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APPLICATION OF INDIRECT HAMILTONIAN TOMOGRAPHY TO COMPLEX SYSTEMS WITH SHORT COHERENCE TIMES

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The identification of parameters in the Hamiltonian that describes complex many-body quantum systems is generally a very hard task. Recent attention has focused on such problems of Hamiltonian tomography for networks constructed with two-level systems. For open quantum systems, the fact that injected signals are likely to decay before they accumulate sufficient information for parameter estimation poses additional challenges. In this paper, we consider use of the gateway approach to Hamiltonian tomography [1, 2] to complex quantum systems with a limited set of state preparation and measurement probes. We classify graph properties of networks for which the Hamiltonian may be estimated under equivalent conditions on state preparation and measurement. We then examine the extent to which the gateway approach may be applied to estimation of Hamiltonian parameters for network graphs with non-trivial topologies mimicking biomolecular systems.

Keywords: Hamiltonian tomography, complex system, dissipation

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1 Introduction

Precise information about the Hamiltonian of many-body quantum systems is crucially important for analysis and prediction of their dynamics, especially to understand the extent to which a given subsystem behaves quantum mechanically. If the subsystem of interest is well isolated from the remainder, i.e., from its environment, in the sense that its dynamics is immune to the effect of noise, then the time evolution is unitary and observable data may be considered 'clean' enough to extract good information on the subsystem Hamiltonian. However this is clearly an idealized situation that is rarely encountered. Furthermore, the general procedures to estimate even a small part of the Hamiltonian that acts on a many-body system are, in general, very complex and require a large number of measurements of different observables. This leads to a further challenge which is that as the data acquisition process becomes more elaborate and accesses more of the system, it is likely to introduce an increasing amount of measurement noise.

Several approaches for Hamiltonian identification, or *Hamiltonian tomography*, have been recently proposed that seek to reduce the complexity of the procedure by making use of some a priori knowledge about the physical system [3, 4, 5, 6, 7, 8, 9, 10, 11]. One approach is to map the many-body system onto a quantum network and to make use of knowledge about the topology of this network to devise protocols that extract desired Hamiltonian parameters from measurements on a restricted portion of the network. Following the demonstration that the Hamiltonian parameters of one-dimensional chain of spin-1/2 particles may be determined by measurements on a single spin [1, 12], this approach has been generalized to more general spin networks with restricted measurement access on a small *gateway* region [2] as well as to more general Hamiltonians [13]. Reference [12] also showed that such an estimation scheme may be robust against noise under weak-coupling conditions. For sparse Hamiltonians, a different approach has recently been developed using the method of compressed sensing [14, 15], which has also been applied to quantum state tomography [16]. Compressed sensing allows determination of both higher order Hamiltonians and system-bath interactions, but is limited to sparse Hamiltonians. Other approaches have been developed that are based on convex optimization [17] and Bayesian estimation [8]. While these Hamiltonian tomography approaches are related to the better known quantum process tomography (QPT) [18, 19,

20, 21, 22] that (together with quantum state and quantum measurement tomographies) provides a complete characterization of quantum dynamics, they differ from QPT in seeking to reconstruct the desired parameters with a minimal amount of resources.

In this paper we explore the use of the gateway scheme outlined in [2] for determination of Hamiltonian parameters for an open quantum system under conditions of restricted access. The approach of Ref. [2] was based on the assumption of long coherence times, which allowed the injected signal (spin wave) to go back and forth in the network many times so that the information about spin interactions may be encoded in the signal. For dissipative systems, we cannot in general expect such a long lifetime of the signal and it will generally be susceptible to decay before coming back to the injection site, even though the initial time evolution for a short time may be seen to be coherent. We therefore limit our attention here to complex systems in which a subsystem does show such coherent short time evolution.

One prototype of this latter situation that is of considerable current interest is the subsystem of pigments in photosynthetic light harvesting systems. Recent spectroscopic experiments have shown that electronic energy transfer dynamics in such systems displays coherence for several hundreds of femtoseconds [23, 24, 25, 26, 27]. Although the extent of vibrational contributions is not entirely clear [28], these coherences are generally accepted to reflect quantum coherences between different excitonic states that may be described by superpositions of single molecule electronic excitations, and are thus amenable to a two-level pseudo-spin representation. In this work we shall consider a network of pseudo-spins that mimics pigments in a light harvesting protein.

We first review the gateway scheme of Refs. [1, 2], introducing the graph theoretic description and notion of infection between different regions of the network (graph) (Sec. 2). We then summarize the minimal restrictions on measurement access via spectroscopic measurements in a pigment-protein complex (Sec. 3). These differ from the measurement requirements for spin networks [2] and thus necessitate an extension of that approach. We present a classification of network topologies that are accessible to Hamiltonian tomography under the current scheme. In Sec. 4 we then investigate the extent to which the scheme may be applied to a network graph mimicking pigments embedded in the Fenna-Matthews-Olson protein of photosynthetic green bacteria [29]. A discussion and analysis of the limitation posed by restriction to short time scales of coherent evolution, together with indications for extensions to remedy this, follows in Sec. 5.

