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Photo-activated biological processes as quantum measurements

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We outline a framework for describing photo-activated biological reactions as generalized quantum measurements of external fields, for which the biological system takes on the role of a quantum meter. By using general arguments regarding the Hamiltonian that describes the measurement interaction, we identify the cases where it is essential for a complex chemical or biological system to exhibit non-equilibrium quantum coherent dynamics in order to achieve the requisite functionality. We illustrate the analysis by considering measurement of the solar radiation field in photosynthesis and measurement of the earth's magnetic field in avian magnetoreception.

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I. INTRODUCTION

The role of quantum dynamical effects in biological processes has generated increasing interest in recent years as time-resolved measurement techniques have allowed probing of dynamics on ultra-short time scales [1]. Photo-induced processes are particularly amenable to such studies, e.g., with pulsed lasers. Many key biological sensing and regulation processes are initiated by absorption of visible or near infrared light: these include vision, photosynthesis and the proposed mechanism for magneto-reception. While the molecular context of these photo-induced biological processes may be quite different, they share several important common features. Most importantly, the excited state dynamics following what is typically an electronic excitation of a chromophore molecule within a pigment-protein complex results in initiation of a sequence of chemical reactions that result in biological functionality - be it signaling of external stimuli as in the cases of vision and magneto-reception, or production of energy rich compounds in the case of photosynthesis. The relevant dynamics following the photo-excitation to the excited state occur in strongly non-equilibrium conditions. An open question that is at the heart of the burgeoning field of quantum biology is whether quantum coherence during this non-equilibrium evolution is relevant in conveying information about the external stimulus to the specific molecular components that initiate subsequent biological function.

In this Article, we analyze the relevance of quantum coherent dynamics in the general class of photo-activated biological processes by embedding the problem in a quantum measurement setting, where the light-sensitive biomolecule takes on the role of a quantum meter that allows the biological organism to acquire information and/or energy from the external stimuli. We shall first outline the key aspects of quantum measurement analogy that will be used in our analysis. Following this we consider two categories of biological quantum measurements. In the first category, the external stimulus for the bio-system consists exclusively of the non-equilibrium radiation field which ensures optical pumping of the pigment-protein complex into a metastable state. This category includes the light harvesting process that initiates photosynthesis, as well as the photo-initiation of vision. In the case of photosynthesis, the requisite biological function is energy storage; the underlying irreversible dynamical process can then be classified as an non-referred quantum measurement, since the information gained about the incident radiation field is per se not directly relevant, although the measurement event and its output of an electron hole pair is essential for the biological function. In contrast, the information gain about the incident light is central to the retinal photo-isomerization in vision. The key feature of all biological processes in this category is that the measurement interaction does not commute with the Hamiltonian describing the eigenstates of an unperturbed quantum meter. In the second category, which includes magneto-reception, the measurement interaction by itself does not lead to coupling of different meter eigenstates prior to optical excitation, i.e., the measurement interaction commutes with the Hamiltonian describing the free quantum-meter evolution. A key conclusion of the present work is that quantum coherence is essential for biological processes belonging to the second category whereas its role in the first category is limited to enhancement of the information/energy extraction rate.

II. QUANTUM MEASUREMENTS AND PHOTO-ACTIVATED BIOLOGICAL PROCESSES

Quantum mechanics postulates that the state of any physical system at time t is described by a density operator $\rho(t)$; the probabilities associated with the possible outcomes of an arbitrary measurement carried out on this system is contained in $\rho(t)$. Quantum mechanics also postulates that the general time evolution of a physical system is describable as a quantum operation, specified by a set of Kraus operators, that relate the initial and final density operator [2]. This formulation allows us to treat the dynamics of a physical system that is in

constant interaction with other, possibly larger, physical systems, which we refer to as the environment; typically, we have no control over the environment degrees of freedom and no possibility to make a measurement. As a consequence of these uncontrolled interactions between the system and the environment, the entropy of the system increases with time, signalling information about the system leaking into the environment degrees of freedom. This process, which is termed decoherence, can encompass both dephasing and relaxation components and is indistinguishable from a measurement carried out on the physical system, provided that the measurement results are discarded. The measurement processes are in turn described by a Positive Operator Valued Measure (POVM), whose elements are directly linked to the Kraus operators associated with the underlying quantum operation. When the elements of the POVM are projection operators onto the eigenstates of the Hermitian operator $\hat{A}$ associated with an observable A, we say that the quantum operation corresponds to the measurement of A.

Even though a quantum measurement is normally perceived as interfacing a system with a classical apparatus, it is convenient to describe the underlying physical process as a quantum mechanical interaction between the system to be measured and a *quantum meter*; as a consequence of the interaction described by the Hamiltonian $\hat{H}_{meas}$, the system and the meter become correlated in a way that the post-measurement state of the meter carries information about the system state. The irreversibility of the measurement process emerges as a consequence of the coupling of the quantum meter to other physical systems with large number of degrees of freedom – the environment of the quantum meter. This formulation was first introduced by von Neumann in 1930s [3].

