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Consistent-histories and dipolar-basis representation of nonlinear response functions

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By expanding optical response functions in the eigenstates of the dipole operator (rather than of the Hamiltonian), we obtain a path-integral representation that lends itself more readily to classical simulations. Connection is made to stochastic (consistent-histories) theories of quantum dynamics of single quantum systems by computing the entire probability distribution of the observed polarization (rather than merely its expectation value). The weight of each Liouville space path contributing to the optical response is complex, and cannot be recast using the joint probabilities used in the consistent-histories approach.

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I. INTRODUCTION

The key quantity in nonlinear spectroscopy is the nonlinear response function $R^{(n)}$ that carries all the relevant molecular information for the interpretation of the signals [1–3]. $R^{(n)}$ is defined by

$$P^{(n)}(\tau_n)=\int_{-\infty}^{\tau_n}d\tau_{n-1}\ldots\int_{-\infty}^{\tau_1}d\tau_0 \times R^{(n)}(\tau_n\ldots\tau_0)E(\tau_{n-1})\ldots E(\tau_0), \qquad (1)$$

where $E(\tau)$ is the external field and $P^{(n)}(\tau_n)$ is the nth-order polarization at time τ_n.

Denoting the coupling of the system to the radiation field by $-\hat{V}E(t)$, $\hat{V}$ being the dipole operator, we have

$$R^{(n)}(\tau_n\ldots\tau_0) =\left(\frac{i}{\hbar}\right)^n\langle\hat{V}(\tau_n)[\hat{V}(\tau_{n-1}),\ldots,[\hat{V}(\tau_1),[\hat{V}(\tau_0),\rho^{eq}]]\ldots]\rangle, \qquad (2)$$

where ρ^{eq} is the equilibrium density matrix. $R^{(n)}$ is thus expressed as a combination of 2^n correlation functions (Liouville space pathways), each representing a sequence of couplings. For a multilevel system $R^{(n)}$ is usually expanded in the eigenstates of the free Hamiltonian H. Each path then consists of n periods of free evolution separated by $n+1$ couplings $\hat{V}$, which change the state of the system. Such expressions for the lowest three-order response functions are given, e.g., in Eqs. (6.17)–(6.19) of Ref. [2]

In this Rapid Communication we explore an alternative physical picture obtained by expanding $R^{(n)}$ in a different basis: the eigenstates of $\hat{V}$. We show that it is then possible to recast it in a path-integral form in Hilbert space, and discuss the connection with the consistent-history interpretation of quantum dynamics [4–7].

II. DIPOLAR-EIGENSTATE REPRESENTATION OF OPTICAL RESPONSE

Introducing the eigenstates $|\alpha_j\rangle$ and eigenvalues V_{α_j} of the dipole operator, we obtain

$$\hat{V}=\sum_{\alpha_j}|\alpha_j\rangle V_{\alpha j}\langle\alpha_j|. \qquad (3)$$

By expanding $\hat{V}(\tau_n)$ in Eq. (2) using Eq. (3), we obtain

$$P^{(n)}(\tau_n)=\sum_{\alpha_n}V_{\alpha_n}\rho^{(n)}_{\alpha_n\alpha_n}(\tau_n),\quad n=1,2,\ldots, \qquad (4)$$

where

$$\rho^{(n)}_{\alpha_n\alpha_n}(\tau_n)=\sum_{\alpha_0,\ldots,\alpha_{n-1}}V_{\alpha_0}\cdots V_{\alpha_{n-1}} \times\int_{-\infty}^{\tau_n}d\tau_{n-1}\int_{-\infty}^{\tau_{n-1}}d\tau_{n-2}\cdots\int_{-\infty}^{\tau_1}d\tau_0 \times K^{(n)}(\tau_n\ldots\tau_0;\alpha_n\ldots\alpha_0) \times E(\tau_{n-1})\cdots E(\tau_0), \qquad (5)$$

with

$$K^{(n)}(\tau_n\ldots\tau_0,\alpha_n\ldots\alpha_0)=\left(\frac{i}{\hbar}\right)^n\langle\alpha_n(\tau_n)|[\hat{V}_{\alpha_{n-1}}(\tau_{n-1}),\ldots[\hat{V}_{\alpha_1}(\tau_1),[\hat{V}_{\alpha_0}(\tau_0),\rho_{eq}]]\ldots]|\alpha_n(\tau_n)\rangle] \qquad (6)$$

