

## Quantum measurement corrections to CIDNP in photosynthetic reaction centers

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*New Journal of Physics* **15** (2013) 075017 (13pp)

Received 30 January 2013

Published 18 July 2013

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/15/7/075017

**Abstract.** Chemically induced dynamic nuclear polarization is a signature of spin order appearing in many photosynthetic reaction centers. Such polarization, significantly enhanced above thermal equilibrium, is known to result from the nuclear spin sorting inherent in the radical pair mechanism underlying long-lived charge-separated states in photosynthetic reaction centers. We will show here that the recently understood fundamental quantum dynamics of radical-ion-pair reactions open up a new and completely unexpected pathway toward obtaining chemically induced dynamic nuclear polarization signals. The fundamental decoherence mechanism inherent in the recombination process of radical pairs is shown to produce nuclear spin polarizations of the order of  $10^4$  times (or more) higher than the thermal equilibrium value at the Earth's magnetic field relevant to natural photosynthesis. This opens up the possibility of a fundamentally new exploration of the biological significance of high nuclear polarizations in photosynthesis.



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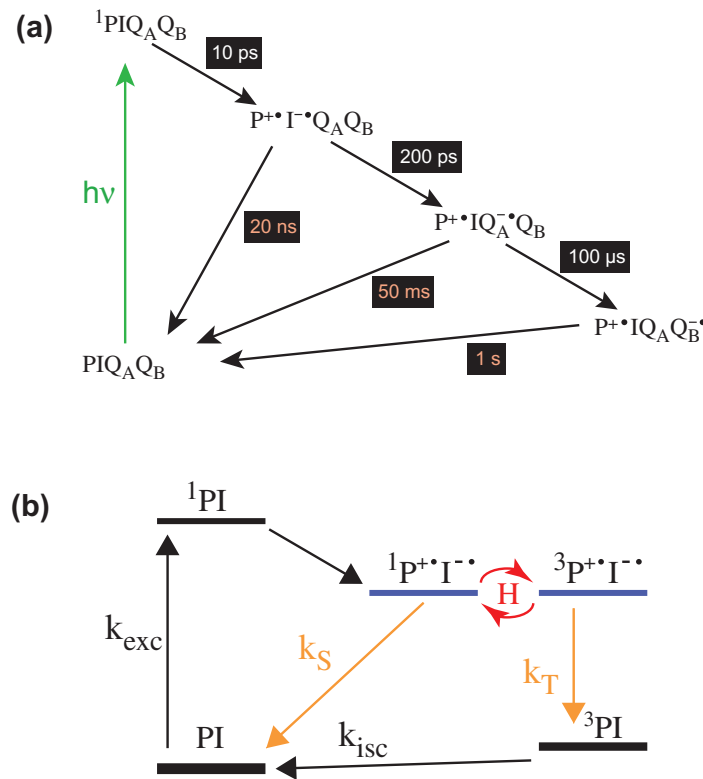
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**1. Introduction**

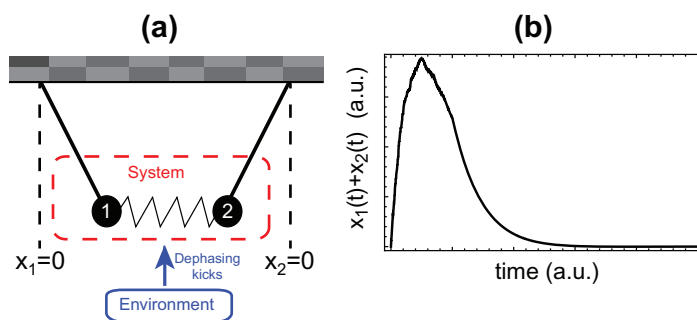
The quantum dynamics of photosynthesis have, quite naturally, attracted a lot of attention recently. Understanding if and how Nature exploits quantum (de)coherence would have tremendous scientific and technological impact. In what follows, photosynthesis can be simply visualized as a two-step process: (i) light harvesting and (ii) photochemical processing. Light harvesting molecules absorb the incident photon and guide the subsequent excitation to the photosynthetic reaction center (RC). It is there where the photochemistry takes place, transforming the initial electronic excitation in a transmembrane proton pump that further drives the life-sustaining chemistry. Regarding step (i), quantum coherence effects in light harvesting complexes (time scales of 1–500 fs) have been addressed theoretically and experimentally [1–10]. We will focus here on step (ii), i.e. on RC quantum dynamics (time scales of 1 ps–10  $\mu$ s) schematically depicted in figure 1(a).

Photosynthetic RCs exhibit a cascade of electron transfer reactions, starting from a photo-excited donor–acceptor dyad PI (chlorophyll-type molecules) and shelving the electron further apart to quinones ( $Q_A$ ,  $Q_B$ ), producing a long-lived charge-separated state driving the transmembrane proton pump. In each of these steps there is a radical-ion pair (RP) formed, further perplexing the dynamics, as RPs exhibit intricate magnetic field effects [11]. RPs [12, 13] are biomolecular ions created from the photo-excited dyad  $^1$ PI. They have two unpaired electrons (denoted by the two dots in figure 1) and any number of magnetic nuclei. The magnetic nuclei of the donor and acceptor molecular ions couple to the ion’s unpaired electron via the hyperfine interaction. This coupling, along with several other intramolecule magnetic interactions, leads to singlet–triplet (S–T) mixing, i.e. a coherent oscillation of the total electronic spin, also affected by the electrons’ Zeeman interaction with the external magnetic field. A spin-dependent charge recombination terminates the coherent S–T mixing and leads to the reaction products, either the original neutral dyad PI (singlet product) or a triplet intermediate ( $^3$ PI). As shown in figure 1(b), singlet (triplet) radical pairs recombine at the singlet (triplet) recombination rate, denoted by  $k_S$  ( $k_T$ ). Triplet products may close the reaction cycle by intersystem crossing into the singlet diamagnetic ground state at a rate  $k_{isc}$ .



