Chirality Induced Spin Coherence in Electron Transfer Reactions

Thomas P. Fay*  

Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory,  
South Parks Road, Oxford, OX1 3QZ, UK  

E-mail: tom.patrick.fay@gmail.com
Abstract

Recently there has been much interest in the chirality induced spin selectivity effect, whereby electron spin polarisation, which is dependent on the molecular chirality, is produced in electrode-molecule electron transfer processes. Naturally, one might consider if a similar effect can be observed in simple molecular charge transfer reactions, for example in light-induced electron transfer from an electron donor to an electron acceptor. In this work we explore the effect of electron transfer on spins in chiral single radicals and chiral radical pairs using Nakajima-Zwanzig theory. In these cases chirality, in conjunction with spin-orbit coupling, does not lead to spin polarisation, but instead the electron transfer generates quantum coherence between spins states. In principle, this chirality induced spin coherence could manifest in a range of experiments, and in particular we demonstrate that the OOP-ESEEM pulse EPR experiment would be able to detect this effect in oriented radical pairs.

Graphical TOC Entry
Recently there has been significant progress in experiments\textsuperscript{1–8} on and theoretical descriptions\textsuperscript{9–11} of the chirality induced spin selectivity (CISS) effect. Much of this has been motivated by the potential for this effect to be exploited in spintronic devices,\textsuperscript{12} in which spins can be used to transfer and store information, with the potential for use in quantum computation and quantum information transfer.\textsuperscript{12,13} The CISS effect involves the generation of electron spin polarisation by the transmission of an electron through a chiral environment, and this effect is generally explained by the presence of the spin-orbit interaction in these systems.\textsuperscript{8–10} The majority of experimental and theoretical studies involve the transmission of electrons between electrodes and chiral molecules,\textsuperscript{1,8,12} however there has been relatively little investigation into the role of chirality on the spin in molecular electron transfers, and so this is precisely what we explore here for reactions in involving radicals and radical pair formation.

It is instructive to first consider a charge transfer reaction in an $S = 1/2$ doublet system,

$$2[D^* - A] \xrightarrow{k_f} 2[DA^*].$$

A simple model for this is a system which can exist in one of two charge transfer (CT) states: $|0\rangle = |D^* - A\rangle$ and $|1\rangle = |DA^*\rangle$.\textsuperscript{14–17} Associated with each of these diabatic states are two spin states $|M_S = \pm 1/2\rangle$, so overall there are four electronic states $|j, M_S\rangle$. For this system we can write the total Hamiltonian as\textsuperscript{14–17}

$$\hat{H} = \hat{H}_0 \hat{I}_0 + \hat{H}_1 \hat{I}_1 + \hat{V}_{\text{DC}} + \hat{V}_{\text{SOC}},$$

where $\hat{I}_j = \sum_{M_S = \pm 1/2} |j, M_S\rangle \langle j, M_S|$ is a projection operator onto charge transfer state $j$, $\hat{H}_j$ is the Hamiltonian for charge transfer state $j$, $\hat{V}_{\text{DC}}$ is the diabatic coupling Hamiltonian and $\hat{V}_{\text{SOC}}$ is the spin-orbit coupling Hamiltonian. The Hamiltonian for each charge transfer state $\hat{H}_j$ can be divided into a nuclear part $\hat{H}_{jn} = \hat{T}_n + V_j(\hat{Q})$ which is a sum of nuclear kinetic energy and potential energy terms, and a spin part $\hat{H}_{js}$, and for simplicity we can assume the spin part is independent of the nuclear coordinates $Q$.\textsuperscript{14,15}
The diabatic coupling term $\hat{V}_{DC}$ does not act on the spin of the system, instead it simply couples the two charge transfer states, and within the Condon approximation (coupling independent of $Q$) this is \textsuperscript{14,15,17}

$$\hat{V}_{DC} = \Delta (|0\rangle \langle 1| + |1\rangle \langle 0|)$$  \hspace{1cm} (2)

where $\Delta$ is a real-valued constant. The spin-orbit coupling also couples the charge transfer states, but it also acts on the spin as follows \textsuperscript{18–20}

$$\hat{V}_{SOC} = -i (|0\rangle \langle 1| \hat{\mathbf{S}} - \Delta \cdot \hat{\mathbf{S}} |1\rangle \langle 0|).$$  \hspace{1cm} (3)

