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Could light harvesting complexes exhibit non-classical effects at room temperature?

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Mounting experimental and theoretical evidence suggest that coherent quantum effects play a role in the efficient transfer of an excitation from a chlorosome antenna to a reaction centre in the Fenna–Matthews–Olson protein complex. However, it is conceivable that a satisfying alternate interpretation of the results is possible in terms of a classical theory. To address this possibility, we consider a class of classical theories satisfying the minimal postulates of macrorealism and frame Leggett–Garg-type tests that could rule them out. Our numerical simulations indicate that even in the presence of decoherence, several tests could exhibit the required violations of the Leggett–Garg inequality. Remarkably, some violations persist even at room temperature for our decoherence model.

Keywords: Leggett–Garg inequality; macrorealism; Fenna–Matthews–Olson protein complex; prosthecochloris aestuarii; quantum effects in biological systems

1. Introduction

Does quantum mechanics play a non-trivial role in evolutionary or molecular processes in biological systems? How could this result be true, when biological systems interact in environments that are ‘hot’ and ‘wet’? Furthermore, how can we frame the first question *rigorously*? These questions have been the subject of intense debate (Abbott *et al.* 2008*a,b*) and a surge of recent interest from both the quantum information community (Briegel & Popescu 2008; Gilmore & McKenzie 2008; Kominis 2008*a,b*, 2009; Mohseni *et al.* 2008; Olaya-Castro *et al.* 2008; Plenio & Huelga 2008; Cai *et al.* 2008, 2009; Caruso *et al.* 2009; Lloyd 2009; Rieper *et al.* 2009) and the experimental quantum chemistry community (Ritz *et al.* 2004; Engel *et al.* 2007; Lee *et al.* 2007; Cheng & Fleming 2009). This active area is sometimes described as ‘quantum biology’ (Abbott *et al.* 2008*a*; Lloyd 2009). Some have suggested that, in addition to the possibility of remarkable new insights into biology, there is the potential to harness naturally occurring coherent quantum effects in biology to engineer new devices.

Two biological processes are playing a particularly important role in fueling interest in this subject: energetic excitation transfer in the Fenna–Matthews–Olson (FMO) light-harvesting protein complex of green

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bacteria (Fenna & Matthews 1975; Leegwater 1996; Chachisvilis *et al.* 1997; Amerongen *et al.* 2000; Renger *et al.* 2001; Adolphs & Renger 2006; Engel *et al.* 2007; Lee *et al.* 2007; Gilmore & McKenzie 2008; Mohseni *et al.* 2008; Olaya-Castro *et al.* 2008; Plenio & Huelga 2008; Caruso *et al.* 2009; Cheng & Fleming 2009; Fassioli *et al.* 2009; Rebentrost *et al.* 2009*a,b*) and the radical ion-pair mechanism in the so-called avian compass (Kominis 2008*a,b*, 2009; Cai *et al.* 2009; Rieper *et al.* 2009). For each system, there are claims of quantum mechanical behaviour in the scientific literature. On the theoretical side, several studies in the literature have proposed an open quantum systems approach to model the dynamics of these biological processes (Mohseni *et al.* 2008; Plenio & Huelga 2008; Caruso *et al.* 2009; Rebentrost *et al.* 2009*b*) and have lent credence to the proposition that coherent quantum effects play a role in their functionality.

Agreement between quantum theoretical models and experiment, however, does not *irrevocably* demonstrate the presence of quantum effects. This point is subtle, but it is a logical fallacy, called the ‘affirmation of the consequent,’ to conclude once and for all that the quantum biological models are the correct models simply because they coincide with the observations of some experiments (Leggett (2002, 2008) stresses this point in several of his papers). It would be useful to *irrevocably* exclude certain classes of classical models that might apply to these biological systems by considering fundamental tests of non-classicality.

One might wonder whether it is well motivated to conduct a test for non-classicality on a system such as the FMO complex, which is clearly microscopic. In fact, is it not obvious that the FMO complex should behave according to quantum-mechanical laws, given that the length scales and time scales are those to which quantum theory applies? We argue that applying a test for non-classicality is valuable here because a significant amount of environmental noise acts on the chromophores of the FMO complex. These decohering effects may ‘wash out’ quantum-mechanical behaviour and make it appear as if the FMO complex behaves according to a class of macrorealistic models (after all, some argue that classical behaviour in general arises owing to such decoherence, Zurek 1991). In some cases (in a high temperature limit), researchers actually have modelled the dynamics of the FMO complex with a classical incoherent hopping model (Förster 1946; Kenkre & Reineker 1982; Leegwater 1996; Chachisvilis *et al.* 1997). Recent results (Mohseni *et al.* 2008; Plenio & Huelga 2008; Caruso *et al.* 2009; Rebentrost *et al.* 2009*b*) suggest that a classical incoherent hopping model is insufficient to explain the ultra-efficient transfer of energy in photosynthesis, but a test for non-classicality could irrevocably exclude the whole class of models to which the classical incoherent hopping model belongs.

In this paper, we frame a test for non-classicality in the FMO protein complex, the molecular complex responsible for the transfer of energetic excitations in a photosynthetic reaction. Quantum chemists have determined a tight-binding Hamiltonian for this simple system (Adolphs & Renger 2006). Phenomenological modifications to the standard Schrödinger equation have allowed an open quantum systems model of its dynamics (Mohseni *et al.* 2008; Plenio & Huelga 2008; Caruso *et al.* 2009; Rebentrost *et al.* 2009*b*). Motivated by experimental results, several theoretical studies have computed the efficiency of energy transfer from the chlorosome antenna to the reaction centre in green bacteria and have asserted that coherent quantum effects play a role. To assess this claim, we frame a test for violation of *macrorealism*, as quantified by the Leggett–Garg (1985)

inequality. In this sense, we are following the program of Leggett outlined in Leggett (2002) and the suggestion of Zeilinger in Abbott *et al.* (2008*b*) that it would be useful to subject biomolecules to tests of non-classicality. The Bell (1964, 1987) and Leggett–Garg¹ tests of non-classicality are benchmarks that determine whether a given dynamical system has stronger-than-classical spatial or temporal correlations, respectively. Each of these tests provides an inequality that bounds the spatial or temporal correlations of a given system—a violation of the inequality implies that the system in question does not behave in a classical manner. The advantage of the Leggett–Garg test over a Bell test is that a Leggett–Garg test applies to a *single* quantum system, easing experimental difficulty. The Leggett–Garg inequality was originally applied to superconducting quantum systems. It was later considered for other systems such as quantum dots (Jordan *et al.* 2006; Ruskov *et al.* 2006; Williams & Jordan 2008), photons (Goggin *et al.* 2009) and atoms (Huelga *et al.* 1995), but, to our knowledge, this is the first application of the Leggett–Garg theory to a biological system.

