Investigating nonclassicality in nonlinear electronic spectroscopy

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In this work, we establish a connection between nonlinear electronic spectroscopy and quantum information protocols for the non-disturbance condition. The non-fulfillment of the later is a witness of nonclassicality. Our approach permits us to express the non-disturbance condition in terms of common observables in the context of electronic spectroscopy experiments, such as the induced polarization. We then provide the theoretical framework allowing one to infer nonclassicality from the detected signals in these experiments. A prominent feature of our proposal is the model independence. In particular, for third-order nonlinear spectroscopies, such as the widely used two-dimensional electronic spectroscopy, we find that the induction of third-order polarization in systems satisfying inversion symmetry automatically implies nonclassicality.

Introduction - Nonlinear spectroscopy techniques such as two-dimensional electronic spectroscopy are well-established both from a theoretical and experimental viewpoint [1]. Among its most noteworthy applications, one could mention its usefulness to reveal electronic couplings and energy transfer pathways in complex molecular aggregates [2]. Consequently, these experimental techniques assume a prominent role in the development of the field of quantum biology [3]. Within this field, a considerable amount of investigation has been undertaken in view of determining whether nonclassical features such as quantum coherence may contribute to optimizing the energy transfer within multichromophoric systems. A paradigmatic example is the so-called Fenna-Matthew-Olson (FMO) complex present in green sulfur bacteria [4–7]. The approaches usually rely on particular theoretical models and are focused on the oscillations of the cross peaks in the 2D electronic spectroscopy signals as a signature of nonclassicality. Nonetheless, alternative ways of witnessing nonclassical effects within these systems, in particular the ones which do not specify a particular model, may permit us to have a clearer and more comprehensive picture of the different aspects of nonclassicality in molecular systems. As a result, we could push the boundaries of the field of quantum biology a little step further.

Classical physics assumes measurement noninvasiveness, which is to say that, in principle, one can perform measurements on classical systems with arbitrarily small disturbance on their dynamics. Conversely, one aspect of the nonclassicality of physical systems is invasiveness, meaning that measurements on these systems often affect their subsequent evolution. Consequently, the statistics of later measurements performed on the same system cannot always be explained by classical theory. Measurement noninvasiveness can be ruled out through the violation of an inequality proposed by Leggett and Garg in 1985 [8, 9]. Specifically, the Leggett-Garg inequality (LGI) consists of a sum of two-time temporal quantum correlations between the results of dichotomic measurements performed on a single physical system as it evolves in time.

Many recent works have further developed and discussed Leggett and Garg original proposition and ideas [10–17]. Alternative witnesses to measure invasiveness have also been proposed. Here, we will explore a protocol for testing noninvasiveness based on the non-disturbance condition [17–19], which can be related to the LGI [17]. By considering the definition of the non-disturbance condition, we explore the extended concept of noninvasiveness of an operation introduced in Ref. [20], where the concept of measurement noninvasiveness is generalized to the notion of noninvasiveness of a general quantum channel. Within this framework, we propose a protocol for testing the non-disturbance condition in the context of electronic spectroscopy experiments, which could be employed with the purpose of witnessing nonclassicality in a vast class of systems wherein electronic spectroscopic is a tremendously useful tool to the study of their properties.

FIG. 1: (Color online) Scheme of a 2D electronic spectroscopy experiment. The laser pulses 1, 2, and 3 are labeled according to the order they are applied. The center of the pulses reach the sample at \( t = 0 \), \( t = t_1 \), and \( t = t_2 \), respectively. The time intervals between the interactions are \( t'_1 = t_1 \) and \( t''_2 - t'_1 = t_2 \), respectively. The time interval between the detection of the signal field by the spectrometer at time \( t \) and pulse 3 is \( t_3 : t - t'_2 = t_3 \).

Nonlinear Response - In typical two-dimensional electronic spectroscopy experiments, three laser pulses, la-
belled as pulse 1, 2 and 3, interact with the sample as sketched in Fig. 1. The quantum mechanical description of the experiment considers a time-dependent Hamiltonian, which can be expressed as

$$H(t) = H_0 + H'(t),$$

(1)

where $H_0$ is time-independent and concerns the molecular system only, while $H'(t)$ is time-dependent and represents the action of the pulses. Before the application of the first pulse, the system is found to be in an equilibrium state $\rho_0$ i.e., a convex combination of the eigenstates of $H_0$. By denoting the electric field at time $t$ by $E(t)$, $H'(t)$ is given by $H'(t) = \mu \cdot E(t)$, where $\mu$ is the molecule dipole operator. Quite important now is the fact that usually the sample-pulse interaction is weak enough to permit the safe use of perturbation theory [1]. Within this approach, the following physical picture emerges.

