

# Cooperative robustness to dephasing: single-exciton Superradiance in a nanoscale ring to model natural light-harvesting systems

G. Luca Celardo,<sup>1,2,3</sup> Paolo Poli,<sup>1</sup> Luca Lussardi,<sup>1</sup> and Fausto Borgonovi<sup>1,2,3</sup>

<sup>1</sup>*Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, via Musei 41, I-25121 Brescia, Italy*

<sup>2</sup>*Interdisciplinary Laboratories for Advanced Materials Physics,*

*Università Cattolica del Sacro Cuore, via Musei 41, I-25121 Brescia, Italy*

<sup>3</sup>*Istituto Nazionale di Fisica Nucleare, Sezione di Pavia, via Bassi 6, I-27100, Pavia, Italy*

(Dated: August 22, 2014)

We analyze a 1-d ring structure composed of many two-levels systems, in the limit where only one excitation is present. The two-levels systems are coupled to a common environment, where the excitation can be lost, which induces super and subradiant behavior. Moreover, each two-levels system is coupled to another independent environment, modeled by a classical white noise, simulating a dephasing bath and described by the Haken-Strobl master equation. Single exciton Superradiance, an example of cooperative quantum coherent effect, is destroyed at a critical dephasing strength proportional to the system size, showing robustness of cooperativity to the action of the dephasing environment. We also show that the coupling to a common decay channel contrasts the action of dephasing, driving the entanglement decay to slow down on increasing the system size. Moreover, after a projective measurement which finds the excitation in the system, the entanglement reaches a stationary value, independent of the initial conditions.

PACS numbers: 71.35.-y, 03.65.Yz, 05.60.Gg

## I. INTRODUCTION

Emergent properties arise due to cooperative behavior of the many constituents of a complex system. They belong to the system as a whole and not to its constituents, and are at the center of many research fields in condensed matter physics. In quantum systems, differently from classical ones, additional emergent properties are possible due to quantum coherence. Among the many fascinating aspects of these properties, one important open question regards their robustness to the effects induced by the presence of an environment. This robustness might enable to exploit coherent quantum effects to build quantum devices for information technologies and basic energy science.

As an example of quantum coherent emergent property, we consider here single exciton Superradiance [1]. Superradiance was originally discovered in the context of atomic clouds interacting with the electromagnetic field (EMF), see the seminal paper by Dicke [2], where Superradiance involved many excited atoms (each modeled as a two-levels system). Dicke showed that, when the wavelength associated with the emitted photon is larger than the system size, there are some states which emit light with an intensity proportional to  $N^2$ , where  $N$  is the number of atoms. This kind of Superradiance would occur also in an ensemble of classical emitters with proper initial conditions. However, Superradiance can occur also when only one excitation is present in the system. In this case it is a purely quantum effect [1], due to exciton states extended over many sites (representing a fully entangled state of the two-levels systems sharing the excitation). The decay rate of such a state is cooperatively enhanced w.r.t. the single system decay rate, in that it is proportional to the system size. For instance, in molec-

ular aggregates [5], and light harvesting complexes [12], the single excitation approximation is valid under natural light intensity since solar light is very dilute. For molecular aggregate if we call  $\gamma$  the radiative decay width of an isolated molecule, an excitation spread coherently over  $N$  molecules has a radiative decay width equal to  $N\gamma$ . Note that Superradiance comes always together with Subradiance, that is the existence of other states with a suppressed decay width (*i.e.* smaller than the single system decay width).

Superradiant behavior with respect to the EMF was found experimentally in many molecular aggregates [6, 7]. Superradiance does not occur only w.r.t. the EMF, as it is commonly considered in literature, but it is a general phenomenon in open quantum systems [3] which can occur whenever many discrete quantum levels are coupled to some common decay channels, characterized by a continuum of states. In particular, its relevance in quantum transport, where the decay channels represent the continuum of scattering states, was pointed out in Ref. [4]. Since the discovery of quantum coherent effects in biological systems even at room temperature [8–12], Superradiance has been thought to have a functional role in photosynthesis, w.r.t. both the absorption of electromagnetic radiation and the transfer of the excitation to another absorbing complex, such as the reaction center [12–16]. In the latter case, the same effects found for the electromagnetic field appear, for instance we can have Sub and Superradiance in transport which implies that the excitation can be transferred to the reaction center or to a lead with an enhanced or suppressed rate. Moreover, proposals of solid state quantum devices for photon sensing and light harvesting based on Superradiance have been made [17].

These systems are usually subject to the effects of dif-

ferent environments. Together with a common decay channel, where the excitation can be lost either by recombination and photon emission or by trapping to a central core absorber, there are also other environments (such as a phonon bath) which induce various kinds of noise characterized by different correlation time-scales, to be compared to the excitonic transport time: i) short-time correlations giving rise to dephasing (homogeneous broadening), and ii) long-time correlations producing on-site static disorder (inhomogeneous broadening). The interplay of different environments is essential to determine the efficiency of light absorption and excitation transfer.

The interplay of dephasing and Superradiance has been considered in many publications, for instance in Ref. [18] the case of many atoms interacting with the EMF in presence of collisional dephasing has been analyzed for many excitations. On the contrary, here, we focus our attention on the relation between dephasing and Superradiance where only one excitation is present in the system. This case turns out to be more relevant for light harvesting complexes, as explained above.

The interplay of single excitation Superradiance and dephasing has been analyzed in Ref. [5] giving more attention to the behavior of populations and not to coherences. Specifically, our main interest is addressing the question of how cooperativity can protect coherences and entanglement.

The coupling to a common decay channel, which induces Superradiance, is taken into account by means of an effective non-Hermitian Hamiltonian [3, 19, 20]. Within this framework, it is possible to recover the generation of entanglement found in the case of two qubits coupled to a common decay channel in Ref. [21].

The coupling to a dephasing environment is modeled as stochastic fluctuations of diagonal energies, a common way to include dephasing in exciton dynamics, and it will be taken into account by using the Haken–Strobl approach [22]. The Haken–Strobl approach has been widely used in the past to include dephasing [5, 23] and it has also been analyzed in many recent applications [24–26] for its simplicity and effectiveness in describing strong dephasing in the high-temperature limit. Despite the essential features captured by this exactly solvable model, concerning the interplay between coherent dynamics and dephasing, its limitations in describing finite temperature experimental data are well known [27]. Indeed it represents the case of strong collisions between excitons and phonons (infinite temperature) thus overestimating the real effect of dephasing on coherences. Even if one may expect that the dephasing induced by stochastic fluctuations hinders quantum coherent effects, and thus Superradiance, we will see that the presence of a common decay channel is able to partially limit the effect of such a noise.