We organize the rest of this paper as follows. We introduce the Leggett–Garg inequality in the next section and review a simple example of a two-level quantum system that violates it. In §3, we review the quantum dynamical model of the FMO complex (we specifically employ the nine-level model of Plenio & Huelga (2008); Caruso *et al.* (2009), which is a modification of the seven-level model of Olaya-Castro *et al.* (2008), Mohseni *et al.* (2008) and Rebentrost *et al.* (2009*b*)). We then discuss several examples of dichotomic observables for the FMO complex to which we can apply the Leggett–Garg inequality. Section 4 begins our study of the Leggett–Garg inequality and the FMO complex. We first study the Leggett–Garg inequality with purely coherent dynamics and are able to derive analytical results. These analytical formulae allow us to determine exactly when coherent dynamics give a violation of the inequality. We then exploit these analytical results in our numerical simulations of the Leggett–Garg inequality and the FMO complex, where we show that it is still possible to violate the inequality even in the presence of noise and potentially even at room temperature. We conclude with some open questions for further study.

2. The Leggett–Garg inequality

The Leggett–Garg inequality applies to any system that obeys the postulates of macrorealism. The postulates of macrorealism for a two-level system are as follows (Leggett & Garg 1985; Leggett 2002):

- *Macrorealism per se.* A macroscopic object is in one of two definite states at any given time.
- *Non-invasive measurement.* It is possible in principle to determine the state of the system without affecting it or any subsequent dynamics.
- *Induction.* The properties of ensembles are determined exclusively by initial conditions (and in particular not by final conditions).

It is reasonable to assume that a classical system, in principle, should obey the postulates of a macrorealistic theory.

¹Leggett points out (Leggett 2002) that single-system Bell-type inequalities (Leggett & Garg 1985) appeared earlier in Home & Sengupta (1984).

The Leggett–Garg inequality bounds the two-time correlation functions of three dichotomic observables $Q(t_1)$, $Q(t_2)$ and $Q(t_3)$ measured at respective times t_1 , t_2 and t_3 . The observables $Q(t_1)$, $Q(t_2)$ and $Q(t_3)$ could be the spin of a particle or the location of the trapped magnetic flux in a double-well potential as in the original application of Leggett & Garg (1985). Let $C_{i,j}$ denote the following two-time correlation function:

$$C_{i,j} \equiv \langle Q(t_i)Q(t_j) \rangle.$$

The Leggett–Garg quantity K is the following combination of three two-time correlations and a constant:

$$K \equiv C_{1,2} + C_{2,3} + C_{1,3} + 1. \quad (2.1)$$

Note that we can obtain the alternate Leggett–Garg quantities

$$-C_{1,2} + C_{2,3} - C_{1,3} + 1, \quad (2.2)$$

$$-C_{1,2} - C_{2,3} + C_{1,3} + 1 \quad (2.3)$$

and

$$C_{1,2} - C_{2,3} - C_{1,3} + 1, \quad (2.4)$$

merely by flipping the sign of the respective observables $Q(t_1)$, $Q(t_2)$ and $Q(t_3)$. The following Leggett–Garg inequality bounds the Leggett–Garg quantity K when the system in question is a macrorealistic system being measured non-invasively:

$$K \geq 0. \quad (2.5)$$

The last correlation function $C_{1,3}$ is to be obtained experimentally by measuring at times t_1 and t_3 but refraining from measuring at time t_2 . By comparing $C_{1,3}$ with correlation functions $C_{1,2}$ and $C_{2,3}$ obtained in the presence of a measurement at t_2 , the Leggett–Garg inequality is sensitive to invasiveness in the t_2 measurement.

An example of a system that violates the Leggett–Garg inequality is a spin- $\frac{1}{2}$ particle with system Hamiltonian $H = \omega\sigma_X/2$ and with the observables $Q(t_1) = Q(t_2) = Q(t_3) = \sigma_Z$. This choice leads to the following value of the Leggett–Garg quantity K in equation (2.1):

$$K = \cos(2\omega\Delta t) + 2\cos(\omega\Delta t) + 1,$$

where the parameter Δt is the uniform time interval between the successive measurements of the observable Q . Observe that choosing the interval $\Delta t = 3\pi/4\omega$ sets $K = -\sqrt{2} + 1$ and leads to a violation of the Leggett–Garg inequality in equation (2.5). Thus, this quantum system does not obey the postulates of a macrorealistic theory when we choose the measurement time intervals as given above. This violation is perhaps unsurprising because a spin- $\frac{1}{2}$ system is a genuine quantum system and ‘cannot have the objective properties tentatively attributed to macroscopic objects prior to and independent of measurements’ (Peres 1995).

3. Model for the FMO complex

Much of the ‘quantum biological’ interest has focused on energy transport in the FMO protein complex (Fenna & Matthews 1975), which is believed to be the main contributor to ultra-efficient energy transfer in photosynthesis. The FMO

protein complex is a trimer in the bacterial species *prosthecochloris aestuarii*. The theoretical models in the literature (Mohseni *et al.* 2008; Olaya-Castro *et al.* 2008; Plenio & Huelga 2008; Caruso *et al.* 2009; Rebentrost *et al.* 2009b) apply to the dynamics of one unit of the trimer. The models assume that a photon impinges on the peripheral antenna of the light harvesting complex. Absorption of the photon produces an electronic excitation, an exciton, that then traverses a network of seven chromophores or *sites* in one unit of the trimer. The exciton can either recombine, representing a loss of the excitation, or it can transfer to a reaction centre, where a light-to-charge conversion occurs before energy storage. Theoretical models (Mohseni *et al.* 2008; Rebentrost *et al.* 2009b) indicate that coherent quantum effects combined with decoherence may lead to a quantum stochastic walk (Rodríguez-Rosario *et al.* 2009) that transports energy efficiently. Rebentrost *et al.* (2009b) provide evidence that coherent quantum effects are responsible for the ultra-high efficiency of photosynthesis, by demonstrating that the transport efficiency is much higher with coherent quantum effects than it is without.

