Measurement-driven reconstruction of many-particle quantum processes by semidefinite programming with application to photosynthetic light harvesting

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Quantum measurements provide a trove of information about a quantum system or process without solution of the Schrödnger equation, and in principle, the associated density matrix is a function of these measurements. Inversion of the measurements can produce an estimate of the density matrix, but this estimate may be unphysical, especially when the measurements are noisy or incomplete. We develop a general approach based on semidefinite programming [D. A. Mazziotti, Phys. Rev. Lett. **106**, 083001 (2011)] for reconstructing the density matrix from quantum measurements which leads naturally to nonnegative solutions, a critical attribute of physically realistic solutions. We discuss the use of this methodology for reconstructing p-particle reduced density matrices (p-RDMs) of N-particle systems where additional semidefinite constraints, known as N-representability conditions, are essential because they ensure that the p-RDM represents an N-particle system. Special attention is given to the N-representability conditions for the experimentally important cases where $p = 1$ or 2. We apply the methodology to reconstructing the time-dependent quantum process of exciton transfer in a photosynthetic light-harvesting complex.

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I. INTRODUCTION

The density matrix encodes probability information about the expected outcome of observations made on a quantum system. Direct calculation of the density matrix by solving the Schrödinger equation is challenging because the dimension of the matrix grows factorially with the system size. Experimental measurement has the ability to provide rich information about a quantum system by accessing only one- and two-particle observables, which provide direct information about the one- and two-particle reduced density matrices (1- and 2-RDMs). The p-particle RDM (p-RDM) can be formally defined from the integration of the N-particle density matrix:

$$ {}^pD(1\cdots p;\bar{1}\cdots\bar{p}) = \int {}^ND(1\cdots N;\bar{1}\cdots N)d(p+1)\cdots dN, \quad (1) $$

where each Arabic number denotes the spin and spatial coordinates of an electron [1,2]. In this study we combine advances in reduced-density-matrix theory [3–13] and semidefinite programming [7,12,14,15] to develop a measurement-driven reconstruction of many-particle quantum processes. We broadly define *quantum-state reconstruction* (QSR) as the reconstruction of the static p-RDM from experimental data and *quantum-process reconstruction* (QPR) as reconstruction of the time-dependent p-RDM from experimental data. Quantum-process reconstruction has important connections to quantum control and inversion [16–18], matrix completion [19,20], and quantum-process tomography (QPT) [21–29]. A wide range of inversion techniques from the area of data reconstruction [19–21] are available to aid the study of quantum processes from quantum measurements, but these techniques do not address the specific challenges of reconstructing reduced density matrices.

Reconstruction from experimental data of the p-RDM of an N-particle system where $p < N$ faces two interwoven challenges: (i) the experimental data may be incomplete or corrupted, and (ii) the p-RDM may not represent the N-particle system. If the data are corrupted or limited in fidelity, the p-RDM estimate may violate necessary physical conditions [21,22]. A p-RDM determined from one- to p-particle observables rather than from the integration of the N-particle density matrix must satisfy certain conditions to guarantee it represents the N-particle system. An RDM must obey fundamental properties shared by any density matrix: it must be (i) Hermitian, (ii) normalized, (iii) symmetric (bosons) or antisymmetric (fermions) upon particle exchange, and (iv) positive semidefinite [30]. A matrix is *positive semidefinite* if and only if all of its eigenvalues are greater than or equal to zero. However, a p-RDM must obey additional constraints, known as *N-representability conditions* [1–5,8–11,13,30–33], to ensure that it represents a physically realistic N-particle system.

The reconstruction of the N-particle density matrix from noisy or incomplete experimental data, we show in Sec. II A, can be expressed as a multiobjective optimization problem in which the density matrix's deviations from experimental data and smoothness in time are jointly minimized while it is constrained at each time to be positive semidefinite. Section II B formulates the direct reconstruction of p-RDMs for $p \leqslant 2$ without the N-particle density matrix through the use of N-representability constraints. Necessary N-representability conditions can be cast in the form of restricting multiple matrix forms of the p-RDM to be positive semidefinite [33]. The N-representability conditions for the fermionic 1-RDM, for example, require that the one-particle and one-hole RDM are positive semidefinite. The precise N-representability conditions depend upon whether the N particles are bosons or fermions [34]. Here we assume that the particles are fermions, but the basic ideas can also be applied when the particles are bosons.

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In Sec. II C the reconstruction problem for the 1- and 2-RDMs constrained by physically important N-representability conditions is recast as a *semidefinite program* whose solution is known as *semidefinite programming* [14,15]. A semidefinite program is a special type of constrained optimization in which a linear function of a matrix is minimized subject to linear constraints on the matrix elements and the restriction that the matrix be positive semidefinite. Semidefinite programming generalizes the well-known family of linear programming by replacing linear scalar inequalities with linear matrix inequalities. Recently, first-order techniques have emerged for performing semidefinite programming [7,12,35–38] efficiently for large systems. We employ algorithms that were developed by one of the authors in the context of computing the ground-state energy of many-electron quantum systems as a direct functional of the 2-RDM [7,12,38]. In this work semidefinite programming serves as a computational engine for forcing N-representability conditions on the 1- or 2-RDM in the face of incomplete and corrupt data.