**Figure 1.** (a) Cascade of electron transfer reactions taking place in photosynthetic RCs. Figure adapted from the review [11]. (b) Primary RP of a quinone-blocked photosynthetic RC. The RP undergoes quantum dynamics due to internal magnetic interactions, embodied by the Hamiltonian  $\mathcal{H}$ , of the two unpaired electrons with each other, the magnetic nuclei and the external magnetic field. These magnetic interactions in long-lived charge-separated states (where the long lifetime is either due to the absence of quinones or due to the large spatial separation of secondary radical pairs) give rise to S–T conversion and spin-dependent recombination, further perplexing the dynamics of the whole reaction. Figure adapted from [21].

It is apparent from figure 1 that when the lifetime of the charge-separated states (which increases with separation) is long enough that magnetic-field effects (with typical time scales of e.g. S–T mixing of the order of 0.1–1  $\mu\text{s}$ ) have time to build up, radical-pair spin dynamics are convolved into the RC dynamics. One aspect of this interrelation pervading a large number of photosynthetic RCs is chemically induced dynamic nuclear polarization (CIDNP) [13–20], the enhancement (by several orders of magnitude) of the ground state (PI) nuclear spin polarization resulting from the RP spin dynamics. CIDNP has emerged as a rather universal signature of spin order in photosynthetic RCs [22] and its possible operational significance for photosynthesis is still an open fundamental question. CIDNP is based on nuclear spin sorting, to be explained shortly, taking place in radical-pair reactions. Regarding solid-state CIDNP in particular, three main mechanisms have so far been known to produce CIDNP signals, the three-spin mixing (TSM) [23], differential decay (DD) and differential relaxation (DR) mechanisms [24].



**Figure 2.** (a) The ‘system’ consists of  $N(t)$  coupled pendulums oscillating out of phase (anti-symmetric mode). The number of such systems  $N(t)$  is a decaying function of time. While they oscillate, the pendulums are perturbed by the ‘environment’, which is here assumed to produce dephasing kicks at random times. (b) For the particular stochastic simulation shown here, every kick from the environment was taken to initialize the amplitude of pendulum 1 to unity and of pendulum 2 to zero. In the absence of the perturbation, all coupled pendulums would be continuously oscillating out of phase, and the ensemble average of the sum of their displacements away from equilibrium,  $x_1 + x_2$ , would be constantly zero. In the presence of the dephasing kicks, however, a non-zero displacement is shown to build up, to later on decay to zero due to the total population decay.

The first is a coherent mechanism resulting from particular magnetic interactions within the RP, while the second is about a nuclear spin imbalance brought about by different recombination rates  $k_S \neq k_T$ . The last mechanism (DR) will not be relevant for the following discussion.

We will demonstrate here that there is yet another, completely unanticipated mechanism at work *at the fundamental quantum dynamical level of RP reactions*. It is due to the inherent quantum measurement of the RP’s spin state continuously going on in the RP as part of the very charge recombination process. The decoherence caused by this ‘internal’ quantum measurement is responsible for a new kind of nuclear spin sorting, particularly efficient at low fields, and completely unrelated to other low-field CIDNP studies [25]. This new mechanism is ubiquitous, as it is largely independent of the particular magnetic interactions in the radical pairs, and thus opens a new pathway toward exploring the biological significance of CIDNP-induced spin order in natural (Earth’s field) photosynthesis. In the following, we will (i) briefly explain the basics of CIDNP signal generation for the general reader and (ii) recapitulate the recent progress in understanding the fundamental quantum dynamics of RP reactions. Combining (i) and (ii), we will then explain the quantum measurement corrections to CIDNP. Before proceeding, we mention a classical analogue of the effect to be discussed, shown in figure 2. We consider an ensemble of coupled pendulums oscillating in the anti-symmetric mode. The ensemble average of the sum of their displacements is  $x_1 + x_2 = 0$  at all times. However, if the ‘environment’ perturbs the system, e.g. with random kicks, while the ensemble population decays, we will observe a non-zero total displacement rising to a maximum and decaying to zero, following suit with the population decay. This displacement is the analogue of the radical-pair nuclear spin to be discussed in the following. The non-zero value of the nuclear spin stems from the particular ‘environment’ pertaining to radical pairs, S–T dephasing, which produces a nuclear spin imbalance along the reaction.