$\hat{\mathbf{S}}$ here is the unitless electron spin operator and the vector coupling $\Delta$ is real valued for the spin-orbit coupling between bound electronic states (a detailed justification of this is given in the SI). Overall this means we can write the total charge transfer state coupling Hamiltonian $\hat{V} = \hat{V}_{DC} + \hat{V}_{SOC}$ as

$$\hat{V} = \Gamma \left( \hat{U}^\dagger |0\rangle \langle 1| + |1\rangle \langle 0| \hat{U} \right),$$  \hspace{1cm} (4)

where $\hat{U}$ is a unitary spin operator given by $\hat{U} = (\Delta + i \Delta \cdot \hat{\mathbf{S}})/\Gamma$, and $\Gamma = \sqrt{\Delta^2 + |\Delta|^2}/4$. This unitary operator rotates the electron spin about the axis $\mathbf{n} = \Delta / |\Delta|$ by an angle $2\theta$, with $\theta$ given by

$$\theta = \text{atan}(|\Delta|/(2\Delta)).$$  \hspace{1cm} (5)

Coherences between the spin states of each charge transfer state will be long-lived because the potential energy surfaces for different spin states $V_{JM_S}(Q) = V_J(Q)$ are identical, but this is not true for coherences between the different charge transfer states, and as such we describe the system with two spin density operators, one for each charge transfer state, $\hat{\sigma}_{js}(t)$ which are related to the
full density operator $\hat{\rho}(t)$ by $^{17}$

$$\hat{\sigma}_{js}(t) = \text{Tr}_a[\langle j | \hat{\rho}(t) | j \rangle].$$

(6)

Our aim is now to find a quantum master equation for these spin density operators. This is done by employing the Nakajima-Zwanzig equation $^{21,22}$ following the same steps as outlined in the derivation of radical pair spin master equations in Ref. 17, which we summarise in the SI. Assuming that the charge transfer coupling $\hat{V}$ can be treated perturbatively, and that the population transfer is described accurately as an incoherent kinetic process, with rates independent of the spin interactions in $\hat{H}_{js}$, the resulting quantum master equations at second order in $\Gamma$ for $\hat{\sigma}_{js}(t)$ are,

$$\frac{d}{dt}\hat{\sigma}_{0s}(t) = -\frac{i}{\hbar} [\hat{H}_{0s}, \hat{\sigma}_{1s}(t)] - k_f \hat{\sigma}_{0s}(t) + k_b \hat{U}^\dagger \hat{\sigma}_{1s} \hat{U}$$

(7)

$$\frac{d}{dt}\hat{\sigma}_{1s}(t) = -\frac{i}{\hbar} [\hat{H}_{1s}, \hat{\sigma}_{1s}(t)] - k_b \hat{\sigma}_{1s}(t) + k_f \hat{U} \hat{\sigma}_{0s} \hat{U}^\dagger,$$

(8)

where $[\cdot, \cdot]$ denotes the commutator. We see that as an electron is transferred, its spin is rotated about the vector $\mathbf{\Lambda}$, and as it is transferred back it is rotated about the vector $-\mathbf{\Lambda}$.

Thus far we do not appear to have included the idea of chirality in any of the above discussion, so we shall now discuss how this manifests in these equations. Chirality of the system determines the relative sign of $\Delta$ and $\mathbf{\Lambda}$. On spatial reflection, the sign of the diabatic coupling $\Delta$ in unchanged, but the sign of the spin-orbit coupling vector $\mathbf{\Lambda}$ is changed because the spin-orbit coupling operator is an axial vector operator. $^{10}$ This means that for an initially spin polarised state of $|0\rangle$, $\hat{\sigma}_{0s}(0) = |\alpha\rangle\langle\alpha|$, $^1$ this polarisation will be transformed into coherence between spin states $|\alpha\rangle$ and $|\beta\rangle$ in CT state $|1\rangle$ if $\mathbf{\Lambda}$ has a component perpendicular to the $z$ axis. $^2$ Interestingly this means that photo-initiated electron transfer in a spatially oriented chiral doublet system, initially at thermal equilibrium in a

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$^1$Here we use the standard notation for the electron spin states $|\alpha\rangle = |M_s = +1/2\rangle$ and $|\beta\rangle = |M_s = -1/2\rangle$.

$^2$This rotation of the electron spin is reminiscent of the $\bar{C}$ term appearing in the theory of Dalum & Hedegård in Ref. 10, derived for spin transport through a molecular junction from the non-equilibrium Green’s function approach. A spin polarisation term analogous to the $D$ term in in Ref. 10 does not appear in our theory for spin transport between bound electronic states because the initial and final electronic states have no linear or angular momentum, so their wavefunctions are real valued and the spin-orbit coupling vector is purely real, so no spin polarisation appears.
magnetic field, would yield $x/y$ magnetisation, and therefore a free-induction decay signal, *without* a microwave pulse. For an achiral system there are equal contributions from configurations with $±\Lambda$, which means that spin polarisation perpendicular to the $\Lambda$ axis is simply lost in the charge transfer process, and as such microwave pulse-free free-induction decay could not be observed.