When the first pulse reaches the sample, at time $t = 0$, it potentially takes the system out of equilibrium, and coherence can be generated. Then, the system continues to undergo a free evolution governed by the Hamiltonian $H_0$ from $t = 0$ to $t'_1$, when the second pulse is applied. Once again the molecular system is let to evolve freely, until the last interaction takes place at $t'_2$. The sample-emitted electric field $E_S$ is detected at time $t$. To be more precise, what is detected is the intensity of the signal $I_S$ which is proportional to the electric field modulus $|E_S|^2$. The source of such emitted field is the third-order nonlinear polarization $P^{(3)}(t)$ resulting from the application of the three pulses. A simple textbook calculation leads to [1]

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 E(t-t_3) \times E(t-t_2-t_3)E(t-t_3-t_2-t_1)S^{(3)}(t_3,t_2,t_1),$$

(2)

where $S^{(3)}(t_1,t_2,t_3)$ is the third-order response function which reads $S^{(3)}(t_1,t_2,t_3) = \langle \mu(t_3 + t_2 + t_1)\mu(t_2 + t_1)\mu(0) \rangle$, with $\mu(t) = U_3^\dagger(t)\mu U_3(t)$. Here, $t'_1 - 0 = t_1$ is the time elapsed between the first and second pulses, $t'_2 - t'_1 = t_2$, the same for second and third pulses, and $t - t'_2 = t_3$, the time elapsed between the last pulse and signal detection. After the rotating wave approximation and Fourier decomposition of the third-order nonlinear polarization as

$$P^{(3)}(t) = \sum_s P_s^{(3)}(t)e^{i\mathbf{k}_s \cdot \mathbf{r} - i\omega_s t},$$

(3)

where $\mathbf{k}_s = \pm \mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3$ and $\omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3$, the choice of one particular Fourier component in (3) (phase matching) leads to $I_S(t) \propto |P_s^{(3)}(t)|^2$. By fulfilling a phase matching condition, we have $|P^{(3)}(t)| = |P_s(t)|$ and then the signal is directly linked to an observable in the sense of quantum mechanics $I_S(t) \propto |P^{(3)}(t)|^2$ [21]. Finally, we remark that the use of narrow pulses or the semi-impulsive limit approximation leads to $I_S(t) \propto |S(t,t_1,t_2)|^2$. All these derivations are detailed in [1].

**Quantum Invasiveness** - As previously mentioned, a classical system is not in a fundamental way disturbed by measurements. Measurement invasiveness is then a signature of quantumness in a physical system. Such nonclassical effects can be unveiled by performing later measurements of a chosen observable, the measurement observable $Q$. By judiciously choosing the measurement observable, one may be able to spot nonclassicality from the measurement statistics. Let us consider the non-disturbance condition proposed in Ref. [17] and schematically shown in Fig. 2. The idea will be presented for a two-level system but it can be easily extended for higher dimensions as in fact we do later in our connection with spectroscopy. The kets $\{|e\rangle, |g\rangle\}$ are the eigenstates of a chosen observable $O$, not necessarily the measurement observable $Q$. They are referred to as classical states in the sense that they are associated with definite values of that observable. In the upper part of the figure, one prepares a input state $\rho$ by subjecting the eigenstate $|g\rangle$ to the transformation $U_1$. For example, if $U_1$ is a unitary, then $\rho = U_1|g\rangle \langle g| U_1^\dagger$. Now, the measurement operation $O$ is performed at $t_1$, and the system undergoes a second transformation labeled as $U_2$. Finally, the observable $Q$ is measured. By repeating the experiment many times, one is able to obtain the expected value $\langle Q \rangle'_\rho$ (the ’ indicates the presence of the measurement operation $O$). In the lower part of the figure, the experiment is now performed without the measurement operation $O$. In this case, the expected value is denoted by $\langle Q \rangle_\rho$. If the measurement operation is performed with arbitrarily small disturbance to the system (classically) we expect

$$d_\rho = \langle Q \rangle'_\rho - \langle Q \rangle_\rho \neq 0$$

(4)

to be zero. As a result, $d_\rho = 0$ works as a witness for quantum invasiveness [17].