Based on this premise, a large class of chemical reactions or biological processes can be described as a quantum measurement where the biological complex of interest assumes the role of a *quantum meter*. The simplest scenario with which one can describe a quantum measurement is the one in which the wave-function describing the quantum meter is in a pure state - which is normally the lowest energy eigenstate of the meter Hamiltonian H_{meter}. This assumption does not require that the overall system wave-function is in a pure state - nor does it assume zero temperature; it is motivated by the fact that to ensure maximal information extraction from the system that is being measured, it is desirable to have complete information about the initial state of the meter. That said, the assumption of an initial pure-state is well justified in a pigment-protein complex where the initial photo excitation produces an electronic excitation of one or more chromophore molecules from a non-degenerate electronic ground-state. The rotational and vibrational degrees of freedom of the bio-molecule on the other hand typically start out and remain in a mixed-state. For the case of a quantum meter measuring a classical field such as the earth's magnetic field, suitable meter degrees of freedom are electronic spin and these may initially be in a pure state, even if the nuclear degrees of freedom are not. We note that such an electron spin quantum meter is currently of interest in other settings, such as a nitrogen-vacancy center used as a quantum meter to measure weak magnetic fields [4, 5].

To proceed with identifying the relevant Hamiltonian describing a light-induced biological process, we shall consider the quantum meter as composed of a system of electrons derived from molecules within a pigment-protein complex, with associated charge (orbital) and spin degrees of freedom. We make the Born-Oppenheimer approximation and treat the vibrational and rotational degrees of freedom of the protein as constituting an environment for the system electrons. The nuclear spins of the environment on the other hand will be treated separately, as they give rise to an effective quasi-static internal magnetic field that acts on the electronic system. In the interaction picture, the general Hamiltonian is then expressed as

$$H = H_{meter} + H_{sys} + H_{meas} + H_{m-env} \tag{1}$$

where H_{m-env} describes the coupling of the quantum meter to its *environment* and H_{sys} is the Hamiltonian of the system to be measured. We shall be concerned here with measurement of external stimuli for biological systems, in particular, measurement of an incident radiation field and of the earth's magnetic field. The coupling between the system and the meter is described by the measurement Hamiltonian H_{meas}. Since we exclusively deal with chemical processes that are triggered by light, we write

$$H_{meas} = H_{m-rad} + H_{int}, \tag{2}$$

where H_{m-rad} is the electric dipole Hamiltonian describing light absorption/emission by the pigment-protein complex and H_{int} the interaction Hamiltonian describing the coupling of the meter to the external stimuli that is not captured by H_{m-rad}.

We assume that the broadband optical excitation arising from H_{m-rad} projects the quantum meter into a superposition of eigenstates $|\Psi_m^{ex}\rangle$ with eigenenergies that are substantially higher than that of the initial ground state $|\Psi_m^{g}\rangle$ of the meter. Before the optical excitation, the meter dynamics is described by $H_{meter} = H_0$. The structural changes induced by the optical excitation are implicit in the post-excitation meter Hamiltonian $H_{meter}^{(ex)} = H_{ex}$. We shall also assume that in general $[H_{ex}, H_0] \neq 0$, implying that a good quantum number for the ground state manifold need not be a conserved quantity for dynamics in the relevant metastable excited state manifold.

The need to assign two non-commuting Hamiltonians to the ground and excited manifolds of the electronic system stems from the influence of the degrees of freedom that are excluded from the description of the quantum meter. This situation can arise when the electronic degree of freedom of interest is spin, which is subject to interactions whose magnitude strongly depend on the

orbital degrees of freedom of the electron. For example, before charge separation in the excited state manifold takes place, the dominant interaction between remote electron spins is electron exchange, whereas following charge separation that results in formation of a radical pair, hyperfine interaction with neighboring nuclear spins could become the leading electron spin interaction term. More generally, optical excitation typically leads to changes in the electronic or nuclear degrees of freedom that are not directly interacting with the external electromagnetic field but are nevertheless indirectly affected by the optical excitation. A mean-field treatment of these additional degrees of freedom would then yield a modified Hamiltonian for the meter, which would be described by H_{ex}, while the pre-optical-excitation Hamiltonian was H_0. This scenario is akin to a quantum quench induced by absorption of a photon [6].