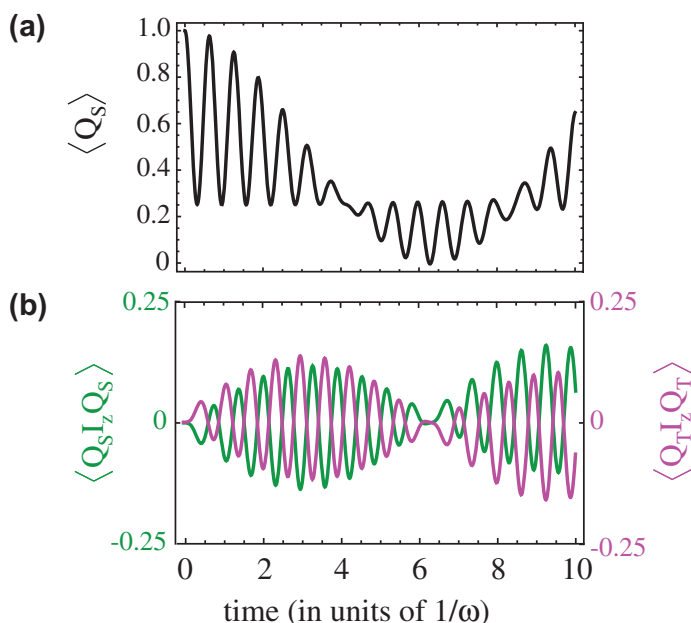
## 2. Nuclear spin sorting

Consider RPs with just one nucleus coupled to the electron of e.g. the donor. At time  $t = 0$  the RPs start out in the electronic singlet state, while the nuclear spins are thermally polarized, which for protons at the Earth's field corresponds to a polarization of about  $10^{-10}$ , practically taken to equal zero. Thus, in the ensemble of RPs half will have the nuclear spin in the  $|+\rangle$  state, while in the other half the nuclear spin will initially be in the  $|-\rangle$  state. The local magnetic field seen by the donor electron will be the external field plus the nuclear magnetic field, while the acceptor electron will only experience the external magnetic field. It is this difference in local magnetic fields experienced by the two electrons that results in a difference in their Larmor frequencies, and hence induces the coherent S–T conversion. Consequently, in the first half radical pairs (with a  $|+\rangle$  nuclear spin) the Larmor precession frequency of the donor electron, and thus the S–T mixing frequency, will be slightly higher than in the other half (due to the opposite contribution of the nuclear spin); hence the coherently formed triplet radical pairs will have their nuclear spins predominantly in the  $|+\rangle$  state, leaving the singlet radical pairs with opposite nuclear polarization. While the nuclear spins are thus sorted among singlet and triplet RPs, and unless there is a coherent mechanism such as TSM producing net nuclear polarization, the expectation value  $\langle I_z \rangle = \text{Tr}\{\rho I_z\}$  of the  $z$ -component of the single nuclear spin under consideration is still zero. Here  $\rho$  is the spin density matrix of the radical pair, describing the electron and nuclear spin degrees of freedom altogether, and  $z$  is the direction of the external magnetic field.

According to the traditional understanding of the radical-pair mechanism and the concomitant CIDNP signal generation, for this nuclear spin sorting to result in a diamagnetic ground state with net nuclear polarization, and in the absence of any coherent mechanism such as TSM, the DD mechanism should be at play in order to observe non-zero CIDNP signals. In the following, we will indeed consider a magnetic Hamiltonian that *does not* exhibit the TSM mechanism, and we will also take  $k_S = k_T$ , so that the DD mechanism is not operational. Hence, according to the traditional theory of RP spin dynamics, no CIDNP signal should be expected. We are then going to show that the opposite is actually true.

### 2.1. Nuclear spin polarization under Hamiltonian evolution

To illustrate the above considerations, we consider a radical pair with one spin-1/2 nucleus *isotropically* coupled to the donor electron. In figure 3(a), we display the undisturbed spin state evolution brought about *just* by the magnetic Hamiltonian  $\mathcal{H} = A\mathbf{I} \cdot \mathbf{s}_1 + \omega(s_{1z} + s_{2z})$ , where  $\omega$  is the electron spin Larmor precession frequency in the external magnetic field defining the  $z$ -axis and  $A$  the donor-electron hyperfine coupling with the donor nuclear spin (in units of frequency). What is plotted in figure 3(a) is the spin state's singlet character, given by the expectation value of the singlet projection operator,  $\langle Q_S \rangle = \text{Tr}\{\rho Q_S\}$ , and assuming an RP with infinite lifetime (in other words, so far we take the recombination rates to be  $k_S = k_T = 0$ ). What figure 3(a) displays are the S–T oscillations brought about by  $\mathcal{H}$ . The nuclear spin,  $I_z$ , of singlet and triplet RPs is given by  $\langle I_z \rangle^S = \langle Q_S I_z Q_S \rangle$  and  $\langle I_z \rangle^T = \langle Q_T I_z Q_T \rangle$ , respectively, and displayed in figure 3(b). The previous considerations regarding nuclear spin sorting are easily visualized by noting in figure 3(b) that although  $\langle I_z \rangle^S \neq 0$  and  $\langle I_z \rangle^T \neq 0$ , the nuclear spin oscillations in the singlet and triplet subspaces are exactly out of phase, so the net RP nuclear polarization  $\langle I_z \rangle = \langle I_z \rangle^S + \langle I_z \rangle^T = 0$ . In case it is not obvious, we prove that  $\langle I_z \rangle = \langle I_z \rangle^S + \langle I_z \rangle^T$

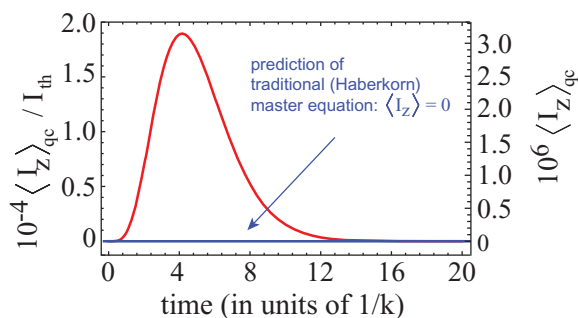


**Figure 3.** Time evolution of (a)  $\langle Q_S \rangle$  and (b) the nuclear spin of singlet RPs  $\langle I_z \rangle^S = \langle Q_S I_z Q_S \rangle$  (green line) and the nuclear spin of triplet RPs  $\langle I_z \rangle^T = \langle Q_T I_z Q_T \rangle$  (pink line), when the radical-pair spin state undergoes unceasing coherent S–T mixing driven by  $d\rho/dt = -i[\mathcal{H}, \rho]$ , where  $\mathcal{H} = A\mathbf{I} \cdot \mathbf{s}_1 + \omega(s_{1z} + s_{2z})$ . For this particular example it was  $\omega = A/10$ . The nuclear spin of singlet RPs is exactly out of phase with the nuclear spin of triplet RPs, so that their sum  $\langle I_z \rangle^S + \langle I_z \rangle^T = 0$ .

in appendix A. We can also show formally that for this particular Hamiltonian  $\mathcal{H}$  it will be  $\langle I_z \rangle = 0$ , as expected since  $\mathcal{H}$  does not qualify for the TSM mechanism [23]. The proof can be found in appendix B.

