Distinguishability and “which pathway” information in multidimensional interferometric spectroscopy with a single entangled photon-pair

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Correlated photons inspire abundance of metrology-related platforms, which benefit from quantum (anti-) correlations and outperform their classical-light counterparts. While such demonstrations mainly focus on entanglement, the role of photon exchange-phase and degree of distinguishability have not been widely utilized in quantum-enhanced applications. Using an interferometric setup we show that even at low degree entanglement, when a two-photon wave-function is coupled to matter, it is encoded with a reliable “which pathway?” information. An interferometric exchange-phase-cycling protocol is developed, which enables phase-sensitive discrimination between microscopic interaction histories (pathways). We find that quantum-light interferometry facilitates utterly different set of time-delay variables, which are unbound by uncertainty to the inverse bandwidth of the wave-packet. We illustrate our findings on an exciton model-system, and demonstrate how to probe intraband dephasing in time-domain without temporal resolution at the detection. The exotic scaling of multiphoton coincidence with respect to the applied intensity is discussed.

I. INTRODUCTION

Interferometric spectroscopy introduces myriad of novel platforms, aiming at revealing quantum information encoded on the wave-function of multiple photons [1–6]. One of the most intriguing aspects of many-body quantum dynamics is the exchange statistics of indistinguishable particles. The wave-function acquires a phase upon the exchange of two particles. This affects their dynamics, and is detectable via unique interference patterns in the correlations of two (or more) particles. Coincidence counting of photons [7], current correlations of electrons [8] and fractional-charges (quantum-hall quasiparticles) [9, 10] are notable examples. In quantum electrodynamics, light-matter coupling can be represented as the sum of all possible interaction histories (pathways). These pathways differ by the order of the events, thus, multiphoton nonlinear processes are potentially imprinted with their relative phases. Although the exchange phase of photons is fixed and solely determined by their bosonic nature, it can be effectively manipulated using a well established interferometric setup for a pair of entangled photons [11]. Here, we develop an exchange-phase-cycling scheme that scans through different values of such a phase. We then, demonstrate the capacity of multiphoton wave-function to encode and decipher matter information inaccessible otherwise. Matter information-gain is physically manifested in a reduced number of light-matter configurations, the ability to switch between them, and a new set of time-delay variables with unique characteristics.

In this article, we study the multidimensional spectral information generated by coupling an entangled photon-pair to matter, via combination of interferometers depicted in Fig. 1. Our scheme is composed of two interferometric setups: state preparation, followed by ‘reading’ the quantum state encoded by light-matter information exchange. This results in several notable differences in comparison to the familiar semiclassical nonlinear optics. (i) While semiclassical techniques scan time-delays between pulses, quantum interferometric setups introduce new type of time-delay variables which are not conjugate to the wave-packet bandwidth. (ii) Interferometric wave-mixing of quantum light generates matter pathways unavailable classically due to simultaneous detection of multiple photon propagation paths generated at different times [3]. (iii) They allow separation to new groups of pathways while delivering phase-sensitive read of each process unmatched with classical light techniques. This allows to reconstruct the temporal dynamics. (iv) The coincidence detection obeys unique scaling relations between the applied intensity $I_p$, the light-sample coupling and the detected signal. This enables to avoid damaging disturbance to the sample, and eliminate unwanted signal contributions (background). (v) Coincidence-counting singles out the two-photon sub-space from the total signal, therefore, it restricts the number of possible microscopic processes (selective). Consequently, two-photon signals are sensitive to collective excitations (harmonic and anharmonic), in contrast to single-photon counting which are generated by matter anharmonicities [12, 13].

Our proposed exchange-phase-cycling protocol projects the information encoded in the multidimensional signal, onto lower dimension data which reveal phase-dependent matter correlation functions. Moreover, we harness the interferometric time-delay to probe the dephasing dynamics of the sample, without resorting to time-resolved detection. The latter is determined by the interferometer optical path-difference and is not conjugate to the frequency measurement; paving the way to joint time-frequency resolution beyond the Fourier limitation.
II. RESULTS

A. The setup

The interferometric spectroscopy setup depicted in Fig. 1 is divided into preparation and detection stages. Both play an essential role in acquisition of the nonlinear signal generated by the sample, through its control parameters. In the preparation process, a modified Michelson interferometer creates a photon-pair with tunable degree of distinguishability, using the exchange-phase engineering described below. At the detection stage, HOM interference is sensitive to the post-coupling degree of distinguishability. Symmetric, antisymmetric and asymmetric optical pathways, each carry valuable matter information corresponding to different light-matter coupling history, enable temporal reconstruction. At the end of this section, we summarize the control parameters available using this setup.