The formulation of the photo-activated measurement process in terms of the general Hamiltonian, Eq. (1), allows us to consider two scenarios:

(i) In the first scenario, the system to be measured is the strength of the incident light field, or equivalently, the number of photons n_i at specific frequencies ω_i incident upon the meter: $H_{sys} = \sum_i \hbar\omega_i n_i$. In this case, $H_{meas} = H_{m-rad}$ and $H_{int} = 0$. Since $[H_0, H_{meas}] \neq 0$, the absorption process in general leads to correlations between the measured system (incident light) and the meter together with its environment (the total pigment-protein complex). Depending on the statistical properties of the incoming light, upon absorption the pigment-protein complex may be in a classical mixture of states, for thermal light, or a coherent superposition of states, for coherent light [7]. Due to the reservoir coupling H_{m-env}, the excited meter states relax over a time scale τ_0 into a metastable eigenstate $|\Psi^d_m(\tau_0)\rangle$ (for notational simplicity we refer to pure states) that constitutes the doorway state for subsequent chemical signaling. We claim that, independent of the coherence in its time evolution, the optical excitation of the meter followed by this non-radiative relaxation into the metastable doorway state is essentially an optical pumping process. The efficiency of the optical pumping is relevant since the metastable states thereby prepared represent the information gained and encoded by the meter and facilitate the relevant conditional chemical reaction which constitutes the signaling step controlling the subsequent biological function. The interplay between incoherent and quantum coherent evolution taking place for $t \leq \tau_0$ quantitatively determines the efficiency of the optical pumping. However, the overall measurement process can nevertheless be efficiently described in terms of rate equations. The best known examples of biological processes that can be described using this scenario are light harvesting and the primary stages of vision.

(ii) In the second scenario, the coupling between the system to be measured and the quantum meter is described by H_{int}, which satisfies $[H_0, H_{int}] = 0$. In this case, both the meter ground state $|\Psi^g_m\rangle$ and the excited state $|\Psi^d_m(\tau_0)\rangle$ that could be reached after the action of H_{m-rad} and H_{m-env} are eigenstates of H_{int} and of $H^{(0)}_{meter} = H_0$. Clearly, if $H_0 = H_{ex}$, the meter cannot aquire information about the system. If on the other hand, the Hamiltonian that governs the dynamics in the optically excited manifold ($H_{meter} = H^{(ex)}_{meter} = H_{ex}$) satisfies $[H_0, H_{ex}] \neq 0$, then the state $|\Psi^d_m(\tau_0)\rangle$ will be a superposition of the eigenstates of H_{ex}. Subsequent evolution under H_{ex} then generates non-trivial quantum dynamics that is sensitive to H_{int} and could allow for an interferometric measurement. To see that the extraction of information about the system in this case relies crucially on the preservation of quantum coherence, we note that an interferometric measurement projecting the system back into the eigenstates of H_0 requires that the coherence time τ_c satisfies

$$\tau_c > 1/||H_{ex}|| \tag{3}$$

assuming $||H_{ex}|| > ||H_{int}||$. A sizeable H_{int} induced coupling, or accumulated relative phase, between the eigenstates of H_{ex} is obtained provided $||H_{int}||\tau_c \sim 1$. Equivalently, a measurement within the lifetime of the excited state is possible if the system retains its quantum coherence on time-scales long compared to the characteristic time-scales of the final-structure Hamiltonian H_{ex}, indicating that non-equilibrium quantum dynamics in the optically excited states is an essential feature. This case presents an especially intriguing situation for measurement of an external magnetic field by a biological quantum meter consisting of electron spins. We note that even though the nature of the information extraction in the measurement process is drastically different in scenario (ii) than in scenario (i), optical pumping also plays a role in scenario (ii), via the preparation of the metastable excited state $|\Psi^d_m(\tau_0)\rangle$.

III. MEASUREMENT OF INCIDENT RADIATION FIELD

First, we consider the scenario (i) where the system observable to be measured is the mean photon number of the incident radiation field. The system-meter correlations that emerge in this case may be interpreted by analogy to a simple three-level system, in which the central dynamical processes are the optical excitation of the pigment-protein complex to a set of high energy states and a subsequent fast non-radiative relaxation to a lower energy metastable state that acts as a doorway state for subsequent chemical and biological signaling processes. Without loss of generality, we may consider incoherent optical excitation from the ground state $|1\rangle$ to a single high energy state $|3\rangle$ which we introduce to represent the set of short-lived excited states. The excitation rate is $\Gamma_{31}\overline{n}_{31}$, where Γ_{31} is the spontaneous emission rate from $|3\rangle$ to $|1\rangle$ and $\overline{n}_{31}$ denotes the steady state mean photon occupancy. Relaxation from state $|3\rangle$ to the lower

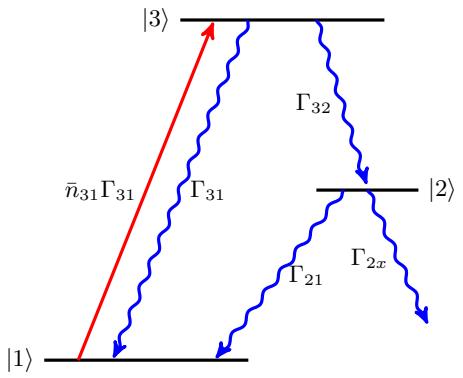
energy doorway state $|2\rangle$ takes place through a combination of quantum coherent evolution due to H_{meter} and coupling to low energy vibrational degrees of freedom of the molecule (H_{m-env}). Postponing the discussion of potential quantum effects, we describe this relaxation with a non-radiative decay rate Γ_{32}. These two rates, together with the relatively slow decay of $|3\rangle$ back to the ground state or the decay of $|2\rangle$ to further reaction product states $|X\rangle$, are features common to each of the photo activated processes that we consider in this paper.

