a transition $(\mu k) \rightarrow (\mu' k + q)$. This information is not explicit in the matrix element (21). Using (22), one finds
\[
\hat{\tau}_{k+q}^{(\lambda)} = \sum_{G} \epsilon^{(0)}_{qG} e^{\Omega r_{\text{eff}}(q + G)} [(q + G) \cdot \varepsilon_{q, \lambda}] [Q + \langle -i\xi \rangle [(q + G) \times (\hbar k + p)] \times \lambda],
\]
where, again, the two terms result from spin–diagonal and explicitly spin-dependent contributions (15) and (16), respectively. The expression (32) together with (35) is an important result, as it shows that only the explicitly spin dependent contribution to the e–pn interaction gives rise to a non-vanishing torque (35). This conclusion does not depend on the single-particle basis $u_{j\mu}$ in the sense that one could apply a $k$-dependent unitary transformation to the $u_{j\mu}$’s and the $g_{j\mu}$’s in (32) and (35). Note that no approximation whatsoever has been made for the dynamics of the phonon assisted quantity. Further, equation (32) and the definition of the torque matrix element is a rather general result for the spin change due to any incoherent electron–boson scattering, for instance, with photons or magnons.

We want to illustrate this result in the language of semiconductor spintronics. Here, the Elliott spin relaxation mechanism refers to the spin relaxation due to a spin–diagonal interaction combined with a spin-mixing in the wavefunction. Our result shows that it is not the spin mixing in the wave functions that determines the Elliott torque matrix element: in this restricted sense, there is no Elliott contribution to spin dynamics in any basis, and the spin dynamics originates exclusively from the spin-dependent Overhauser (or Yafet) contribution. When we evaluate the phonon-assisted density matrix in the scattering limit, an electron–phonon matrix element appears, which contains both spin–diagonal and spin-dependent contributions. For this regular matrix element, the spin diagonal (‘Elliott’) contribution is likely much bigger than the spin–dependent (‘Overhauser’ or ‘Yafet’) contribution.

The torque operator $\hat{\tau}_{k+q, \lambda}$, which is due to the spin-dependent contribution only, has the long-wavelength limit
\[
\hat{\tau}_{k+q, \lambda}^{(\lambda)} = -i\xi \epsilon^{(0)}_{q, \lambda} v_{\text{eff}} (q \rightarrow 0) (q \cdot \varepsilon_{q, \lambda}) [Q + \langle -i\xi \rangle [(q + G) \times (\hbar k + p)] \times \lambda].
\]

3.4. Dynamics of the average spin in the scattering limit

To compare the results of the present approach with the conventional EY analysis, we specialize the dynamical equation (32) for $S_{\alpha}$, for the case of incoherent scattering. To this end, we need to evaluate the phonon-assisted density matrix $\langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | k\lambda j \rangle$. Its equation of motion couples to higher order correlation functions of the type $(b^\dagger b c^\dagger c)$ and $(c^\dagger c c^\dagger c)$. This equation-of-motion hierarchy is truncated at the scattering level according to the dynamical coupled-cluster method, and by performing a Markov approximation, see [34, 38]. Details of this procedure are given in appendix B. With these approximations we find for the ensemble averaged spin
\[
\frac{\partial}{\partial t} S = 2 \text{Re} \sum_{kqj} \sum_{\mu
u'} \sum_{\lambda} \langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | kq j \rangle \Omega \langle \mu, \nu'| \hat{\Sigma}_{\lambda}^{\alpha} \mu, \nu' | kq j \rangle \Omega \times \langle B_{q, \lambda}^{\alpha} \mu, \nu'| \lambda \rangle \Omega \times \langle B_{-q, \lambda}^{\alpha} \mu, \nu'| \lambda \rangle \Omega \bigg|_{e-pn}.
\]
where $N_{q, \lambda} = b(h\omega_{q, \lambda})$ are phonon occupation numbers. We will assume that the phonon system is not changed appreciably by the electronic dynamics so that the $N_{q, \lambda} = b(h\omega_{q, \lambda})$ are the equilibrium phonon
occupations given by the Bose function \( b(\langle \omega_{\text{kin}} \rangle) \). In the result (37) the full reduced density matrix appears on the right-hand side, which needs to be determined to obtain the spin dynamics.

4. Relaxation time for Kramers degenerate bands

We now specialize to the case of a pair of Kramers degenerate bands with a quasi-equilibrium spin-expectation value to obtain a relation for the spin relaxation time, which generalizes Yafet’s treatment.