The observation of long-lived coherence in photosynthetic light-harvesting complexes suggests that the energy-transfer dynamics in these complexes is fundamentally quantum mechanical. The investigation of energy transfer as a *quantum process* has been the subject of extensive theoretical and experimental effort [39–51]. As an illustration of the present tomography method, the time-dependent 1-RDM for the energy-transfer dynamics in a model photosynthetic complex is reconstructed from corrupted and incomplete data (see Sec. III). Reconstruction with N-representability constraints and regularization is capable of improving the accuracy of the 1-RDM estimate by approximately two orders of magnitude relative to the error from a least-squares fit to the data. Furthermore, we show that reconstruction at the same level of accuracy is achievable from incomplete measurements.

II. THEORY

A general theory for reconstruction of the N-particle density matrix from quantum measurements is developed in the first section. Because building the complete density matrix for an N-particle system is both computationally and experimentally difficult, we reformulate the theory in terms of 1- or 2-RDMs constrained by representability conditions in Sec. II B. In Sec. II C we discuss expressing the reconstruction as a semidefinite program that can be solved in polynomial time using efficient recently developed algorithms [7,12]. Finally, a theoretical model for the exciton-transfer dynamics in a photosynthetic light-harvesting complex is described in Sec. II D. In Sec. III this model is employed to test the reconstruction of RDMs from noisy and/or incomplete data.

A. Quantum-process reconstruction

Full information of the time evolution of an N-particle quantum system is given by the N-particle density matrix $D(t)$. The expectation value of any observable at time t for the quantum system is a linear functional of the density matrix,

$$\langle \hat{A} \rangle_t = \mathrm{Tr}[\hat{A}\, D(t)], \tag{2}$$

which is to say that observable outcomes provide a linear map to the density matrix. The results of a measurement can be seen as providing a set of linear constraints on the density matrix, and the elements of the density matrix can be found by minimizing

$$\epsilon_i = \left(\left| \int_{t_i}^{t_f} \{\mathrm{Tr}[\hat{A}_i(t)\, D(t)] - b_i(t)\}\, dt \right|^2 \right)^{\frac{1}{2}}, \tag{3}$$

where b_i is the ith measurement outcome and ϵ_i is the magnitude of the ith residual. The details of performing optimal measurements for QPT are beyond the scope of this work, but they have been discussed for a variety of physical systems [22,24,25,52–55]. Because minimization of Eq. (3) is accomplished by linear least-squares inversion (see, for example, Ref. [21]), a density-matrix estimate from minimizing Eq. (3) will be denoted D_{LS}.

Estimating the density matrix in this manner faces the following obstacles: (i) the measured data set may be *corrupted* so that there is error associated with each density-matrix element, that is,

$$D_{\mathrm{LS}}(t) = D(t) + f(\sigma), \tag{4}$$

where $f(\sigma)$ represents error with a standard deviation of σ that arises from imperfect measurements, and (ii) the set of measurements $\{b_i\}$ may not provide sufficient information to estimate every element of the density matrix, and hence, D_{LS} may be *incomplete*. The challenge addressed in this work is to reconstruct the true density matrix as accurately as possible from quantum measurements that may be corrupted and incomplete. In practice, the starting point may be experimental information, whereby the objective is to minimize Eq. (3) directly from a set of corrupted and incomplete measurements, or the starting point may be a prior quantum-state estimate (i.e., a density matrix) which may itself be corrupted and incomplete.

Any physically realistic solution to the reconstruction problem must satisfy conditions of a density matrix [56]. Furthermore, physically realistic solutions should be continuously differentiable in time. Because straightforward minimization of Eq. (3) often leads to a matrix D_{LS} which violates properties requisite of a physical density matrix, the attempt to reconstruct D from experimental data should seek to find the matrix that minimizes Eq. (3) while constrained to be normalized, Hermitian, antisymmetric (fermions) in particle exchange, positive semidefinite, and continuously differentiable in time. We demonstrate in Sec. II C that these conditions may be enforced through semidefinite programming (SDP), and thus, the density matrix that is reconstructed with these conditions will be denoted D_{SDP}. We define the matrices E and R as

$$E(t) = D_{\mathrm{SDP}}(t) - D_{\mathrm{LS}}(t), \tag{5}$$

$$R(t) = D_{\mathrm{SDP}}(t+1) - D_{\mathrm{SDP}}(t), \tag{6}$$

where E measures the error between the reconstructed SDP density matrix D_{SDP} and the least-squares density matrix D_{LS} at time t and R measures the variability between elements of the reconstructed SDP density matrix at time t and time $t+1$. Using these definitions, the reconstruction problem can be framed as a multiobjective optimization where the norms of E

and R are minimized while enforcing constraints to guarantee the reconstructed solution is a proper density matrix,

$$\begin{aligned} &\min\ (\alpha||E|| + \beta||R||) \\ &\text{such that } D_{\text{SDP}}(t) \succeq 0, \\ &\text{Tr}[D_{\text{SDP}}(t)] = N. \end{aligned} \tag{7}$$

Minimization of the first objective E directs instantaneous solutions $D_{\text{SDP}}(t)$ to a matrix which is close to the elements of $D_{\text{LS}}(t)$ while minimization of the second objective directs the global solution $D_{\text{SDP}}(t)$ to one that varies smoothly in time.