Our physical model for excitation transfer is the nine-level model in Caruso *et al.* (2009) and Plenio & Huelga (2008), a modification of the seven-level model in Olaya-Castro *et al.* (2008), Mohseni *et al.* (2008) and Rebentrost *et al.* (2009b). We can restrict dynamics to the single-excitation space because the excitation number is a conserved quantity in the absence of light-matter interaction events (within the exciton recombination time scale of 1 ns (Owens *et al.* 1987)). The possible states for the exciton can be expressed in the *site basis* $\{|m\rangle\}_{m=1}^7$, where the state $|m\rangle$ indicates that the excitation is present at site m . The incoherent dynamics include a ‘ground’ state $|G\rangle$ corresponding to the loss or recombination of the excitation and a sink state $|S\rangle$ corresponding to the trapping of the exciton at the reaction centre. The excitation evolves into one of the two states $|G\rangle$ or $|S\rangle$ in the limit of infinite time. The density operator ρ for this open quantum system admits the following representation in the site basis:

$$\rho = \sum_{m,n \in \{G,1,\dots,7,S\}} \rho_{m,n} |m\rangle\langle n|.$$

We simplify our analysis by assuming that the dynamics of the density operator are Markovian. Thus, a Lindblad master equation, with coherent and incoherent components, models the dynamics (Lindblad 1976; Breuer & Petruccione 2007). Coherent evolution occurs according to the following Hamiltonian H (Adolphs & Renger 2006; Caruso *et al.* 2009):

$$H \equiv \begin{bmatrix} 215 & -104.1 & 5.1 & -4.3 & 4.7 & -15.1 & -7.8 \\ -104.1 & 220 & 32.6 & 7.1 & 5.4 & 8.3 & 0.8 \\ 5.1 & 32.6 & 0 & -46.8 & 1.0 & -8.1 & 5.1 \\ -4.3 & 7.1 & -46.8 & 125 & -70.7 & -14.7 & -61.5 \\ 4.7 & 5.4 & 1.0 & -70.7 & 450 & 89.7 & -2.5 \\ -15.1 & 8.3 & -8.1 & -14.7 & 89.7 & 330 & 32.7 \\ -7.8 & 0.8 & 5.1 & -61.5 & -2.5 & 32.7 & 280 \end{bmatrix}, \quad (3.1)$$

where the above matrix representation of H is with respect to the site basis $\{|m\rangle\}_{m=1}^7$ and the units of energy are cm^{-1} (the typical units of choice in spectroscopy experiments). The diagonal terms in H correspond to the site energies and the off-diagonal terms correspond to intersite couplings. The order of magnitude of the energies in the above Hamiltonian is 100 cm^{-1} , implying that we should observe dynamics on the order of 300 fs. Engel *et al.* (2007) experimentally observed behaviour on this order.

Three Lindblad superoperators (Lindblad 1976; Breuer & Petruccione 2007) also contribute to the dynamics of the density operator in the nine-level model in Caruso *et al.* (2009) and Plenio & Huelga (2008). The general form of a Lindblad superoperator $\mathcal{L}(\rho)$ is as follows:

$$\mathcal{L}(\rho) \equiv \sum_m \zeta_m (2A_m \rho A_m^\dagger - \{A_m^\dagger A_m, \rho\}),$$

where ζ_m is a rate and A_m is a Lindblad operator.

The first Lindblad superoperator $\mathcal{L}_{\text{diss}}$ in our model corresponds to the dissipative recombination of the exciton (loss of energy in the system):

$$\mathcal{L}_{\text{diss}}(\rho) \equiv \sum_{m=1}^7 \Gamma_m (2|G\rangle\langle m|\rho|m\rangle\langle G| - \{|m\rangle\langle m|, \rho\}). \quad (3.2)$$

An excitation at site $|m\rangle$ recombines with rate Γ_m , and $|G\rangle\langle m|$ is the Lindblad operator that effects this dissipation.

The next Lindblad superoperator $\mathcal{L}_{\text{sink}}(\rho)$ accounts for the trapping of the exciton in the reaction centre:

$$\mathcal{L}_{\text{sink}}(\rho) \equiv \Gamma_{\text{sink}} (2|S\rangle\langle 3|\rho|3\rangle\langle S| - \{|3\rangle\langle 3|, \rho\}). \quad (3.3)$$

The Lindblad superoperator $\mathcal{L}_{\text{sink}}$ includes the operator $|S\rangle\langle 3|$ because evidence suggests that site three in the FMO complex plays a crucial role in transferring the exciton to the reaction centre (Adolphs & Renger 2006), where it is later exploited for energy storage.

The final Lindblad superoperator $\mathcal{L}_{\text{deph}}$ accounts for the unavoidable dephasing interaction with the environment:

$$\mathcal{L}_{\text{deph}}(\rho) \equiv \sum_{m=1}^7 \gamma_m (2|m\rangle\langle m|\rho|m\rangle\langle m| - \{|m\rangle\langle m|, \rho\}), \quad (3.4)$$

where γ_m is the rate of dephasing at site m . Discussion of this rough treatment of the decoherence appears in Rebentrost *et al.* (2009b), Haken & Strobl (1973) and Leegwater (1996).

The following Lindblad quantum master equation governs the evolution of the density operator ρ :

$$\dot{\rho} = -i[H, \rho] + \mathcal{L}_{\text{diss}}(\rho) + \mathcal{L}_{\text{sink}}(\rho) + \mathcal{L}_{\text{deph}}(\rho), \quad (3.5)$$

where we explicitly see the contribution of the Hamiltonian equation (3.1) and the noise superoperators (3.2)–(3.4) to the dynamics, and we implicitly set $\hbar = 1$. Evolution according to the above Lindblad evolution equation is completely

positive and trace-preserving (CPTP) for any time (Breuer & Petruccione 2007), and we let $\mathcal{N}_{t,t_0}(\rho)$ denote the induced CPTP map corresponding to the evolution of the density operator ρ from an initial time t_0 to some later time t .