To the extent that the relaxation of the doorway state $|2\rangle$ is slow, this level scheme together with their relevant couplings corresponds to an optical pumping scheme (see Figure 1 for two specific examples). A steady state rate equation analysis for the state populations ρ_{ii} shows that in all cases that we consider, the population of the doorway state $|2\rangle$ is proportional to the number density of the incident radiation field $\overline{n}_{31}$. In our measurement-based description of photo activated processes in biology, optical pumping from the ground state $|1\rangle$ to the metastable excited state $|2\rangle$ is thus equivalent to a measurement of the incident solar radiation field observable $\overline{n}_{31}$, or equivalently its temperature.

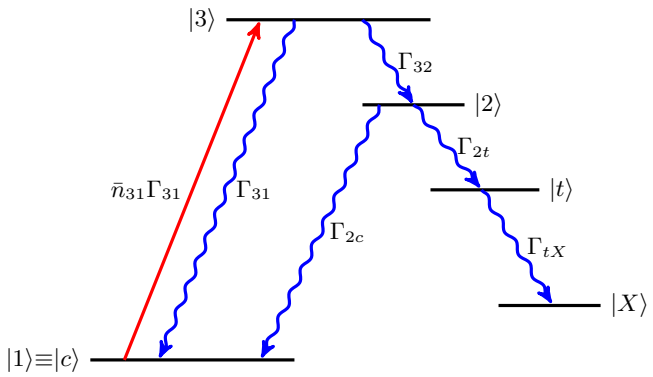
A. Light harvesting complexes in photosynthesis

To illustrate this measurement of incident light intensity via optical pumping in a biological setting, we first consider the light harvesting step in photosynthesis. Here the quantum meter is the chromophore component of a pigment-protein complex known as the light harvesting complex (LHC) or the 'antenna complex', whose role is to transfer the energy from absorbed photons to the reaction center where subsequent separation of the electron-hole pair occurs. The system to be measured is the out-of-equilibrium source of light – typically sunlight filtered by the earth's atmosphere, although some bacteria living deep below the ocean near hydrothermal vents employ black body radiation from these vents [8]. The information extraction in this case is accompanied by energy storage in the quantum meter. This is brought about by subsequent steps transferring the electronic energy from the antenna complex to the reaction center where charge separation occurs, generating electrons that initiate chemical reactions leading to energy rich products. The average population of the photo-generated electrons in the reaction center can then be considered to represent the encoding of information gained from a measurement of the mean number of absorbed photons (typically visible or near infrared).

Figure 2a shows the basic scheme for interpretation of light harvesting as optical pumping of the doorway state leading to charge separation. In the notation of scenario (i), the LHC meter is initially in state $|1\rangle$ in which the pigments are in their electronic ground states. The meter is excited into a metastable state $|3\rangle$ corresponding to a superposition of excitonic eigenstates of the pigment sub-



(a) Optical pumping in light harvesting



(b) Optical pumping in vision

FIG. 1: (a) Schematic of optical pumping for light harvesting. The rate constants for this optical pumping scheme are as follows: $\Gamma_{31}, \Gamma_{21} \sim (ns)^{-1}, \Gamma_{2X} \sim (1-4\ ps)^{-1}, \Gamma_{32} \sim (100-800\ ps)^{-1}$ [9, 10].
(b) Optical pumping scheme corresponding to photon-absorption induced dynamics of rhodopsin. The magnitude of the key decay rates are $\Gamma_{32} \sim (80\ fs)^{-1}$ [11], $\Gamma_{2t} \sim (140\ fs)^{-1}, \Gamma_{2c} \sim (280\ ps)^{-1}$ [12], while the remaining rate constants are $\Gamma_{31} \sim (20\ ps)^{-1}$ [13] and $\Gamma_{tX} \sim (1\ ps)^{-1}$ [14].

system by absorption of broadband photons. The meter then exhibits complex non-equilibrium quantum dynamics during which this initial superposition relaxes into the doorway state $|2\rangle$. This may may then undergo radiative decay back to the ground state (fluorescence) with rate Γ_{21}, or non-radiative transformation to further products X, with rate Γ_{2X}. The relaxation process from $|3\rangle$ to $|2\rangle$ is known to be characterized by a remarkable near-unity quantum efficiency; within our optical pumping model, this implies that the short time dynamics must yield complete transfer of ρ_{33} to ρ_{22}. Unlike most optical pumping schemes in atomic physics though, the ambient conditions relevant for biological processes ensure that $\rho_{22} \ll \rho_{11}$.