B. Reduced density matrices and N representability

Measurements on the full N-particle manifold are not always realizable, and often measurements are made on the one- or two-particle space where the p-RDM with $p = 1$ or 2 is the appropriate variable to characterize the system. Care must be taken in computing the p-RDM to ensure it corresponds to a realistic N-particle system [1–5,8–11,13,30–33]. The N-electron density matrix in the reconstruction of Eq. (7) can be replaced with a p-RDM only if the positive semidefinite condition $D_{\text{SDP}}(t) \succeq 0$ is replaced by N-representability conditions. Importantly, the most important of these conditions are also expressible as semidefinite constraints. In the following two sections the N-representability conditions on the 1- and 2-RDMs are briefly reviewed.

Traditionally, quantum-process tomography has been associated with the generation of a complete map of the system's dynamics in time, but recent work has emphasized the importance of partial quantum-process tomography to retrieve the most important information without the cost of computing a complete map [26–28]. For many-particle systems the use of RDMs provides a natural framework for extracting the most important information from the available experimental measurements.

1. N representability of the 1-RDM

A reduced density matrix must satisfy special conditions known as N-representability conditions to guarantee that it corresponds to an N-particle density matrix [1–5,8–11,13, 30–33]. A set of necessary conditions, called the p-positivity conditions, is known for the p-particle RDM. For p equal to 1, one-positivity of the 1-RDM requires that the 1-RDM and the one-hole RDM (1-HRDM) are positive semidefinite [30,33]; that is,

$${}^1D(t) \succeq 0, \tag{8}$$

$${}^1Q(t) \succeq 0, \tag{9}$$

where the elements of the one-particle RDM ${}^1D$ and 1-hole RDM ${}^1Q$ are given by

$${}^1D^p_q(t) = \text{Tr}[\hat{a}^\dagger_p \hat{a}_q, {}^N D(t)], \tag{10}$$

$${}^1Q^p_q(t) = \text{Tr}[\hat{a}_p \hat{a}^\dagger_q, {}^N D(t)], \tag{11}$$

and $\hat{a}^\dagger_p$ ($\hat{a}_p$) denotes a creation (annihilation) operator that creates (destroys) a particle in orbital p. Taking the expectation value of the anticommutation relation for fermion creation and annihilation operators yields the following linear mapping between the one-particle and one-hole RDMs:

$${}^1D(t) + {}^1Q(t) = {}^1I, \tag{12}$$

where ${}^1I$ is the one-particle identity matrix. For the 1-RDM, one-positivity is both *necessary and sufficient* to guarantee N representability for systems with at most one-particle interactions [30], and these conditions guarantee that the probabilities of finding one particle and one hole are between 0 and 1.

2. N representability of the 2-RDM

Necessary N-representability conditions on the 2-RDM, known as two-positivity conditions, require that the two-particle RDM, two-hole RDM, and the particle-hole RDM are positive semidefinite [1–5,8–11,13,30–33]:

$${}^2D(t) \succeq 0, \tag{13}$$

$${}^2Q(t) \succeq 0, \tag{14}$$

$${}^2G(t) \succeq 0, \tag{15}$$

where the elements of these matrices are given by

$${}^2D^{pq}_{rs}(t) = \text{Tr}(\hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r, {}^N D), \tag{16}$$

$${}^2Q^{pq}_{rs}(t) = \text{Tr}(\hat{a}_p \hat{a}_q \hat{a}^\dagger_s \hat{a}^\dagger_r, {}^N D), \tag{17}$$

$${}^2G^{pq}_{rs}(t) = \text{Tr}(\hat{a}^\dagger_p \hat{a}_q \hat{a}^\dagger_s \hat{a}_r, {}^N D). \tag{18}$$

The matrix elements of the two-particle, two-hole, and particle-hole RDMs in Eq. (16) are related by linear mappings which can be derived from the fermion anticommutation relations. Keeping the ${}^2D(t)$, ${}^2Q(t)$, and ${}^2G(t)$ matrices positive semidefinite corresponds to restricting the probability distributions for finding two particles, two holes, and a particle-hole pair nonnegative. The two-positivity conditions are necessary but not sufficient conditions for the N representability of the 2-RDM.