1. Preparation

A pump beam is directed into a modified Michelson interferometer using a dichroic mirror, as shown in Fig. 1b and first introduced in Ref. [11]. The beam passes through a BBO (β - barium borate) crystal, that generates a pair of orthogonally (linearly) polarized entangled photons denoted as signal and idler. The pair is fully characterized by the joint spectral amplitude (JSA) \( \Phi(\omega_a, \omega_b) \). The JSA used in our calculations is given by \( \Phi(\omega_a, \omega_b) = A_p (\omega_a + \omega_b) \varphi(\omega_a, \omega_b) \) where \( A_p(\omega) = \exp\left[ (\omega - \omega_p)^2 / 2\sigma_p^2 \right] \) is a symmetric pump Gaussian envelope with bandwidth \( \sigma_p \), centered around \( \omega_p \) [14]. The phase-matching factor \( \varphi(\omega_a, \omega_b) = \text{sinc} \left[ (\omega_a - \omega_{\text{ac}})T_a + (\omega_b - \omega_{\text{ac}})T_b \right] \) breaks the frequency exchange symmetry. Here \( \omega_{\text{ac}} / L \) is the central frequency of the signal and idler, and \( T_{a/b} = L \left( v_a^{-1} - v_p^{-1} \right) \), where \( L \) is the nonlinear crystal length and \( v \) is the inverse group velocity at the relevant central frequency \( \omega_{\text{ac}} / L \). The JSA can exhibit strong exchange asymmetry, imprinting the horizontal \( |H\rangle \) and the vertical \( |V\rangle \) polarization quantum channels with distinct spectral signatures. All beams (pump, signal and idler) are then split by a 50:50 BS, and each path is manipulated separately. On one arm the polarizations are swapped by passing twice through a \( \lambda / 4 \) plate, while the other undergoes a controlled path delay introducing the phase \( \theta \). In the second passing through the BBO crystal (first during the generation), due to the exchanged polarizations, the spectral profile is flipped from \( \Phi(\omega_a, \omega_b) \) to \( \Phi(\omega_b, \omega_a) \). The transmitted part of the beam from the DM is then given by the \( \theta \)-symmetrized amplitude, resulting in the two-photon wave-function

\[
|\Psi_\theta\rangle = \int d\omega_a d\omega_b \Phi_\theta(\omega_a, \omega_b) a^\dagger(\omega_a) b^\dagger(\omega_b) |\text{vac}\rangle \quad (1a)
\]

\[
\Phi_\theta(\omega_a, \omega_b) = \frac{1}{\sqrt{2}} \left[ \Phi(\omega_a, \omega_b) + e^{i\theta} \Phi(\omega_b, \omega_a) \right], \quad (1b)
\]
Figure 2. Joint spectral amplitude. The JSA in Eq. 1b is presented for selection of \( \theta \) values used on the excitation model system. (a) The non-symmetrized amplitude two photon amplitude in frequency domain, with Schmidt number \( \kappa = 1.01 \). Symmetrized amplitude using (b) \( \theta = \frac{\pi}{2} \) with \( \kappa = 1.06 \), (c) \( \theta = 0 \) with \( \kappa = 1.58 \) and (d) antisymmetric \( \theta = \pi \) with \( \kappa = 2.87 \). Each bar-plots signify the Schmidt decomposition resulting from the corresponding amplitude.