## 2.2. Prediction of the traditional theory

Now, besides the coherent RP dynamics producing the oscillations in figure 3, which are driven by  $d\rho/dt = -i[\mathcal{H}, \rho]$  as discussed in the previous paragraph, the spin-selective charge recombination of RPs has to be accounted for. This is done by a master equation of the form  $d\rho/dt = -i[\mathcal{H}, \rho] + \mathcal{L}(\rho)$ , where  $\mathcal{L}(\rho)$  is the reaction super-operator, written in terms of the singlet and triplet projection operators,  $Q_S$  and  $Q_T$ , and the singlet and triplet recombination rates,  $k_S$  and  $k_T$ , respectively. Recently, quantum measurement theory has been shown [26, 27] to fundamentally describe the reaction dynamics of RPs, resulting in a new form of  $\mathcal{L}(\rho)$ , conceptually departing from the traditional theory used until now [28]. The main physical point of departure is the fact that the very charge recombination process of RPs damps their coherent S–T mixing, i.e. it brings about an unavoidable intramolecule decoherence in their spin state evolution. The traditional theory for the reaction operator of RPs, although successful in accounting for a large volume of experimental data, does not embody this decoherence process, neglectation of which leads to several conceptual problems [29, 30]. In any case, in the example treated above, if the nuclear spin expectation value is evaluated according to the full master



**Figure 4.** Evolution of  $\langle I_z \rangle$  according to the full density matrix equation of Kominis [27], with  $k_S = k_T = 4A$ . The absolute value of the nuclear polarization is shown in the right y-axis, while its enhancement relative to the thermal equilibrium polarization, of the order of  $10^4$ , is shown in the left y-axis. Qualitatively the same result (only higher by about a factor of 2) is obtained from the Jones–Hore theory [31]. In contrast, the traditional theory predicts  $\langle I_z \rangle = 0$ , exactly the same as the sum of the two traces in figure 3(b) that applies to the case of zero recombination rates. Note the different time scales in this figure from figure 3: since  $k \gg \omega$ , the build-up of  $\langle I_z \rangle_{qc}$  in this plot takes place at the very beginning of the S–T mixing oscillations shown in figures 3(a) and (b).

equation of the traditional theory, taking  $k_S = k_T$ , it is found to be identically equal to zero, exactly as it is if only the Hamiltonian evolution is taken into account. This is formally shown in appendix C. According to common wisdom, this should be perceived as an obvious result, since with  $k_S = k_T$  the DD mechanism cannot lead to any net nuclear polarization. To recapitulate, the statement that  $\langle I_z \rangle = 0$  at all times when considering *just* the Hamiltonian evolution remains true *according to the traditional master equation of spin chemistry*, that is, if we *also* take into account the recombination reaction that gradually diminishes the radical-pair population to zero.

### 3. Nuclear polarization induced by singlet–triplet decoherence

The counter-intuitive new result presented here is this: according to the new master equation describing the fundamental quantum dynamics of RP reactions [27], there actually is a non-zero RP nuclear spin polarization, depicted in figure 4. A similar result, different by just a factor of 2, follows from another variant of the quantum-measurement-based stochastic Liouville equation [31]. In this particular example, the nuclear polarization is about  $10^4$  times higher than the thermal equilibrium proton polarization (left y-axis of figure 4) and roughly independent of  $\omega$  as long as  $\omega$  is relatively small (to be further discussed later). What is the source of this new kind of CIDNP signal? We will now go beyond the particular example considered above and provide the explanation for the general case of this new channel for photochemically enhancing nuclear polarizations *at the Earth’s field*: the fundamental S–T decoherence underlying the radical-pair mechanism.

To visualize this mechanism, suppose that at time  $t$  the single-nuclear-spin RP ensemble is described by the density matrix  $\rho$ . Assuming a magnetic Hamiltonian *not* supporting any coherent generation of *net* RP nuclear polarization, as in the example considered previously, it will be  $\langle I_z \rangle = \text{Tr}\{\rho I_z\} = 0$ . This, as already mentioned, implies that  $\langle I_z \rangle^S = -\langle I_z \rangle^T$ . The idea

behind the new kind of CIDNP signal generation is the following. The intramolecule S–T decoherence is equivalent to some RPs being *projected* to either the singlet or the triplet RP manifold of states, exactly due to the continuous quantum measurement of  $Q_S$  induced by the RP recombination dynamics, the measurement rate being  $(k_S + k_T)/2$  [26]. The result of this measurement is either  $Q_S = 1$ , i.e. the RP is projected to the singlet manifold, or  $Q_S = 0$ , i.e. the RP is projected to the triplet manifold. The probability for a singlet or a triplet projection is  $\langle Q_S \rangle$  or  $\langle Q_T \rangle$ , respectively. Hence, at time  $t + dt$  the state of the radical pairs will be (ignoring the RPs that recombine into neutral products during  $dt$ ) a new mixture comprised of (a) radical pairs in the state  $\rho + d\rho$ , with  $d\rho = -i dt[\mathcal{H}, \rho]$ , plus (b) the singlet-projected radical pairs described by  $Q_S \rho Q_S$ , plus (c) triplet-projected radical pairs described by  $Q_T \rho Q_T$ . The nuclear polarization of states (a) will still be zero, since again, the Hamiltonian  $\mathcal{H}$  does not generate *net* nuclear polarization. The combined nuclear polarization of projected states (b) and (c), denoted by  $\langle I_z \rangle^{\text{proj}}$ , will be the *weighted* sum of singlet RP nuclear polarization,  $\langle I_z \rangle^S$ , and triplet RP nuclear polarization,  $\langle I_z \rangle^T$ , the sum being weighted by the respective projection probabilities, i.e.