4.1. Eigenstates for Kramers degenerate bands

Kramers degenerate states including spin–orbit coupling can be assumed to have the form \([39–41]\)

\[
\begin{align*}
    u_{k\uparrow}(x) &= a_k(x) |\uparrow\rangle + b_k(x) |\downarrow\rangle, \\
    u_{k\downarrow}(x) &= a_k^*(x) |\downarrow\rangle - b_k^*(x) |\uparrow\rangle.
\end{align*}
\]

(38) (39)

In semiconductors and metals with relatively weak spin–orbit coupling, these spin-mixed states can be considered to be mostly spin-up and spin-down for the vast majority of the Brillouin zone, which is indicated by the labels \(\uparrow\), \(\downarrow\). More precisely, \(\frac{1}{\Omega} \int_{\Omega} |b_k(x)|^2 \, d^3x\) is much smaller than \(\frac{1}{\Omega} \int_{\Omega} |a_k(x)|^2 \, d^3x\). Because of the degeneracy, there is an ambiguity in the definition of these states, as any superposition will also be an eigenstate. In accordance with [39–41], we choose them to fulfill

\[
\langle u_{\uparrow,k} | \hat{S}_z | u_{\downarrow,k} \rangle = 0.
\]

(40)

This is equivalent to the statement that the chosen states \(u_{\uparrow,k}, u_{\downarrow,k}\) diagonalize \(\hat{S}_z\) in the degenerate subspace. The choice is important, if one wants to attach some importance to the magnitude of \(\hat{S}_z\) as spin mixing parameter. In \textit{ab initio} calculations one often uses a small external magnetic field to enforce a quantization direction so that (40) is fulfilled.

The condition (40) does not imply that the electrons are in pure spin-up or spin-down states characterized by the same two-dimensional spinors at each \(k\). In fact, we have

\[
\begin{align*}
    u_{\uparrow,k} &\approx |\uparrow\rangle \quad \text{and} \quad u_{\downarrow,k} \approx |\downarrow\rangle,
\end{align*}
\]

(41)

as well as \(|\langle u_{\downarrow,k} | \hat{S}_z | u_{\uparrow,k} \rangle| \leq \hbar / 2\) for \(\lambda = \uparrow, \downarrow\). For more details, see appendix A.

4.2. Quasi-equilibrium with spin polarization

In order to derive a characteristic rate for the relaxation of a small excess spin polarization \(\delta S_z\) at a temperature \(T\), we first need to determine the reduced density matrix for this case. We assume the system to be in a quasi-equilibrium with a given spin-expectation value \(\delta S_z\). Thus we must determine the quasi-equilibrium distribution for the eigenenergies of the generalized grand-canonical \(k \cdot p\) hamiltonian

\[
\hat{\epsilon}(k) \equiv \hat{h}_{\text{eff}}(k) - \mu - \zeta_z \hat{S}_z.
\]

(42)

Here, \(\zeta_z\), the spin accumulation, is the Lagrange parameter needed to obtain the finite spin expectation value. Since \(\hat{h}_{\text{eff}}(k)\) includes spin–orbit coupling it does not commute with \(\hat{S}_z\), so that the eigenstates and eigenenergies of

\[
\hat{\epsilon}(k) \psi_{jk} = E_{jk} \psi_{jk}
\]

are, in general, \textit{not} identical to the \(u_{jk}\)’s that result as eigenfunctions of \(\hat{h}_{\text{eff}}(k)\), see equation (26).

We assume that \(\zeta_z\) is small and determine \(E_{jk}\) perturbatively in the degenerate subspace of the \(u_{jk}\)’s. Since we chose the \(u_{jk}\)’s that diagonalize \(\hat{S}_z\) in the degenerate subspace, see (40), this gives

\[
E_{jk} \approx \epsilon_k - \mu - \zeta_z \langle u_{jk} | \hat{S}_z | u_{jk} \rangle.
\]

(44)

If we also assume that other bands are sufficiently far away, the eigenvectors are \(\psi_{jk} \approx u_{jk}\). If there are other bands close to the bands for which the spin relaxation is computed, one needs to include an eigenvector correction for \(\psi_{jk}\).