where \( |\text{vac}\rangle \) is the noninteracting vacuum. Broadband pumping of type-II parametric down-converter, is known to generate photon-pairs with strong spectral distinguishing information (see [11, 15], and Sec. S1 of the SM). We shall show in Sec. II B3 that the asymmetric part of the JSA to \( (\omega_a, \omega_b) \) exchange plays a significant role in recovering the real part of the matter correlation function for microscopic matter processes that are symmetric to exchange. Fig. 2a depicts the non-symmetrized JSA in frequency domain. Fig. 2b-d then present \( \theta = \pi/2, 0 \) and \( \pi \) used in the cycling protocols presented below. The JSA was computed with \( \omega_p = 4 \) eV, with a 4 mm nonlinear crystal with \( T_a = 6.1 \) fs and \( T_b = 230 \) fs. The Schmidt number \( \kappa_\theta \equiv \left[ \sum_n p^2 \langle n|\theta\rangle \right]^{-1} \) computed by a diagonalization of the discretized single photon reduced density matrix, following the procedure in Ref. [14]. Here, \( p \langle n|\theta\rangle \) is an eigenvalue that can be interpreted as the \( n^{th} \) mode probability using \( \theta \)-symmetrized JSA. It provides a measure for the effective two-photon Hilbert space [14]. The Schmidt decomposition resulting from each JSA is plotted in the bar-plots showing relatively low number of participating modes, hence low degree of entanglement. Note that for \( \theta = \pi \) Schmidt modes appear in pairs, as reported in Ref. [14, 16].

2. Detection and coupling

The coincidence signal is obtained by a two-photon expectation-value at the detection plane. Since the detection event is represented by an annihilation of a photon by the detector, it is useful to begin the analysis from the detection stage. We then describe the light-matter interaction stage using the joint density operator. Interferometric setups can be simply described by a basis transformation between the detection and interaction stages [3]. Two separate coincidence detection protocols are considered; as depicted in Fig. 1. The coincidence observables corresponding to the two detection protocols \( U_D^I \) and \( U_D^R \) reflect two-photon population in their respective domain (time-frequency). Both setups contain several independent control parameters that manipulate the excitation and detection mechanisms. Detection related control parameters include the HOM relative delay \( T \), and when resolved \( (U_D^I)^\dagger \), the detected frequencies \( (\omega_a, \omega_b) \). The exchange phase \( \theta \), pump bandwidth \( \sigma_p \), pump central frequency \( \omega_p \) and the pair central frequencies \( (\omega_a, \omega_b) \) constitute the excitation related control parameters. The first three \( (\theta, \sigma_p, \omega_p) \) can be scanned continuously in a single setup. Additional control parameters are the entangled pair central frequencies \( (\omega_a, \omega_b) \), which require a special quasi-phase-matching preparation procedure [17].

Total coincidence signal – \( U_D^I \) The total coincidence count is described as annihilation of two modes by two detectors. When the signal is not temporally resolved, the annihilation time is integrated over. The corresponding observable is given by the operator

\[
\hat{O}_I(t_a, t_b) = E^\dagger_{a,R}(r_a, t_a) E_{b,R}(r_b, t_b) E_{a,L}(r_a, t_a) E^\dagger_{b,L}(r_b, t_b) \quad (2)
\]

Here, \( E_R \) and \( E_L \) are electric field superoperators, corresponding to Hilbert-space operators that act from the right \( E_R^\dagger \equiv E^\dagger_R \), and left \( E^\dagger_L \equiv E_L^\dagger \) of the density operator. The Hilbert-space polarization-dependent field operator is given by \( E_{\sigma} (r, t) = \sum_k \sqrt{\frac{\Omega_k}{2\pi}} \hat{\epsilon}_\sigma (k) a_{k,\sigma}^\dagger (t) e^{i k \cdot r} \), where \( \hat{\epsilon}_\sigma (k) \) is the \( \sigma \)-polarization vector, \( \Omega_Q \) is the quantization volume \( (c = 1) \), and \( a_{k,\sigma}^\dagger (t) \) are annihilation (creation) operators obeying the bosonic commutation relations \( [a_{k,\sigma}, a_{k',\sigma'}^\dagger] = \delta_{\sigma,\sigma'} \delta_{k, k'} \). \( \hat{O}_I \) expresses annihilation of two-modes from the left and right of the density operator, projecting the two-photon subspace in the measurement. The coincidence signal is finally obtained by taking the expectation value of Eq. 2 in the interaction picture

\[
\mathcal{C}[\Lambda_I] = \int dt_a dt_b \quad \times \left\langle \left[ \mathcal{T} \hat{O}_I (t_a, t_b) \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^{t} ds H_{\text{int},-} (s) \right\} \right] \right\rangle , \quad (3)
\]