$$\langle I_z \rangle^{\text{proj}} = \langle Q_S \rangle \langle I_z \rangle^S + \langle Q_T \rangle \langle I_z \rangle^T. \quad (1)$$

Taking into account that  $\langle I_z \rangle^T = -\langle I_z \rangle^S$  and using the completeness relation  $\langle Q_T \rangle = 1 - \langle Q_S \rangle$ , it follows that

$$\langle I_z \rangle^{\text{proj}} = \langle I_z \rangle^S (2\langle Q_S \rangle - 1). \quad (2)$$

Thus, if  $\langle Q_S \rangle \neq \langle Q_T \rangle \neq 1/2$ , more (when  $\langle Q_S \rangle > 1/2$ ) or less (when  $\langle Q_S \rangle < 1/2$ ) projections will take place to the singlet state than to the triplet, and  $\langle I_z \rangle_t^{\text{proj}}$  will be non-zero, if of course  $\langle I_z \rangle^S$  is non-zero.

To recapitulate the physics of this new effect, the S–T dephasing inherent in the radical-pair quantum dynamic evolution randomly projects radical pairs into either the singlet or the triplet subspace. The projection probability at time  $t$  depends on the singlet (or triplet) character of the electronic spin state; hence the projections will be asymmetric if  $\langle Q_S \rangle \neq 1/2$ . Nuclear spin sorting, i.e. the fact that  $\langle I_z \rangle^S = -\langle I_z \rangle^T \neq 0$ , combined with the asymmetric projections produces a non-zero nuclear spin expectation value.

#### 4. Estimate of the quantum measurement corrections to CIDNP for the general case

We can now theoretically estimate the quantum measurement corrections to CIDNP, to be denoted by  $\langle I_z \rangle_{\text{qc}}$ , shown in figure 4. Letting  $k = k_S = k_T$ , the rate of singlet or triplet projections (the ‘quantum measurement’ rate) is just  $(k_S + k_T)/2 = k$ . We will focus on low magnetic fields and assume, as is the case most often, that  $k > A, \omega$ . Toward the estimate, consider the following three steps. (i) As the RPs start out in the singlet state, and the S–T mixing frequency  $\Omega \ll k$ , in the short reaction time of  $1/k \ll 1/\Omega$  the singlet character will not have enough time to change appreciably, so it will be  $\langle Q_S \rangle \approx 1$ . This means that the RPs will be projected predominantly to the singlet state. (ii) The electron spin of the donor molecule, which contains the one and only nuclear spin of the RP under consideration, will precess at frequency  $|\omega \pm A|$  when the nuclear spin is in the  $|\pm\rangle$  state. So at time  $t$ , the number of singlet RPs with the nuclear spin in the  $|\pm\rangle$  state will be  $N_{\pm} \approx \cos[(\omega \pm A)t]^2$ . The nuclear polarization of singlet RPs at time  $t = 1/k$  will thus be  $\langle I_z \rangle^S = (N_+ - N_-)/(N_+ + N_-)$ , easily seen to be

$$\langle I_z \rangle^S \approx -\frac{\omega A}{k^2}. \quad (3)$$



(iii) S–T projections taking place at the rate  $k$  will be a source term for  $d\langle I_z \rangle_{\text{qc}}/dt$ . The source term, proportional to  $\langle I_z \rangle^{\text{proj}}$ , starts at  $t = 0$  from zero and oscillates at a rate  $\Omega$  while it is drained at a rate  $k$ ; thus  $d\langle I_z \rangle_{\text{qc}}/dt = k\langle I_z \rangle^{\text{proj}} e^{-kt} \sin \Omega t$ , yielding at time  $t \approx 1/k$  that  $\langle I_z \rangle_{\text{qc}} \approx -\langle I_z \rangle^{\text{proj}} \Omega^2/k^2$ . Putting everything together and using equation (2), we finally arrive at

$$\langle I_z \rangle_{\text{qc}} \approx \frac{\omega \Omega^2 A}{k^4}. \quad (4)$$

For the particular example depicted in figure 3 it is  $\Omega \approx A/10$ ; hence according to the estimate of equation (4), it is  $\langle I_z \rangle_{\text{qc}} \approx 4 \times 10^{-6}$ , in good agreement with the exact value shown in the right y-axis of figure 4. Furthermore, the result of equation (4) can be recast in terms of the thermal polarization  $I_{\text{th}} = \hbar\omega/4\gamma k_{\text{B}}T$  (the expression for  $I_{\text{th}}$  is valid for  $\hbar\omega \ll \gamma k_{\text{B}}T$ ), where  $\omega = \gamma_e B$  is the electron Larmor frequency in the external magnetic field  $B$ , with  $\gamma_e = 2\pi \times 2.8 \text{ MHz G}^{-1}$  being the electron gyromagnetic ratio and  $\gamma = |\mu_e/\mu_p| = 658.5$  being the ratio of electron-to-proton magnetic moment. The enhancement factor  $\langle I_z \rangle_{\text{qc}}/I_{\text{th}}$  is thus seen to be independent of  $\omega$  and equal to

$$\frac{\langle I_z \rangle_{\text{qc}}}{I_{\text{th}}} \approx 10^3 \frac{(\Omega/0.01 \text{ ns}^{-1})^2 (A/0.1 \text{ ns}^{-1})}{(k/1 \text{ ns}^{-1})^4}. \quad (5)$$

For ease of use, in the previous expression we provided the enhancement factor in terms of the S–T mixing frequency  $\Omega$  (in units of  $0.01 \text{ ns}^{-1}$ ), the hyperfine coupling  $A$  (in units of  $0.1 \text{ ns}^{-1}$ ) and the recombination rate  $k$  (in units of  $1 \text{ ns}^{-1}$ ). For typical hyperfine couplings of about 10 G and recombination times of the order of 1 ns, it is seen that the quantum measurement corrections to chemically induced dynamic nuclear polarization amount to a significant enhancement of at least four orders of magnitude over the thermal polarization.