4. The Leggett–Garg inequality and the FMO complex

In the forthcoming subsections, we consider the application of the Leggett–Garg inequality to the FMO complex. We first discuss several observables that one might measure in a Leggett–Garg protocol. We then obtain analytical results when the dynamics are purely coherent. These analytical results allow us to determine the time intervals between measurements in a Leggett–Garg protocol that lead to the strongest violation of the inequality. We finally use these time intervals in a numerical simulation of the FMO dynamics that includes the effects of noise. The result is that several observables exhibit a strong violation of the inequality for temperatures below room temperature, and the violation persists in some cases up to room temperature.

(a) Observable for the Leggett–Garg inequality in the FMO complex

Recall that the Leggett–Garg quantity in equation (2.1) involves any three dichotomic observables $Q(t_1)$, $Q(t_2)$ and $Q(t_3)$ measured at respective times t_1 , t_2 and t_3 .

We have freedom in choosing both the observables that we measure and the times at which we measure them. Perhaps the simplest dichotomic observable that we can construct corresponds to the question (Peres 1995):

‘Is the system in state $|\psi\rangle$ or not?’

The two-element set of measurement operators for this question are as follows: $\{|\psi\rangle\langle\psi|, I - |\psi\rangle\langle\psi|\}$. We assign the value +1 if the system is in the state $|\psi\rangle$ and the value –1 otherwise. Let $Q_{|\psi\rangle}$ denote the resulting observable where

$$Q_{|\psi\rangle} \equiv |\psi\rangle\langle\psi| - (I - |\psi\rangle\langle\psi|) = 2|\psi\rangle\langle\psi| - I. \quad (4.1)$$

We might build a dichotomic observable from states in the *exciton basis*. The exciton basis is the energy eigenbasis $\{|\phi_m\rangle\}_{m=1}^7$ of the Hamiltonian H in equation (3.1) where

$$\forall m \quad H|\phi_m\rangle = E_m|\phi_m\rangle.$$

Then the dichotomic observable constructed from an energy eigenstate is $Q_{|\phi_m\rangle}$. Note that observables of this form commute with the Hamiltonian H in equation (3.1).

Another possibility is to build the dichotomic observable from the site basis. This type of observable asks the question, ‘Is the excitation at site m ?’ where $m \in \{G, 1, \dots, 7, S\}$. The dichotomic observable constructed from a site state is the *site observable* $Q_{|m\rangle}$. Observables of this form do not commute with the Hamiltonian H in equation (3.1).

(b) *Analytical results for coherent dynamics*

Let us first suppose that evolution of the FMO complex is coherent and does not include the noisy Lindblad evolution terms in equations (3.2)–(3.4). This assumption is unrealistic, but it gives a starting point for understanding the Leggett–Garg inequality and the FMO complex before proceeding with the full-blown evolution in equation (3.5).

The general form of the two-time correlation functions appearing in the Leggett–Garg quantity K in equation (2.1) are as follows for a coherent evolution:

$$C_{1,2} = \frac{1}{2} \text{Tr}[Q(t_2)e^{-iH(t_2-t_1)}\{Q(t_1), \rho_{t_1}\}e^{iH(t_2-t_1)}],$$

$$C_{2,3} = \frac{1}{2} \text{Tr}[Q(t_3)e^{-iH(t_3-t_2)}\{Q(t_2), \rho_{t_2}\}e^{iH(t_3-t_2)}]$$

and
$$C_{1,3} = \frac{1}{2} \text{Tr}[Q(t_3)e^{-iH(t_3-t_1)}\{Q(t_1), \rho_{t_1}\}e^{iH(t_3-t_1)}],$$

where H is the Hamiltonian in equation (3.1), ρ_{t_1} the initial density operator of the FMO complex, $\rho_{t_2} \equiv e^{-iH(t_2-t_1)}\rho_{t_1}e^{iH(t_2-t_1)}$ and $\{\cdot, \cdot\}$ is the anticommutator. As indicated in §2, the correlator $C_{1,3}$ characterizes an experiment in which measurements occur at times t_1 and t_3 but no measurement occurs at time t_2 .

Suppose first that we prepare the FMO complex in some state $|\psi\rangle$ and take the Leggett–Garg observable to be $Q_{|\psi\rangle}$ as in equation (4.1). Thus, this measurement is a ‘survival probability’ measurement (Peres 1995; Kofler 2008; Kofler & Brukner 2008). Suppose further that we measure $Q_{|\psi\rangle}$ at uniform time intervals Δt . A straightforward calculation (Kofler 2008; Kofler & Brukner 2008) shows that the Leggett–Garg quantity in equation (2.3) is equal to

$$4|\langle\psi|\psi_{2\Delta t}\rangle|^2 - 4\text{Re}[(\langle\psi|\psi_{\Delta t}\rangle)^2\langle\psi_{2\Delta t}|\psi\rangle], \quad (4.2)$$

where $|\psi_t\rangle \equiv e^{-iHt}|\psi\rangle$. Recall that a violation of the Leggett–Garg inequality occurs when the above quantity drops below zero.

If the state $|\psi\rangle$ is an eigenstate $|\phi_m\rangle$ in the exciton basis we should not expect to violate the Leggett–Garg inequality because the observable $Q_{|\phi_m\rangle}$ commutes with the Hamiltonian. We can confirm this intuition by plugging the eigenstate $|\phi_m\rangle$ into equation (4.2). Doing so gives a value of zero for equation (4.2), thereby saturating the Leggett–Garg inequality, but yielding no violation.

Thus, we set the Leggett–Garg observable to a site observable $Q_{|m\rangle}$ where $m \in \{1, \dots, 7\}$. Sites 1 and 6 are the chromophores that are closest to the chlorosome antenna and are thus most likely to be the initial state of the FMO complex (Rebentrost *et al.* 2009*b*). The initial state ρ_{t_1} of the FMO complex can be a pure state $|1\rangle\langle 1|$ or $|6\rangle\langle 6|$ or a uniform classical mixture of sites $|1\rangle$ and $|6\rangle$:

$$\pi_{1,6} \equiv \frac{1}{2}(|1\rangle\langle 1| + |6\rangle\langle 6|). \quad (4.3)$$

One might also consider setting the initial state to the maximally mixed state

$$\pi \equiv \frac{1}{7}(|1\rangle\langle 1| + \dots + |7\rangle\langle 7|).$$

Table 1 lists exact expressions for the Leggett–Garg quantity in equation (2.3) for these different cases.