The quasi-equilibrium reduced density matrix in the eigenbasis of the grand canonical hamiltonian is diagonal and depends only on the grand-canonical energies \(E_{jk}\), i.e.,

\[
\rho^{ij}_{\text{eq}} = \delta_{\mu,\nu} f(E_{jk}),
\]

(45)

where \(f(\epsilon) = [\exp(\beta \epsilon) + 1]^{-1}\) is the Fermi function. Since \(\zeta_z\) is small, we keep only the first order result in \(\zeta_z\) and with (44) we find for the quasi-equilibrium distribution
\[ \rho_{k}^{\mu\nu} = \delta_{\mu,\nu} [ f (\epsilon_k - \mu) + \Delta_k \zeta_z \langle \eta_{jk} | \hat{\gamma}_z u_{jk} \rangle ] \]  
(46)

where we have defined \( \Delta_k \equiv -\frac{df}{d\epsilon}|_{k_\perp = \mu} \). For low temperatures, this function approaches a \( \delta \)-function concentrated at \( \epsilon_k = \mu \). From the reduced density matrix (46) we find the relation \( \zeta_{z} = \frac{\delta S_{z}}{\mathcal{N}} \) between \( \delta S_z \) and \( \zeta_z \) with the normalization

\[ \mathcal{N} = \sum_{j} \langle \eta_{jk} | \hat{\gamma}_z u_{jk} \rangle^2 \Delta_k. \]  
(47)

4.3. EY relaxation time

To obtain the close-to-equilibrium spin relaxation rate defined by

\[ \frac{\partial}{\partial t} \delta S_{z} = -\frac{\delta S_{z}}{T_{SR}}, \]  
(48)

we insert (46) in (37) and linearize. Then, as in Yafet’s original treatment and its extension by Fähnle and coworkers,[20] \( \zeta_z \) drops out and we find

\[ \frac{1}{T_{SR}} = -\frac{2}{\mathcal{N}} \text{Re} \sum_{kq} \sum_{\lambda} g_{\lambda}^{(L)} \langle \eta_{jk}^{(L)} | \hat{\gamma}_z u_{jk}^{(L)} \rangle \Delta_{k+q} \times \left\{ \frac{N_{q,\lambda} + f (\epsilon_{jk} - \mu)}{\epsilon_{jk} + \hbar \omega_{q,\lambda} + i\gamma} + \frac{1 + N_{q,\lambda} - f (\epsilon_{jk} - \mu)}{\epsilon_{jk} - \hbar \omega_{q,\lambda} + i\gamma} \right\}. \]  
(49)

This expression for the spin relaxation, or \( T_1 \), is a more physically transparent result compared to Yafet’s because it relates the spin dynamics directly to a torque matrix element. It improves on the original Yafet result by including the correct bookkeeping for spin instead of counting the contribution of spin mixed states as if they were pure spin states. Instead of \( | g_{\lambda}^{(L)} \rangle \langle \eta_{jk}^{(L)} | \), i.e., the squared modulus of the e–pn matrix element, as it occurs in Yafet’s result, here matrix elements of the torque, the electron–phonon interaction and the spin appear.

In Yafet’s original result, only one matrix element, namely our \( g \) appears, and the spin diagonal and explicitly spin–dependent contributions to this matrix element are conventionally called, respectively, the Elliott and Overhauser (or Yafet) contributions. In our derivation, two different matrix elements occur. If we stick to the established language, the torque matrix element only has an Overhauser contribution, whereas the g matrix element both Elliott and Overhauser terms contribute. Thus we do not have a ‘pure’ Elliott contribution, but the leading term is a mixed one with an Elliott contribution in \( g \), but Overhauser in \( t \). Regarding the g matrix element in the long wavelength limit, Yafet[5] and numerical evaluations[41] of his spin–relaxation result find a cancellation between Elliott and Overhauser contributions in the short range contribution, whereas Grimaldi and Fulde[23] find for the long-wavelength limit a dominating long-range Elliott contribution to \( g \).

Our result (49) is not limited to small spin mixing and is qualitatively different from the original Yafet formula. It will make it easier to compute accurate EY spin relaxation times numerically and to compare different contributions to spin dynamics by computing the relevant combination of torque and g matrix elements.

5. Conclusion

In conclusion, we have presented an investigation of the carrier–spin dynamics due to incoherent electron–phonon scattering in the presence of spin–orbit coupling, as originally considered by Overhauser, Elliott, and Yafet. We examined the dynamical equation for the reduced density matrix in terms of the phonon assisted density matrix including the contributions of the spin–diagonal (electrostatic) electron–phonon interaction as well as the phonon–modulated spin–orbit coupling. We showed that the central quantity to account for the spin change is a torque matrix element, which gives a physically more appealing picture of spin dynamics due to the EY mechanism. This important result is missed if one works only with distribution functions for spin-mixed single particle states, because one needs the whole spin–density matrix to characterize the spin completely. Our results show that the spin mixing in the Bloch states has no impact on the torque matrix element for the electron–phonon interaction. This result clarifies how spin mixing in the wavefunctions affects spin relaxation due to a spin–diagonal scattering mechanism, which is commonly called the Elliott contribution to the EY mechanism. Only the explicitly spin-dependent phonon-induced modulation of the spin–orbit coupling as introduced by Overhauser gives rise to a non-vanishing torque due to an incoherent scattering mechanism. As an application of this general result, we derived for Kramers degenerate bands an explicit expression for the spin relaxation, or \( T_1 \), time close to equilibrium, which is valid for arbitrary spin mixing.
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Appendix A. Spin expectation values for degenerate bands