We note for the reader who would worry about angular momentum conservation that the RP's nuclear spin polarization is exactly balanced by an opposite and equal electronic spin polarization, i.e. the sum  $\langle s_{1z} + s_{2z} + I_z \rangle = 0$  at all times, as it should be, since it is zero at time  $t = 0$  (the initial state is  $\rho_0 = Q_S/\text{Tr}\{Q_S\}$ , which is a singlet state with zero nuclear polarization). The non-zero electronic spin polarization necessarily involves the admixture of the  $|T_+\rangle = |\uparrow\uparrow\rangle$  and  $|T_-\rangle = |\downarrow\downarrow\rangle$  triplet states; therefore, this new CIDNP mechanism is a low-magnetic-field effect, because at high fields the  $|T_{\pm}\rangle$  states are out of reach from the singlet state  $|S\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ . How low a magnetic field depends on the recombination rate  $k$ , since the triplet RP decay broadens the triplet energy levels by about  $k$ ; hence the mechanism is appreciable for magnetic fields  $B$  such that  $B < k/\gamma_e$ , i.e. when the Zeeman energy separation of  $|T_{\pm}\rangle$  is within the broadening  $k$ . For  $k \approx 1 \text{ ns}^{-1}$ , the effect is appreciable for fields  $B \leq 50 \text{ G}$ .

## 5. Conclusions

In closing, the following comments should be made.

1. We stress that the new CIDNP signal is a fundamental phenomenon attributed to the inherent quantum dynamics of RPs.
2. Kaptein's rules [32] provide a compact relation of the main features of the CIDNP signal to the system's parameters. For this case, the sign of the effect, i.e. whether it is emissive (+) or absorptive (–), is the same as the sign of the hyperfine coupling  $A$ .

3. The new CIDNP effect reported here does not require any particular combination or fine-tuning of magnetic interactions, such as the coherent TSM low-field effect analyzed in [25], but is rather general and shows up whenever there is a non-zero nuclear spin polarization of singlet RPs,  $\langle I_z \rangle^S$ , as in figure 3(b). The rather general requirement for this to happen is that the oscillation frequencies  $\omega_m - \omega_n$  of the non-zero matrix elements  $[Q_S]_{mn} = \langle m | Q_S | n \rangle$  must have terms linear in the hyperfine couplings. Here  $|n\rangle$  and  $\omega_n$  are the eigenvectors and eigenvalues of  $\mathcal{H}$ , with  $n = 1, \dots, 4M$ , where  $M$  is the nuclear spin multiplicity of the radical pair.
4. Regarding experimental detection of the new CIDNP effect, we note the following. While NMR measurements at low fields suffer loss of sensitivity, recent methods of ultra-sensitive magnetometry using superconducting quantum interference devices (SQUIDs) [33, 34] or atomic magnetometers [35, 36] have demonstrated the ability to sensitively detect NMR signals at near-zero magnetic fields. To provide a rough estimate of the magnetic field  $B_n$  produced by the polarized nuclear spins, we note that in the solid phase the concentration of RCs can be as large as 1 mM. Assuming just a single proton spin per RC (which will heavily underestimate the magnitude of the effect), choosing a magnetic field of 1 G and taking into account that the considered enhancement will boost the thermal nuclear polarization by a factor of  $10^4$ , we find that the magnetic field just outside a spherical volume will be  $B_n \approx 10^4 P_{\text{th}} \mu_p \mu_0 [\text{RC}]$ , where [RC] is the RC concentration. At 1 G the thermal polarization is  $P_{\text{th}} \approx 10^{-10}$ ; hence  $B_n \approx 20$  fT, already 200 times higher than what state-of-the-art atomic magnetometers can do [37]. In fact, this seems to be yet another exciting application of ultra-sensitive magnetometry in the biological realm [38, 39].
5. Although we considered the special case  $k_S = k_T$ , the new kind of CIDNP signal we predict will ubiquitously affect all sorts of radical pairs, including of course the ones with asymmetric recombination rates  $k_S \neq k_T$ , which predominantly occur in photosynthetic RCs [22]. We have chosen to deal with the special case  $k_S = k_T$  and a magnetic Hamiltonian unable to support coherent generation of CIDNP signals in order to be able to focus exclusively on this fundamentally new CIDNP process. Establishing how this mechanism attributed to S–T decoherence affects, qualitatively and quantitatively, the cases where *there exists* a CIDNP signal according to the mechanism's traditional understanding (e.g. TSM, DD or DR scenarios) is a more involved exercise that will be undertaken elsewhere.
6. We have considered the CIDNP signal in the RP state, and not in the diamagnetic ground state of the molecule in a closed reaction cycle as the one shown in figure 1(b). In other words, in figure 4 we depicted the transient nuclear polarization of the RPs in between their creation at time  $t = 0$  and the time their population has decayed to zero due to charge recombination. However, it is easily seen that the same results hold true for the diamagnetic ground state in the steady state under continuous excitation (i.e. continuous illumination) and a closed reaction cycle, as long as the intersystem crossing rate  $k_{\text{isc}}$  (see figure 1(b)) is fast enough.