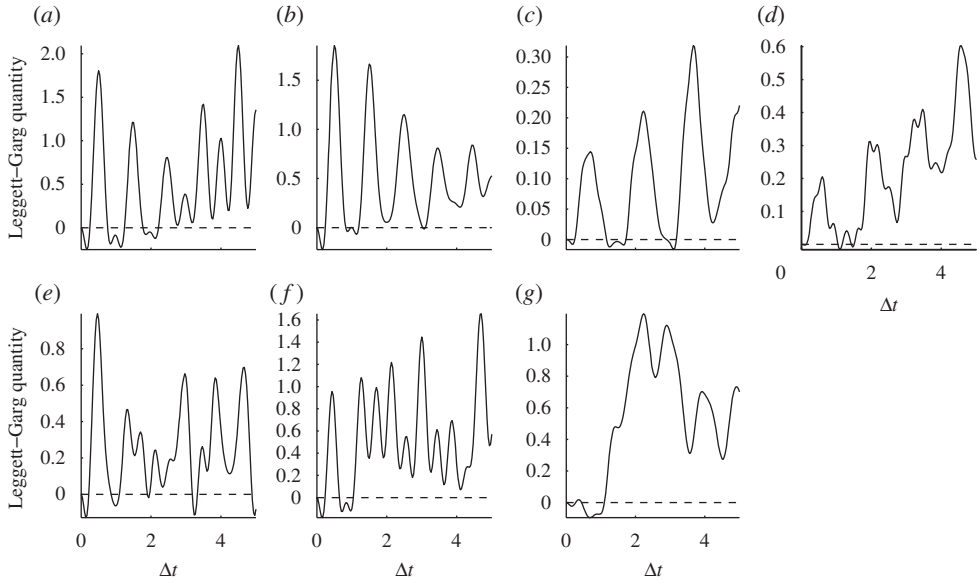


Figure 1. The Leggett–Garg quantity as a function of the uniform time interval Δt for all seven sites in the FMO complex when evolution is coherent and the initial state is the classical mixture $\pi_{1,6}$. The units of Δt are ps. A dotted line divides each plot into two regions. Points above a dotted line are in a ‘no violation’ region while points below are in a ‘violation’ region. The convention is the same in figures 2–4. To show overall behaviour, the Δt axis has a coarse scale up to 5 ps. However, an experimental test would require control of Δt to hundreds of femtoseconds. (a) Site 1, (b) site 2, (c) site 3, (d) site 4, (e) site 5, (f) site 6 and (g) site 7.

Table 1. The first column lists the initial state of the FMO complex. The second column lists the site that we measure in a Leggett–Garg protocol. The third column gives the analytical form of the corresponding Leggett–Garg quantity as a function of the uniform time interval Δt when dynamics are purely coherent. We use these formulae to compute the results of figure 1 and table 2.

ρ_{t_1}	measurement	Leggett–Garg quantity
$\pi_{1,6}$	$ 1\rangle$	$2(\langle 1 6_{\Delta t}\rangle ^2 + \langle 1 1_{2\Delta t}\rangle ^2 - \text{Re}\{\langle 1 (\langle 1_{\Delta t}\rangle\langle 1_{2\Delta t} + 6_{\Delta t}\rangle\langle 6_{2\Delta t}) 1\rangle\langle 1 1_{\Delta t}\rangle\})$
$\pi_{1,6}$	$ 6\rangle$	$2(\langle 6 1_{\Delta t}\rangle ^2 + \langle 6 6_{2\Delta t}\rangle ^2 - \text{Re}\{\langle 6 (\langle 1_{\Delta t}\rangle\langle 1_{2\Delta t} + 6_{\Delta t}\rangle\langle 6_{2\Delta t}) 6\rangle\langle 6 6_{\Delta t}\rangle\})$
$\pi_{1,6}$	$ 2\rangle, \dots, 5\rangle, 7\rangle$	$2(\langle m 1_{\Delta t}\rangle ^2 + \langle m 6_{\Delta t}\rangle ^2 - \text{Re}\{\langle m (\langle 1_{\Delta t}\rangle\langle 1_{2\Delta t} + 6_{\Delta t}\rangle\langle 6_{2\Delta t}) m\rangle\langle m m_{\Delta t}\rangle\})$
$ 1\rangle\langle 1 $	$ 1\rangle$	$4 \langle 1 1_{2\Delta t}\rangle ^2 - 4\text{Re}\{\langle 1_{2\Delta t} 1\rangle\langle 1 1_{\Delta t}\rangle\}^2$
$ 1\rangle\langle 1 $	$ 2\rangle, \dots, 7\rangle$	$2 \langle m 1_{\Delta t}\rangle ^2 - 4\text{Re}\{\langle m 1_{\Delta t}\rangle\langle 1_{2\Delta t} m\rangle\langle m m_{\Delta t}\rangle\} + 2\text{Re}\{\langle 1_{2\Delta t} m_{\Delta t}\rangle\langle m 1_{\Delta t}\rangle\}$
$ 6\rangle\langle 6 $	$ 6\rangle$	$4 \langle 6 6_{2\Delta t}\rangle ^2 - 4\text{Re}\{\langle 6_{2\Delta t} 6\rangle\langle 6 6_{\Delta t}\rangle\}^2$
$ 6\rangle\langle 6 $	$ 1\rangle, \dots, 5\rangle, 7\rangle$	$2 \langle m 6_{\Delta t}\rangle ^2 - 4\text{Re}\{\langle m 6_{\Delta t}\rangle\langle 6_{2\Delta t} m\rangle\langle m m_{\Delta t}\rangle\} + 2\text{Re}\{\langle 6_{2\Delta t} m_{\Delta t}\rangle\langle m 6_{\Delta t}\rangle\}$
π	all sites	$\frac{4}{d} - \frac{8}{d} \langle m m_{\Delta t}\rangle ^2 + \frac{4}{d} \langle m m_{2\Delta t}\rangle ^2$