In this paper we will not consider the effect of a static disorder (inhomogeneous broadening), which has been analyzed by some of the Authors of this paper [28]. The interplay of dephasing (homogeneous broadening) and

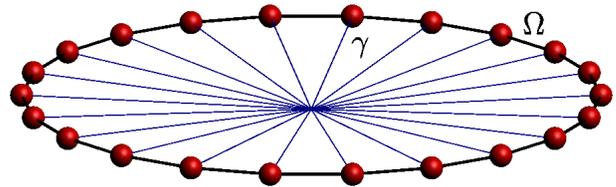


FIG. 1: (Color online)  $N$  sites with coupling  $\Omega$  connected to a common decay channel with the same coupling strength  $\gamma$ .

static disorder has also been analyzed in Refs. [26, 29].

## II. THE MODEL

We consider here a paradigmatic model with  $N$  two-level systems arranged in a ring structure, which has been also analyzed in several papers [5, 17, 26, 30–32] to describe different systems, such as molecular J-aggregates [6], bio-inspired devices for photon sensing [17], and efficient light-harvesting systems [30]. In particular, it has been often considered in the frame of exciton transport in natural photosynthetic complexes, such as LHI, LHII, where chlorophyll molecules are held in a ring-like structure by a protein scaffold [33].

Usually, under low light intensity, only one excitation is considered and the system becomes equivalent to a tight binding model where the excitation can hop from site to site, as described in Fig. 1. Specifically, we consider a ring with nearest neighbors coupling,  $\Omega$ , described by the following periodic tight binding Hamiltonian:

$$H^{tb} = \sum_{j=1}^N E_j |j\rangle \langle j| + \Omega \sum_{j=1}^N (|j\rangle \langle j+1| + |j+1\rangle \langle j|). \quad (1)$$

We also fix the energy scale taking  $\Omega = 1$  and, for simplicity,  $E_j = 0$ , for  $j = 1, \dots, N$ . Here  $|j\rangle$  represents a state in which the excitation is at the site  $j$ , while all the other sites are unoccupied. In terms of two-level system states ( $|0\rangle, |1\rangle$ ) it can be written as

$$|j\rangle = |0\rangle_1 |0\rangle_2 \dots |1\rangle_j \dots |0\rangle_N.$$

Each site is coupled to a common decay channel with coupling strength  $\gamma$ , as shown in Fig. 1.

$$\mathcal{H} = H^{tb} - i\frac{\gamma}{2}Q, \quad Q_{ij} = 1, \quad i, j = 1, \dots, N. \quad (2)$$

In the case of molecular aggregate this common decay channel can represent the coupling with the EMF [5] where the excitation can be lost. Indeed the non-Hermitian Hamiltonian used to model the coupling of molecular aggregates with the EMF [5] reduces to Eq.(2), in the limit of large wavelength with respect to the system size and for molecular aggregates with parallel dipoles. For instance the wavelength of the absorbed light (hundreds of nanometers) is much larger than the system size of natural complexes such as LHI, LHII (few tens of nanometers) [12].

We stress that while in the case of the EMF,  $\gamma$  and  $\Omega$  have a common origin, since they both arise from the interaction with the EMF, here we take a more general point of view:  $\gamma$  can also represent the coupling with a different environment, so that it can be varied independently of  $\Omega$ . For instance in molecular aggregates  $\gamma$  can also represent the coupling to a central core absorber, such as the reaction center [15, 16] or a semi-infinite lead where the excitation can be trapped [4, 17, 19, 34].

Due to its specific structure, the operator  $Q$  in Eq.(2) has only one eigenstate with a non-zero eigenvalue: this is the fully extended state with eigenvalue equal to  $N$ ,

$$|S\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^N |i\rangle. \quad (3)$$

This eigenstate also corresponds to the ground state of  $H^{tb}$ . All the other eigenstates of  $Q$  are degenerate with null eigenvalues and, since  $[Q, H^{tb}] = 0$ , they can be chosen to match the other eigenstates of  $H^{tb}$ , see Ref. [28]. This implies that only the state  $|S\rangle$ , Eq. (3), has a non-vanishing decay width equal to the total decay width of the system:  $\Gamma_N = N\gamma$ . This is the superradiant state and the dependence on  $N$  of the decay width is the hallmark of the cooperative nature of Superradiance. All the other states with zero decay width are called sub-radiant. Clearly, this perfect segregation of the decay widths will not persist in presence of dephasing or of any other source of disorder which breaks the symmetry of the model.

Thus in our model, in absence of disorder, we are in a superradiant regime for any  $\gamma$  and we have:

- a superradiant state,  $|S\rangle$  with a decay width given by  $N\gamma$ ,
- $N - 1$  subradiant states, orthogonal to the superradiant one, with zero decay width for any value of  $\gamma$ .

Note that this situation is a peculiarity of the model: usually, the superradiant regime sets in only above a critical value of the coupling with the continuum of states. This fact shows that ring-shaped nanostructures are ideal to exploit Superradiance, and it might also explain why they appear in natural photosynthetic complexes.

The effect of the dephasing environment is taken into account in the frame of the Haken-Strobl (HS) model [22]. In the HS model considered below, dephasing arises due to uncorrelated fluctuations of site energies,

$$\langle E_i(t)E_j(t') \rangle = \hbar\delta_{ij}\delta(t-t')\gamma_\phi. \quad (4)$$

where  $\gamma_\phi$  is the dephasing rate measured in units of energy, proportional to the intensity of site energy fluctuations. Finally, the master equation for the density matrix  $\rho$  (setting  $\hbar = 1$ ) can be obtained adding both the non-Hermitian term and the dephasing term:

$$\frac{d\rho_{hk}}{dt} = -i(\mathcal{H}\rho - \rho\mathcal{H}^\dagger)_{hk} - \gamma_\phi(1 - \delta_{hk})\rho_{hk}. \quad (5)$$

Usually, in molecular aggregates, energy is measured in units of  $\text{cm}^{-1}$ , corresponding to energy divided by  $\hbar c$ . In these units, time is measured in cm which corresponds to the mapping  $t \rightarrow 2\pi ct$  ( $c \simeq 0.03 \text{ cm/ps}$  is the speed of light) and Eq. (5) remains the same. In the following all units of energy will be given in  $\text{cm}^{-1}$  and in order to have time in ps we need to divide it by  $2\pi c$ .