In conclusion, this is the first step of a very promising research program, namely the particular repercussions of the recently unraveled fundamental quantum dynamics of the radical-pair mechanism for understanding the dynamics of photosynthetic RCs. We have extended the fundamental understanding of CIDNP by pointing to a new and qualitatively different way of obtaining enhanced nuclear spin polarization. Interestingly, this polarization *naturally* turns out to be significant at low magnetic fields pertinent to natural photosynthesis. It stems from

the random singlet or triplet projections *naturally* taking place during the quantum evolution of radical pairs and leading to spin decoherence. Thus, an intriguing point raised is if and how the quantum mechanical process of spin decoherence affects the biological workings of photosynthetic RCs. In other words, what is the biological significance of Earth-field CIDNP produced by S–T decoherence?

## Appendix A

Since  $I_z$  commutes with the electron spins  $\mathbf{s}_1$  and  $\mathbf{s}_2$ , it also commutes with  $Q_S = 1/4 - \mathbf{s}_1 \cdot \mathbf{s}_2$  and with  $Q_T = 1 - Q_S$ . Thus, since the two projection operators are orthogonal, i.e.  $Q_S Q_T = Q_T Q_S = 0$ , it will be  $Q_S I_z Q_T = Q_T I_z Q_S = 0$ . Furthermore, since  $Q_S + Q_T = 1$ , it will be  $\text{Tr}\{\rho I_z\} = \text{Tr}\{\rho(Q_S + Q_T)I_z(Q_S + Q_T)\}$  and by using the previous relations it follows that indeed  $\langle I_z \rangle = \langle I_z \rangle^S + \langle I_z \rangle^T$ .

## Appendix B

Since  $I_z$  commutes with  $\mathbf{s}_1$  and  $[I_z, I_x] = iI_y$ ,  $[I_z, I_y] = -iI_x$ , it follows that  $[I_z, \mathcal{H}] = iA(s_{1x}I_y - s_{1y}I_x)$ . Then, Heisenberg's equation of motion  $dI_z/dt = i[I_z, \mathcal{H}]$  leads to

$$d\langle I_z \rangle/dt = -A\langle s_{1x}I_y - s_{1y}I_x \rangle. \quad (\text{B.1})$$

The most general pure spin state of the RP can be written as  $|\psi\rangle = \sum_{i=S, T_0, T_{++}, T_{--}} |i\rangle|\chi_i\rangle$ , where  $|i\rangle$  are the four electron-spin S–T basis states and  $|\chi_i\rangle$  is a nuclear spin state. It is straightforward to show that  $\langle \psi | s_{1x}I_y - s_{1y}I_x | \psi \rangle = 0$ ; therefore  $d\langle I_z \rangle/dt = 0$  at all times. The same holds true for any mixture of pure states. Since at time  $t = 0$  we have an RP mixture with zero nuclear polarization, at all times it will be  $\langle I_z \rangle = \langle [\mathcal{H}, I_z] \rangle = 0$ .

## Appendix C

The traditional master equation is  $d\rho/dt = -i[\mathcal{H}, \rho] - k_S(Q_S\rho + \rho Q_S)/2 - k_T(Q_T\rho + \rho Q_T)/2$ . For the case under study  $k_S = k_T = k$ , and taking into account that  $Q_S + Q_T = 1$ , the traditional master equation becomes  $d\rho/dt = -i[\mathcal{H}, \rho] - k\rho$ . After multiplying by  $I_z$  and taking the trace, it follows that according to the traditional theory it will be  $d\langle I_z \rangle/dt = -i\text{Tr}\{[\mathcal{H}, \rho]I_z\} - k\langle I_z \rangle$ . But  $\text{Tr}\{[\mathcal{H}, \rho]I_z\} = -\text{Tr}\{[\mathcal{H}, I_z]\rho\} = -\langle [\mathcal{H}, I_z] \rangle$ , which was shown to equal zero in appendix B. Therefore,  $d\langle I_z \rangle/dt = -k\langle I_z \rangle$ . Since at  $t = 0$  it is  $\langle I_z \rangle = 0$ , the same is true at all times.

## Acknowledgments

I warmly acknowledge helpful comments from Professors Gunnar Jeschke and Ulrich Steiner, and several comments clarifying CIDNP-related issues from Professor Jörg Matysik.

## References

- [1] Collini E *et al* 2010 Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature *Nature* **463** 644
- [2] Scholes G D, Fleming G R, Olaya-Castro A and van Grondelle R 2011 Lessons from nature about solar light harvesting *Nature Chem.* **3** 763