![FIG. 2: (Color online) Scheme of the main experiment: in the upper part, a system initially in the state $|g\rangle$ is subjected to the transformation $U_1$ at $t = 0$ and a measurement operation $O$ at $t'_1$. Finally, the measurement of the observable $Q$ is performed at $t'_2$. The same realization is considered in the lower part of the figure, except for the fact that $O$ is not carried out at $t'_1$. However, this is an idealized scenario which does not...](image-url)
take into account the fact that in any real experiment one does not have perfect control of all classical variables which may lead to classical disturbance or errors. As proposed in Ref. [17], control experiments can be used to handle such classical disturbances occurring alongside the measurement at \( t_1 \) (clumsy measurement). A scheme for such control experiments is depicted in Fig. 3. Now the inputs are the classical states, defined as the eigenstates of \( O \). In this way, one can spot classical disturbances through non null values of \( d_g = \langle Q \rangle_g - \langle Q \rangle_g \) and \( d_e = \langle Q \rangle_e - \langle Q \rangle_e \), which are caused by classical disturbances that incoherently mix the classical states. Thus, nonclassical effects can be witnessed only if the following inequality is violated

\[
\min(d_g, d_e) \leq d_\rho \leq \max(d_g, d_e).
\]  

(5)

In these case, coherence is present in the basis formed by eigenstates \( O \). Specifically, it means that \( \rho \) is different from a convex combination of these eigenstates. As an important note, nothing that has been said so far relies on the nature of the measurement operation \( O \) at \( t'_1 \). Actually, the measurement \( O \) can be replaced by a general quantum channel without any loss of significance [20]. Even a unitary operation replacing \( O \) can be used to infer the nonclassicality of the input state \( \rho \) through violation of (5) [20].

\[
\begin{array}{c|c|c|c}
|g\rangle \text{ or } |e\rangle & O & \begin{cases} \langle Q \rangle_g \\ \langle Q \rangle_e \end{cases} \\
|g\rangle \text{ or } |e\rangle & U_2 & \begin{cases} \langle Q \rangle_g \\ \langle Q \rangle_e \end{cases} \\
\hline
\end{array}
\]

\begin{align*}
\quad & \quad \quad t = 0 \quad t'_1 \quad t_2 \quad t \\
\text{FIG. 3: (Color online) Scheme of the control experiment: in} \\
\text{the upper part, the classical states } |g\rangle \text{ and } |e\rangle \text{ prepared at} \\
\text{t = 0 are subjected to the measurement operation } O \text{ at } t'_1. \\
\text{The measurement of the observable } Q \text{ is performed at } t'_2. \text{ The} \\
\text{same realization is considered in the lower part of the figure,} \\
\text{except for the fact that } O \text{ is not carried out at } t'_1.
\end{align*}

Nonclassicality in spectroscopy experiments - We now establish a connection between disturbance and nonlinear electronic spectroscopy experiments. As discussed above, the interactions of the system with the laser pulses will be treated within the framework of the standard perturbative approach, which is the theoretical framework used to analyze these experiments [1]. We then identify observables in the context of the spectroscopical experiments that are suitable for the nonclassicality test, what represents a meaningful advantage from the point of view of experimental viability. It is important to remark that there are alternative theoretical descriptions for electronic spectroscopy that could have been taken into account [22, 23], and this can be investigated elsewhere.

We take \( U_1, O, \) and \( U_2 \) depicted in Fig. 2 as the three laser pulses in Fig. 1. For the classical states, we will be considering the eigenstates of the multichromophoric system Hamiltonian, i.e., \( O = H_0 \) with \( |g\rangle \) being the ground state and \( |i\rangle \) with \( i = 1, 2, \ldots, n \) the excited states (exciton states). This choice helps us to spot the presence of quantum coherence in the exciton basis, a topic of interest to the quantum biology community [4–6]. Finally, we consider the intensity of the signal \( I_S(t) \propto |P^{(3)}(t)|^2 \) as \( \langle Q \rangle \) [21]. As pointed out above, approximations such as the semi-impulsive limit can be considered what makes \( P^{(3)}(t) \propto S^{(3)}(t) \) in the semi-impulsive limit. Hence, the invasiveness witness of Eq. (4) can be expressed in terms of the induced polarizations as

\[
d_\rho = I'_S(t) - I_S(t) = |P^{(3)}(t)|^2 - |P^{(2)}(t)|^2.
\]  

(6)

If semi-impulsive limit is considered, one finds \( d_\rho = |S^{(3)}(t, t_1, t_2)|^2 - |S^{(2)}(t, t_1, t_2)|^2 \).