### III. EXACT SOLUTION FOR MACROSCOPIC VARIABLES

Let us define the following macroscopic variables:

$$p = \text{tr}\rho = \sum_{h=1}^N \rho_{hh}, \quad q = \sum_{h \neq k} \rho_{hk}. \quad (6)$$

As for their physical meaning,  $p(t)$  describes the probability of finding the excitation in the ring (which will decay to zero since the system is open) and  $q(t)$  is related to the presence of quantum coherences and it is a real number, being the sum of all the off-diagonal elements of the Hermitian density matrix. Those variables completely characterize the radiative behavior of the system.

Following what is commonly done in literature in the case of interaction with the EMF [35], we give an analytical expression of the decay width for a given state  $\rho$ . Since in our case the state  $|S\rangle$ , Eq. (3), is the only decaying states, while the others do not decay at all, the decay width of any state  $\rho$  can be written as the probability to be the state  $|S\rangle$  times its decay width  $N\gamma$ ,

$$\Gamma_\rho = N\gamma\langle S|\rho|S\rangle = \gamma \sum_{n,m} \rho_{nm} = \gamma(p+q). \quad (7)$$

From the last expression it is clear that, if  $p = 1$  and  $q = 0$ , we have the decay width  $\Gamma_\rho = \gamma$ , and that we need  $q \neq 0$  to have Superradiance or Subradiance. For instance, for the superradiant state in Eq. (3), we have:  $p = 1, q = N - 1$ , so that  $\Gamma_\rho = N\gamma$ . Since  $|S\rangle$  is also a fully entangled state, this shows that  $q$  represents the coherences responsible for Superradiance.

The system of  $N^2 \times N^2$  differential equations (5) decouples, so that we can write a close set of equations for the macroscopic variables:

$$\begin{cases} \dot{p} = -\gamma p - \gamma q, \\ \dot{q} = -(N\gamma - \gamma)p - (N\gamma - \gamma + \gamma_\phi)q. \end{cases} \quad (8)$$

The dynamics of  $p(t)$  and  $q(t)$  can be obtained easily starting from the initial conditions

$$p(0) = \sum_{h=1}^N \rho_{hh}(0) = 1, \quad q(0) = q_0 = \sum_{h \neq k} \rho_{hk}(0), \quad (9)$$

and it is given by

$$p(t) = -p_- e^{\lambda_+ t} + p_+ e^{\lambda_- t}, \quad (10)$$

$$q(t) = p_- \left(1 + \frac{\lambda_+}{\gamma}\right) e^{\lambda_+ t} - p_+ \left(1 + \frac{\lambda_-}{\gamma}\right) e^{\lambda_- t}, \quad (11)$$

where

$$p_{\pm} = \frac{\gamma + \lambda_{\pm} + \gamma q_0}{\lambda_{+} - \lambda_{-}}, \quad (12)$$

and  $\lambda_{\pm}$  are the eigenvalues of the linear system (8),

$$\lambda_{\pm} = \frac{-N\gamma - \gamma_{\phi} \pm \sqrt{N^2\gamma^2 + \gamma_{\phi}^2 + (2N - 4)\gamma\gamma_{\phi}}}{2}. \quad (13)$$

Note that Eq. (10) for the population  $p(t)$  is in agreement with the results obtained in Ref. [5], while the results for coherences have not been discussed so far. Note also that, for  $\gamma = 0$ , we have  $\dot{p} = 0$  and  $\dot{q} = -\gamma_{\phi}q$ , so that coherences would simply decay exponentially as  $q(t) = q(0)\exp(-\gamma_{\phi}t)$ . A very different situation arises because of the coupling with a common decay channel. It is interesting to study the limit for small and large  $\gamma_{\phi}/N\gamma$ . In the regime,  $\gamma_{\phi}/N\gamma \ll 1$ , we have:

$$\lambda_{+} = -\frac{\gamma_{\phi}}{N} + o\left(\frac{\gamma_{\phi}}{N\gamma}\right), \quad (14)$$

$$\lambda_{-} = -N\gamma - \gamma_{\phi}\frac{N-1}{N} + o\left(\frac{\gamma_{\phi}}{N\gamma}\right).$$

This means that, in this regime, the dynamics are characterized by a cooperative (proportional to the system size  $N$ ) exponentially fast decay with rate  $-N\gamma$  (superradiant), and a strongly suppressed decay with slope  $\gamma_{\phi}/N$  (subradiant). We will call this the *superradiant regime*.

On the other hand, for  $N\gamma/\gamma_{\phi} \ll 1$  one has

$$\lambda_{+} = -\gamma + o(N\gamma/\gamma_{\phi}), \quad (15)$$

$$\lambda_{-} = -\gamma_{\phi}[1 + o(N\gamma/\gamma_{\phi})].$$

In this regime any cooperative effect on the decay is lost and the long-time dynamics are dominated by the smallest exponent between  $\gamma$  and  $\gamma_{\phi}$ . This is the *non-superradiant regime*.

#### IV. SURVIVAL PROBABILITY

The critical dephasing strength separating the *superradiant regime* from the *non-superradiant regime* can be studied by means of the survival probability,  $p(t)$ , for the excitation to be still in the system at time  $t$ . Note that, for  $\gamma_{\phi} = 0$ , assuming as initial condition a superradiant state ( $p_0 = 1, q_0 = N - 1$ ), Eq. (3), we have  $p(t) = e^{-N\gamma t}$ , while for any subradiant initial state we have:  $p(t) = p_0 = 1$ .

In Fig. 2 we show the survival probability,  $p(t)$ , as a function of time for different  $\gamma_{\phi}$  values, starting from the superradiant state. As one can see, for  $\gamma_{\phi}/N\gamma \ll 1$ , it decreases in time initially as  $e^{-N\gamma t}$  and, for  $t > t^*$ , as  $e^{-\gamma_{\phi}t/N}$  independently of  $\gamma$ . It is relatively easy to estimate the transition time,  $t^*$ , as the intersection, in logarithmic scale, between the lines with slope  $-N\gamma$  and

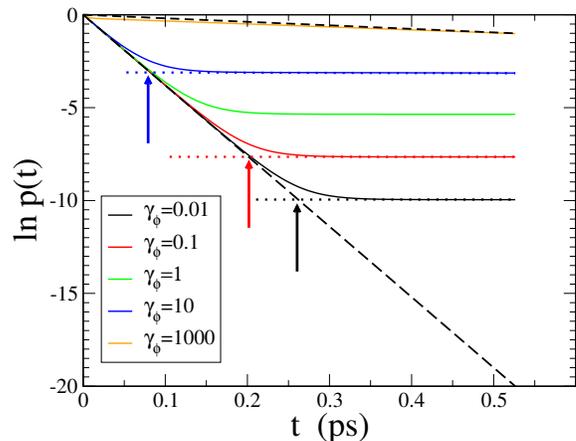


FIG. 2: (Color online) Survival probability,  $p(t)$ , as a function of time,  $t$ , measured in  $ps$ , see discussion below Eq. (5). Different values of the dephasing rate  $\gamma_{\phi}$  are shown as solid lines. The superradiant decay with rate  $N\gamma$  and the decay with rate  $\gamma$  are also shown as dashed lines. Parameters are  $\Omega = 1$ ,  $\gamma = 10$  and  $N = 20$ . The vertical arrows indicate the analytical expressions for the time  $t^*$ , Eq. (16), at which the superradiant decay ends. Dotted lines represent exponential decays with exponents  $\gamma_{\phi}/N$ . Initial state is the superradiant extended state  $|S\rangle$ .