Figure 1 plots the Leggett–Garg quantity for each site observable as a function of the uniform time interval Δt , when the initial state is $\pi_{1,6}$. The result is that each of the seven site measurements gives a violation of the Leggett–Garg inequality for some intervals Δt when the dynamics are purely coherent. These

Table 2. The first column lists the initial state of the FMO complex. The second column lists the site observable that the Leggett–Garg protocol measures. The third column lists the strongest violations for each site observable and the fourth column gives the corresponding time interval Δt that leads to this violation. (For comparison, the strongest possible violation of the inequality is -0.5 .) We obtained these values assuming that evolution is coherent (though, we examined times up to $\Delta t = 5$ ps only). The last row in the table indicates that we do not obtain a violation for any site observable when the initial state is the maximally mixed state.

initial state ρ_0	site	K	Δt (ps)
$\pi_{1,6}$	1	-0.25053	0.16678
$\pi_{1,6}$	2	-0.22321	0.16678
$\pi_{1,6}$	3	-0.016389	3.1021
$\pi_{1,6}$	4	-0.01574	1.1008
$\pi_{1,6}$	5	-0.12782	0.13343
$\pi_{1,6}$	6	-0.17994	0.16678
$\pi_{1,6}$	7	-0.094719	0.70048
$ 1\rangle\langle 1 $	1	-0.4935	0.16678
$ 1\rangle\langle 1 $	2	-0.44335	0.16678
$ 1\rangle\langle 1 $	3	-0.065461	3.1355
$ 1\rangle\langle 1 $	4	-0.091838	1.7345
$ 1\rangle\langle 1 $	5	-0.08013	2.2015
$ 1\rangle\langle 1 $	6	-0.0097707	0.16678
$ 1\rangle\langle 1 $	7	-0.085607	1.034
$ 6\rangle\langle 6 $	1	-0.0077476	0.13343
$ 6\rangle\langle 6 $	2	-0.0043891	1.034
$ 6\rangle\langle 6 $	3	-0.0032073	0.13343
$ 6\rangle\langle 6 $	4	-0.034082	1.4677
$ 6\rangle\langle 6 $	5	-0.27786	4.9701
$ 6\rangle\langle 6 $	6	-0.35011	0.16678
$ 6\rangle\langle 6 $	7	-0.18045	0.70048
π	all	0	all times

results may not be particularly surprising (Kofler 2008; Kofler & Brukner 2008), given that the system is quantum, the measurements are sharp, and the dynamics are purely coherent.

Table 2 lists the time intervals that lead to the strongest violation for $\Delta t \in [0, 5]$ ps. We only consider times up to 5 ps because it is likely that the exciton will trap by this time for the case of incoherent dynamics in the next section. Table 2 also lists the time intervals that lead to the strongest violation when the initial state is $|1\rangle\langle 1|$, $|6\rangle\langle 6|$, or π . We now use these time intervals for the more realistic case, where the excitation in the FMO complex experiences the noisy contributions in equations (3.2)–(3.4) from dissipation and dephasing.

(c) Numerical results for incoherent dynamics

The Lindblad evolution in equation (3.5) is a more realistic model for evolution of the excitation in the FMO complex. It incorporates the effects of excitonic recombination, trapping to the reaction centre and environmental dephasing noise,

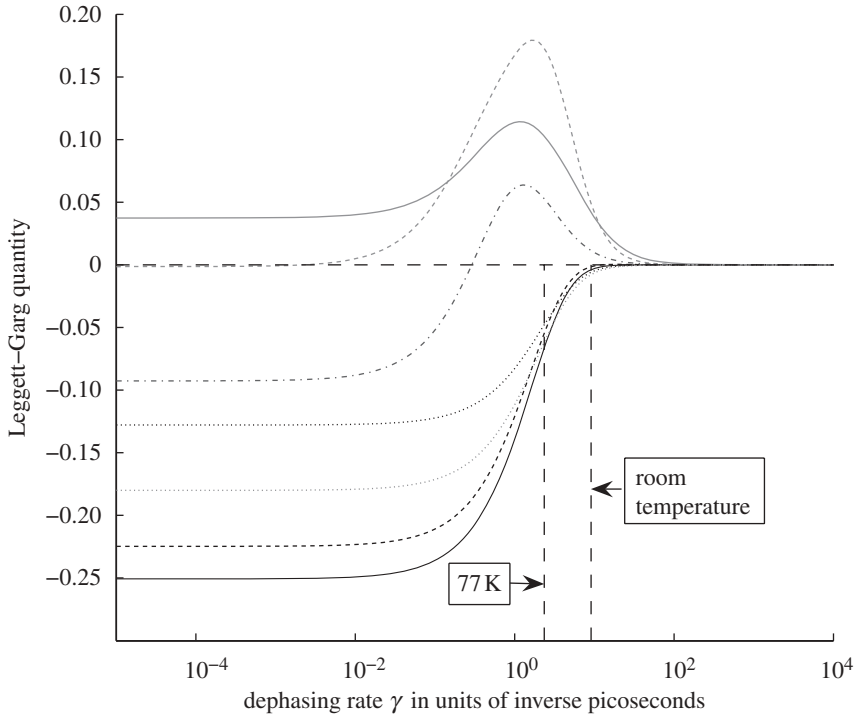


Figure 2. Displays the Leggett–Garg quantity as a function of the dephasing parameter γ for each site observable $Q_{|m\rangle}$, where $m \in \{1, \dots, 7\}$. The site observables $Q_{|3\rangle}$ and $Q_{|4\rangle}$ do not give a violation of the Leggett–Garg inequality for any amount of dephasing noise, even though we observed a violation in figure 1 with purely coherent dynamics. Site observables $Q_{|1\rangle}$, $Q_{|2\rangle}$, $Q_{|5\rangle}$, $Q_{|6\rangle}$ and $Q_{|7\rangle}$ give a strong violation of the inequality for low dephasing noise. Each of their corresponding Leggett–Garg quantities has a smooth, monotonic transition to the ‘no violation’ region for stronger dephasing noise, with the Leggett–Garg quantity for site observables $Q_{|1\rangle}$, $Q_{|2\rangle}$, $Q_{|5\rangle}$, $Q_{|6\rangle}$ withstanding the strongest amount of dephasing noise before they make a transition to the ‘no violation’ region. Using the temperature analysis of the environment in Reberstrost *et al.* (2009b), a dephasing rate of 2.1 ps^{-1} corresponds to a temperature of around 77 K and a dephasing rate of 9.1 ps^{-1} corresponds to a temperature of around 298 K (room temperature). Site observables $Q_{|1\rangle}$, $Q_{|2\rangle}$, $Q_{|5\rangle}$ and $Q_{|6\rangle}$ give a violation for room temperature, with the Leggett–Garg quantity respectively equal to -0.0039 , -0.0015 , -0.0059 and -0.0079 . In this figure, the initial state is taken to be $\pi_{1,6}$ (solid black line, site 1; dashed black line, site 2; solid grey line, site 3; dashed grey line, site 4; black dotted line, site 5; grey dotted line, site 6; dashed dotted line, site 7).