2 Gateway scheme of Hamiltonian tomography

In the 'gateway scheme' of Hamiltonian identification [1, 2], we consider a network of spin 1/2 pseudo-spins subject to a unitary dynamics generated by a Hamiltonian containing pairwise interaction terms and Zeeman terms. For clarity and conciseness we describe here only the case of excitation-conserving Hamiltonians, namely those satisfying $[H, \sum_n Z_n] = 0$, i.e., conserving the total magnetization of the pseudo-spin network. We further assume that all coupling strengths c_n between spins are real and the (relative) signs of these, but not the magnitudes, are known. We shall consider the determination of the Hamiltonian parameters in the first excitation subspace, i.e., the subspace in which there is only one 'up' pseudo-spin and all other pseudo-spins are 'down'. (Note that this places a restriction on the interaction between pseudo-spins.) The basis states describing one excitation localized on a single pseudo-

spin will be denoted by $|\mathbf{1}\rangle \equiv |\uparrow\downarrow\ldots\downarrow\rangle = |10\ldots0\rangle$, where N is the number of pseudo-spins. Other states with a single up-spin will be denoted similarly hereafter, i.e., $|\mathbf{n}\rangle = |\downarrow\ldots\uparrow\ldots\downarrow\rangle$ contains only a single spin up at the n-th site. The energy eigenstates will be denoted $|E_j\rangle$. We define $\rho_n(t) = \mathrm{tr}_{\neq n}[U(t)|\psi_0\rangle\langle\psi_0|U(t)^\dagger]$ to be the reduced density matrix on site n, where $U(t) = \exp(-iHt)$ is a time evolution operator for the network.

We illustrate the scheme here for a 1D spin chain with nearest-neighbor interactions.The Hamiltonian in the first excitation subspace is given by

$$H_{1\mathrm{D}} = \begin{pmatrix} b_1 & c_1 & & \\ c_1 & b_2 & c_2 & \\ & & \ddots & c_{N-1} \\ & & c_{N-1} & b_N \end{pmatrix}. \tag{1}$$

For a 1D chain, we start our procedure by measuring all eigenenergies $\{E_j\}$ and coefficients $\{\langle E_j|\mathbf{1}\rangle\}$ for $j = 1, 2, \ldots, N$. First we initialize the state of the chain as $|\psi_0\rangle := 1/\sqrt{2}(|\mathbf{0}\rangle+|\mathbf{1}\rangle)$, i.e., $1/\sqrt{2}(|0\rangle + |1\rangle) \otimes |0\ldots0\rangle$. Such an initialization is possible by accessing only the first spin [30]. We then perform state tomography on the first spin after a time lapse t to extract the reduced density matrix $\rho_1(t)$ and repeat this at various time delays to obtain $\rho_1(t)$ as a function of time. Up to an irrelevant phase factor, the diagonal element of $\rho_1(t)$ can be written as

$$f_{11}(t) := \langle\mathbf{1}|\exp(-iHt)|\mathbf{1}\rangle = \sum_j \exp(-iE_jt)|\langle E_j|\mathbf{1}\rangle|^2.$$

The eigenenergies $\{E_j\}$ and the coefficients $\{|\langle E_j|\mathbf{1}\rangle|\}$ can then be obtained by performing the time Fourier transform of $f_{11}(t)$. Due to the arbitrariness of the global phase, we can choose all $\langle E_j|\mathbf{1}\rangle$ to be real and positive. Detailed discussion of the factors determining the efficiency of the Fourier transform are discussed in Ref. [1]. As noted there, it is necessary to observe repeated reflections of the signal (at least N times) in order to obtain an adequate signal to noise ratio. Consequently a long time coherence is necessary for implementation of Hamiltonian tomography with measurements only on a single spin.

With the information about $\{E_j\}$ and $\{\langle E_j|\mathbf{1}\rangle\}$ obtained from these single spin measurements, we can proceed to the parameter estimation by constructing a set of N^2 equations representing $\langle E_j|H_{1\mathrm{D}}|\mathbf{n}\rangle$ for $1 \leq j, n \leq N$. These equations are given by

$$E_j\langle E_j|\mathbf{1}\rangle = b_1\langle E_j|\mathbf{1}\rangle + c_1\langle E_j|\mathbf{2}\rangle, \tag{2}$$

$$E_j\langle E_j|\mathbf{n}\rangle = c_{n-1}\langle E_j|\mathbf{n}-\mathbf{1}\rangle + b_n\langle E_j|\mathbf{n}\rangle + c_n\langle E_j|\mathbf{n}+\mathbf{1}\rangle \quad (1 < n < N), \tag{3}$$

$$E_j\langle E_j|\mathbf{N}\rangle = c_{N-1}\langle E_j|\mathbf{N}-\mathbf{1}\rangle + b_N\langle E_j|\mathbf{N}\rangle. \tag{4}$$