where \( \Lambda_I = (\omega_p, \sigma_p, \theta, T) \) represents the set of control parameters available in this measurement protocol. \( \langle \hat{O} \rangle \equiv \text{tr} \{ \hat{O} \rho_0 \} \) denotes the trace with respect to the
initial state of the joint density operator $\rho_0 = \rho(t_0)$ and $T$ is the time ordering superoperator. The light-matter coupling is described by the interaction superoperator, corresponding to the commutator of the Hilbert-space interaction Hamiltonian and the density operator, $H_{\text{int}} - \rho \equiv [H_{\text{int}}, \rho]$. We adopt the the multipolar interaction Hamiltonian in the rotating wave approximation (RWA) $H_{\text{int}} = \mathbf{E} \cdot \mathbf{V} + \text{H.c.}$, where $\mathbf{V}$ is the dipole lowering-operator. Within RWA, emission of a photon is associated with energy decrease of the sample while absorption with an increase. Note that the total coincidence counting signal $C_I$ is obtained by integration over photon arrival times – unresolved due to the lack of temporal gating.

The frequency-resolved coincidence-counting – $U^\dagger_{II}$

The frequency-resolved signal is obtained by a double annihilation of optical modes, and defined by the corresponding frequency-domain superoperators. These are related to time-domain counterparts using Fourier transform $E_\sigma(r,t) = \int \frac{d\omega}{2\pi} e^{i\omega t} E_\sigma(r,\omega)$. Similarly, the observable $\hat{O}_{II}$ is given by

$$\hat{O}_{II} (\omega_a, \omega_b) = E^\dagger_{a,R}(r_a,\omega_a) E^\dagger_{b,R}(r_b,\omega_b) E_{b,L}(r_b,\omega_b) E_{a,L}(r_a,\omega_a),$$

and the coincidence signal is obtained by the respective expectation value

$$C[\Lambda_{II}] = \left\langle T \hat{O}_{II} (\omega_a, \omega_b) \exp \left\{-\frac{i}{\hbar} \int_{t_0}^{t} ds H_{\text{int}} - \rho (s) \right\} \right\rangle.$$  (5)

Here $\Lambda_{II} = \{\omega_a, \omega_b, \omega_p, \sigma_p, \theta, T, \}$ are the corresponding control parameters.

When implementing Eqs. 3 and 5, it is crucial to note that the light-matter coupling are taken at different stages of the interferometer. Consequently, they are given in different basis sets and require the linear transformation described next.

**Interferometric photon basis-transformation**

Due to the HOM interferometer, the optical modes involved in the light-matter coupling, and the detected modes are given in different basis sets. The transformation Jordan-Schwinger map can be represented using an $SU(2)$ rotation in the frequency-domain [18–22], resulting in the input-output relation

$$\hat{R}_{T} = \begin{pmatrix} t & ire^{i\omega T} \\ ire^{-i\omega T} & t \end{pmatrix}.$$  (6)

Here $t$ and $r$ are the transmission and reflection coefficients obeying $|t|^2 + |r|^2 = 1$, and $T$ is the relative time-delay. For the 50:50 BS considered here, $t = r = 1/\sqrt{2}$. The field in vector notation is given by

$$(\mathbf{E}(r,\omega) = (E_a(r,\omega), E_b(r,\omega))^T,$$ under the HOM rotation the detected field is expressed by $E_{\text{det}}(r,\omega) = \hat{R}_{T} \mathbf{E}_{\text{interaction}}(r,\omega)$. In the following, we express all field operators in the basis set of the interaction domain $E_{\text{interaction}} = E(r,\omega)$, which requires the inverse rotation of the observable in Eq. 2 (see SI for detailed derivation) [3].