albeit in a Markovian context. The two-time correlation functions appearing in the Leggett–Garg quantity K in equation (2.1) must now be evaluated using the following more general forms:

$$C_{1,2} = \frac{1}{2} \text{Tr}[Q(t_2) \mathcal{N}_{t_2, t_1}(\{Q(t_1), \rho\})],$$

$$C_{2,3} = \frac{1}{2} \text{Tr}[Q(t_3) \mathcal{N}_{t_3, t_2}(\{Q(t_2), \mathcal{N}_{t_2, t_1}(\rho)\})]$$

and

$$C_{1,3} = \frac{1}{2} \text{Tr}[Q(t_3) \mathcal{N}_{t_3, t_1}(\{Q(t_1), \rho\})],$$

where \mathcal{N} is the superoperator that propagates the density operator forward in time according to the evolution in equation (3.5).

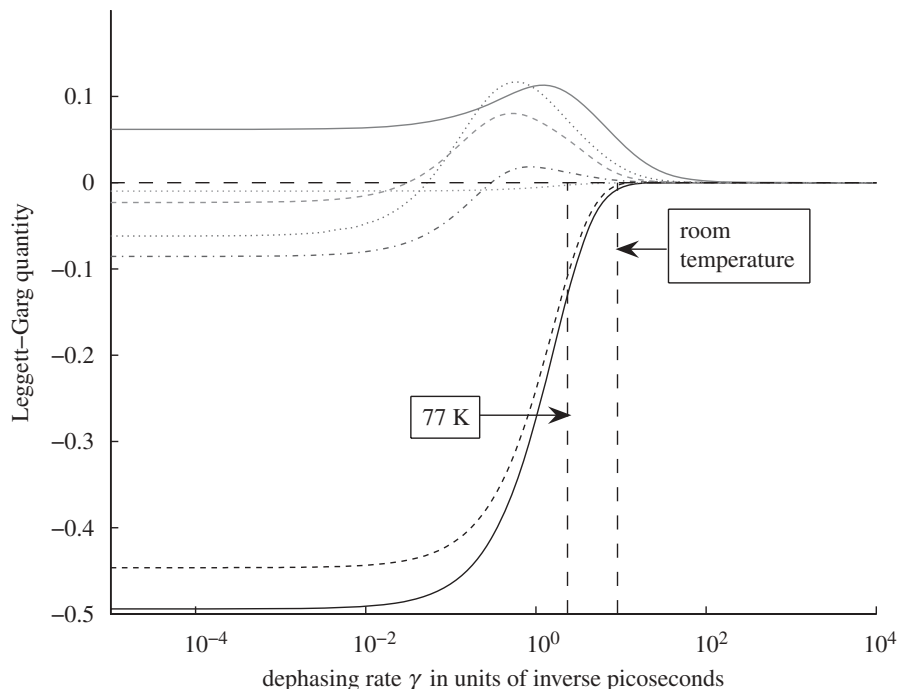


Figure 3. This figure is similar to figure 2, with the exception that the initial state of the FMO complex is a pure state at site 1. Site observables $Q_{|1\rangle}$ and $Q_{|2\rangle}$ give a violation for room temperature, with the Leggett–Garg quantity, respectively, equal to -0.0077 and -0.003 (solid black line, site 1; dashed black line, site 2; solid grey line, site 3; dashed grey line, site 4; black dotted line, site 5; grey dotted line, site 6; dashed dotted line, site 7).

In order to perform a numerical simulation for the incoherent dynamics equation (3.5), we need to fix the trapping rate Γ_{sink} , the recombination rates Γ_m and the dephasing rates γ_m . We take these rates from Caruso *et al.* (2009) and Plenio & Huelga (2008). Unless otherwise stated, the trapping rate $\Gamma_{\text{sink}} = 62.8/1.88 \text{ cm}^{-1}$, corresponding to about $2\pi c\Gamma_{\text{sink}} \approx 6 \text{ ps}^{-1}$, where c is the speed of light in units of cm ps^{-1} . The recombination rates Γ_m are uniform for all sites in the FMO complex so that $\Gamma_m = \Gamma_{\text{recomb}} = 1/(2 \cdot 188) \text{ cm}^{-1}$, corresponding to about $2\pi c\Gamma_{\text{recomb}} \approx 5 \times 10^{-4} \text{ ps}^{-1}$. We assume that the dephasing rate is uniform so that $\gamma_m = \gamma$ for all sites m .

As in the previous subsection, we choose the Leggett–Garg observable to be a site observable $Q_{|m\rangle}$ where $m \in \{1, \dots, 7\}$. The initial state ρ_{t_i} can either be the pure state $|1\rangle\langle 1|$, $|6\rangle\langle 6|$, or a uniform classical mixture of sites $|1\rangle$ and $|6\rangle$ as in equation (4.3), for the same reasons mentioned in the previous subsection (we do not consider the maximally mixed state because we should not expect it to give any violation given that it does not give a violation even in the coherent dynamics case). The time interval Δt between measurements of the Leggett–Garg observable is taken from table 2. Figures 2–4 display the Leggett–Garg quantity as a function of the dephasing parameter γ for each site observable $Q_{|m\rangle}$, where $m \in \{1, \dots, 7\}$.