We show here in detail that, for the case of degenerate bands, the electron spin operator can be diagonalized in the space of the degenerate bands, even if spin-mixing due to spin–orbit coupling is present. This is not a new result, but it is important to keep this in mind when dealing with Kramers degenerate wave functions.

We assume we have arbitrary \( u_{ik} \)'s of the general form

\[
u_{ik}(\mathbf{x}) = a_{ik}(\mathbf{x})|\uparrow\rangle + b_{ik}(\mathbf{x})|\downarrow\rangle,
\]

which are Kramers degenerate. In this subspace, for fixed \( \mathbf{k} \) the matrix of the spin operator \( \hat{s}_z \) is

\[
\frac{\hbar}{2} \begin{pmatrix} c_k & d_k \\ c_k & -d_k \end{pmatrix}
\]

with the real diagonal elements

\[
d_k \equiv \langle u_{ik} | \hat{s}_z | u_{ik} \rangle = \int_{\Omega} \frac{d^3x}{\Omega} |a_{ik}(\mathbf{r})|^2 - |b_{ik}(\mathbf{r})|^2
\]

and complex off-diagonal elements

\[
c_k \equiv \langle u_{ik} | \hat{s}_z | u_{ik} \rangle = -\int_{\Omega} \frac{d^3x}{\Omega} (a_{ik}(\mathbf{r}) b_{-k}(\mathbf{r}) + a_{-k}(\mathbf{r}) b_{ik}(\mathbf{r})].
\]

If \( c_k = 0 \), diagonalization leads to the eigenstates \( u_{\pm k} \) with \( \lambda = \uparrow, \downarrow \)

\[
u_{\pm k}(\mathbf{x}) = \frac{c_k}{L} |\lambda\rangle \pm \frac{d_k + d_{-k}}{2L} \left[ 1 - \sqrt{1 + \frac{4 |c_k|^2}{(d_k + d_{-k})^2}} \right] |\downarrow\rangle,
\]

\[
u_{\pm k}(\mathbf{x}) = \frac{c_k}{L} |\lambda\rangle + \frac{d_k + d_{-k}}{2L} \left[ 1 - \sqrt{1 + \frac{4 |c_k|^2}{(d_k + d_{-k})^2}} \right] |\uparrow\rangle,
\]

where \( L \) normalizes the \( u_{ik} \)'s. The corresponding spin eigenvalues are

\[
\frac{\hbar}{2} \times \left[ \frac{1}{2}(d_k - d_{-k}) \pm \sqrt{\frac{1}{4}(d_k + d_{-k})^2 + |c_k|^2} \right].
\]

In the presence of inversion symmetry, as in aluminium and silicon, these expressions simplify further. Then \( d_k = d_{-k} \) and the eigenvalues are \( \pm (\hbar/2) \sqrt{d_k^2 + |c_k|^2} \) for \( \lambda = \uparrow, \downarrow \), respectively. This result shows that the \( \uparrow, \downarrow \) labels are justified as these states generally have an expectation value of \( \hat{s}_z \) of modulus smaller than (or almost equal to) \( \pm \hbar/2 \). At the same time, the spin-mixed states are not just rotated pure spin states, which would lead to a spin projection of exactly \( \pm \hbar/2 \) along the quantization axis. Further, these states may have non-vanishing \( \hat{s}_x \) and \( \hat{s}_y \) expectation values.

Appendix B. Truncation scheme for EOMs

In this appendix, we give some intermediate results for the derivation of the scattering limit of the equation of motion for the spin–density matrix and the average spin. These results are the lowest order of a standard systematic coupled-cluster scheme to truncate the equations of motion, see e.g., [34, 38].