Noting that $b_1 = \langle\mathbf{1}|H|\mathbf{1}\rangle = \sum_j E_j|\langle E_j|\mathbf{1}\rangle|^2$, each factor of which has been determined by state tomography on spin 1, the expansion of $|\mathbf{2}\rangle$ in the basis $|E_j\rangle$ can be obtained up to the constant c_1. The value of c_1 can then be obtained within a sign factor by requiring that $|\mathbf{2}\rangle$ be normalized to unity. All other parameters b_l, c_m and $\langle E_j|\mathbf{n}\rangle$ are then subsequently obtained in the same manner from Eq. (3) (for $l = N-1, m = N$) and Eq. (4). The intensities of any local magnetic fields (which will be assumed imposed in the z-direction) can be then estimated from $\{b_l\}$.

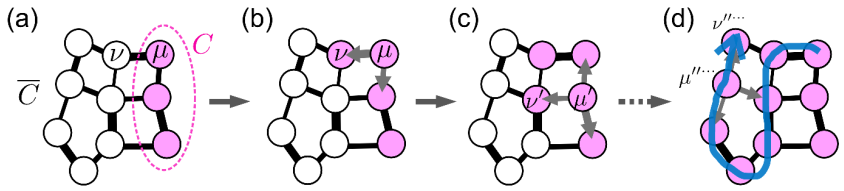

Fig. 1. An example of graph infection. (a) Initially, three colored nodes in the region C are 'infected'. (b) Since the node ν is the only uninfected node among the neighbors of μ, it becomes infected as time evolves. (c) In a similar manner, ν' becomes infected by μ'. (d) Eventually all nodes will be infected sequentially.

This scheme can be generalized to more complex graphs by enlarging the accessible area C as was shown in Ref. [2]. In that work the Hamiltonian tomography of a general graph formed by a network of spin-1/2 systems was found to be possible if C *infects* the entire graph. The infection process is defined as follows. Starting with a subset C of a larger set of nodes V, suppose that all nodes in C possess, i.e., are *infected* with some property. This property then spreads and infects other nodes according to the following rule: an infected node infects a *healthy* (uninfected) neighbor if and only if the latter is the *unique* healthy neighbor of the former. If eventually all nodes are infected by this process, the initial set C is referred to as an *infecting subset*. Figure 1 depicts the infecting process with a simple example.

We will see below that in general, although this requirement of infection is a necessary condition of the graph, it is not always a sufficient condition for Hamiltonian tomography under arbitrary measurements. In particular, we will show that there exist graphs that are not amenable to tomography under the spectrally restricted measurement assumptions employed in the current work.

3 Spectrally restricted Hamiltonian tomography for pseudo-spin networks

We now discuss an extension of the gateway scheme for Hamiltonian tomography of a subsystem, given access to a restricted set of spectral measurements and some short time subsystem coherence.

We consider a pseudo-spin network with XY-type interactions and local external magnetic fields, namely

$$\begin{aligned} H &= \frac{1}{2}\sum_{(m,n)\in E} c_{mn}(X_mX_n + Y_mY_n) + \sum_{m\in V} b_mZ_m \\ &= \sum_{(m,n)\in E} c_{mn}(\sigma_m^+\sigma_n^- + \sigma_m^-\sigma_n^+) + \sum_{m\in V} b_mZ_m. \end{aligned} \tag{5}$$

This defines a graph $G = (V, E)$ with V the set of pseudo-spin sites and E the links defined by the spin hopping between sites. The Hamiltonian parameters are the coupling strengths c_{mn}, and the energy gaps $2b_m$ due to the Zeeman terms, $\sum b_mZ_m$. We employ the notation, X_i, Y_i, and Z_i, for the standard Pauli matrices throughout this paper: $\sigma_m^{\pm} = (1/2)(X_m \pm iY_m)$ are thus the raising and lowering operators for the m-th pseudo-spin.

For a network of pigments such as that considered later in this paper (Sec. 4), the pseudo-spin sites are individual molecules with pseudo-spin states $|0\rangle, |1\rangle$ corresponding to the ground

and first excited electronic states, with energy gaps $2b_m$, while the links are given by the matrix elements of coupling between transition dipole moments on different molecules. This corresponds to the usual Heitler-London description of excitonic coupling between pigments [31]. Since we restrict the analysis here to short times during which the dynamics are coherent, we do not explicitly include other degrees of freedom here (but see discussion in Sec. 5).

Given a finite window of quantum coherence of subsystem dynamics, we may develop a variant of the gateway Hamiltonian tomography scheme via a set of spectral measurements at short times. This is possible with the following set of assumptions.