We are now in a position to consider the effect of spin-orbit coupling and chirality on the charge transfer process between a singlet photoexcited precursor state $DA^+$ and a charge separated radical pair state $D^{++}A^{*-}$,

$$^1[DA^+] \xrightarrow{k_f/k_b} 2S+1[D^{++}A^{*-}].$$

Analogous to the above situation, a simple model for this includes the excited precursor diabatic state $|0\rangle = |DA^+\rangle$ and a charge separated radical pair state $|1\rangle = |D^{++}A^{*-}\rangle$. We assume that the state $|0\rangle$ can only exist in a singlet spin state, so only $|0, S = 0, M_S = 0\rangle$ exists, but the radical pair state $|1\rangle$ can exist in both singlet and triplet states which lie very close in energy, therefore there are four (near-)degenerate $|1, S, M_S\rangle$ states which exist, with $S = 0$ and $S = 1$. The total Hamiltonian for this system has the same form as Eq. (1), $\hat{H} = \hat{H}_0\hat{\Pi}_0 + \hat{H}_1\hat{\Pi}_1 + \hat{V}_{DC} + \hat{V}_{SOC}$, where again $\hat{H}_j = \hat{H}_{js} + \hat{H}_{jn}$ is the Hamiltonian for state $j$ and $\hat{\Pi}_j$ is a projection operator onto the $j$ states of the allowed spin multiplicity for that charge transfer state, i.e. $\hat{\Pi}_0 = |0\rangle\langle 0|\hat{P}_S$ and $\hat{\Pi}_1 = |1\rangle\langle 1| (\hat{P}_S + \hat{P}_T)$, where $\hat{P}_S$ and $\hat{P}_T$ are singlet and triplet spin state projection operators. As before

$$\hat{V}_{DC} = \Delta(\hat{P}_S |0\rangle\langle 1| + |1\rangle\langle 0| \hat{P}_S) \quad (9)$$

is the diabatic coupling Hamiltonian, which now comes with a singlet projection operator $\hat{P}_S$ because the diabatic coupling is spin conserving. The electron transfer can be regarded as a one electron transfer process, where only electron 1 transfers, and therefore the spin-orbit coupling term can be written as

$$\hat{V}_{SOC} = -i(\hat{P}_S |0\rangle\langle 1| \Lambda \cdot \hat{S}_1 - \Lambda \cdot \hat{S}_1 |1\rangle\langle 0| \hat{P}_S). \quad (10)$$
where $\hat{S}_1$ is the spin operator for electron 1 (this is justified in more detail in the SI). This means the total charge transfer Hamiltonian can be written as

$$\hat{V} = \Gamma (\hat{P}_S \hat{U}^\dagger |0\rangle |1\rangle + |1\rangle |0\rangle \hat{U} \hat{P}_S) \tag{11}$$

where now $\hat{U} = (\Delta + i \mathbf{A} \cdot \hat{S}_1)/\Gamma$ only acts on electron 1.

From this we can obtain the quantum master equations for the spin density operators of the two charge transfer states, once again using the Nakajima-Zwanzig equation as in Ref. 17, which gives

$$\frac{d}{dt} \sigma_{0s}(t) = -\frac{i}{\hbar} [\hat{H}_{0s}, \sigma_{0s}(t)] - k_f \sigma_{0s}(t) + k_b \hat{P}_S \hat{U}^\dagger \sigma_{1s} \hat{U} \hat{P}_S \tag{12}$$

$$\frac{d}{dt} \sigma_{1s}(t) = -\frac{i}{\hbar} [\hat{H}_{1s}, \sigma_{1s}(t)] - \left\{ \frac{k_b}{2} \hat{U} \hat{P}_S \hat{U}^\dagger, \sigma_{1s}(t) \right\} - i \hbar \left[ 2\delta J \hat{U} \hat{P}_S \hat{U}^\dagger, \sigma_{1s}(t) \right] + k_f \hat{P}_S \sigma_{0s}(t) \hat{P}_S \hat{U}^\dagger. \tag{13}$$

Here $\{ , \}$ denotes the anti-commutator, and $2\delta J \hat{U} \hat{P}_S \hat{U}^\dagger$ is an effective spin coupling term in the radical pair state (expressions for the master equation parameters $k_f, k_b$ and $\delta J$ are given in the SI).