C. Quantum-process reconstruction as a semidefinite program

Semidefinite programming is a generalization of linear programming in which a linear function of a matrix is minimized subject to linear constraints on the matrix elements and the condition that the matrix be positive semidefinite [14,15,38,57]. A semidefinite program is expressible in its primal form as

$$\begin{aligned} &\min\ (c^T x) \\ &\text{such that } Ax = b, \\ &M(x) \succeq 0, \end{aligned} \tag{19}$$

where M is an operator that maps the solution vector x to a matrix. Importantly, in this formulation multiple matrices, as arise in the N-representability conditions of Sec. II B, can be kept positive semidefinite by making $M(x)$ a block-diagonal matrix containing these matrices [38]. Semidefinite programs can be solved by primal-dual interior-point methods which have been implemented in several software packages (see, for example, Refs. [35–37,58]), but the computational scaling of such methods is prohibitive for large-scale systems. In the context of 2-RDM-based electronic structure methods, one of the authors has developed more efficient methods for solving

the SDP based on nonlinear programming [7,38,59], which we use in this application, as well as a method based on a boundary-point algorithm [12,60].

The reconstruction problem was framed in Secs. II A and II B as a multiobjective optimization in which the solution's proximity to the experimental data and its smoothness in the time domain are minimized while it is constrained to satisfy physical conditions, such as the N-representability conditions. Significantly, the nonconvex optimization in Eq. (7) can be reformulated as a convex optimization, more specifically, a semidefinite program. Assuming that time is discretized, we must define the solution x of the SDP in Eq. (19) to have three parts for each point in time: $x_E(t)$, $x_R(t)$, and $x_D(t)$, which correspond to the errors in the fit to the quantum measurements, the errors in the smoothness of the solution, and the vector form of the RDMs, respectively.

While the squared Frobenius norm of the error $E(t)$ in Eq. (5) is *quadratic* in the RDMs, the minimization of the norm can be formulated as *linear* in the solution x of the SDP. Minimizing the squared Frobenius norm of $E(t)$ can be relaxed to minimizing the trace of $M(x_E(t))$ [61],

$$M(x_E(t)) = \begin{pmatrix} I & E(t) \\ E^*(t) & F(t) \end{pmatrix} \succeq 0, \tag{20}$$

where I is the identity, $F(t)$ is a matrix of free variables, and $E(t)$ depends linearly upon $x_D(t)$ as defined in Eq. (5). Taking the determinant of the 2×2 block matrices in the positive semidefinite, $M(x_E(t))$ yields

$$F(t) - E^*(t)\, E(t) \succeq 0 \tag{21}$$

or

$$F(t) \succeq E^*(t)\, E(t), \tag{22}$$

and taking the trace of Eq. (22) yields

$$\mathrm{Tr}[F(t)] \geqslant \mathrm{Tr}[E^*(t)\, E(t)]. \tag{23}$$

Hence, because the Frobenius norm of the error matrix is

$$||E||_F = \sqrt{\mathrm{Tr}[E(t)E(t)^*]}, \tag{24}$$

minimizing the trace of $F(t)$ provides a *semidefinite relaxation* for the problem of minimizing the Frobenius norm. Furthermore, we can minimize the errors at all points in time by minimizing over the sum of $F(t)$ over all t. Similarly, the optimization of the Frobenius norm of $R(t)$ defined in Eq. (6) may be performed by minimizing the trace of

$$M(x_R(t)) = \begin{pmatrix} I & R(t) \\ R^*(t) & F'(t) \end{pmatrix} \succeq 0, \tag{25}$$

where $F'(t)$ is a second matrix of free variables and $R(t)$ depends linearly upon $x_D(t)$ as defined in Eq. (6). As in the previous case, we can minimize the errors at all points in time by minimizing over the sum of $F'(t)$ over all t.

For reconstruction of the 1-RDM, at each point in time the solution has a block of the form

$$M(x_D(t)) = \begin{pmatrix} {}^1D(t) & 0 \\ 0 & {}^1Q(t) \end{pmatrix} \succeq 0, \tag{26}$$

and for reconstruction of the 2-RDM with two-positivity conditions, at each point in time the solution has a block of the form

$$M(x_D(t)) = \begin{pmatrix} {}^2D(t) & 0 & 0 \\ 0 & {}^2Q(t) & 0 \\ 0 & 0 & {}^2G(t) \end{pmatrix} \succeq 0. \tag{27}$$

In addition to the semidefinite conditions, linear constraints of the form $Ax = b$ are required to enforce trace relations, the contraction of 2-RDM to the 1-RDM, and the linear mappings connecting ${}^1D(t)$ and ${}^1Q(t)$ or ${}^2D(t)$, ${}^2Q(t)$, and ${}^2G(t)$. This formalism may be generalized to include higher-particle RDMs as well, but we will show in the following section that the 1-RDM is an appropriate choice for the current application.

D. Model for photosynthetic light harvesting

Photosynthetic light-harvesting systems are collections of chromophores that capture and transfer energy from photons. The energy-transfer process can be understood in terms of the dynamics of a delocalized excitation (or exciton). The dynamics of the exciton density matrix can be modeled by a Liouville equation of motion supplemented with a Lindblad operator [62],

$$\frac{dD(t)}{dt} = -\frac{i}{\hbar}[\hat{H},\, D(t)] + \hat{L}(D(t)), \tag{28}$$

where $\hat{H}$ is the system Hamiltonian and $\hat{L}$ is the Lindblad operator accounting for the interaction between the system and its surroundings. A model for the system Hamiltonian in the site basis of the chromophores [63,64] is

$$\hat{H} = \sum_j^M \hbar\omega_j \hat{a}_j^\dagger \hat{a}_j + \sum_{j \neq i} \hbar v_{j,l} (\hat{a}_j^\dagger \hat{a}_l + \hat{a}_j \hat{a}_l^\dagger), \tag{29}$$

where $\hat{a}_i^\dagger$ ($\hat{a}_i$) creates (kills) an excitation on site i. The Lindblad operator $\hat{L}$ models the effects of dephasing, dissipation, and transfer to the sink; further details are reported elsewhere [63,64]. If the initial state of the system contains a single excitation, then the dynamics is restricted to the Hilbert space spanned by the set of singly excited states, and consequently, the 1-RDM is sufficient to fully characterize the quantum state.