Here $\hat{V}_{\alpha_j}\equiv|\alpha_j\rangle\langle\alpha_j|$, $\hat{V}_{\alpha_j}(\tau)=\exp(iH\tau)\hat{V}_{\alpha_j}\exp(-iH\tau)$ and $\alpha_n(\tau_n)=\exp(-iH\tau_n)|\alpha_n(0)\rangle$. $\rho^{(n)}_{\alpha_n\alpha_n}(\tau_n)$ is the probability of observing the value α_n of the polarization when measured at time τ_n. Note that the equilibrium density matrix is normalized to have a unit trace $\Sigma_{\alpha_n}\rho^{eq}_{\alpha_n\alpha_n}=1$, whereas $\rho^{(n)}$ has a zero trace $\Sigma_{\alpha_n}\rho^{(n)}_{\alpha_n\alpha_n}=0$, $n=1,2,\ldots$.

$K^{(n)}$ has 2^n independent terms known as Liouville-space pathways. Bulk measurements only yield the expectation

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value of the polarization $P^{(n)}$, and are adequately described by the ordinary response function $R^{(n)}$. However, measurements conducted on a single molecule (or a few molecules) may yield the entire probability distribution $\rho_{\alpha_n\alpha_n}$ of observing the value α_n, which is a more detailed quantity [8].

Equation (5) assumes the form of a classical average over all possible realizations V_{α_n} of the dipole operator. For the linear response $(n=1)$ we have

$$K^{(1)}(\tau_1\tau_0;\alpha_1\alpha_0)=\frac{i}{\hbar}\langle\hat{V}_{\alpha_1}(\tau_1)\hat{V}_{\alpha_0}(\tau_0)\rangle+\text{c.c.}, \qquad (7)$$

This can be recast in the form

$$K^{(1)}(\tau_1\tau_0;\alpha_1\alpha_0)=\frac{i}{\hbar}\sum_{\alpha_2} G_{\alpha_1\alpha_0}(\tau_{10})G^{\dagger}_{\alpha_0\alpha_2}(\tau_{10})\rho^{eq}_{\alpha_2\alpha_1}+\text{c.c.}, \qquad (8)$$

where we have defined $\tau_{jk}\equiv\tau_j-\tau_k$, and the Green function is given by

$$G_{\alpha_j\alpha_k}(\tau)\equiv\langle\alpha_j|\exp(-iH\tau)|\alpha_k\rangle. \qquad (9)$$

Equations (4), (5), and (8)show that $P^{(1)}$ involves a triple sum over α_0, α_1, and α_2. Each choice of α_0, α_1, and α_2 represents a path in the dipole-eigenstate space and the summations can viewed as a path integral. $G_{\alpha_j\alpha_k}$ represents a conditional amplitude of going from α_k to α_j. Even though it is not a probability, the statistical weight of a given path is given by a product of two Green functions and ρ^{eq}.

Using the eigenstates $|\kappa\rangle$ of the Hamiltonian we have

$$G_{\alpha_j\alpha_k}(\tau)=\sum_{\kappa}\langle\alpha_j|\kappa\rangle\langle\kappa|\alpha_k\rangle\exp(-i\varepsilon_{\kappa}\tau). \qquad (10)$$

The higher-order response functions depend on the same ingredients. For the second-order response, we have

$$K^{(2)}(\tau_2,\tau_1\tau_0;\alpha_2\alpha_1\alpha_0)=\left(\frac{i}{\hbar}\right)^2[\langle\hat{V}_{\alpha_2}(\tau_2)\hat{V}_{\alpha_1}(\tau_1)\hat{V}_{\alpha\_0}(\tau_0)\rangle$$
$$-\langle\hat{V}_{\alpha_1}(\tau_1)\hat{V}_{\alpha_2}(\tau_2)\hat{V}_{\alpha_0}(\tau_0)\rangle]$$
$$+\text{c.c.} \qquad (11)$$