Now assuming the radical pair, state $|1\rangle$, is formed very rapidly and irreversibly from an excited singlet precursor $|0\rangle$, as is often the case for radical pairs formed by photoexcitation of a singlet ground state, then we can take $k_b = 0$, and the radical pair spin density operator as being formed in the state

$$\sigma_{1s}(0) = \sigma_{ns} \hat{U} \hat{P}_S \hat{U}^\dagger \tag{14}$$

where $\sigma_{ns}$ is the initial nuclear spin state of the precursor state. The initial electron spin state can be written as $\hat{U} \hat{P}_S \hat{U}^\dagger = |\psi_0\rangle \langle \psi_0|$, where the initial spin state $|\psi_0\rangle = \hat{U} |S\rangle$ is

$$|\psi_0\rangle = \cos \theta |S\rangle + i \sin \theta |T_0(n)\rangle, \tag{15}$$

in which $|S\rangle$ is an electron spin singlet state and $|T_0(n)\rangle$ is a $T_0$ triplet state defined with respect to
The axis $\mathbf{n} = \mathbf{\Lambda}/|\mathbf{\Lambda}|$, and $\theta$ is given by Eq. (5). Once again for the opposite enantiomer the sign of $\mathbf{\Lambda}$ changes. Denoting the different enantiomers $+$ and $-$, this means that $\mathbf{n}_+ = -\mathbf{n}_-$, or equivalently we can write the initial state as

$$|\psi_0^\pm\rangle = \cos \theta_+ |S\rangle \pm i \sin \theta_+ |T_0(\mathbf{n}_+)|.$$  \hspace{1cm} (16)

This means that the phase of the initial coherence between singlet and triplet states is changed by the chirality in the radical pair. In an achiral system, there will be equal but opposite contributions to charge transfer from configurations with opposite signs of $\mathbf{n}$, and therefore there will be no initial coherence between singlet and triplet electron spin states. It is well known that spin-orbit coupled charge transport (SOCT) in radical pair reactions leads to the formation of triplet radical pairs, 20,23–28 but this shows that in chiral systems spin coherence between singlet and triplet states is also generated by SOCT.

We will now consider how chirality induced spin coherence could be detected experimentally by EPR. Because the spin coherence generated is orientation dependent, any experiment probing this would have to be performed on radical pairs somehow fixed in a specific spatial orientation. Here we consider the OOP-ESEEM (out of phase electron spin echo envelope modulation) EPR experiment,
which has been developed as a technique for probing zero-quantum coherences in photo-generated radical pairs, with the applied field $B$ parallel to $\mathbf{A}$ for oriented radical pairs as illustrated in Fig. 1 (A). The standard OOP-ESEEM experiment consists a laser flash ($h\nu$), in which the radical pairs are generated, followed by a waiting time of $t_0$, followed by a non-selective $(\pi/4)_x$ microwave pulse, and another $(\pi)_x$ pulse after a time $\tau$, and after another waiting time $\tau$ the free-induction decay spin echo is recorded over times $t$. This $h\nu - t_0 - (\pi/4)_x - \tau - (\pi)_x - \tau - \text{FID}$ pulse sequence is illustrated schematically in Fig. 1 (B). This pulse sequence gives access to information about the zero quantum coherences in the spin density operator, which evolve in the waiting times $t_0$ and $\tau$. If we are interested in the initial state of the spin density operator, in particular the phases of the initial zero-quantum coherences, then we should minimise the time for the coherences to evolve on their own, as well as any decoherence processes, and therefore here we only consider the case of $t_0 = 0$, as shown in Fig. 1 (B).

Using the standard high-field radical pair spin Hamiltonian in the rotating frame, and invoking the Schulten-Wolynes semiclassical approximation for the nuclear spins in the radical pair, we can obtain expressions for the $x$-channel OOP-ESEEM signal $f_x(t) = \text{Tr}_s[(\hat{S}_{1x} + \hat{S}_{2x})\hat{r}_{1s}(t)]$ (details of this are given in the SI). In the weak coupling limit ($|\Omega_1 - \Omega_2| \gg |J|, |d|$) we find the OOP-ESEEM FID signal to be,

$$
 f_x(t) = \frac{1}{2} \sin (\theta) \sin \left(\left(J - \frac{d}{3}\right)(t + 2\tau)\right) \sum_{i=1,2} e^{-t^2/(2\tau_i^2)} \left(\sin (\theta) \cos (\Omega_i t) - \sqrt{2} \cos (\theta) \sin (\Omega_i t)\right).
$$