**B. Application to an exciton model**

Consider the three-level exciton model-system depicted in Fig. 3a, with energy manifolds corresponding to the ground, singly and doubly excited states $(g, e, f)$ respectively. We expand Eqs. 3, 5 to $4^{th}$ order light-matter coupling $H_{\text{int}}$. In Fig. 3b we show two groups of light-matter

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**Figure 3. Exciton model system and coupling pathways.** (a) Three-level model system composed of ground $\{\{g\}\}$, single $\{\{e\}\}$ and doubly excited $\{\{f\}\}$ manifolds. The (red) arrows pointing interchangeably up and down correspond to Raman pathways. The (purple) arrows arranged in two consecutive absorption followed by two emissions correspond to two-photon resonances. (b) Diagrammatic representation of the contributing microscopic light-matter processes. Straight arrows represent an interaction corresponding to both fields. Curved arrows represent the detection (annihilation) process. Diagram $D_1$ involve double excitations (reaching the $f$-manifold) and referred to as two-photon resonance (TPR). $D_2$ and $D_3$ describe single excitations (e-manifold) and denoted Raman processes (RP). The two distinct sub-groups of processes are depicted in panel (a).
coupling pathways; two-photon resonance (TPR) and Raman processes (RP), represented in loop diagrams $D_1,$ and $D_2,$ $D_3$ respectively. TPR interaction sequences begin with two-photon absorption events $|\{g\}\rangle \rightarrow |\{e\}\rangle \rightarrow |\{f\}\rangle,$ while RPs involve $|\{g\}\rangle \leftrightarrow |\{e\}\rangle$ transitions (and do not involve the $f$ manifold). The diagrams describe the light-matter interaction on a closed time-contour (Keldysh) in which the ket (bra) evolve forward (backward) in time $[23, 24].$ The sample is taken to be initially in the ground-state $\rho (\infty) = |g_i\rangle \langle g_i|,$ each inward (outward) arrow denotes interaction-induced excitation (de-excitation) of the sample, and the final state of the sample is stated at the top of each diagram. Note that the reflection (interchanging the bracket arrows) of all $D_i$ is obtained by complex conjugation. We assume initially uncorrelated field-matter density operator $\rho (\infty) = \rho_{gf} (\infty) \otimes \rho_{\mu} (\infty),$ where $\rho_{gf} (\infty) = |\Psi_f\rangle \langle \Psi_f|$ is the two-photon initial pure-state.

Below, we show the signals obtained using the two coincidence-counting detection protocols presented in Fig. 1, $U_D^{\dagger/11}.$ The probability of observing each of the microscopic processes $(D_i)$ varies with the number of detected photons, consequently it is sensitive to the final state of the sample; in contrast to a similar signal obtained with a classical source. When single photons are detected, all the processes contribute regardless to the number of generated photons $[25, 26].$

1. Total-coincidence – probing intraband dephasing

The celebrated HOM dip, is an interference pattern of the total coincidence-count of photon-pairs, obtained by varying their relative path-delay $T$ $[27].$ The count obtains its minimal value for $T = 0,$ and vanishes altogether when the pair is completely indistinguishable. Detection protocol $U_D^{\dagger}$ manifests a HOM interference of the pair posterior to the interaction with a sample. A signature of matter energy-fluctuations shape the interference pattern in the presence of the field. Under the conditioned elaborated below, it is possible to isolate the contribution of diagram $D_3$ and probe the intraband dephasing in time-domain. This measurement contains no time resolved detection, using exclusively the HOM relative delay, which is not conjugate to any frequency variable.

The coincidence signal is derived for general pulse parameters and corresponding symmetrization procedure (initial state) in Sec. S1 of the SM. The signal is derived using diagrams $D_1,$ $D_2$ and $D_3$ resulting in Eq. S7. Simpler expressions are obtained for a narrowband pump pulse, using degenerate phase-matching condition for the entangled pair, fixing $\omega_a = \omega_b = \omega / 2.$ In this case, the phase-matching condition $\varphi (\omega_a, \omega_b)$ is maximal for identical central frequencies $\omega_a = \omega_b$ of the entangled pair. We assume a narrowband pump of bandwidth (FWHM) $\Delta \lambda / \lambda_p \leq 10^{-7}$ where $\lambda_p$ is the central frequency of the pump. The central frequency is scanned in the range of $0.1 - 3eV$ attainable by pulse-duration in the order of $\tau_p \approx 10$ ps.