Using the Green functions, this assumes the form

$$K^{(2)}(\tau_2,\tau_1\tau_0;\alpha_2\alpha_1\alpha_0)$$
$$=\left(\frac{i}{\hbar}\right)^2\sum_{\alpha_3}[G_{\alpha_2\alpha_1}(\tau_{21})G_{\alpha_1\alpha_0}(\tau_{20})G^{\dagger}_{\alpha_0\alpha_3}(\tau_{20})\rho^{eq}_{\alpha_3\alpha_2}$$
$$-G^{\dagger}_{\alpha_1\alpha_2}(\tau_{21})G_{\alpha_2\alpha_0}(\tau_{10})G^{\dagger}_{\alpha_0\alpha_3}(\tau_{10})\rho^{eq}_{\alpha_3\alpha_1}]+\text{c.c.} \qquad (12)$$

For the third-order response, which represents four-wave-mixing processes, we get

$$K^{(3)}(\tau_3\tau_2,\tau_1\tau_0;\alpha_3\alpha_2\alpha_1\alpha_0)$$
$$=\left(\frac{i}{\hbar}\right)^3[\langle\hat{V}_{\alpha_1}(\tau_1)\hat{V}_{\alpha_2}(\tau_2)\hat{V}_{\alpha_3(\tau_3)\hat{V}_{\alpha_0}(\tau_0)}\rangle$$
$$+\langle\hat{V}_{\alpha_0}(\tau_0)\hat{V}_{\alpha_2}(\tau_2)\hat{V}_{\alpha_3}(\tau_3)\hat{V}_{\alpha_1}(\tau_1)\rangle$$
$$+\langle\hat{V}_{\alpha_0}(\tau_0)\hat{V}_{\alpha_1}(\tau_1)\hat{V}_{\alpha_3}(\tau_3)\hat{V}_{\alpha_2}(\tau_2)\rangle$$
$$+\langle\hat{V}_{\alpha_3}(\tau_3)\hat{V}_{\alpha_2}(\tau_2)\hat{V}_{\alpha_1}(\tau_1)\hat{V}_{\alpha_0}(\tau_0)\rangle]+\text{c.c.},(13)$$

which gives

$$K^{(3)}(\tau_3\tau_2,\tau_1\tau_0;\alpha_3\alpha_2\alpha_1\alpha_0)=\left(\frac{i}{\hbar}\right)^3\sum_{\alpha_4}[G^{\dagger}_{\alpha_1\alpha_2}(\tau_{21})G^{\dagger}_{\alpha_2\alpha_3}(\tau_{32})G_{\alpha_3\alpha_0}(\tau_{30})G^{\dagger}_{\alpha_0\alpha_4}(\tau_{10})\rho^{eq}_{\alpha_4\alpha_1}$$
$$+G^{\dagger}_{\alpha_0\alpha_2}(\tau_{20})G^{\dagger}_{\alpha_2\alpha_3}(\tau_{32})G_{\alpha_3\alpha_1}(\tau_{31})G^{\dagger}_{\alpha_1\alpha_4}(\tau_{10})\rho^{eq}_{\alpha_4\alpha_0}$$
$$+G^{\dagger}_{\alpha_0\alpha_1}(\tau_{10})G^{\dagger}_{\alpha_1\alpha_3}(\tau_{31})G_{\alpha_3\alpha_2}(\tau_{32})G^{\dagger}_{\alpha_2\alpha_4}(\tau_{20})\rho^{eq}_{\alpha_4\alpha_0}$$
$$+G^{\dagger}_{\alpha_3\alpha_2}(\tau_{32})G^{\dagger}_{\alpha_2\alpha_1}(\tau_{21})G_{\alpha_1\alpha_0}(\tau_{10})G^{\dagger}_{\alpha_0\alpha_4}(\tau_{30})\rho^{eq}_{\alpha_4\alpha_3}]+\text{c.c.} \qquad (14)$$

Generally the products in Eqs. (8), (12), and (14) should be averaged over all other (e.g., nuclear) degrees of freedom to which the system may be coupled.