The key question of interest for us is the role of quantum coherence during this measurement process. In particular, to what extent does the quantum nature of the meter (LHC) play an enabling role in the measurement

of the incident light field? The non-equilibrium energy transfer dynamics of light harvesting have been extensively studied in recent years [15–17] and a full description was shown to require simulation of complex open quantum system dynamics with both coherent and incoherent components. We note however, that the interplay between dipole-dipole interaction (H_{ex}) mediated interchromophore exciton hopping and the coupling to vibrational degrees of freedom (H_{m-env}) ensure the energy transfer from the initially excited chromophore state $|3\rangle$ to the reaction-center state $|2\rangle$, irrespective of the relative magnitude of the coherence time τ_c to characteristic quantum coherent evolution timescale $||H_{ex}||^{-1}$. In fact, theoretical studies have shown that preserving quantum coherence, or equivalently, reducing the effects of dephasing and dissipation in the light harvesting produces a relatively small quantitative change in efficiency rather than an on/off switch of functionality [18].

B. Photo-activated isomerization in vision

Photo-activated isomerization constitutes another class of biological processes that may be understood in terms of optical pumping realizing a measurement of incident mean visible photon number ($\overline{n}_{31}$) by a biological quantum meter. Light activated isomerization reactions play an important role in control and switching of biological function in a broad range of organisms, including vision in animals and photosynthesis in halo bacteria. A prime example of such a photo-activated isomerization based quantum meter is the rhodopsin pigment-protein complex which plays the key role in the primary steps of animal vision [19].

Figure 1b shows the energy level diagram of the relevant states involved in the photo activation of vision by retinal in rhodopsin protein. In the ground state $|1\rangle \equiv |c\rangle$ of rhodopsin, the retinal pigment is in the cis-conformation. Experimental studies have shown that the transformation from initial Franck-Condon photo-product $|3\rangle$ reached by photon absorption, to the metastable all-trans isomer of retinal proceeds via a conical intersection, which is reached within ~ 80 fs[11]. The system returns to the ground electronic state nuclear potential energy surface V_{S_0} by traversing the conical intersection, arriving in the transitory state, labeled $|2\rangle$ in Fig 1b. This state then undergoes rapid bifurcation, with approximately 65% chance of undergoing nuclear dynamics transforming it into the trans isomer $|t\rangle$ which constitutes the doorway state signalling photon absorption; the remaining 35% returns to the cis-isomer of the electronic ground state, $|1\rangle$. The overall transformation of $|3\rangle$ to $|t\rangle$ takes place in ~ 200 fs. Combined with a 50% absorption probability for a single photon by an ensemble of rhodopsin molecules contained within a rod cell [20], the overall process results in a remarkable $\sim 30\%$ probability of detection of single photons. While the electronic and vibrational degrees of freedom are expected to be entangled around the conical intersection [21], it is not clear what role, if any, the underlying quantum correlations play for the creation of the signalling trans state.

IV. MAGNETORECEPTION AS A QUANTUM MEASUREMENT OF A CLASSICAL FIELD

Magnetoreception refers to the ability of living organisms to detect the magnitude and/or orientation of the earth's magnetic field. Typically found in migrating species, it has been most widely studied in birds which are capable of navigating distances of thousands of kilometers [22, 23]. This is quite remarkable, given that the earth's magnetic field is very weak ($\sim 50\mu$T) and the Zeeman interaction energy of a molecule with such a field is typically more than 6 orders of magnitude smaller than k_BT. Several biophysical mechanisms have been proposed to rationalize this remarkable ability [24–26]. One proposed mechanism, the radical pair hypothesis, is equally remarkable in that it requires maintenance of coherent quantum spin dynamics over nm distances on time scales (well) exceeding 10 ns [27]. While there is so far no unambiguous evidence for this mechanism *in vivo*, there is circumstantial evidence that it contributes at least partially to avian magnetoreception in some species [28, 29], as well as mounting evidence of feasibility from *in vitro* studies with biomimetic molecular model systems [30]. It thus presents an intriguing and dramatic instance of non-equilibrium quantum dynamics that may be essential for biological function.

The molecular basis of the radical pair mechanism is described in a number of review articles [23, 27, 31]. We note that magnetoreception is widely accepted to be photo-activated, allowing it to be mapped directly into the general framework for photo-induced biological processes. Here we present an analysis of the proposed mechanism within the formalism for measurement of an external field by a biological quantum meter described above. We shall illustrate this with specific reference to the cryptochrome protein, a photoreceptor which is the leading candidate for hosting the radical pair in the retina of birds. This protein contains a co-factor, FAD, which absorbs incident light centered around 450 nm to form an excited singlet state FAD*. The unstable FAD* triggers a rapid charge transfer across a chain of three tryptophan amino acids, leading to the formation of a radical pair state [FAD$^{\bullet -}$ + TrpH$^{\bullet +}$] in which the electron spins are located on spatially separated and distinct molecules. The total electron spin is conserved during this fast electron transfer, which takes place on a ps time-scale τ_0.