\[ C [\Lambda] = C (\omega_p, 0, T) \]

\[ \propto \text{Re} \text{tr} \left\{ VG V^\dagger \left( - \frac{\omega_p}{2} \right) V^\dagger \left[ 1 - iG (T) \right] VG \left( \frac{\omega_p}{2} \right) \right\}, \]

where we have used the fully symmetric initial state for the field ($\theta = 0$), selectively isolating $D_3.$ Here $G (t) = -i \theta (t) e^{-iH_{\mu} t}$ is the Green function of the sample and its Fourier transform $G (\omega) = \frac{1}{2} (\omega - H_{\mu} + i\epsilon),$ introducing the phenomenological dephasing rate $\gamma$ ($h = 1$). It is convenient to read Eq. 7 from the density matrix, the sample optically excited to a populated excited state than de-
excited back to the ground manifold where the observable $1 - iG(T)$ is measured (see Eq. S9 of the SI for the full sum-over-states expression). The time domain Green’s function is evaluated at the ground state (initial energy manifold), and thus reveals its temporal dynamics at time $T$. Scanning $\omega_p$ and performing the Fourier transform of the signal with respect to the pair $\{\omega_p, T\}$, we obtain the spectra presented in Fig. 4a-b

$$S = \int \frac{d\omega_\gamma}{2\pi} C[\Lambda_I] e^{i\omega_\gamma T}. \quad (8)$$

Note that $T$ and $\omega_p$ are non-conjugate pair and in principle can be resolved to arbitrary accuracy. Fig. 4a depicts the spectrum obtained for intraband dephasing $\gamma_g = 1\text{meV}$ (4ps) and more rapid interband dephasing $\gamma_{eg} = 10\text{meV}$ (0.4ps). The latter contribute to the line-shape broadening, limiting the frequency resolution. Fig. 4b presents the same for equal interband and intraband dephasing $\gamma_{eg} = \gamma_g = 1\text{meV}$ (4ps). Fig. 4b depicts the spectrum obtained for equal interband and intraband dephasing $\gamma_{eg} = \gamma_g = 1\text{meV}$ (0.4ps). Fig. 4c presents the coincidence-count $C[\Lambda_I]$, obtained by varying the delay HOM delay parameter $T$ and tracing over $\omega_p$,

$$C_T = \int \frac{d\omega_p}{2\pi} C[\Lambda_I]. \quad (9)$$

We note that similar plot is obtained using monochromatic $\omega_p$. Exponentially decaying envelope of the intraband dephasing is visible (time-domain) is modulated by the fast oscillations at the transition frequencies. Two possible dephasing rates are illustrated $\gamma_g = 1$ and $2\gamma_g = 2\text{meV}$, as well as the fast decay of $\gamma_{eg}$.

### 2. Frequency-resolved coincidence

A natural extension of the coincidence-counting above, includes frequency resolution of the detected photons depicted as detection protocol $(U_D^{\text{II}})$ in Fig. 1. The detected photons add two dimensions to the above signal, resulting in a set of control parameters $\Lambda_{II} = \{\omega_a, \omega_b, \theta, T, \omega_p, \sigma_p\}$. Expansion of Eq. 5 to 4th order, introduces another characteristic phase-factor $\exp\{i\eta\}$ due to the HOM delayed-path trajectories, where $\eta = (\omega_a - \omega_b) T$ (see Sec. III of the SM for full derivation). There are multiple ways to explore the high dimensional signal, one way is by fixing the pair $(\theta, \eta)$. For brevity we use the shorthand notation $C_0(\pi) \equiv C[\Lambda_{II}]$ where $\eta$ can be fixed for any pair of frequencies $(\omega_a, \omega_b)$ using the delay variable $T$. Also, it is convenient to introduce the auxiliary functions corresponding to the real $\mathcal{R}_i = \Re\{\Xi_i\}$ and imaginary $\mathcal{I}_i = \Im\{\Xi_i\}$ parts of the respective pathway contributions. Here $i = \{\text{TPR, RP}\}$, and $\Xi_i$ encapsulate all the microscopic processes that contribute to each of the respective pathways (see Sec. III of the SM for explicit expressions). Explicitly, the choice $(\theta, \eta) = (0, \pi)$ results in

$$C_0(\pi) = \mathcal{I}_{\text{TPR}}(\omega_a, \omega_b) + \mathcal{I}_{\text{RP}}(\omega_a, \omega_b), \quad (10)$$

