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Inter-state coupling and definitions of bright and dark states

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Abstract

Contrary to a standard definition of diabatic states (i.e., those without momentum-dependent coupling), based on the construction from adiabatic ones, we defined diabatic states as bright and dark states of a given experiment. Namely, they are defined as states providing maximum, respectively, zero value of electronic transition dipole moments projected to a given polarization vector. Second, the state from (or to) which the optical transition is performed is not from the space of investigated electronic excited state manifold, but it is chosen by the observer. It is shown, for this case, that the inter-state coupling is a general function of vibrational coordinates. The explicit dependence of the inter-state coupling on vibrational coordinates is particularly important for system with strong Stokes shift. The role of exact definitions of bright and dark states as well as the inter-state coupling is discussed with respect to the coherent structure of electronic population observed in optical spectroscopy.

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1. Introduction

It has been shown recently [1,2] that the amplitude and frequency of Rabi oscillations of the time-dependent population of excited state are very sensitive to a form of inter-state coupling between excited state and other states in the electronic states manifold (ground state and higher excited states). A model with a constant value of inter-state coupling with respect to vibrational coordinates provides a significantly different pattern of electronic and vibrational coherence in the electronic population than the model, where the inter-state coupling is linearly (or quadraticaly) dependent on a vibrational coordinates [1,2]. Namely, for the case of linear or quadratic dependence of the inter-state coupling on vibrational coordinate, the Rabi oscillations exhibit a more pronounced vibrational modulation. This means that vibrational dependence of the inter-state coupling should be taken into account when experimental data are simulated theoretically. Pisliakov et al. [3] calculated theoretically the spectra of time- and frequency-gated spontaneous emission of an electron-transfer (ET) system. They assumed the model of donor–acceptor system consisting of two excited diabatic states with constant inter-state coupling. The first state corresponded to the donor excited state and it was assumed to be optically bright. The second state, corresponding to the acceptor state, was assumed to be optically dark. Authors of Ref. [3] concluded that obtained theoretical simulations were not observed, at least to their knowledge, to be in a quantitative agreement with any experiment. Namely, the structure of Rabi oscillations caused by the time dependence of the population of the bright excited state was not found in known time-resolved luminescence signals. In our work the possible explanation of these discrepancies is outlined. It is shown, that both the choice of the dark and bright states as well as definitions of the form of inter-state coupling are formally independent and they correspond to different choice of the basis of diabatic states. One of the physical consequences is that whenever we assume a certain

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form of the inter-state coupling, it corresponds to a fixed definition of diabatic states. This diabatic basis can provide, in general, arbitrary values of elements of transition dipole moments and we couldn't say definitely that some states are bright and others are dark. On the other hand, when the diabatic states are defined as bright and dark states of experiment we can obtain a quite general dependence of the inter-state coupling on vibrational coordinates. In what follows, if a concrete optical experiment is modeled theoretically, the bright and dark states should be defined with respect to this experiment, and the form of inter-state coupling of bright and dark states should be chosen accordingly. It is shown analytically, that the standard assumption of a constant inter-state coupling yields very unstable solutions for systems with large Stokes shift, which is the typical case for, e.g., charge transfer-complexes [4].

The paper is organized as follows. In Section 2 an alternative definition of diabatic basis of bright and dark states is defined from the transition dipole moments projected to a given polarization vector. Connection of such a non-standard approach to the experiments of the pump-probe category is outlined in brief. In Section 3 the transformation from the diabatic basis with constant inter-state coupling to the bright-dark basis is discussed. In Section 4 the diabatic basis corresponding to the vertical excitation is discussed with respect to the adiabatic transition dipole moments and other optical experiments (IR, Raman, luminescence, vibrational side-bands) where these adiabatic transition dipole moments are relevant.