Mapping this onto our measurement scenario (ii), we identify the electrons of the radical pair as the quantum meter, characterized by Hamiltonians H_0 in the ground state and H_{ex} in the excited state. For $r < 1$ nm, the dominant term in H_{ex} is well approximated by the exchange interaction

$$H_{ex} \simeq J(r)\vec{S}_1 \cdot \vec{S}_2 \simeq H_0 \tag{4}$$

where $J(r)$ depends exponentially on the inter-electron separation r. The dominant contribution to H_{ex} for $r > 1$ nm on the other hand, is given by the anisotropic hyperfine interaction of the two electron spins with the proximal nuclear spins in their local environments:

$$H_{ex} \simeq \sum_{i_1,k} A_{i_1,k} S_{1,k} I_{i_1,k} + \sum_{i_2,k} A_{i_2,k} S_{2,k} I_{i_2,k}. \quad (5)$$

Here I_{i_1}, I_{i_2} denote the nuclear spins with non-negligible coupling to the spin of the unpaired electrons localized at FAD ($\vec{S}_1$) and tryptophan ($\vec{S}_2$), respectively. $\mathbf{A}_{i,k}$ is the corresponding hyperfine coupling constant along $\hat{k}$ ($k = x, y, z$). The system to be measured here is the earth's magnetic field: this classical field B_{ext} appears in the system-meter interaction term H_{int} of H_{meas}:

$$H_{int} = g_e \mu_B \vec{B}_{ext} \cdot (\vec{S}_1 + \vec{S}_2), \quad (6)$$

where we assume that the g-factor of the electron g_e is independent of its location within the pigment-protein complex [32]. We also discard the much smaller coupling of nuclear spins to $\vec{B}_{ext}$. Since measurement of the earth's magnetic field is initiated by sunlight, H_{meas} must also include H_{m-rad}, which is given here by the electric dipole Hamiltonian describing sun light absorption by the FAD chromophore. The environmental Hamiltonian H_{m-env} is given by the interactions of the radical pair electrons with the vibrations and rotations of the cryptochrome protein. In fact, the preparation of the cryptochrome in the long-lived [$FAD^{\bullet -}$ + $TrpH^{\bullet +}$] singlet state (state $|2\rangle$ in Fig. 1a) is accomplished by an optical pumping process that is based on H_{m-rad} and H_{m-env}.

We emphasize that since the meter starts out in a singlet state and since $[H_0, H_{int}] = 0$, there are no system-meter correlations before optical excitation. After the optical pumping process prepares the pigment-protein complex in the metastable radical-pair [$FAD^{\bullet -}$ + $TrpH^{\bullet +}$] with an inter-electron distance of $r \sim 1.5$ nm, the relevant meter Hamiltonian becomes H_{ex}, given by Eq. (5). Since the timescale for completion of optical pumping, i.e., the optical excitation followed by radical pair formation, is much shorter than $||H_{ex}||^{-1}$, the radical pair is initially in the singlet state, ^{S}[$FAD^{\bullet -}$ + $TrpH^{\bullet +}$]. However, since the strength and the anisotropy of the hyperfine interactions in the FAD and tryptophan molecules are different, the total electron spin is no longer conserved. Consequently the singlet state is not an eigenstate of H_{ex} and the hyperfine interactions give rise to dynamic inter-conversion of singlet and triplet radical states ^{S}[$FAD^{\bullet -}$ + $TrpH^{\bullet +}$]$\longleftrightarrow^T$[$FAD^{\bullet -}$ + $TrpH^{\bullet}$].

This inter-conversion requires a full quantum mechanical description over the time scale of the spin coherence of the radical pair. Since $[H_{ex}, H_{int}] \neq 0$, the weak magnetic field of the earth B_{ext} modifies the coherent singlet-triplet inter-conversion provided that its orientation is not parallel to that of the hyperfine (difference) field [33]. Since the singlet and triplet states possess different reaction pathways, this modulation can cause changes in the populations of the resulting products. In cryptochrome, both singlet and triplet states can convert to a long-lived ($\geq 100\mu$s) protonated state [$FADH^{\bullet}$ + $Trp^{\bullet}$], while only the singlet state can undergo relaxation by back electron transfer to the initial (singlet) ground state FAD + TrpH [28]. This singlet relaxation occurs on a timescale of $\tau_p \geq 1\mu s$, so that modulations on shorter time scales can cause observable changes in the combined singlet and triplet population that is converted into the long-lived protonated state. Consequently a detection of the changes in the protonated radical pair singlet and triplet states or products of subsequent chemical reactions, constitutes a measurement of $\vec{B}_{ext}$. The essential feature of this radical-pair based magnetoreception is thus the dependence of the long-time-scale ($> 1\mu s$) protonated state population on the relative orientation of the earth's magnetic field $\vec{B}_{ext}$ with respect to the radical pair axis.