For the 1-RDM, N representability is ensured by keeping the 1-RDM and the 1-HRDM positive semidefinite [30,33]. In the special case that only single excitons are considered, the one-particle RDM in the basis set of excited orbitals traces to unity. Using the relation in Eq. (12), we perceive that when the one-particle RDM traces to 1, the one-hole RDM is automatically positive semidefinite. Hence, in this case constraining the one-particle RDM to be positive semidefinite is sufficient for N representability of the 1-RDM. The solution block x_D simplifies because only ${}^1D(t)$ needs to be explicitly computed and constrained to be positive semidefinite. Alternatively, because we consider only one exciton in the system, the 1-RDM for excitons is equivalent to the complete exciton density matrix, and hence only the density matrix needs to be held positive semidefinite.

III. APPLICATIONS

A. Methodology

The model quantum process in this application is the one-exciton dynamics of a seven-chromophore model of the Fenna-Matthews-Olson (FMO) complex. The SDP is encoded with quantum-process information from a simulation of the exciton-transfer process in FMO. The Liouville equation is solved for the 1-RDM with a fourth- and fifth-order Runge-Kutta method with variable step size [61]. The initial density matrix describes a single excitation on chromophore 1, and the time evolution of the 1-RDM is simulated for 1 ps with a 1-fs time step. The parameters for the system Hamiltonian in Eq. (29) and the Lindblad operator are taken from a study done by Plenio and coworkers [63]. From solving Eq. (28), we obtain 1000 instantaneous 1-RDMs from $t = 0$ to 1000 fs, which we will consider the exact 1-RDMs for the quantum process discretized in time. We introduce corruption and incompleteness of the quantum-process information as postprocessing steps following the solution of Eq. (28). Corruption in the data is simulated by adding Gaussian noise to each 1-RDM element for each time step in the data set. A Gaussian random number generator is implemented as described in Ref. [65] with $\mu = 0$ and $\sigma = 0.005$. Incompleteness of the data set is simulated in two ways: (i) by omitting the coherences ${}^1D_2^1(t)$ and ${}^1D_1^2(t)$ for each t between 1 and 1000 fs and (ii) by omitting a randomly chosen population (diagonal 1-RDM element) for each t between 1 and 1000 fs. This corrupted and incomplete quantum-process information constitutes our model for a 1-RDM obtained by least-squares inversion ${}^1D_{\mathrm{LS}}(t)$ and enters into the SDP calculation through the matrix block defined in Eq. (20).

The objective of the SDP, as formulated in Sec. II C, involves a matrix block of dimension 7 and two matrix blocks of dimension 14 at each time t, so each time step has 441 variables and 295 constraints. This SDP is intractable by primal-dual interior-point methods for more than approximately 10 time steps, but it is easily solvable with first-order methods [7,12]. The first-order algorithm for solving SDP in Ref. [7] is implemented for real-valued problems while the data set is complex valued, and so one additional step is taken to map the complex-valued data set to a real data set. The complex-to-real mapping increases the rank of each matrix block by a factor of 2, but because of the efficiency of the first-order algorithm, this has a negligible impact on computational cost. The details of this mapping are described in the Appendix.

B. Results

We consider reconstruction of the 1-RDM by semidefinite programming using three models for corrupted or incomplete information in the least-squares inversion ${}^1D_{\mathrm{LS}}(t)$. All three models for ${}^1D_{\mathrm{LS}}(t)$ introduce corruption through Gaussian noise. The second and third models also introduces data loss. The second model omits the coherences between chromophores 1 and 2 at each t, and the third model omits a randomly selected population at each t. The semidefinite reconstruction is performed using information from each model of ${}^1D_{\mathrm{LS}}$ in combination with restrictions from N representability and/or regularization.