$\gamma_{\phi}/N$ , obtaining

$$t^* \approx -\frac{1}{N\gamma} \log \frac{\gamma_{\phi}}{N\gamma}. \quad (16)$$

The time  $t^*$ , which represents the timescale at which the superradiant transfer ends, becoming subradiant, has been shown in Fig. 2 by vertical arrows. On the other side, for large enough dephasing rate  $\gamma_{\phi} > N\gamma$ , Superradiance is destroyed and the survival probability decays as  $e^{-\gamma t}$ , see Fig. 2.

To determine the critical dephasing strength at which the super and subradiant effect is destroyed, we analyze the decay of both the superradiant state, Eq. (3), and of a particular subradiant state,

$$|A\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^N (-1)^i |i\rangle, \quad (17)$$

which is clearly orthogonal to the superradiant one, ( $\langle S|A\rangle = 0$ ). Let us consider the time,  $\tau$ , at which  $p(\tau) = 1/e$ : it is clear that Superradiance is completely destroyed when  $\Lambda \equiv 1/\tau \simeq \gamma$ . Note that  $\Lambda/\gamma$  has also been called effective cooperation number ( $N_{\text{eff}}$ ) in literature[5].

As it is shown in Fig. 3, the ratio  $\Lambda/\gamma$ , for the superradiant initial state, goes to 1 when  $\gamma_{\phi}/N\gamma \approx 1$ . For the anti-symmetric initial state Eq. (17), we have that:

- for  $\gamma_{\phi}/N\gamma < 1$ ,  $\Lambda \propto \gamma_{\phi}/N$ ;
- for  $\gamma_{\phi}/N\gamma > 1$ , the ratio  $\Lambda/\gamma$  approaches 1, in agreement with the analytical results presented above.

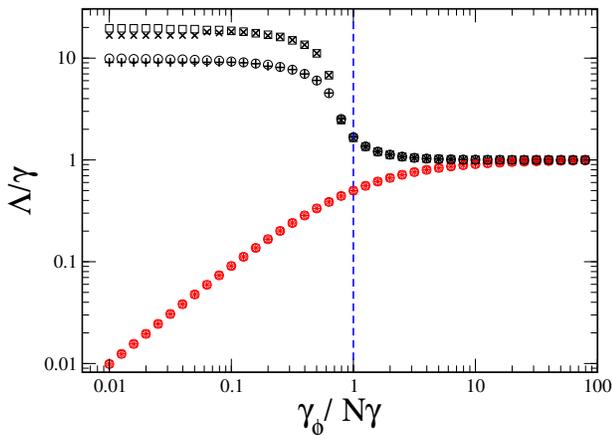


FIG. 3: (Color online)  $\Lambda/\gamma$  as a function of  $\gamma_\phi/N\gamma$  for an initial state: extended,  $|S\rangle$ , (upper black symbols); antisymmetric  $|A\rangle$ , (lower red symbols). Different symbols correspond to different parameters: plus ( $N = 10, \Omega = 1, \gamma = 100$ ), crosses ( $N = 20, \Omega = 1, \gamma = 100$ ), circles ( $N = 10, \Omega = 100, \gamma = 1$ ), squares ( $N = 20, \Omega = 100, \gamma = 1$ ). The vertical dashed line is the critical threshold  $\gamma_\phi/N\gamma = 1$ .

We also checked (not shown in Fig. 3) that this behavior is independent of  $\gamma$  and shared by all of the subradiant initial states.

Fig. 3 also shows the robustness of super and subradiant emergent effects to dynamical disorder: the amount of dephasing needed to destroy the superradiant behavior increases with the system size. Note that the same robustness was found in the presence of static disorder [20, 28], so that it appears to be a general property of such coherent emergent effects. Another interesting result is that, at fixed dephasing rate, the decay rate of the subradiant states decreases on increasing the system size (as  $\gamma_\phi/N$ ). This indicates that some kind of quantum coherence is cooperatively preserved in presence of Superradiance.

## V. ENTANGLEMENT

Here we would like to address the question whether other kinds of quantum coherence, different from that needed to sustain Superradiance, are preserved by the coupling to a common decay channel. Therefore, we will base our analysis on a quantity used to quantify the global entanglement [10]:

$$E[\rho] = -\sum_i \rho_{ii} \ln \rho_{ii} + \sum_i \lambda_i \ln \lambda_i, \quad (18)$$

where  $\lambda_i$  are the eigenvalues of the density matrix. Note that  $E[\rho]$  measures the entanglement between the many two-levels systems which share the excitation. Let us stress that, for an extended state, see Eq. (3), we have  $E[\rho] = \ln(N)$ , while, for a separable state, we have  $E[\rho] = 0$ . Moreover, the von Neumann entropy,  $-\sum_i \lambda_i \ln \lambda_i$ , van-

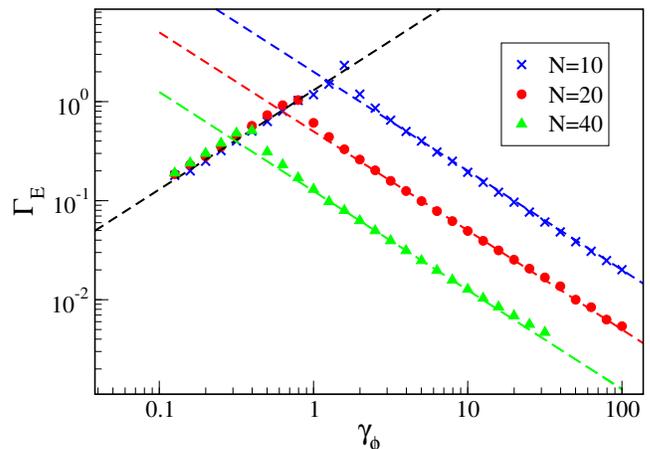


FIG. 4: (Color online) Dependence of the decay rate of the global entanglement for the closed system as a function of the dephasing  $\gamma_\phi$  for different  $N$  values, as indicated in the legend. Here is:  $\gamma = 0, \Omega = 1$ , and as initial state we chose the single site  $|k\rangle$ . Dashed (black) line is the fitting  $\Gamma_E = 1.3\gamma_\phi$ , red, blue and green dashed lines stand for  $\Gamma_E = C(N)/\gamma_\phi$ , where  $C(10) = 2, C(20) = 1/2, C(40) = 1/8$ .

ishes for pure states, so that  $E[\rho] = -\sum_i \rho_{ii} \ln \rho_{ii}$ .