2. From arbitrary diabatic states to bright and dark states

The time- and frequency-gated spectroscopy (time up-conversion technique) may be under condition of sufficiently short pulses described as a sequence of several steps: first, the molecular system is excited with a laser pump pulse; second, the excited molecules spontaneously emit light; third, the emitted light is mixed with a coherent gate pulse with exactly defined time delay t with respect to the pump pulse. The mixed signal is analyzed. It can be proved analytically in the limit of sufficiently short gate pulses that for coupled two-level system consisting of bright and dark states the frequency-integrated signal corresponds to the occupation probability of the bright state. In what follows, the initial excitation is dependent on the polarization of the pump pulse. For different orientations of molecules the different hot initial excitation conditions are obtained. In the same way, the analysis of the collected signal is also dependent on the polarization vector. Hence, the total signal is dependent on the statistical averaging of the orientation of molecules and on directions of polarization vectors during the pump and the reading process.

In this paragraph we show, how to construct the optically bright and dark states from arbitrarily selected basis of diabatic states. Let $\left|f\right\rangle$ be a state, from (or to) which the optical transition is performed and $\{\varphi_i\}_{i=1}^{N}$ denotes the orthonormal basis of diabatic states, which are involved in the dynamics of initially excited system. These states are determined by the experimental conditions. For example, in the case of time- and frequency-gated spontaneous emission, $\left|f\right\rangle$ is the ground state. Dimension N of the Hilbert subspace formed by states $\{\varphi_i\}_{i=1}^{N}$ is given by states, which are either optically coupled to the initial electronic state during the pump pulse or by the number of states coupled non-adiabatically during the excited state dynamics [5–7]. Then, the bright state $\left|\psi_1\right\rangle$ is defined in the following way

$$\left|\psi_1\right\rangle = \frac{\sum_{i=1}^{N}\left|\varphi_i\right\rangle\left\langle\varphi_i\right|(\vec{d}.\vec{e})\left|f\right\rangle}{\sqrt{\sum_{i=1}^{N}\left|\left\langle f\right|(\vec{d}.\vec{e})\left|\varphi_i\right\rangle\right|^2}}, \tag{1}$$

where $\vec{d}$ is the operator of dipole moment and $\vec{e}$ is the vector of polarization. It can be also seen directly that any arbitrary vector $|X\rangle$ taken from the Hilbert space that is spanned onto states $\{\varphi_i\}_{i=1}^{N}$ and, simultaneously, orthogonal to $\left|\psi_1\right\rangle$, i.e., when the vector $|X\rangle$ satisfies the condition $\left\langle X|\psi_1\right\rangle = 0$, it automatically satisfies also the relation

$$\langle X|(\vec{d}.\vec{e})\left|f\right\rangle = 0. \tag{2}$$

In other words, it behaves as optically dark in the experiment. The dimension of the space of dark states is $N-1$. For $N=2$, as it is discussed below, we get also unambiguous definition of dark state. For higher values of N we have a partial freedom of the choice of unitary transformation, which can be related to the suitable choice of the elements of the potential energy matrix U in a new basis.

For the case of non-orthogonal basis we define $\left|\psi_1\right\rangle$ as

$$\left|\psi_1\right\rangle = \frac{P_e(\vec{d}.\vec{e})\left|f\right\rangle}{\sqrt{\left\langle f\right|(\vec{d}.\vec{e})P_e(\vec{d}.\vec{e})\left|f\right\rangle}}, \tag{3}$$

where P_e is the projector onto the Hilbert subspace of relevant electronic states. Non-orthogonality of original diabatic states can be found, e.g., if these states are defined from the adiabatic states of a given potential energy surfaces (PES), corresponding to different nuclear coordinates (e.g., local minima on adiabatic PES). Number of coupled diabatic states, which should be taken into account, is exactly equal to the number of coupled adiabatic PESs [5–7].

For the sake of clarity let's study a simple model with a basis of three orthonormal diabatic states consisting of a ground state $\left|g\right\rangle$ and two excited states $\left|\varphi_1\right\rangle$ and $\left|\varphi_2\right\rangle$. The transition dipole moments of diabatic states, projected to a vector of polarization $\vec{e}$, are given as follows:

$$\left\langle g\right|\vec{d}.\vec{e}\left|\varphi_1\right\rangle = d_{g1}, \tag{4}$$

$$\left\langle g\right|\vec{d}.\vec{e}\left|\varphi_2\right\rangle = d_{g2}. \tag{5}$$