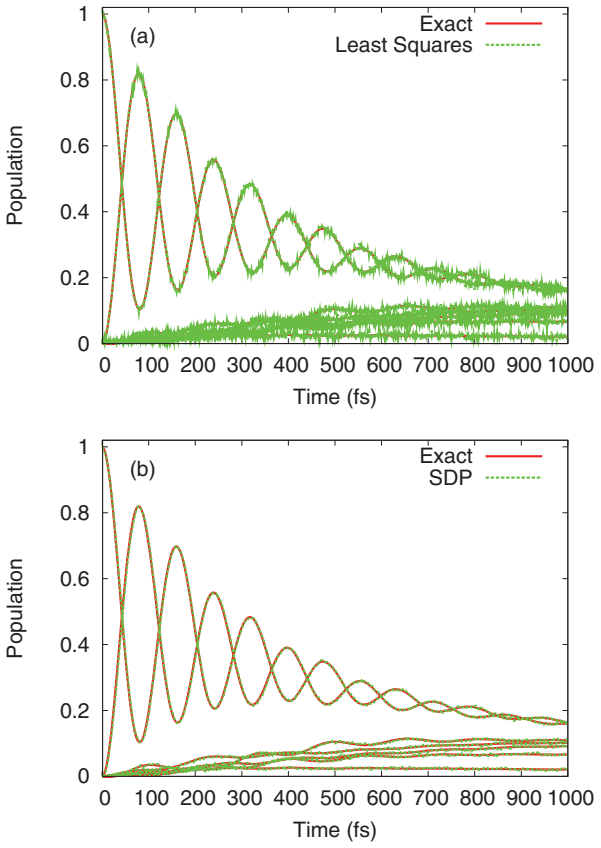

FIG. 1. (Color online) Two reconstructions methods, (a) least-squares fit and (b) SDP fit with N-representability conditions and regularization, are compared in their reconstruction of an energy transfer in light harvesting from noisy data. While the least-squares reconstruction results in a poor resolution of the population dynamics, the SDP reconstruction recovers the exact population dynamics [shown in red (dark gray)] for all of the chromophores. Corruption is introduced through Gaussian noise with $\sigma = 0.005$.

The reconstruction of the quantum process from the corrupted (first) model of ${}^1D_{\mathrm{LS}}$ is shown in Fig. 1. The corruption (Gaussian noise with $\sigma = 0.005$) in the least-squares 1-RDM results in poor resolution of the population dynamics in all seven chromophores. For chromophores 3 through 7 the corruption severely obscures the individual population dynamics. Nevertheless, by enforcing N representability and regularization through SDP reconstruction, we can unambiguously recover the population dynamics for all of the chromophores. Figure 2 plots the Frobenius norms of (i) the error in the least-squares 1-RDM, (ii) the error in the SDP 1-RDM reconstructed with N representability, and (iii) the error in the SDP 1-RDM reconstructed with N representability and regularization. The error matrix for a given 1-RDM estimate is defined as the difference between the 1-RDM estimate and the exact 1-RDM; for example, $E_{\mathrm{LS}}(t) = {}^1D_{\mathrm{LS}}(t) - {}^1D(t)$ is the error matrix for the 1-RDM obtained from least-squares inversion. From Fig. 2 we see that applying the ${}^1D \succeq 0$ condition alone decreases the Frobenius norm of the error matrix at each time step by at least half an order of magnitude, while including regularization further decreases the error by at least another half an order of

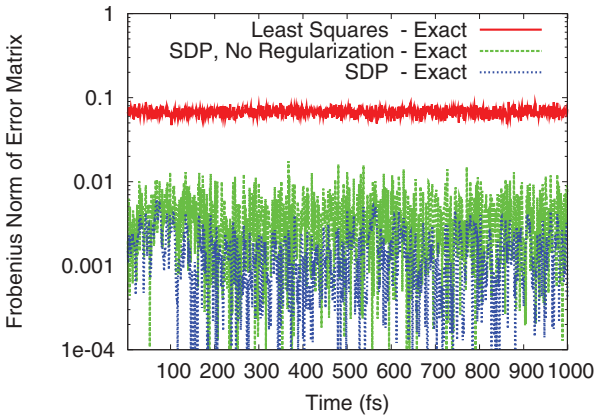

FIG. 2. (Color online) The Frobenius norms of (i) the error in the least-squares 1-RDM [red (medium gray)], (ii) the error in the SDP 1-RDM reconstructed with N representability [green (light gray)], and (iii) the error in the SDP 1-RDM reconstructed with N representability and regularization [blue (dark gray)] are shown. Applying the ${}^1D \succeq 0$ condition decreases the Frobenius norm of the error at each time step by at least half an order of magnitude, while also including regularization further decreases the error by half an order of magnitude.

magnitude. Finally, Fig. 3 demonstrates that the model of ${}^1D_{\mathrm{LS}}$ corrupted with Gaussian noise is not N representable and that semidefinite reconstruction successfully enforces the N-representability conditions. Many ${}^1D_{\mathrm{LS}}(t)$ have eigenvalues as small as -0.03, whereas the smallest eigenvalues of ${}^1D_{\mathrm{SDP}}$ are greater than or equal to zero for all t.