In the single exciton approximation it is also possible to compute the concurrence [36] for any pair of two-levels systems  $i \neq j$ , which is simply given by [10]

$$C_{ij} = 2|\rho_{ij}|.$$

Before analyzing the effect of opening on the global entanglement, let us discuss the case without opening ( $\gamma = 0$ ). Since the off-diagonal matrix elements are exponentially suppressed, the steady state solution of Eq. (5), is given by,  $\rho_{ij} = \delta_{ij}/N$ . Thus, in our model of decoherence, the density matrix becomes diagonal with a homogeneous distribution, all the off-diagonal matrix elements and  $E[\rho]$  (which represent the coherences) vanish for large enough times. Typically, one has that  $E_\rho(t) \sim e^{-\Gamma_E t}$ , for  $t$  large. The dependence of  $\Gamma_E$  on  $\gamma_\phi$  for the different parameters has been obtained by an exponential fitting in time and is shown in Fig. 4. As one can see,  $\Gamma_E$  is not monotone with  $\gamma_\phi$ , since it firstly increases linearly with  $\gamma_\phi$  and then, for large dephasing, it decreases as  $1/\gamma_\phi$ . This fact has been interpreted in literature as a manifestation of the so-called quantum Zeno effect [24]. To summarize, in the case  $\gamma = 0$  we numerically found:

$$\Gamma_E = \begin{cases} 1.3 \gamma_\phi & \text{for } \gamma_\phi < 12.4 \Omega/N, \\ \frac{200 \Omega^2}{N^2 \gamma_\phi} & \text{for } \gamma_\phi > 12.4 \Omega/N. \end{cases} \quad (19)$$

Let us now consider the case  $\gamma \neq 0$ . Under very general assumptions, see Appendix A, it is possible to obtain the asymptotic behavior (for  $t \rightarrow \infty$ ) of the density matrix:

$$\rho_{ij}(t) = e^{\lambda+t} [a\delta_{ij} + (1 - \delta_{ij})b], \quad (20)$$

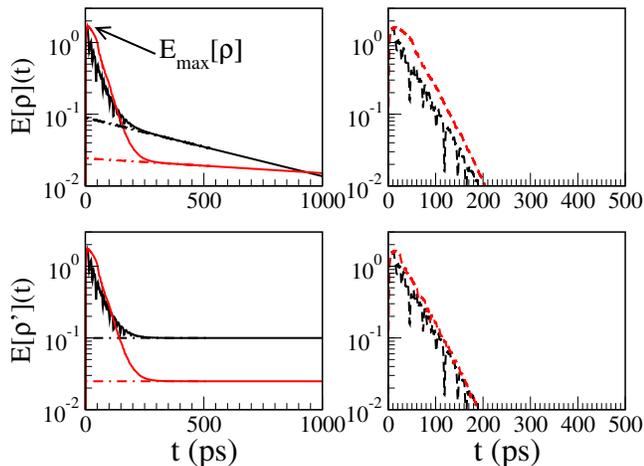


FIG. 5: (Color online) Upper panels: Global entanglement,  $E[\rho]$ , as function of time,  $t$ , starting from a single site,  $|i\rangle$ , for the open system with  $\gamma = 1$  (left panel) and for the closed system with  $\gamma = 0$  (right panel). In the left panel the analytical results for the asymptotic global entanglement are shown as dot-dashed lines. Different system sizes are considered:  $N = 10$  (black curves) and  $N = 40$  (red curves). Lower panel: the same quantities for the normalized density matrix,  $\rho'$ , see text. Data are  $\Omega = 1$  and  $\gamma_\phi = 0.1$ .

where

$$a = -\frac{p_-}{N}, \quad b = \frac{p_-}{N(N-1)} \left(1 + \frac{\lambda_+}{\gamma}\right), \quad (21)$$

and  $p_-$ ,  $\lambda_+$  are defined in Eqs (12,13). Eq. (20) has been numerically verified in a very large range of parameters.

From the analytical expression, Eq. (20), it is easily deduced that both global entanglement and concurrence decay exponentially in time, as  $\exp(\lambda_+ t)$ . In more detail, one gets the asymptotic ( $t \rightarrow \infty$ ) behavior for the concurrence,

$$C_{ij} \sim 2e^{\lambda_+ t} \left[ \frac{p_-}{N(N-1)} \left(1 + \frac{\lambda_+}{\gamma}\right) \right], \quad (22)$$

and for the global entanglement,

$$E[\rho] \sim \frac{-p_-}{N} e^{\lambda_+ t} \left\{ \left(2 + \frac{\lambda_+}{\gamma}\right) \ln \left(2 + \frac{\lambda_+}{\gamma}\right) + \left(N - 2 - \frac{\lambda_+}{\gamma}\right) \ln \left[1 - \frac{1}{N-1} \left(1 + \frac{\lambda_+}{\gamma}\right)\right] \right\}. \quad (23)$$

This means that, in the superradiant regime, where  $\lambda_+ = -\gamma_\phi/N$ , see (14), the decay of the entanglement is suppressed as we increase the system size. On the other hand, for large dephasing,  $\gamma_\phi \gg N\gamma$ , where Superradiance is destroyed, the entanglement decays as  $\exp(-\gamma t)$ , independently of the system size. Thus entanglement decay displays a transition from a size-independent decay (for  $\gamma_\phi \gg N\gamma$ ) to a *cooperative sustained* decay (for  $\gamma_\phi \ll N\gamma$ ), where the entanglement decay becomes independent of  $\gamma$  and is suppressed on increasing the system

size,  $N$ , as  $\gamma_\phi/N$ . This proves that, in the superradiant regime, also other kinds of coherences are affected by cooperativity.