(17)

$\Omega_i$ is the resonant frequency of electron spin $i$ (in the rotating frame), $J$ is the scalar coupling constant and $d$ is the effective dipolar coupling constant, and $\tau_i^{-2} = \frac{1}{3} \sum_{k=1}^{N_i} a_{i,k}^2 I_i,k (I_i,k + 1)$, where $a_{i,k}$ and $I_i,k$ are the hyperfine coupling constants and spin quantum numbers for the hyperfine coupled nuclei in radical $i$. For simplicity we have ignored spin relaxation and radical pair recombination processes. Importantly here we see that changing the sign of $\theta$ changes the sign of certain terms in the $x$ channel FID signal after the OOP-ESEEM pulse sequence. This means the signal would
be sensitive to the chirality of the molecule. As described in the SI, we can also calculate the OOP-ESEEM signal in the intermediate–strong coupling limit numerically. Often in OOP-ESEEM experiments, the waiting time $\tau$ is varied, so we also consider the integrated FID echo signal as a function of $\tau$, $F_x(\tau) = \int_0^\infty f_x(t) \, dt$.

As an example of this we plot the $t$ dependent OOP-ESEEM signal of two enantiomers of a chiral radical pair with $\theta = \pm \pi/16$ in Fig. 2. This corresponds to an initial triplet fraction of $\sim 4\%$ which is typical of organic radical pairs in solution.\textsuperscript{35–37} We see that the two OOP-ESEEM signals are very different even in the case of a modest SOCT contribution. The signals are not the exact negative of each other because the spin Hamiltonian is chirality independent but chirality does change the sign of the phase of coherences in the initial state, leading to a phase shift in the OOP-ESEEM signals. In Fig. 3 we show these signals for the same model in the intermediate coupling regime, calculated by sampling $10^6$ realisations of the hyperfine fields, where again we
Figure 3: OOP-ESEEM signals for chiral radical pairs with $\Omega_1 = -\Omega_2 = 1.5 \text{ mT} \gamma_e$, $J - d/3 = 3 \text{ mT} \gamma_e$ and $\tau_1 = \tau_2 = 2.0 \text{ mT}^{-1} \gamma_e^{-1}$. Achiral signals are an average of the $\theta = \pm \pi/16$ signals. Top panel: the FID echo for $\tau = 200 \text{ ns}$ calculated using Eq. (S.25). Bottom panel: the integrated echo as a function of $\tau$ calculated using Eq. (S.25).

see that there is a phase shift between the $F_x(\tau)$ signals.

In this work we have discussed how spin-orbit coupling can lead to chirality induced spin coherence in radicals and radical pair systems, an effect which has not before been explored in spin chemistry. In contrast to the case of electrode-molecule electron transfers, where chirality induces spin polarisation, chirality in intramolecular electron transfers generates specific coherent superpositions of spin states. This effect should manifest in certain EPR experiments and other experiments such as those that probe magnetic field effects (which we describe briefly in the SI).

Chirality induced spin coherence could be important in a range of systems. For example, it has been suggested that radical pair reactions in cryptochrome proteins form the basis of the magnetic compass sense of migratory birds, and because chirality induced spin coherence is orientation dependent, this effect could hypothetically play a role in avian magnetoreception. Radical-based systems have also been proposed as potential molecular qubits, and various quantum information theoretic ideas have been explored using these molecules. Electron
transport in chiral molecular systems could provide a way of further manipulating spin coherences in these systems. Other chiral open-shell molecular systems, aside from radicals and radical pairs, could potentially display chirality induced spin coherence effects. For example it has been demonstrated that spin-orbit coupling can play a role in singlet fission \(^{47}\) and triplet-triplet up-conversion, \(^{48}\) so it stands to reason that in chiral systems spin-orbit coupling could lead to interesting effects on these processes. Furthermore chirality induced spin coherence effects could manifest in the photophysics of open-shell chiral transition metal complexes with \(S > 0\). Overall we hope that this work will lay foundations for exploring chirality induced spin effects in a wide variety of molecular systems, beyond what has already been studied in electrode-molecule interfaces.

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**Supporting Information**

Discussion and derivation of the spin-orbit coupling Hamiltonian in the diabatic representation used here, an outline of the second order Nakajima-Zwanzig master equation theory, expressions for OOP-ESEEM signals of chiral radical pairs in the intermediate-strong coupling limit, and a brief discussion of the effect of chirality induced spin coherence on quantum yields of radical pair reactions.
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