(i) The network topology is known. That is, the set of interacting pairs of sites which play a dominant role in the overall dynamics is known without precise information on the values of the coupling strengths, c_{mn}. The latter may, without loss of generality, be assumed real.
(ii) The sign of each c_{mn} is known, but not the magnitude.
(iii) The energy gaps between the two pseudo-spin levels are known for the specific sites that we need to access.
(iv) Single site excitation is possible when we have the information on energy gaps.
(v) The energy eigenvalues of the system are known.
(vi) Measurement in the energy eigenbasis $\{|E_j\rangle\}$ is possible, i.e., the probability of finding an eigenstate $|E_j\rangle$ in a state with a single site excitation $|\mathbf{n}\rangle$, i.e., $|\langle E_j|\mathbf{n}\rangle|^2$, can be measured.

Assumptions (i) and (ii) are the same as in the original scheme described in the previous section. Assumption (iii) is necessary for the single site excitation in Assumption (iv). Assumptions (iv) and (v) differ from the assumptions of the original gateway scheme of Refs. [1, 2], which required waiting for a signal to travel back and forth in the chain/network (Sec. 2). Since that procedure requires long coherence times, in situations where the time over which the quantum dynamics are coherent is limited, a *global* measurement in the energy basis provides an alternative route to acquire information about the subsystem before the excitation decays, provided that such a measurement may be implemented on a fast enough timescale. With use of such a global measurement, the term "to access the site n" then gains a slightly different meaning, namely "to prepare a state" or "to excite the molecule" at the site n, rather than to "to measure at site n" as was implicitly understood in Ref. [1].

The motivation for this measurement in the energy eigenbasis is that all necessary information for the gateway scheme are the sets of $\{E_j\}$ and $\langle E_j|\mathbf{n}\rangle$ for all $n \in C$. In Section 4 below, we discuss the feasibility of measurements in the different bases for the case of biomolecular networks. Clearly, which variant of the Hamiltonian tomography scheme is chosen for a particular physical realization of a pseudo-spin network, i.e., the spectrally restricted version presented here or the original gateway scheme of Refs. [1, 2], will depend on the relative ease of making measurements in site or energy bases.

The fact that the quantities we obtain are the modulus of $\langle E_j|\mathbf{n}\rangle$ gives rise to modifications to the choice of sites that should be accessed and the class of graphs to which the scheme is applicable, as we discuss below. For 1D chains, it still suffices to access an end site, as in the original proposal in Ref. [1]. If the graph derived from the pseudo-spin network has branches without loops, the end sites of all branches should be accessed. Figure 2(a) shows an example

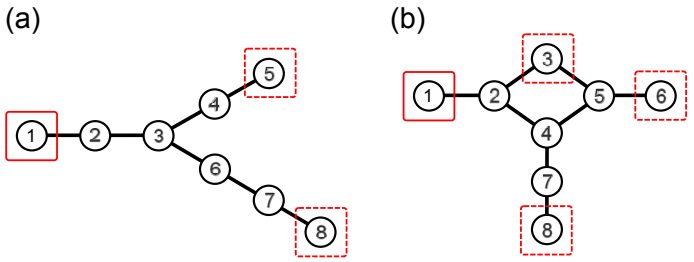

Fig. 2. Two examples of graphs to which the present spectrally restricted Hamiltonian tomography scheme can be applied. (a) For graphs with branches, the end pseudo-spin of each branch should be accessed, i.e., this pseudo-spin should locally excited before the measurement in the $|E_j\rangle$-basis. In this example, sites 1, 5, and 8 (each encircled with red lines) need to be accessed. A measurement at one of them defines the global phase, e.g., the site 1. The coefficients $|\langle E_j|\mathbf{n}\rangle|$ are measured after exciting the red encircled sites at the other end of the graph. (b) If there is a loop in the graph, then in addition to the end sites of branches emerging from the loop (sites 1, 6 and 8), the remaining sites contributing to the loop (e.g., site 3, also encircled in red) need to be accessed. Note that in both examples we need to access a larger set of sites than the smallest infecting set.

of such a situation. If we set the global phase by $\langle E_j|\mathbf{1}\rangle$, then measurements can only give the modulus of $\langle E_j|\mathbf{5}\rangle$ (and $\langle E_j|\mathbf{8}\rangle$), without their relative phases. At site 5 we have

$$(E_j - b_5)\langle E_j|\mathbf{5}\rangle = c_{45}\langle E_j|\mathbf{4}\rangle. \tag{6}$$

Summing up the modulus squared of this equation over j, we can find c_{45}^2. With the assumed knowledge of the sign, we then obtain the value of c_{45}, which can then be used to obtain the value of $|\langle E_j|\mathbf{4}\rangle|$. The procedure is repeated until we reach the branching site, i.e., site 3 in Figure 2(a) where two branches meet. The coupling strength between sites 3 and 4 in Figure 2(a), for instance, can be obtained by evaluating $\sum_j |\cdot|^2$ of $(E_j - b_4)\langle E_j|\mathbf{4}\rangle = c_{34}\langle E_j|\mathbf{3}\rangle + c_{45}\langle E_j|\mathbf{4}\rangle$, resulting in $c_{34}^2 = \sum_j (E_j - b_4)^2 |\langle E_j|\mathbf{4}\rangle|^2$, from which b_4 can be obtained as before. (See text after Eq. (4).)