In Fig. 5 we analyze the behavior of  $E[\rho]$ , starting from a wave function localized on a single site,  $|\psi_0\rangle = |i\rangle$ . Since this state overlaps with the superradiant state with a small probability,  $1/N$ , it can be considered mostly subradiant for large  $N$ . In Fig. 5 (upper panels) we fix  $\gamma_\phi = 0.1$  and we consider two different situations: with opening (left panel  $\gamma = 1$ ) and without opening (right panel  $\gamma = 0$ ), both for different system sizes,  $N = 10, 40$ . As one can see, the presence of the coupling to a common decay channel produces the following effects:

1. it slows down the entanglement decay (compare the left panel with the right one);
2. it decreases the decay rate on increasing the system size, since the entanglement decays as  $e^{-\gamma_\phi t/N}$  (compare the black with the red line in the left panel).

The asymptotic expansion, Eq. (23), represents the entanglement at the time  $t$  for a system that can decay into the continuum. This means that the global entanglement decays not only because of the destruction of coherences, but also due to the loss of probability into the continuum. It is interesting to consider what would be the global entanglement after a measurement which finds the excitation in the ring. To this end, one should consider the density matrix  $\rho'(t) = \rho(t)/\text{Tr}[\rho(t)]$  after the measurement given by the projection operator  $\sum_i |i\rangle\langle i|$ . In this case one obtains a stationary entanglement

$$E[\rho'] = \frac{1}{N} \left(2 + \frac{\lambda_+}{\gamma}\right) \ln \left(2 + \frac{\lambda_+}{\gamma}\right) + \left(1 - \frac{2}{N} - \frac{\lambda_+}{N\gamma}\right) \ln \left[1 - \frac{1}{N-1} \left(1 + \frac{\lambda_+}{\gamma}\right)\right], \quad (24)$$

(see Eq. (B3) in Appendix B), which is independent of time and initial conditions. This finding is confirmed by our numerical results for the entanglement of the normalized density matrix, shown in Fig. 5 (lower left panel). Note that the entanglement of the normalized density matrix indicates the entanglement present in the system at time  $t$ , after a measurement which finds the excitation in the system. Note that while all the coherences  $\rho_{ij} \rightarrow 0$ , as  $t \rightarrow \infty$ , the same does not happen for the normalized density matrix  $\rho'_{ij}$ . The mathematical reason is that also  $\text{Tr}(\rho) \rightarrow 0$  for  $t \rightarrow \infty$ .

## VI. MAXIMAL ENTANGLEMENT

Another interesting quantity to be studied is the maximal entanglement (value at the peak) obtained during the whole evolution, see Fig. 5. In absence of coupling to the continuum,  $\gamma = 0$ , the coupling,  $\Omega$ , between neighboring sites creates entanglement (with those initial conditions we have  $E[\rho(0)] = 0$ ), which is then exponentially suppressed in time by any chosen dephasing rate,

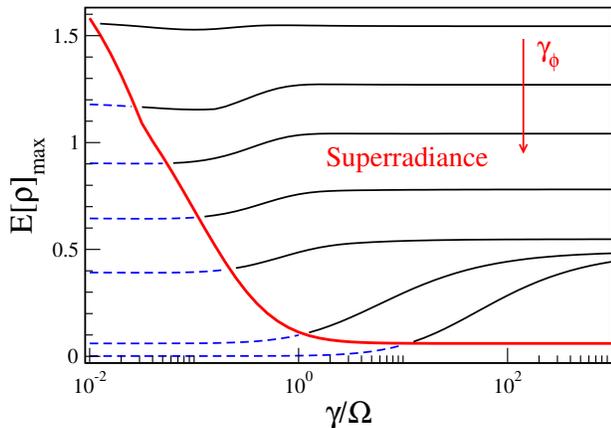


FIG. 6: (Color online) Maximal global entanglement  $E[\rho]_{max}$  as a function of the degree of opening  $\gamma$  for fixed  $N = 10$  and  $\Omega = 1$ . Each curve has been obtained at fixed  $\gamma_\phi = 0.1, 0.25, 0.5, 1, 2, 10, 100$  (from the upper curve to the lower one), and it is shown as blue dashed in the regime characterized by  $\gamma_\phi > N\gamma$  and as full black in the superradiant regime  $\gamma_\phi < N\gamma$ . The thick red curve represents the superradiant transition  $\gamma_\phi = N\gamma$ , so that the superradiant region is above that curve. As initial state we chose a single site  $|i\rangle$ .

$\gamma_\phi \neq 0$ , see Fig. 5. Maximal entanglement occurs at the time  $\tau \simeq \hbar/\Delta E$ , where  $\Delta E \simeq 4\Omega/N$  is the unperturbed energy spacing, and its maximal value decreases on increasing the dephasing rate  $\gamma_\phi$ . On the other hand, the competing effects due to the coupling with the continuum of states,  $\gamma \neq 0$ , result in different behaviors depending on the choice of the parameters. Results for maximal entanglement  $E_{max}[\rho]$  are presented in Fig. 6. As one can see, in the non-superradiant region,  $N\gamma < \gamma_\phi$  (below the thick red line),  $E_{max}[\rho]$  is almost independent of the coupling  $\gamma$ , while, on entering the superradiant region,  $N\gamma > \gamma_\phi$ , there is a strong enhancement of the maximal entanglement (mainly in the region of large dephasing), up to reach a saturation value. In conclusion, we can say that, even in presence of a dephasing environment, an optimal coupling to the continuum of states exists, such that a maximal global entanglement is reached.

## VII. CONCLUSIONS

We have analyzed a ring of two-level systems in the limit where only one excitation is present. We studied the combined effect of different environments on such a ring structure. The two-level systems are coupled to a common decay channel, which induces super and subradiant behavior; moreover, they are also coupled to a dephasing environment, modeled by a classical white noise (Haken-Strobl approach). We have shown that coherent emergent properties, such as Superradiance and Subradiance, display a cooperative robustness to dephasing, in

the sense that the critical dephasing rate needed to destroy these coherent effects increases with the system size. By analyzing the global entanglement, we have demonstrated that the coupling to a common decay channel is able to prevent the loss of coherences. Indeed, we have shown that the entanglement decay is suppressed, in the superradiant regime, as we increase the system size. We have also derived an analytical expression for the asymptotic evolution of the density matrix. In the future it will be interesting to understand how this asymptotic form depends on the details of the coupling to the common decay channel. This would allow to control the state of a quantum system and its degree of entanglement by suitably coupling it to one or more dissipative environments.