To elucidate the essential role played by quantum coherence in magneto-reception, we may consider the well-known simplified problem of two electron spins, (e.g., one at FAD (F) and the other at Tryptophan (T)), with only one of these electron spins (e.g., F) interacting with a single nuclear spin $I^F = 1/2$. H_{ex} is then given by the anisotropic hyperfine interaction at site F:

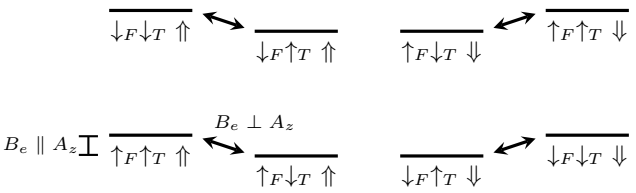
$$H_{ex} = A_z S_z^F \cdot I_z^F \quad (7)$$

Even though the nuclear spin is in a completely mixed state, its state remains unchanged during the time scale over which the electron spin evolves; we may therefore assume that it is initially oriented along z, i.e., $|\Uparrow\rangle_F$, without loss of generality. The energy levels for this simplified scheme are shown in Figure 2a.

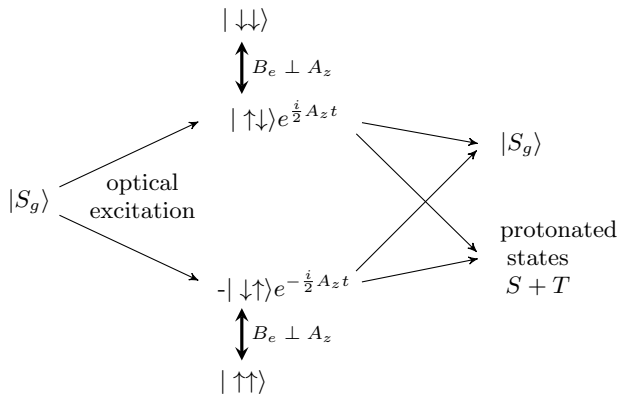
Starting out in the singlet state of the electrons at sites F and T at time $t = 0$, the wave-function of the coupled electron-nuclear system for $B_{ext} = 0$ is

$$|\Psi(t)\rangle = \frac{1}{\sqrt{2}} |\uparrow, \Uparrow\rangle_F \otimes |\downarrow\rangle_T e^{-iA_z t} - \frac{1}{\sqrt{2}} |\downarrow, \Uparrow\rangle_F \otimes |\uparrow\rangle_T. \quad (8)$$

If $B_{ext} \parallel \hat{z}$, then the initial singlet state can couple only to a single triplet state, $|T_0\rangle$: assuming equal slow decay of the singlet and triplet states into distinct chemical products, this will yield a long-time singlet ($|S\rangle$) yield of 50%. However, when $B_{ext} \perp \hat{z}$ and in the low field regime where $B_{ext} \ll A_z$, the Zeeman interaction only influences the electron at site T, which is not coupled to a nuclear spin. In this case, all three triplet states are populated with a long-time singlet yield of 25%, provided $A_z \gg B_{ext} \sim \tau_c^{-1}$. In the opposite limit of $A_z \ll \tau_c^{-1}$ on the other hand, the singlet-triplet transition probability vanishes to lowest order. We can therefore conclude that preservation of quantum coherence over the dynamical timescales associated with H_{ex} is essential for magneto-reception. Figure 2b illustrates the relevant energy level diagram for $B_{ext} \ll A_z$: the electron spin at site T precesses around the external field, leading to excitation of



(a) Energy levels of simplified radical pair model



(b) External field modification of singlet-triplet conversion

FIG. 2: (a) Schematic of energy levels relevant to magnetoreception in cryptochrome, within the simplified radical pair model of two electron spins, S^F at FAD and S^T at Tryptophan (single up/down arrows) with a single nuclear spin I^F (double up/down arrow) interacting with the FAD electron spin. With an anisotropic hyperfine tensor $A \equiv A_z$, a weak external field $B_e \parallel \hat{z}$, just shifts the energy levels (vertical bars), while $B_e \perp \hat{z}$ induces transitions between spin levels with different z-projection of $S = S^F + S^T$ (double headed arrows). For $A_z \gg B_e$, the resulting eight total spin levels are divided into two groups separated by a gap of order A_z. (b) Schematic of the resulting external magnetic field modified singlet-triplet conversion in optically excited cryptochrome for $B_e \perp \hat{z}$. Upon optical excitation and the subsequent fast relaxation leading to radical pair formation, the protein-chromophore complex is prepared in a coherent superposition of its eigenstates $|\uparrow,\downarrow\rangle$ and $|\downarrow,\uparrow\rangle$. While the hyperfine interaction modifies the relative phase accumulated by $|\uparrow,\downarrow\rangle$ and $|\downarrow,\uparrow\rangle$, $B_e \perp A_z$ leads to coherent excitation of the the other two triplet states $|\uparrow,\uparrow\rangle$ and $|\downarrow,\downarrow\rangle$, thereby modifying the probability that the molecule ends up in the protonated state.

all 3 triplet states whenever B_{ext} is not parallel to $\hat{z}$. The analogy with a simple interferometer is imperfect since all four two-electron spin states are in general coupled by the dynamics (see also [34]).