The reconstruction of the quantum process from a corrupted and incomplete (second) model of ${}^1D_{\mathrm{LS}}$ is shown in Fig. 4, where incompleteness is introduced by omission of the coherences between chromophores 1 and 2. The results show that it is possible to reconstruct the population dynamics very accurately even without information about the coherences between the channels with the largest populations, chromophores 1 and 2. Finally, we consider the third model

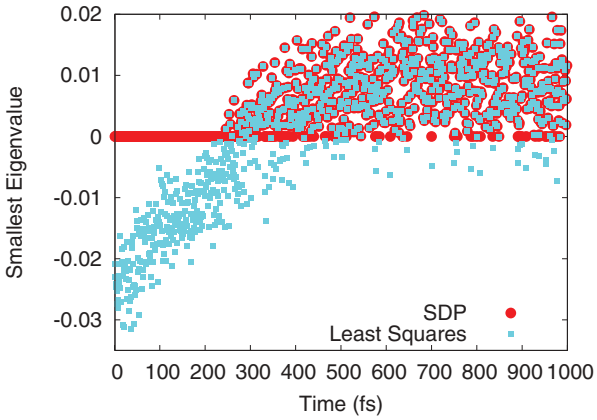

FIG. 3. (Color online) The lowest eigenvalues of the least-squares 1-RDM (blue squares) and the SDP 1-RDM (red dots) are shown. Both models are reconstructed from noisy data. The least-squares 1-RDM is not N representable because its lowest eigenvalues are as negative as -0.03, especially at early t, while the SDP 1-RDM has nonnegative eigenvalues (N representable) for all t.

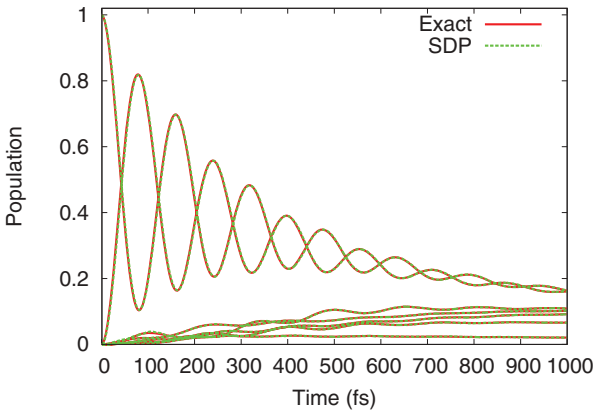

FIG. 4. (Color online) Chromophore populations [green (light gray)] from semidefinite reconstruction using N representability and regularization are compared with the exact populations [red (dark gray)]. Reconstruction is from corrupted and incomplete data. Incompleteness is introduced by omitting the coherences between chromophores 1 and 2 for each t from 1 to 1000, while corruption is introduced through Gaussian noise with $\sigma = 0.005$.

of ${}^1D_{\mathrm{LS}}$ in which a randomly selected population is omitted at each t. Reconstructing the 1-RDM with N-representability conditions alone, shown in Fig. 5(a), leads to wild fluctuations in the values of the elements and a large error relative to the model data. However, using N representability and regularization, shown in Fig. 5(b), provides sufficient information to reconstruct the 1-RDM accurately.

IV. DISCUSSION AND CONCLUSIONS

Experimental measurements offer the opportunity to access quantum-state and quantum-process information directly without computational solution of the Schrödinger equation. In particular, experiment provides information that can be used to build the one- or two-particle reduced density matrix without construction of the N-particle density matrix. Major obstacles facing reconstruction of RDMs, and therefore QST and QPT, include corruption and incompleteness of experimental data and the challenge of constraining the solution to satisfy necessary N-representability conditions [1–3,8,30–33], that is, constraints that are necessary for the RDM to represent an N-particle system. We have shown that a general reconstruction methodology that overcomes these obstacles is possible through semidefinite programming [14,15,38,57]. The reconstruction methodology developed encodes N-representability conditions through a combination of positive semidefinite and linear constraints. Optimization is performed with respect to two objectives: (i) the least-squares fit to measured data and (ii) the smoothness of the solution in time. Both objectives are expressed as *linear* objectives, suitable for a semidefinite program, through a relaxation of the Frobenius norms [61]. The smoothness criterion (or regularization) and the N-representability conditions allow accurate reconstruction from data sets which are corrupted and incomplete.

Interesting parallels exist between the reconstruction of one- and two-electron RDMs from experimental measurements and the variational calculation of the two-electron RDM