In order to compare our results with experimental data about molecular aggregates and natural photosynthetic complexes one needs to estimate the dephasing rate. Typically, the superradiant regime described in this paper could be reached in realistic systems such as J-aggregates, at low temperature or for a very large number of molecules in the aggregates. For instance in PIC Br J-aggregates we have  $(\hbar/\gamma)^{-1} = 3.7$  ns and a dephasing rate of 10 ps at 1.5 K [6, 27]. Thus the superradiant regime occurs for  $N > 370$ , which is easily reachable in J-aggregates. On the other hand one should be careful to apply the results from Haken-Strobl master equation blindly, see discussion in the Introduction.

At room temperature the dephasing rate for natural photosynthetic complexes, such as LHI and LHII, is estimated to be on the order of  $100 \text{ cm}^{-1}$  [23, 32], which is much larger than the superradiant decay rate. Indeed for the LHI complex, we have  $N = 32$  and  $\gamma \approx 10^{-3} \text{ cm}^{-1}$  [5] for the coupling w.r.t. the electromagnetic field, and  $\gamma \approx 10^{-2} \text{ cm}^{-1}$  [28] for the coupling w.r.t. to reaction center. Thus the superradiant decay rate,  $N\gamma$ , w.r.t. both environments is much smaller than the dephasing rate. In this range of parameters the Haken-Strobl master equation predicts the total quenching of Superradiance. On the other hand Superradiance w.r.t. the electromagnetic field has been found experimentally at room temperature in LHI and LHII complexes [7]. For J-aggregates [6] Superradiance has also been found in presence of a dephasing rate which is one order of magnitude larger than the superradiant decay rate [27]. These facts have been explained in Ref. [27] by introducing a more sophisticated model of the interaction with the phonon bath, showing that the Haken-Strobl approach overestimates the detrimental effect of dephasing.

In the future it would be interesting to verify the main results obtained here, which are the cooperative robustness to disorder and the possibility to preserve coherences through the coupling with a common decay channel, with more sophisticated models of exciton-phonon interaction.

*Acknowledgments.* We would like to thank Giulio Gius-teri, Robin Kaiser, Mohan Sarovar, Rosario Fazio and Diego Ferrari for providing many useful discussions.

- [1] M. O. Scully and A. A. Svidzinsky, *Science* **325**, 1510 (2009);
- [2] R. H. Dicke, *Phys. Rev.* **93**, 99 (1954).
- [3] V. V. Sokolov and V. G. Zelevinsky, *Nucl. Phys.* **A504**, 562 (1989); *Phys. Lett. B* **202**, 10 (1988); I. Rotter, *Rep. Prog. Phys.* **54**, 635 (1991); V. V. Sokolov and V. G. Zelevinsky, *Ann. Phys. (N.Y.)* **216**, 323 (1992).
- [4] G.L. Celardo and L. Kaplan, *Phys. Rev. B* **79**, 155108 (2009); G. L. Celardo, A. M. Smith, S. Sorathia, V. G. Zelevinsky, R. A. Senkov, and L. Kaplan, *Phys. Rev. B* **82**, 165437 (2010).
- [5] J. Grad, G. Hernandez, and S. Mukamel, *Phys. Rev. A* **37**, 3835 (1988).
- [6] H. Fidler, J. Knoester and D. A. Wiersma, *J. Chem. Phys.* **95**, 7880 (1991); J. Moll, S. Daehne, J. R. Durrant and D. A. Wiersma, *J. Chem. Phys.* **102**, 6362 (1995); S. De Boer and D.A. Wiersma, *Chem Phys. Lett.*, **165**, 45 (1990).
- [7] R. Monshouwer, M. Abrahamsson, F. van Mourik and R. van Grondelle, *J. Phys. Chem. B* **101**, 7241 (1997).
- [8] G.S. Engel et al., *Nature* **446**, 782 (2007).
- [9] G. Panitchayangkoon et al., *PNAS* **107**, 12766 (2010).
- [10] M. Sarovar, A. Ishizaki, G.R.Fleming and K.B.Whaley, *Nat. Phys.* **6**, 462 (2010).
- [11] H. Hossein-Nejad and G. D. Scholes, *New J. Phys.* **12**, 065045 (2010).
- [12] J. Strumpfer, M. Sener, and K. Schulten. *J. Phys. Chem. Lett.*, **3**, 536 (2012).
- [13] S. Lloyd and M. Mohseni, *New J. Phys.* **12**, 075020 (2010).
- [14] G. D. Scholes, *Chem. Phys.* **275**, 373 (2002).
- [15] G.L.Celardo, F. Borgonovi, V.I. Tsifrinovich, M. Merkli and G.P. Berman, *J. Phys. Chem. C* **116**, 22105 (2012).
- [16] D. Ferrari, G. L. Celardo, G.P. Berman, R.T.Sayre, F. Borgonovi, *J. Phys. Chem. C* **118**, 20 (2014).
- [17] K. D. B. Higgins, S. C. Benjamin, T. M. Stace, G. J. Milburn, B. W. Lovett, E. M. Gauger, arXiv:1306.1483.
- [18] J.J. Maki et al, *Phys. Rev. A* **40**, 5135 (1989); L. Yuan et al, *Phys. Rev. A* **87**, 023826 (2013).
- [19] A. F. Sadreev and I. Rotter, *J. Phys. A* **36**, 11413 (2003).
- [20] G.L. Celardo, A. Biella, L. Kaplan, F. Borgonovi *Fortschr. Phys.* **61**, No. 2-3, 250-260 (2013); A. Biella, F. Borgonovi, R. Kaiser, G.L. Celardo, *Europhys. Lett.* **103** 57009 (2013).
- [21] F. Francica, S. Maniscalco, J. Piilo, F. Plastina and K.-A. Suominen, *Phys. Rev. A* **79**, 032310; S. Maniscalco, F. Francica, R. L. Zaffino, N. Lo Gullo and F. Plastina, *Phys. Rev. Lett.* **100**, 090503 (2008).
- [22] H.Haken, G. Strobl, *Z. Physik*, **262**, 135 (1973).
- [23] J.A. Leegwater, *J. Phys. Chem*, **100**, 14403 (1996).
- [24] P. Rebentrost, M. Mohseni, I.Kassal, S. Lloyd and A. Aspuru-Guzik, *New J. Phys.* **11**, 033003 (2009); P. Rebentrost, M. Mohseni and A. Aspuru-Guzik, *J. Phys. Chem. B* **113**, 9942 (2009).
- [25] M. B. Plenio and S. F. Huelga, *New J. Phys.* **10**, 113019 (2008); F. Caruso, A. W. Chin, A. Datta, S. F. Huelga and M. B. Plenio, *J. Chem. Phys.* **131**, 105106 (2009).
- [26] J. M. Moix, M. Khasin, and J. Cao, *New J. Phys.*, **15**, 085010 (2013); J. Wu, R.J. Silbey and J. Cao, *Phys. Rev. Lett.*, **110**, 200402 (2013).
- [27] F. C. Spano, J. R. Kuklinski and S. Mukamel, *Phys. Rev. Lett.* **65**, 211 (1990); F. C. Spano, J. R. Kuklinski and S. Mukamel, *J. Chem. Phys.* **94**, 7534 (1991).
- [28] G.L. Celardo, G.G. Giusteri and F. Borgonovi, *Cooperative Robustness to Static Disorder*, arXiv:1403.1779, (2014).
- [29] D. J. Heijs, V. A. Malyshev, and J. Knoester, *Phys. Rev. Lett.* **95**, 177402 (2005).
- [30] M. Sarovar, K. B. Whaley, *New J. Phys.* **15**, 013030 (2013).
- [31] A. Olaya-Castro, C. F. Lee, F. Fassioli Olsen, and N. F. Johnson, *Phys. Rev. B* **78**, 085115 (2008).
- [32] F. C. Spano and S. Mukamel, *J. Chem. Phys.* **91**, 683 (1989).
- [33] X. Hu, T. Ritz, A. Damjanovic, K. Schulten, *J. Phys. Chem. B* **101**, 3854 (1997).
- [34] F. Mattiotti, G.L. Celardo, G.G. Giusteri, In preparation.
- [35] Y. Zhao, T. Meier, W. M. Zhang, V. Chernyak and S. Mukamel *J. Phys. Chem. B* **103**, 3954 (1999).
- [36] W. K. Wootters, *Phys. Rev. Lett.* **80**, 2245 (1998).