If there is a loop in the graph, all sites n that contribute the loop need to be accessed in order to determine $|\langle E_j|\mathbf{n}\rangle|$. The necessity of knowing all $|\langle E_j|\mathbf{n}\rangle|$ for the loop-forming sites n derives from the requirement of having sufficient equations to determine the couplings. If branches extrude from the loop, the access sites should be chosen to be the end sites of these branches, just as in the case of simple graphs having branches. (See Figure 2(b).)

These examples show that the present variant of the gateway scheme for Hamiltonian tomography cannot be applied once there are two or more loops in a connected graph. The constraint on the available measurement given by Assumption (v) above poses a further condition on the network topologies to which the current scheme is applicable. We illustrate this for two simple examples of graphs in Figure 3. Because the original gateway scheme is based on the fact that only one unknown term, e.g., $c_{mn}\langle E_j|\mathbf{n}\rangle$, appears in the equation deriving from the factor $\langle E_j|H|\mathbf{m}\rangle$, we are able to obtain the value of one new coupling strength, c_{mn}, by using the previously obtained knowledge on parameters for sites other than n. The property of infection then guarantees that all coupling strengths can be estimated recursively in this manner, provided that all coefficients $\langle E_j|\mathbf{m}\rangle$ are known for all sites $m \in C$, as well as all eigenvalues $\{E_j\}$. However, when there is no information on the relative phase of $\langle E_j|\mathbf{m}\rangle$, the number of sites needs to be larger than or equal to the number of edges. The

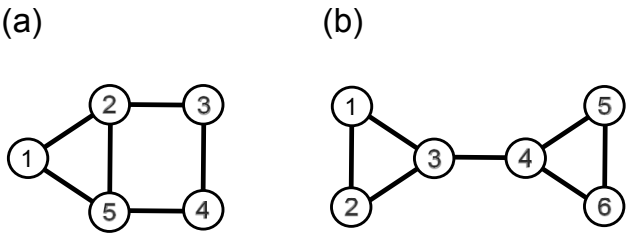

Fig. 3. Graphs containing more than one loop. In both examples here, the number of sites is less than the number of edges, rendering the Hamiltonian unestimable with the spectrally restricted approach using measurements in the energy basis.

graphs in Figure 3 do not fulfill this condition and as a result their Hamiltonians cannot be estimated with the current approach.

4 Application to a molecular network

We now apply the gateway scheme with restricted spectral access outlined above for a network of pseudo-spins to Hamiltonian tomography of a network graph with nontrivial topology mimicking a pigment-protein complex. As an example, we take the geometry of the seven coupled pigments embedded in the Fenna-Mathews-Olson (FMO) protein [29] and use the dominant electronic couplings between pigments as in Refs. [32, 33]. This leads to the network graph shown in Figure 4. Recent investigations have demonstrated that electronic quantum coherence in such a pigment-protein complex persists for several hundreds of femtoseconds even at physiological temperatures [24, 25, 26, 27]. This means that application of the present Hamiltonian tomography scheme is restricted to measurements on the timescale of a few hundred femtoseconds.

We note that the presence of quantum coherence does not necessarily imply purely unitary dynamics. If the evolution is indeed unitary, the values of $|\langle E_j|\mathbf{n}\rangle|$ are constant in time. However, in the presence of dissipation, the measured values of $|\langle E_j|\mathbf{n}\rangle|$ may vary. Provided that the measurement can be made within the timescale in which the dynamics of $|E_j\rangle$ may be characterized by a phenomenological factor Γ_j, then this time dependence would be reflected in measurement of time dependent coefficients $|\langle E_j|\mathbf{n}\rangle|\exp(-\Gamma_j t/2)$. Measuring these quantities at various times within the relevant timescale would then allow estimations of the values $|\langle E_j|\mathbf{n}\rangle|$ by extrapolation back to $t = 0$. Current technology allows controlled shaping of pulses with time duration 10–20 femtoseconds [34, 35, 36, 37], suggesting that such an estimation might be feasible.

