Updated Derivation of Second Order Response to Arbitrary Light*

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We derive the general form of the reduced statistical operator describing the excited state of a molecular system driven by an arbitrary (classical) light as discussed in T. Mančal and L. Valkunas, New J. Phys. 12 (2010) 65044.

We consider a general molecular system in interaction with its environment

$$H_0 = H_S + H_B + H_{S-B} \tag{1}$$

and subject to the influence of an external optical field through the interaction Hamiltonian

$$H_I = -\hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{E}}(t). \tag{2}$$

Here, we assume that we already work in the interaction picture with respect to the light Hamiltonian, and the operator $\hat{\boldsymbol{E}}$ is therefore time-dependent. We assume that the interaction between the light and the system is non-entangling, which is well satisfied by the coherent light of the laser and by the black body radiation. For this reason, the combined state of the system (including the environment) and light can be written in terms of a product of their respective state vectors

$$|\psi(t)\rangle = |\phi(t)\rangle|\Xi(t)\rangle, \tag{3}$$

where $|\phi(t)\rangle$ is the state of the molecular system and its environment, and $|\Xi(t)\rangle$ is the state of light.

The state $|\psi(t)\rangle$ satisfies the Schrödinger equation

$$\frac{\partial}{\partial t}|\psi(t)\rangle = -\frac{i}{\hbar}\left(H_0 - \hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{E}}(t)\right)|\psi(t)\rangle. \tag{4}$$

Solving this equation to the first order in $\hat{\boldsymbol{E}}$ we obtain

$$|\psi(t)\rangle = U_0(t)|\psi(0)\rangle - \frac{i}{\hbar}\int\limits_0^t \mathrm{d}\tau\, U_0(t-\tau)\hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{E}}(\tau)|\psi(0)\rangle, \tag{5}$$

where we assume that the initial condition for the system state at $t = 0$ reads as $|\psi(0)\rangle = |\psi_{B,\mathrm{eq}}\rangle|g\rangle$, where $|g\rangle$ is the electronic ground state of the molecular system and $|\psi_{B,\mathrm{eq}}\rangle$ is the equilibrium bath state relative to $|g\rangle$. This state effectively does not evolve under $U_0(t)$.

Now, we will construct the statistical operator $\hat{W}_e(t)$ corresponding to the excited state manifold of the singly excited molecular states. We define a projection operator $\hat{P}_e = \sum_n |n\rangle\langle n|$, where the states $|n\rangle$ represent all the electronic states of the system that can be reached by optical excitation from the ground state $|g\rangle$, and all the states that can be reached by non-radiative processes from them (excluding the ground state). We have

$$\hat{W}_e(t) = \hat{P}_e\langle\Xi(t)|\psi(t)\rangle\langle\psi(t)|\Xi(t)\rangle\hat{P}_e. \tag{6}$$

Here, we also average over the state of the light. The statistical operator $\hat{W}_e(t)$, which describes the system in the excited state and its environment, reads as

$$\hat{W}_e(t) = -\frac{1}{\hbar^2}\int\limits_0^t \mathrm{d}\tau' \int\limits_0^t \mathrm{d}\tau U_0(t-\tau')\hat{\mu}|g\rangle$$
$$\times \hat{w}_{eq}\langle g|\hat{\mu}U_0^\dagger(t-\tau)\langle\hat{E}(t-\tau')\hat{E}(t-\tau)\rangle \tag{7}$$

The excited state reduced density matrix describing the electronic excited state dynamics of the system is obtained by tracing over the bath

$$\hat{\rho}_e(t) = \mathrm{tr}_B\{\hat{W}_e(t)\}. \tag{8}$$

Applying the trace over the bath to Eq. (7) we get

$$\hat{\rho}_e(t) = -\frac{1}{\hbar^2}\int\limits_0^t \mathrm{d}\tau' \int\limits_0^{\tau'} \mathrm{d}\tau\ \mathrm{tr}_B\{U_0(t-\tau')\hat{\mu}|g\rangle\hat{w}_{\mathrm{eq}}$$
$$\times\langle g|\hat{\mu}U_0^\dagger(t-\tau'+\tau)\}G_E(t-\tau', t-\tau'+\tau) + \text{h.c.}.$$

Here, $G_E(t-\tau', t-\tau'+\tau)$ is the two-point field correlation function of quantum optics (up to a normalization)

$$G_E(t-\tau', t-\tau'+\tau) = \langle\hat{E}(t-\tau')\hat{E}(t-\tau'+\tau)\rangle.$$

The operator

$$\hat{R}(\tau'', \tau) = \mathrm{tr}_B\{U_0(\tau'')\hat{\mu}|g\rangle\hat{w}_{\mathrm{eq}}\langle g|\hat{\mu}U_0^\dagger(\tau''+\tau)\}, \tag{9}$$

has matrix elements

$$R_{ab}(\tau'', \tau) = d_{gc}d_{dg}$$
$$\times\sum_{cd}\mathrm{tr}_B\{\langle c|U_0^\dagger(\tau''+\tau)|b\rangle\langle a|U_0(\tau'')|d\rangle\hat{w}_{\mathrm{eq}}\}. \tag{10}$$

These elements can be recognized as consisting of the first two intervals of the third-order response functions that form the signal measured in the third-order non-linear spectroscopies. If the non-linear response interval times are denoted by t_1, t_2 and t_3 (the so-called coherence time,

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[*] This is supporting information for my Nobel Symposium Poster

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waiting time and the second coherence time), than the $\hat{R}$ operator can be obtained from the (ideal) measured response at $t_1 = \tau$ and $t_2 = \tau''$ and $t_3 = 0$. If a 2D electronic spectrum $S(\omega_3, t_2, t_1)$ represented in the time domain is measured (with ideal ultrashort pulses), the second order response is related to its integral over the detection frequency ω_3, i.e.

$$\hat{R}(t_2, t_1) \approx \int\limits_{-\infty}^{\infty} \mathrm{d}\omega_3 \; S(\omega_3, t_2, t_1). \tag{11}$$

Theoretically, a system's driven second-order excited state can be calculated from the same ingredients as the time-resolved spectra. How to do this directly from the experimental spectrum is a subject of ongoing research.