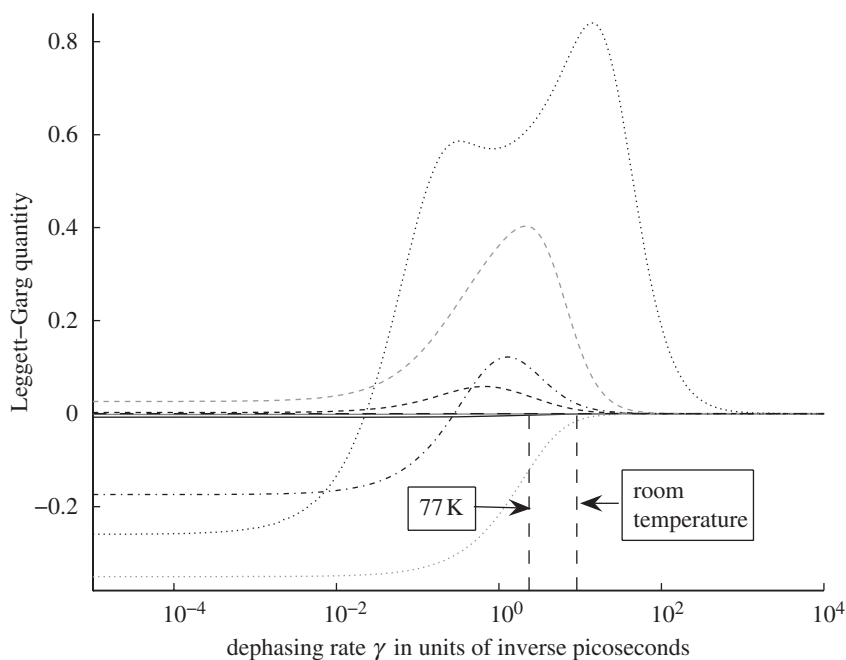


Figure 4. This figure is similar to figure 2, with the exception that the initial state of the FMO complex is a pure state at site 6. Site observable $Q_{(6)}$ gives a violation for room temperature, with the Leggett–Garg quantity equal to -0.0155 (solid black line, site 1; dashed black line, site 2; solid grey line, site 3; dashed grey line, site 4; black dotted line, site 5; grey dotted line, site 6; dashed dotted line, site 7).

The figures demonstrate that several site observables exhibit a violation even as γ increases. The temperature analysis of the environment in Reberstrost *et al.* (2009b) indicates that a dephasing rate of 2.1 ps^{-1} corresponds to a temperature of around 77 K and a dephasing rate of 9.1 ps^{-1} corresponds to a temperature of 298 K (room temperature). Under the assumption that this is approximately correct, figures 2–4 predict a violation at both temperatures. However, it might be difficult for an experimentalist to observe these violations at room temperature given that they are weak.

We have verified the robustness of these predictions against variations in the dynamical parameters in equation (3.5). Adolphs & Renger (2006) mention that the site energies of their calculated Hamiltonian are accurate within $\pm 2 \text{ cm}^{-1}$. We therefore conducted several simulations that added independent, zero-mean Gaussian noise with variance 2 to each entry in the Hamiltonian matrix in equation (3.1) to determine whether the violations would still hold under this slight perturbation. The result is that all room temperature violations in figures 2–4 still hold, and in fact, the values of the Leggett–Garg quantities are the same up to the fourth decimal place. The trapping rates in the literature vary substantially, including 0.25 ps^{-1} (Adolphs & Renger 2006), 1 ps^{-1} (Mohseni *et al.* 2008) or 4 ps^{-1} (Olaya-Castro *et al.* 2008), so we have checked our results for all of these choices. The plots for all these cases are similar to figures 2–4 and have

approximately the same values for violations at room temperature. This finding is reasonable given that most of our measurement times are less than the average trapping times corresponding to these other trapping rates.

Our numerical simulations demonstrate that several choices of measurements lead to a violation of the Leggett–Garg inequality, even when noise processes act on an excitation in the FMO complex. Experimental confirmation could irrevocably exclude a class of macrorealistic theories from describing the dynamics of the excitation.

5. Conclusions

We have framed tests that could be used to experimentally exclude a class of macrorealistic theories, including a classical incoherent hopping model, from describing the room-temperature dynamical behaviour of an excitation in the FMO complex. To do so, we have introduced several examples of observables that one might apply in a test of macrorealism, and our numerical simulations predict that these observables lead to a violation of the Leggett–Garg inequality.

We discuss several ideas for furthering this research. The Leggett–Garg measurements that we have considered here are projective measurements in the site basis. Measurements in the site basis, especially measurements that could eliminate the considerable uncertainties about the exciton initial state, are currently experimentally infeasible.² After all, such measurements would require spatial resolution on the order of 12 Å (Fenna & Matthews 1975), while the photons in current experiments have much lower energies corresponding to cm spatial resolution (the scale of the Hamiltonian matrix elements). And even if an experimentalist were to manage a ‘noisy’ or ‘fuzzy’ measurement of the sites in the FMO complex, Kofler & Brukner (2008) and Kofler (2008) have shown that ‘fuzzy’ measurements may lead to our observation of a classical world even in the presence of quantum dynamics. A more promising direction would be to perform measurements in a spatially extended basis, distinct from either the site basis or the exciton basis, and to derive time-averaged Leggett–Garg inequalities (Ruskov *et al.* 2006) for the two-dimensional spectroscopy signal currently employed in FMO complex experiments.

Furthermore, future work should consider more realistic models of noise in the FMO complex, potentially including correlated noise (Fassioli *et al.* 2009; Nazir 2009) and non-Markovian effects (Rebentrost *et al.* 2009*a*). One might also consider an application of Bell’s inequality to study the ability of the FMO complex to preserve entanglement.

We have applied the Leggett–Garg inequality to the FMO complex, and it would be valuable to apply the Leggett–Garg test to the dynamics of magnetoreception in the avian compass (Kominis 2008*a,b*, 2009; Cai *et al.* 2009). It would also be interesting to explore the Leggett–Garg inequality in artificial quantum networks with particular noisy interactions. A study of this sort might lead to an increased understanding of the dividing line between macrorealism

²Informative communications on this point with Alán Aspuru-Guzik and Patrick Rebentrost are gratefully acknowledged.

and non-classicality in more complicated systems. One might be able to apply the ideas in Kofler & Brukner (2008), Kofler (2008), Caruso *et al.* (2009) and Plenio & Huelga (2008) here.

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