There are several additional aspects of the scheme and in particular, of the six assumptions laid out in the previous section, that need to be carefully considered for application to a biomolecular network. Assumptions (i) and (ii) are satisfied for a well-studied system such as FMO, for which crystal structures have been determined [38, 39]. For this system, there is also considerable experimental spectroscopic and theoretical information on the pseudo-spin energy levels [40] (Assumption (iii)) and on the energy eigenvalues of the system [41] (Assumption (v)). The key requirements to consider are thus Assumption (iv), that single site excitation is possible, and Assumption (vi), that measurement in the energy eigenbasis is possible. Achieving single site addressability in a multichromophoric pigment-protein com-

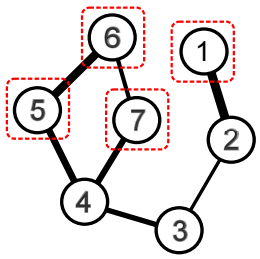

Fig. 4. An example of the set of pigment molecules to be excited in a small pigment-protein complex. Exciting those at sites 1, 5, 6 and 7 (encircled by red dashed lines) individually is sufficient to determine all the Hamiltonian parameters.

plex where chromophores are typically separated by 1-5 nm is a challenging task. Several theoretical studies have addressed the extent to which selective electronic excitation of one chromophore in FMO may be realized by use of phase, amplitude and polarization shaped pulses, both in ensemble and single molecule settings [42, 43, 44]. While theoretical optimization of such coherently controlled excitation generally relies on knowledge of the transition dipole matrix elements, such optimization may also be implemented experimentally without this knowledge, by so-called "learning control" [45]. The requirement of measurement in the energy basis, while readily satisfied by fluorescence detection for the lowest lying energy eigenstate, might also be facilitated for other eigenstates by coherent control, e.g., using pump-probe spectroscopy with shaped probe pulses to select the energy of interest. Effects of homogeneous broadening may be reduced by working at low temperatures and effects of inhomogeneous broadening and orientational disorder by doing single molecule studies. In future work it will be important to examine the effects of incomplete initialization and imperfect measurements, as well as uncertainties in the energy parameters, with a robustness analysis of the gateway scheme.

Using the data of $\{E_j\}$ and $\{\langle E_j|\mathbf{m}\rangle\,(m \in C)\}$ and following the procedure described above with Eqs. (2)-(4), we can then construct the matrix elements of the symmetric matrix corresponding to the Hamiltonian in the one-excitation subspace.

Since the network in Figure 4 contains a loop formed by four sites, we need to access at least four sites, 1, 5, 6, and 7, as described in Sec 3. Let us follow the estimation procedure again briefly for clarity. Suppose that we start from $|\mathbf{1}\rangle$, that is, we set the global phase of $|E_j\rangle$ so that $\langle E_j|\mathbf{1}\rangle$ are real and positive for all j. Then, using Eq. (2), we have

$$\sum_j |(E_j - b_1)\langle E_j|\mathbf{1}\rangle|^2 = c_{12}\langle E_j|\mathbf{2}\rangle, \tag{7}$$

where b_1 can be known from E_j and $\langle E_j|\mathbf{1}\rangle$, thus the left-hand side of Eq. (7) is equal to $\sum_j E_j^2\langle E_j|\mathbf{1}\rangle^2 - b_1^2$. The estimation process then proceeds to site 4 according to Eq. (3), obtaining the values of c_{34} and $\langle E_j|\mathbf{4}\rangle$ with a correct phase. With the measured values of $|\langle\mathbf{5}|E_j\rangle|$, $|\langle\mathbf{6}|E_j\rangle|$, and $|\langle\mathbf{7}|E_j\rangle|$, we can then make use of the following set of equations to obtain the coupling strengths:

$$(E_j - b_4)\langle E_j|\mathbf{4}\rangle - c_{34}\langle E_j|\mathbf{3}\rangle = c_{45}\langle E_j|\mathbf{5}\rangle + c_{47}\langle E_j|\mathbf{7}\rangle, \tag{8}$$

$$(E_j - b_5)\langle E_j|\mathbf{5}\rangle = c_{45}\langle E_j|\mathbf{4}\rangle + c_{56}\langle E_j|\mathbf{6}\rangle, \tag{9}$$

$$(E_j - b_6)\langle E_j|\mathbf{6}\rangle = c_{56}\langle E_j|\mathbf{5}\rangle + c_{67}\langle E_j|\mathbf{7}\rangle, \tag{10}$$

$$(E_j - b_7)\langle E_j|\mathbf{7}\rangle = c_{67}\langle E_j|\mathbf{6}\rangle + c_{47}\langle E_j|\mathbf{4}\rangle. \tag{11}$$

Summing up the modulus squared of each equation over j gives four equations with four unknown parameters, c_{45}^2, c_{56}^2, c_{67}^2, and c_{47}^2. Together with the a priori knowledge on the signs of the set $\{c_n\}$ that was assumed initially, all coupling strengths c_{ij} can now be estimated. The remaining parameters, i.e., b_5, b_6, and b_7, may be evaluated from $|\langle E_j|\mathbf{n}\rangle|$ $(n = 5, 6, 7)$. For example, $b_5 = \langle\mathbf{5}|H|\mathbf{5}\rangle = \sum_j E_j|\langle E_j|\mathbf{5}\rangle|^2$. Thus all parameters of the Hamiltonian have now been identified, despite the lack of the precise information about the phase of $\langle E_j|\mathbf{n}\rangle$.