We should also take into consideration the control experiments shown in Fig. 3. A total of \( n + 1 \) control experiments should be carried out, each of them corresponding to one of the eigenstates of \( H_0 \) as input. As we can see, in the upper part of Fig. 3, given one of the aforementioned eigenstates as input, only \( O \) and \( U_2 \) are applied. In the lower part, in turn, only \( U_2 \) is carried out for the same eigenstate as input. As a result, we obtain \( d_g = |P^{(2)}_g(t)|^2 - |P^{(1)}_g(t)|^2 \) for the ground state as input and \( d_i = |P^{(2)}_i(t)|^2 - |P^{(1)}_i(t)|^2 \) for the excited states. Consequently, the nondisturbance condition of Eq. (5) now reads

\[
\min_i \{d_g, d_i\} \leq d_\rho \leq \max_i \{d_g, d_i\}.
\]  

(7)

We therefore found a sound connection between disturbance and electronic spectroscopy experiments, since \( d_\rho \) is given in terms of the polarization, an observable which is commonplace in the context of these experiments.

As an illustrative example, let us consider an electronically coupled dimer with the Hamiltonian (\( \hbar = 1 \)) [24]

\[
H_0 = \omega_A a_A^\dagger a_A + \omega_B a_B^\dagger a_B + J(a_A^\dagger a_B + a_B^\dagger a_A),
\]  

(8)
where $a_i^\dagger$ and $a_i$ are, respectively, creation and annihilation operators for electronic excitations at the chromophore $i \in \{A, B\}$. $\omega_A$ and $\omega_B$ are the first and second site energies, and $J$ is the coupling between the chromophores. By defining the parameters $\omega = (\omega_A + \omega_B)/2$, $\Delta = (\omega_A - \omega_B)/2$, and $\theta = \arctan(J/\Delta)/2$, one can diagonalize the dimer Hamiltonian with the help of the transformed operators $a_{\alpha} = \cos \theta a_A + \sin \theta a_B$, and $a_{\beta} = -\sin \theta a_A + \cos \theta a_B$ [23, 24]. In this way, the Hamiltonian (8) becomes

$$H_0 = \hbar \omega_{\alpha}|\alpha\rangle\langle\alpha| + \hbar \omega_{\beta}|\beta\rangle\langle\beta| + \hbar \omega_f|f\rangle\langle f|,$$

with the eigenvalues $\omega_{\alpha} = \omega + \Delta \sec 2\theta$, $\omega_{\beta} = \omega - \Delta \sec 2\theta$, and $\omega_f = \omega_A + \omega_B$. Without any loss of generality, the ground state $|g\rangle$ is associated with the eigenvalue $\omega_g = 0$. In (9), we also have $|\alpha\rangle = a_{\alpha}^\dagger |g\rangle$ and $|\beta\rangle = a_{\beta}^\dagger |g\rangle$ as single exciton states and $|f\rangle = a_{\alpha}^\dagger a_{\beta}^\dagger |g\rangle$ the two-exciton state. The energy eigenstates of the system, $\{|g\rangle, |\alpha\rangle, |\beta\rangle, |f\rangle\}$, constitute the exciton basis and are the classical states in our protocol to witness nonclassicality. By assuming inversion symmetry, the even-order nonlinearity (7), quantum invasiveness would in principle be witnessed whenever

$$|P^{(3)}(t)| \neq 0.$$  

(10)

Therefore, for the particular case where $P^{(2)}(t) = 0$, $|P^{(3)}(t)| \neq 0$ implies nonclassicality. Moreover, if the semi-impulsive limit applies, (10) can be written as $S^{(3)}(t,t_1,t_2) \neq 0$. In this example, one can see that the whole protocol, including both the main and control experiments, were reduced to one single condition: $|P^{(3)}(t)| \neq 0$. 

Violations of the LGI for the multichromophoric systems were found theoretically in Ref. [25], where projective measurements in the site-basis were employed. However, as pointed out by the authors, such measurements are not realistic when it comes to experimental implementations. Our proposal aims to bridge this gap by linking nonclassicality tests to experimental techniques in a direct and fundamental way. Additionally, given that our work investigate quantum invasiveness in driven systems [26], it deals with setups which are not conventionally considered in Leggett-Garg scenarios. At the same time, by proposing sound protocols which employ well-established experimental techniques such as electronic spectroscopy, we expect that the present work will pave the way for new and exciting experimental investigations in quantum biology and quantum technologies that rely on time-dependent Hamiltonians.

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