The electron–phonon interaction leads to the following equation of motion for the phonon assisted density matrix \( \chi^{(\lambda)}_{\mu\kappa\mu'\kappa'\mathbf{q}} \)

\[
i\hbar \frac{\partial}{\partial t} \chi^{(\lambda)}_{\mu\kappa\mu'\kappa'\mathbf{q}} \left|_{\mathbf{x}=\mathbf{p}=\mathbf{n}} \right. \approx \sum_{\mathbf{k}\mathbf{k'}} \delta_{\kappa\kappa'} \left\{ \langle \hat{c}_{\mu\kappa'}^\dagger \hat{c}_{\nu\kappa} | \mathbf{p}^{(\lambda)}_{\mu\mu'\mathbf{q}} \hat{c}_{\mu'\kappa'}^\dagger \hat{c}_{\nu'\kappa} \rangle \right. \\
+ \delta_{\mu'\nu'} \left\{ \langle \hat{b}_{\nu'\kappa'}^\dagger \hat{b}_{\mu'\kappa} | \mathbf{p}^{(\lambda)}_{\mu\mu'\mathbf{q}} \hat{b}_{\mu'\nu'}^\dagger \hat{b}_{\nu\kappa} \rangle - \delta_{\mu\nu'} \langle \hat{b}_{\nu'\kappa'}^\dagger \hat{b}_{\mu'\kappa} | \mathbf{p}^{(\lambda)}_{\mu\mu'\mathbf{q}} \hat{c}_{\mu'\kappa'}^\dagger \hat{c}_{\nu'\kappa} \rangle \right\},
\]

where we have already neglected terms containing two \( \hat{b} \) or two \( \hat{b}^\dagger \) operators. The higher-order correlation functions are approximated by the truncation prescriptions.
\[
\langle c_{i',k'}^{-\dagger}c_{i,k}^{-\dagger} c_{i',k} c_{i,k'} \rangle \simeq \delta_{i,i'} \delta_{k,k'} \langle c_{i',k'}^{-\dagger} c_{i,k}^{-\dagger} c_{i',k} c_{i,k'} \rangle - \langle c_{i',k'}^{-\dagger} c_{i,k}^{-\dagger} c_{i',k} c_{i,k'} \rangle = \delta_{k,k'} [\hat{\rho}_{\nu''}(k)] \rho_{\nu''}(k - q)
\] (B.2)

and
\[
\langle b_{i',k'}^{-\dagger} b_{i,k}^{-\dagger} c_{i,k} \rangle = \langle (1 + \hat{b}_{i',k'}^{-\dagger} b_{i,k}^{-\dagger}) c_{i,k} \rangle \simeq (1 + N_{i,k}) \rho_{\nu''}(k)
\]
\[
\langle \hat{b}_{i',k'}^{-\dagger} b_{i,k}^{-\dagger} c_{i',k'} c_{i,k} \rangle \simeq (1 + N_{i,k}) \rho_{\nu''}(k - q) \quad \text{(B.3)}
\]

This leads to
\[
\frac{i\hbar}{\partial t} X_{\nu',\nu; k',k}^{(\lambda)} \left|_{pn} \right. = \sum_{s,\sigma'} \left[ \delta_{\nu',\nu} - \rho_{\nu''}(k) \right] \rho_{\nu''}(k - q) = [\delta_{\nu',\nu} - \rho_{\nu''}(k)] + \Delta(\nu,\nu'') (k - q) \quad \text{(B.4)}
\]

If we call the RHS of the above equation \( \Gamma_{\nu',\nu; k',k}^{(\lambda)} \), the full equation of motion (including coherent rotation terms) for the phonon-assisted density matrix is
\[
i\hbar \frac{\partial}{\partial t} X_{\nu',\nu; k',k}^{(\lambda)} = \left( \epsilon_{\nu',k'} - \epsilon_{\nu,k} + \hbar \omega_{\nu''} \right) X_{\nu',\nu; k',k}^{(\lambda)} + \Delta(\nu,\nu'') (k - q) \quad \text{with solution (B.5)}
\]

\[
X(t) = \frac{1}{i\hbar} \int_{-\infty}^{t} e^{i(E + \hbar \gamma)(t'-t)/\hbar} \Gamma(t') dt'.
\]

The Markov approximation assumes that \( \Gamma(t') \) varies slowly compared to the rotation frequency and can be approximated by \( \Gamma(t) \) in the integral. Letting \( \gamma \rightarrow 0 \) we get
\[
X(t) \simeq \Gamma(t) \left(-\frac{1}{E + i\hbar \gamma} \right) \Gamma(t) \left[\frac{-i\pi \delta(E) + \mathcal{P} \frac{1}{E}}{E} \right]
\]

where \( \mathcal{P} \) denotes a principal value. Finally, neglecting the real part, which only results in energy shifts, this result is inserted into equation (29) to obtain the equation of motion for the density matrix at the scattering level. To get the spin dynamics at this level, this result is inserted into (32).

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