To quantify the role of quantum coherence in this simple model, we have carried out a calculation assuming $A_z = 1000$ μT and compared the long-time triplet yields for the cases where the external field ($B_{ext} = 50$ μT) is parallel or perpendicular to z. We have assumed that the relaxation time back to the initial ground state as well as to the long-lived protonated states is 1 μs. We find that the difference in the triplet yield between the two configurations increases by a factor of 10^8 when the electron spin coherence time is increased from $\tau_c = 0.1A_z^{-1} = 1$ ns to $\tau_c = 10A_z^{-1} = 100$ ns. The strongly nonlinear increase in the sensitivity confirms the essential role played by the quantum coherence.

We emphasize that this description is overly simplistic, since it neglects the presence of multiple nuclear spins which reduce the overall directional sensitivity of cryptochrome. In principle, H_{ex} should also include contributions from exchange and magnetic-dipole interaction between the separated electrons; we neglect these contributions here for simplicity, noting however that exchange interactions could reduce the sensitivity of the pigment-protein complex to B_{ext}. The dipole-dipole interactions on the other hand could facilitate magnetoreception without the need for hyperfine coupling due to their inherent anisotropic nature. Indeed, using numerical calculations assuming isotropic hyperfine interaction ($A = A_x = A_y = A_z$) and strong dipolar interaction with strength $V_{dip} = A = 1000$ μT in the same simplistic model, we find that the difference in the triplet yield is comparable to that of the anisotropic hyperfine case discussed earlier for $\tau_c = 10A_z^{-1} = 100$ ns.

The above analysis of avian reception presents a picture of an array of quantum meters located in the retina of the bird, each of which measures the magnitude and orientation of the magnetic field relative to its own orientation and produces a classical signal in the form of a chemical population derived from the integrated time dependence of the protonated radical pair population. One of the underlying assumptions in radical-pair-based magnetoreception is that the bird's brain undertakes processing and integration of all such classical signals deriving from an array of quantum meters [35]: it thus generates visual modulation patterns via chemical signaling of the intrinsically quantum protonated state yield. It is these variations in the modulation patterns that yield the desired magnetic field information [31]. An interesting aspect of this biological quantum measurement is that it is continuous in time, with the cumulative protonated-state population providing the calibration for the classical field.

V. CONCLUSION

In this Article, we have developed a general formalism for describing photo-activated biological processes as a quantum measurement, where a protein-pigment complex takes on the role of a quantum meter. We argued that this formulation allowed us to identify the conditions under which preservation of quantum coherence and the associated non-equilibrium quantum dynamics becomes essential for the biological function. Description of the initial step of the measurement where the protein is prepared in a doorway state as an optical pumping process enabled us to highlight the common features of the photo-activated processes.

We have argued that the preservation of quantum coherence during the time-scale in which the metastable doorway state $|\Psi_m^d(\tau_0)\rangle$ is formed is not essential for the primary biological function when $[H_0, H_{meas}] \neq 0$; the presence or absence of quantum coherence during this time window only leads to modest quantitative improvements in the efficiency of the energy storage in light harvesting. Nevertheless, we emphasize that there may be scenarios in which a small quantitative increase in efficiency could provide a major advantage to the organism. There is also the possibility that presence of quantum coherence plays an important role in imposition of unidirectional energy flow, quantum ratcheting of energy over uphill steps and enabling long range transport [36].

The relevance of the formulation we present here depends strongly on the identification of further biological processes for which the preservation of quantum coherence and the ensuing non-equilibrium quantum dynamics is essential, i.e. $[H_0, H_{int}] = 0$ and $[H_{ex}, H_{int}] \neq 0$. At present, the proposed mechanism for magnetoreception is the only candidate system that is in this class. On the other hand, we note that optically induced radical pairs are also sensitive to weak electric fields; this sensitivity is due to the different electric dipole moments of the singlet and triplet states, which in turn results in an external electric field dependent relative phase between the two spin states. As a consequence, the singlet-triplet oscillations in the excited state can be altered by external electric fields. In fact, it is well known that fluctuating electric fields can lead to dephasing of singlet-triplet coherence [37]. Taken alone, such dephasing is equivalent to a non-referred quantum measurement of the electric field. However, in the context of an optically induced radical pair in a biological setting with chemical reaction products dependent on the singlet-triplet dynamics, the underlying electric field sensitivity of the singlet-triplet energy difference may facilitate measurement of a local electric field.

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