5 Discussion

We have developed an extension of the gateway scheme of Hamiltonian tomography to estimation of Hamiltonian parameters for subsystems of complex quantum systems that show coherent dynamics for a limited period of time. We circumvent the problem of decay of quantum coherence preventing the observation of reflections of the injected signal that was required in the original scheme of Ref. [1] by employing instead a measurement in the $\{|E_j\rangle\}$-basis. Assuming the feasibility of such a spectrally restricted measurement, we then showed that by choosing the right set of accessible (i.e., spectroscopically excitable) sites, the Hamiltonian of a given network of pseudo-spins can be estimated. These constraints on measurable quantities, in particular the lack of feasibility of measurements in the site basis, were found to modify the requirements for the graph properties. While the Hamiltonians of one-dimensional chains are still estimable by accessing, i.e., preparing, a state at the end site only, as in the original gateway scheme, we now find that, in general, the set of accessible sites needs to be larger than an infecting set. Furthermore, there exist networks to which the current estimation scheme cannot be applied, regardless of the choice of accessible sites, because of the detailed structure of the network topology. This major difference results from the constraint on feasible measurements imposed here and raises interesting questions for the interplay between network topology and measurement capabilities in Hamiltonian identification schemes in general.

As noted in Section 1, when the Hamiltonian matrix for the pseudo-spin system is a sparse matrix, Hamiltonian estimation techniques based on compressed sensing [14, 15, 16] might also be applicable. The Hamiltonian for our one-dimensional example, Eq. (1), is indeed sparse, but in this and the biomolecular applications considered in this work (which may not be sparse in general), the pattern of non-zero elements and their range is known. Furthermore the Hamiltonians are in general not of low rank. Therefore for such systems the use of compressed sensing does not appear to offer benefits, although for large scale general pseudo-spin networks satisfying the requirements on sparsity with unknown pattern of couplings and/or range of couplings, combining compressed sensing approaches with the current Hamiltonian tomography approach may provide a fruitful avenue of exploration.

Application of this spectrally restricted Hamiltonian tomography approach to a small scale network of molecular pigments indicated that provided the spectral measurements can be made on a timescale significantly shorter than the characteristic time for loss of coherence, the Hamiltonian tomography approach may yield useful estimates for parameters of the electronic Hamiltonian describing excitonic energy transfer through a well-characterized aggregate of pigments or pigment-protein complexes. We note nevertheless that realistic application to such systems will require extension of the current approach to include dissipation

and decoherence in a more quantitative manner, e.g., as in Refs. [4, 8, 12, 15, 46, 47, 48], to account for the lack of unitarity that is associated with the subsystem dynamics despite the appearance of quantum coherences at short times. It will also be useful to investigate the robustness of the present scheme to uncertainties in the known parameters and to imperfections in the state initialization and measurement.