III. DISCUSSION

To discuss the physical significance of the dipolar representation of the response function, we recast it in the form

$$P^{(n)}(\tau_n)=\sum_{\alpha_0\cdots\alpha_n}V_{\alpha_0}V_{\alpha_1}\cdots V_{\alpha_n}$$
$$\times\int_{-\infty}^{\tau_n}d\tau_{n-1}\int_{-\infty}^{\tau_{n-1}}d\tau_{n-2}\cdots\int_{-\infty}^{\tau_1}d\tau_0K^{(n)}(\tau_n\ldots\tau_0;\alpha_n\ldots\alpha_0)E(\tau_{n-1})\cdots E(\tau_0). \qquad (15)$$

This has the appearance of a classical stochastic average over $n+1$ measurements of a random variable V. However, this impression is misleading. To see that, let us consider a sequence of $n+1$ measurements of the dipole, carried out at times $\tau_0 \ldots \tau_n$ and resulting in the values $\alpha_0, \ldots, \alpha_n$, respectively. The probability for this sequence (''history'') is [4–7]

$$\begin{aligned} W^{(n+1)}(\alpha_0 \ldots \alpha_n ; \tau_0 \ldots \tau_n) &= |G_{\alpha_n \alpha_{n-1}}(\tau_n - \tau_{n-1})|^2 \ldots |G_{\alpha_2 \alpha_1}(\tau_2 - \tau_1)|^2 \\ &\times |G_{\alpha_1 \alpha_0}(\tau_1 - \tau_0)|^2 \rho^{eq}_{\alpha_0 \alpha_0}. \end{aligned} \tag{16}$$

We shall now compare $W^{(n+1)}$ with $K^{(n)}$. $W^{(n+1)}$ has all the properties of a classical joint probability distribution. It is the basic quantity in the consistent history description of quantum dynamics. At each time τ_j the system is in the state $|\alpha_j\rangle$ and its density matrix is $|\alpha_j\rangle\langle\alpha_j| j=0, \ldots, n$. In contrast, in $K^{(n)}$ we measure the dipole only at the last time τ_n and find the value α_n. At the earlier times $\tau_j (j=0, \ldots, n-1)$ we only pass through α_j at time τ_j, but the density matrix could be either $|\alpha_j\rangle\langle\alpha_k|$ or $|\alpha_k\rangle\langle\alpha_j|$ with $k \neq j$. $K^{(n)}$ is thus a pseudo-joint-probability. Other notable differences are that W depends only on diagonal elements $\rho^{eq}_{\alpha_0 \alpha_0}$, whereas K only depends on off-diagonal elements $\rho^{eq}_{\alpha_1 \alpha_2}$ (diagonal elements do not contribute). In addition, W only depends on $|G|^2$ (which is real), whereas K depends on G itself, which is a complex quantity.

Both W and K are real but have different normalizations. For a fixed choice of $\tau_0 \ldots \tau_n$, $W^{(n+1)}$ is normalized as $\Sigma_{(\alpha_0 \ldots \alpha_n)} W^{(n+1)}(\alpha_0 \ldots \alpha_n ; \tau_0 \ldots \tau_n) = 1$, whereas K represents the deviation of the density matrix from equilibrium and has a zero trace $\Sigma_{(\alpha_0 \ldots \alpha_n)} K^{(n)}(\tau_n \ldots \tau_0 ; \alpha_n \ldots \alpha_0) = 0$.

The dipole-eigenstates representation of $K^{(n)}$ provides a path-integral picture that could be used in semiclassical numerical simulations [9]. It is interesting to note that, even though the response functions (and $K^{(n)}$) are experimental observables that may be obtained by using carefully timed and tuned pulses, they may not be represented by the joint probability $W^{(n+1)}$ used to describe conventional measurements in the consistent-histories approach. $W^{(n+1)}$ does not carry enough information for representing this type of observables.

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