## Appendix A: Asymptotic form of the density matrix

Let us write the master equation Eq. (5) in the form of a linear system

$$\dot{\rho}_{hk} = (\mathcal{L}\rho)_{hk} = \sum_{nm} \mathcal{L}_{hknm} \rho_{nm}, \quad (\text{A1})$$

where the  $N^2 \times N^2$  elements  $\mathcal{L}_{hknm}$  are time independent. It is easy to see that for large time,  $t \rightarrow \infty$ , and generic initial conditions the asymptotic behavior of  $\rho_{hk}(t)$  will be dominated by the smallest eigenvalue  $\lambda_0 = -\min_k |\lambda_k|$  of the four-indexes matrix  $\mathcal{L}$ , so that

$$\rho_{hk}(t) \sim e^{\lambda_0 t} c_{hk}, \quad (\text{A2})$$

where the coefficients  $c_{hk}$  depend on the initial conditions and on the labels  $(hk)$ .

Let us now assume a kind of ergodicity, in the sense that all diagonal and off-diagonal elements equal some real ( $a$ ) and complex ( $b+ic$ ) constant, respectively. More specifically, we assume that the constants  $a, b$  might be dependent on the initial conditions, but not on the position  $(hk)$ . We therefore conjecture the following asymptotic behavior:

$$\rho_{ij}(t) \sim e^{\lambda_0 t} [a\delta_{ij} + (1 - \delta_{ij})(b + ic)]. \quad (\text{A3})$$

Since the asymptotic density matrix, Eq. (A3), should be a solution of the master equation, Eq. (5), the following system for the real part should hold:

$$\begin{cases} \lambda_0 a = -\gamma[a + (N-1)b], \\ a(\lambda_0 + \gamma) = -\gamma(N-1)b. \end{cases} \quad (\text{A4})$$

Requiring the determinant to be zero, in order to have a

non-null solution, we obtain

$$\lambda_0 = \frac{-N\gamma - \gamma\phi \pm \sqrt{N^2\gamma^2 + \gamma\phi^2 + (2N-4)\gamma\gamma\phi}}{2}.$$

Since  $|\lambda_+| < |\lambda_-|$ , one gets  $\lambda_0 = \lambda_+$ . In the same way, it is easy to show that the imaginary part of the system can be solved only by  $c = 0$ .

Using Eqs. (10) and (11), and taking into account that  $|\lambda_+| < |\lambda_-|$ , one gets immediately Eq. (20):

$$\rho_{ij}(t) \sim e^{\lambda_+ t} \left[ -\frac{p_-}{N} \delta_{ij} + \frac{(1 - \delta_{ij})p_-}{N(N-1)} \left( 1 + \frac{\lambda_+}{\gamma} \right) \right]. \quad (\text{A5})$$

### Appendix B: Asymptotic expression for renormalized density matrix and entanglement

From the asymptotic form of the density matrix, Eq. (20), we easily get the asymptotic form of  $\rho' = \rho/\text{Tr}(\rho)$ :

$$\rho_{ij}(t)' \sim \left[ \frac{1}{N} \delta_{ij} + (1 - \delta_{ij}) \frac{1}{N(N-1)} \left( 1 + \frac{\lambda_+}{\gamma} \right) \right]. \quad (\text{B1})$$

To compute the global entanglement, one has to compute the von Neumann entropy, namely the eigenvalues of such

a matrix, which are given by:

$$\begin{cases} \xi_1 = \frac{1}{N} \left( 2 + \frac{\lambda_+}{\gamma} \right), \\ \xi_k = \frac{1}{N} \left[ 1 - \frac{1}{N-1} \left( 1 + \frac{\lambda_+}{\gamma} \right) \right], \quad \text{for } k = 2, \dots, N. \end{cases} \quad (\text{B2})$$

Simple algebra then gives

$$\begin{aligned} E[\rho'] &= \frac{1}{N} \left( 2 + \frac{\lambda_+}{\gamma} \right) \ln \left( 2 + \frac{\lambda_+}{\gamma} \right) + \\ &+ \left( 1 - \frac{2}{N} - \frac{\lambda_+}{N\gamma} \right) \ln \left[ 1 - \frac{1}{N-1} \left( 1 + \frac{\lambda_+}{\gamma} \right) \right]. \end{aligned} \quad (\text{B3})$$

In the limit of large  $N$ , one easily finds

$$E[\rho'](t) \sim \frac{1}{N} (2 \ln 2 - 1) + o(1/N^2), \quad (\text{B4})$$

where terms of order  $1/N^2$  have been neglected.

Finally, for the asymptotic behavior of concurrence we get

$$C_{ij} = 2|\rho'_{ij}| \sim 2 \left[ \frac{1}{N(N-1)} \left( 1 + \frac{\lambda_+}{\gamma} \right) \right]. \quad (\text{B5})$$