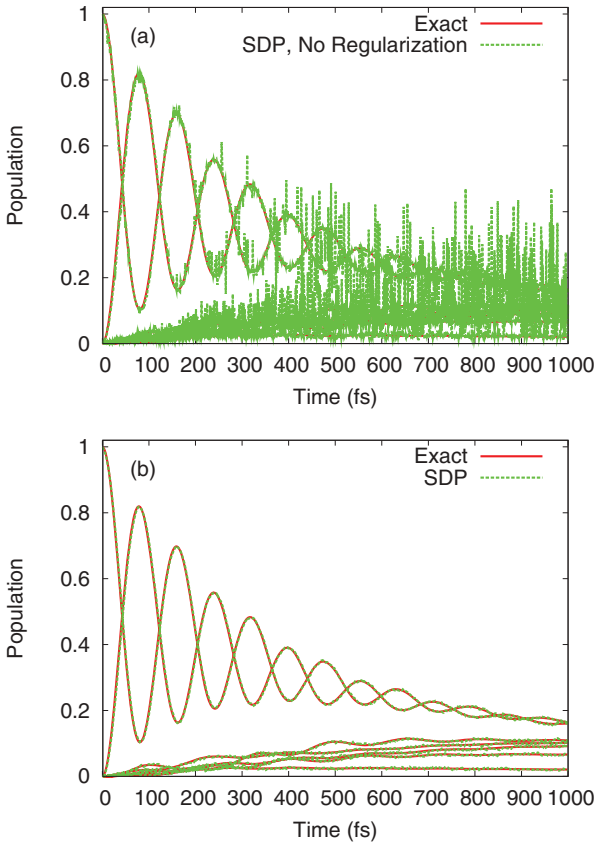

FIG. 5. (Color online) Chromophore populations [green (light gray)] from semidefinite reconstruction using N representability (a) without and (b) with regularization are compared with the exact populations [red (dark gray)]. Reconstruction is from corrupted and incomplete data. Incompleteness is introduced by omitting the coherences between chromophores 1 and 2 for each t from 1 to 1000, while corruption is introduced through Gaussian noise with $\sigma = 0.005$.

of many-electron systems [3–5,8–11,33,66–68]. Because both methods attempt to compute RDMs without calculation of the N-electron density matrix, they both need N-representability conditions that are necessary for the computed RDM to represent an ensemble N-electron density matrix. The N-representability conditions on the 1-RDM, keeping its eigenvalues (natural occupation numbers) between 0 and 1, were first proven sufficient by Coleman in 1963 [30], while the N-representability conditions on the p-RDM for $p > 1$, involving much more complicated non-negativity conditions, were only recently characterized and proven sufficient [13]. Because the N-representability conditions involve linear and linear matrix (semidefinite) constraints, both the reconstruction of 2-RDMs from experimental measurements and the variational calculation from an energy functional for many-electron systems are naturally formulated as semidefinite programs, solvable by semidefinite programming. The N-representability constraints for the 1-RDM have a polynomial scaling with system size, while the complete constraints for the 2-RDM have a nondeterministic polynomial complete (NP-complete) scaling with system size [13]. In practice, however, by using a subset of the N-representability conditions on the 2-RDM, both 1-RDM and 2-RDM reconstruction can be performed with polynomial scaling.

We applied the reconstruction methodology to characterizing the energy-transfer dynamics of the photosynthetic light-harvesting complex in green sulfur bacteria [39–51]. Reconstruction of the one-electron RDM was performed from data that were corrupted with Gaussian noise. The semidefinite reconstruction improved the accuracy of the 1-RDM by approximately two orders of magnitude compared to the least-squares estimate, which did not consider the representability of the 1-RDM. We observed similar accuracy when reconstruction was performed from data that were both corrupted and incomplete.

Unlike reconstruction from linear least-squares inversion, reconstruction by semidefinite programming can be formulated to constrain the solution to satisfy the physical requirements of an RDM. Importantly, this reconstruction can be formulated directly with experimental data as well as with an estimate of the RDM. The semidefinite programming filters the quantum measurements to remove noise and incompleteness through a combination of regularization (smoothness) and N-representability conditions. The reconstructed N-representable RDMs provide a compact description of the quantum system and process, including information about coherence lifetimes and energy-transfer efficiency. The present work can be readily generalized to interacting many-boson systems [34] as well as the determination of higher-particle RDMs [1,8]. Quantum-process reconstruction by semidefinite programming provides an important tool for reconstructing realistic, N-representable reduced density matrices of many-particle quantum processes.

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APPENDIX: REAL REPRESENTATION OF A COMPLEX MATRIX

Consider the complex number $z_1 = a_1 + b_1 i$, where $\mathrm{Re}(z_1) = a_1$ and $\mathrm{Im}(z_1) = b_1$. A matrix representation for z_1 is [69]

$$M(z_1) = \begin{pmatrix} a_1 & -b_1 \\ b_1 & a_1 \end{pmatrix}. \tag{A1}$$

For two complex numbers z_1 and z_2 this mapping preserves arithmetic operations such as

$$\begin{aligned} M(z_1 + z_2) &= M(z_1) + M(z_2), \\ M(z_1 z_2) &= M(z_1) M(z_2), \\ M(z_1 - z_2) &= M(z_1) - M(z_2), \\ M(z_1/z_2) &= M(z_1) M(z_2)^{-1}. \end{aligned} \tag{A2}$$

This idea can be generalized to represent a Hermitian matrix by a real symmetric matrix by either applying the above mapping

to each complex entry of the matrix or noticing an equivalent representation,

$$\bar{M}(Z_1) = \begin{pmatrix} \mathrm{Re}(Z_1) & -\mathrm{Im}(Z_1)^T \\ \mathrm{Im}(Z_1) & \mathrm{Re}(Z_1) \end{pmatrix}. \tag{A3}$$

The rank of $\bar{M}(Z_1)$ is twice the rank of Z_1 with each eigenvalue being doubly degenerate, but the mapping preserves both Hermiticity and positive semidefiniteness. Hence, solving an SDP for the real symmetric matrix $\bar{M}(Z_1)$ is equivalent to solving an SDP for the Hermitian matrix Z_1 [58].

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