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References

1. D. Burgarth, K. Maruyama, and F. Nori, Phys. Rev. A **79**, 020305(R) (2009).
2. D. Burgarth and K. Maruyama, New J. Phys. **11**, 103019 (2009).
3. J. H. Cole, S. G. Schirmer, A. D. Greentree, C. J. Wellard, D. K. L. Oi, and L. C. L. Hollenberg, Phys. Rev. A **71**, 062312 (2005).
4. J. H. Cole, A. D. Greentree, D. K. L. Oi, S. G. Schirmer, C. J. Wellard, and L. C. L. Hollenberg, Phys. Rev. A **73**, 062333 (2006).
5. M. Mohseni and D. A. Lidar, Phys. Rev. Lett. **97**, 170501 (2006).
6. M. Mohseni, A. T. Rezakhani, and D. A. Lidar, Phys. Rev. A **77**, 032322 (2008).
7. B. Lévi, C. C. López, J. Emerson, and D. G. Cory, Phys. Rev. A **75**, 022314 (2007).
8. S. G. Schirmer and D. K. L. Oi, Phys. Rev. A **80**, 022333 (2009).
9. S. Ashhab, J. R. Johansson, and F. Nori, New J. Phys. **8**, 103 (2006).
10. N. P. Oxtoby, A. Rivas, S. F. Huelga, and R. Fazio, New J. Phys. **11**, 063028 (2009).
11. C. T. Schmiegelow, A. Bendersky, M. A. Larotonda, and J. P. Paz, Phys. Rev. Lett. **107**, 100502 (2011).
12. C. D. Franco, M. Paternostro, and M. S. Kim, Phys. Rev. Lett. **102**, 054304 (2009).
13. D. Burgarth, K. Maruyama, and F. Nori, New J. Phys. **13**, 013019 (2011).
14. A. Shabani, R. L. Kosut, M. Mohseni, H. A. Rabitz, M. A. Broome, M. P. Almeida, A. Fedrizzi, and A. G. White, Phys. Rev. Lett. **106**, 100401 (2011).
15. A. Shabani, M. Mohseni, S. Lloyd, R. L. Kosut, and H. A. Rabitz, Phys. Rev. A **84**, 012107 (2011).
16. D. Gross, Y.-K. Liu, S. T. Flammia, S. Becker, and J. Eisert, Phys. Rev. Lett. **105**, 150401 (2010).
17. K. C. Young, M. Sarovar, R. Kosut, and K. B. Whaley, Phys. Rev. A **79**, 062301 (2009).
18. M. A. Nielsen and I. L. Chuang, Quantum Computation and Quantum Information (Cambridge University Press, Cambridge, 2000).
19. G. M. D'Ariano and P. Lo Presti, Phys. Rev. Lett. **86**, 4195 (2001).
20. J. B. Altepeter, D. Branning, E. Jeffrey, T. C. Wei, P. G. Kwiat, R. T. Thew, J. L. OfBrien, M. A. Nielsen, and A. G. White, Phys. Rev. Lett. **90**, 193601 (2003).
21. J. Yuen-Zhou and A. Aspuru-Guzik, J. Chem. Phys. **134**, 134505 (2011).
22. J. Yuen-Zhou, J. J. Krich, M. Mohseni, and A. Aspuru-Guzik, Proc. Natl. Acad. Sci. USA **108**, 17615 (2011).
23. S. Savikhin, D. Buck, and W. Struve, Chem. Phys. **223**, 303 (1997).
24. G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Man.cal, Y.-C. Cheng, R. E. Blankenship, and G. R. Fleming, Nature **446**, 782 (2007).
25. G. Panitchayangkoon, D. Hayes, K. A. Fransted, J. R. Caram, E. Harel, J. Wen, R. E. Blankenship, and G. S. Engel, Proc. Natl. Acad. Sci. USA **107**, 12766 (2010).
26. E. Collini, C. Y. Wong, K. E. Wilk, P. M. G. Curmi, P. Brumer, and G. D. Scholes, Nature **463**,

644 (2010).
27. T. R. Calhoun, N. S. Ginsberg, G. S. Schlau-Cohen, Y.-C. Cheng, M. Ballottari, R. Bassi, and G. R. Fleming, J. Phys. Chem. B **113**, 16291 (2009).
28. N. Christensson, H. Kauffmann, T. Pullerits, and T. Mancal, Arxiv preprint arXiv:1201.6325 (2012).
29. R. E. Fenna and B. W. Matthews, Nature **258**, 573 (1975).
30. D. Burgarth and V. Giovannetti (2007), proceedings, M. Ericsson and S. Montangero (eds.), Pisa, Edizioni della Normale 2008 (arXiv:0710.0302).
31. V. M. Agranovich, Excitations in Organic Solids (Oxford University Press, 2008).
32. A. Ishizaki and G. R. Fleming, Proc. Natl. Acad. Sci. USA **106**, 17255 (2009).
33. S. Hoyer, M. Sarovar, and K. B. Whaley, New J. Phys. **12**, 065041 (2010).
34. J. Vaughan, T. Hornung, T. Feurer, and K. Nelson, Optics letters **30**, 323 (2005).
35. K. Gundogdu, K. Stone, D. Turner, and K. Nelson, Chem. Phys. **341**, 89 (2007).
36. K. Nelson, in Nonlinear Optics: Materials, Fundamentals and Applications (Optical Society of America, 2011).
37. J. Dawlaty, D. Bennett, V. Huxter, and G. Fleming, J. Chem. Phys. **135**, 044201 (2011).
38. R. Fenna and B. Matthews, Nature **258**, 573 (1975).
39. Y. Li, W. Zhou, R. Blankenship, and J. Allen, J. Mol. Bio. **271**, 456 (1997).
40. J. Adolphs and T. Renger, Biophysical journal **91**, 2778 (2006).
41. D. Hayes and G. Engel, Biophysical Journal **100**, 2043 (2011).
42. B. Brüggemann and V. May, J. Phys. Chem. B **108**, 10529 (2004).
43. B. Brüggemann, T. Pullerits, and V. May, Journal of Photochemistry and Photobiology A: Chemistry **180**, 322 (2006).
44. B. Brüggemann, T. Pullerits, and V. May, Journal of Photochemistry and Photobiology A: Chemistry **190**, 372 (2007).
45. H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, Science **288**, 824 (2000).
46. S. Schirmer, D. Oi, and S. Devitt, Institute of Physics: Conferences Series **107**, 012011 (2008).
47. D. Brivio, S. Cialdi, S. Vezzoli, B. T. Gebrehiwot, M. G. Genoni, S. Olivares, and M. G. A. Paris, Phys. Rev. A **81**, 012305 (2010).
48. S. G. Schirmer and D. Oi, Laser Phys. **20**, 1203 (2010).