- [3] Nalbach P, Braun D and Thwart M 2011 Exciton transfer dynamics and quantumness of energy transfer in the Fenna–Matthews–Olson complex *Phys. Rev. E* **84** 041926
- [4] Wilde M M, McCracken J M and Mizel A 2010 Could light harvesting complexes exhibit non-classical effects at room temperature? *Proc. R. Soc. Lond. A* **466** 1347
- [5] Ishizaki A and Fleming G R 2009 Theoretical examination of quantum coherence in a photosynthetic system at physiological temperature *Proc. Natl Acad. Sci. USA* **106** 17255
- [6] Panitchayangkoon G *et al* 2011 Direct evidence of quantum transport in photosynthetic light-harvesting complexes *Proc. Natl Acad. Sci. USA* **108** 20909
- [7] Mosheni M, Rebentrost P, Lloyd S and Aspuru-Guzik A 2008 Environment-assisted quantum walks in photosynthetic energy transfer *J. Chem. Phys.* **129** 174106
- [8] Chin A W, Huelga S F and Plenio M B 2012 Coherence and decoherence in biological systems: principles of noise-assisted transport and the origin of long-lived coherences *Phil. Trans. Act. R. Soc.* **370** 3638
- [9] Sarovar M, Ishizaki A, Fleming G R and Whaley K B 2010 Quantum entanglement in photosynthetic light-harvesting complexes *Nature Phys.* **6** 462
- [10] Rozzi C A *et al* 2013 Quantum coherence controls the charge separation in a prototypical artificial light-harvesting system *Nature Commun.* **4** 1602
- [11] Boxer S G, Chidsey E D and Roelofs M G 1983 Magnetic field effects on reaction yields in the solid state: an example from photosynthetic reaction centers *Annu. Rev. Phys. Chem.* **34** 389
- [12] Schulten Z and Schulten K 1977 The generation, diffusion, spin motion and recombination of radical pairs in solution in the nanosecond time domain *J. Chem. Phys.* **66** 4616
- [13] Steiner U and Ulrich T 1989 Magnetic field effects in chemical kinetics and related phenomena *Chem. Rev.* **89** 51
- [14] Closs G L and Closs L E 1969 Induced dynamic nuclear spin polarization in reactions of triplet diphenylmethylene *J. Am. Chem. Soc.* **91** 4549
- [15] Kaptein R and Oosterhoff J L 1969 Chemically induced dynamic nuclear polarization: II. Relation with anomalous ESR spectra *Chem. Phys. Lett.* **4** 195
- [16] Zysmilich M G and McDermott A 1994 Photochemically induced dynamic nuclear-polarization in the solid-state N-15 spectra of reaction centers from photosynthetic bacteria *J. Am. Chem. Soc.* **116** 8362
- [17] Polenova T and McDermott A E 1999 A coherent mixing mechanism explains the photoinduced nuclear polarization in photosynthetic reaction centers *J. Phys. Chem. B* **103** 535
- [18] Prakash S *et al* 2006 Photo-CIDNP MAS NMR in intact cells of *Rhodobacter sphaeroides* R26 *J. Am. Chem. Soc.* **128** 12794
- [19] Diller A *et al* 2007 N-15 photochemically induced dynamic nuclear polarization magic-angle spinning NMR analysis of the electron donor of photosystem II *Proc. Natl Acad. Sci. USA* **104** 12767
- [20] Daviso E *et al* 2009 Electron-nuclear spin dynamics in a bacterial photosynthetic reaction center *J. Phys. Chem. C* **113** 10269
- [21] Daviso E *et al* 2009 The electronic structure of the primary electron donor of reaction centers of purple bacteria at atomic resolution as observed by photo-CIDNP <sup>13</sup>C NMR *Proc. Natl Acad. Sci. USA* **106** 22281
- [22] Matysik J, Diller A, Roy E and Alia A 2009 The solid-state photo-CIDNP effect *Photosynth. Res.* **102** 427
- [23] Jeschke G 1997 Electron–electron-nuclear three-spin mixing in spin-correlated radical pairs *J. Chem. Phys.* **106** 10072
- [24] Jeschke G and Matysik J 2003 A reassessment of the origin of photochemically induced dynamic nuclear polarization effects in solids *Chem. Phys.* **294** 239
- [25] Jeschke G, Anger B C, Bode B E and Matysik J 2011 Theory of solid-state photo-CIDNP in the Earth’s magnetic field *J. Phys. Chem.* **115** 9919
- [26] Kominis I K 2009 The quantum Zeno effect explains magnetic-sensitive radical–ion-pair reactions *Phys. Rev. E* **80** 056115
- [27] Kominis I K 2011 Radical–ion-pair reactions are the biochemical equivalent of the optical double slit experiment *Phys. Rev. E* **83** 056118

- [28] Haberkorn R Density matrix description of spin-selective radical pair reactions *Mol. Phys.* **32** 1491
- [29] Kominis I K 2012 Magnetic sensitivity and entanglement dynamics of the chemical compass *Chem. Phys. Lett.* **542** 143
- [30] Kominis I K 2012 Reactant-product quantum coherence in electron transfer reactions *Phys. Rev. E* **86** 026111
- [31] Jones J A and Hore P J 2010 Spin-selective reactions of radical pairs act as quantum measurements *Chem. Phys. Lett.* **488** 90
- [32] Kaptein R 1971 Simple rules for chemically induced dynamic nuclear polarization *J. Chem. Soc.: Chem. Commun.* **1971** 732
- [33] McDermott R *et al* 2002 Liquid-state NMR and scalar couplings in microtesla magnetic fields *Science* **295** 2247
- [34] Matlachov A N, Volegov P L, Espy M A, George J S and Kraus R H 2004 SQUID detected NMR in microtesla magnetic fields *J. Magn. Res.* **170** 1
- [35] Savukov I M and Romalis M V 2005 NMR detection with an atomic magnetometer *Phys. Rev. Lett.* **94** 123001
- [36] Xu S J *et al* 2006 Magnetic resonance imaging with an optical atomic magnetometer *Proc. Natl Acad. Sci. USA* **103** 12668
- [37] Dang H B, Maloof A C and Romalis M V 2010 Ultrahigh sensitivity magnetic field and magnetization measurements with an atomic magnetometer *Appl. Phys. Lett.* **97** 151110
- [38] Xia H, Baranga A B A, Hoffman D and Romalis M V 2006 Magnetoencephalography with an atomic magnetometer *Appl. Phys. Lett.* **89** 211104
- [39] Corsini E *et al* 2011 Search for plant biomagnetism with a sensitive atomic magnetometer *J. Appl. Phys.* **109** 074701