in which both pathway-groups are observed, as shown in 5a. The calculations executed for an entangled pair generated by a broadband pump with $\sigma_p = 0.9eV$ ($\approx 1fs$ pulse). The central frequency $\omega_p$ is scanned in the range of $2 - 5eV$ and all dephasing rates are identical $\gamma_{ij} = 5\text{meV}$. The Schmidt number $\kappa_{G} \approx 2.7$ for the above parameters, with a $L = 0.4\text{mm}$. Fig 5a depicts all contributing pathways, where we observe Fano-like resonances [28] located along the diagonal in which $\omega_a + \omega_b = \omega_{f,gi}$, such that $\omega_{a/b} = \omega_{f,gi}$, $\omega_{p/a} = \omega_{f,cj}$. The RP pathways are observed along the lines corresponding to the transitions $\omega_{c,gi}$. Similar results are obtained with doubled bandwidth ($\sigma_p$) corresponding to $\kappa_{G} \approx 1.7$. The coincidence-count vanishes for $(\theta, \eta) = (0, 0)$ as we would expect for indistinguishable photons.

### 3. Exchange-phase-cycling

Pathway selectivity enables to study the dynamics in greater detail, categorizing microscopic processes into distinguishable families related by permutations of the light-matter interaction sequence. Frequency-resolved detection $(U_D^{\text{II}})$ depicted in Fig. 1 achieves just that – isolating the real and imaginary part of each process exclusively – thanks to exchange-phase-cycling protocols introduced below.

We propose exchange-phase-cycling method whereby several signals with different control parameters are combined to selectively observe desired pathways. These exploit both interferometers; manipulating the effective exchange phases prior and after the interaction respectively $(\theta, \eta)$. The (modified) Michelson interferometer (Fig. 1b) imprints any permutation of the initial photon-pair with a relative phase-factor. The HOM detection interferometer introduces path-related phase factor to the detected photons. Certain combinations of $(\theta, \eta)$ are useful in reconstructing the real and imaginary parts of the signals individually (See Sec. III of the SM for full derivation and final expressions). For this purpose, it is useful to introduce the Fourier transform of the coincidence signal $D_\theta = \int d\Omega e^{-i\omega_\gamma \theta} C_0(\eta)$ (presenting 2D spectral map along the lines $\Omega = \omega_a - \omega_b$). Combinations of $C_0(\eta)$ and $D_\theta$ render phase-sensitive reconstruction of the TPR and RP processes possible exclusively.

The cycling protocols are not unique, there are multiple choices of linearly-dependent cycling protocols to achieve path selectivity. Here, we display one cycling protocol resulting in the 2D spectra presented in Fig. 5a-e. 5d-g depicts the cycling protocol corresponding to the real $\mathcal{R}_i$ and imaginary $\mathcal{I}_i$ parts of the respective con-
The imaginary (d) and real (e) part of the RP pathway following the cycling protocols in Eqs. 11c.

The Schmidt number κ that ω along the diagonal lines in which we observe Fano-like resonances [28] located using an ultrafast pump with varying bandwidth; from a narrowband σp = 1.8meV corresponding to ≈ 1ps pulse, to broadband σp = 0.9meV using a ≈ 1fs pulse. The central frequency ωp is scanned in the range of 2−5eV and all dephasing rates are identical γij = 5meV. Due to the cycling parameters, the real part of the response is strongly dependent on the degree of asymmetry of the initial state. The asymmetric part of the JSA gains stronger expression in the ultrafast regime, and become negligible for a narrowband [11, 29]. Therefore, the signal corresponding to the protocols in Eqs. 11a−11d are calculated using an ultrafast pump with σp = 0.9meV and depicted in Fig. 5b−e respectively. The Schmidt number κθ for the above parameters and a L = 0.4mm, varies between 1−5 (depending on θ).

In our calculations we have used an entangled pair generated by a pump with varying bandwidth; from a narrowband σp = 1.8meV corresponding to ≈ 1ps pulse, to broadband σp = 0.9meV using a ≈ 1fs pulse. The central frequency ωp is scanned in the range of 2−5eV and all dephasing rates are identical γij = 5meV. Due to the cycling parameters, the real part of the response is strongly dependent on the degree of asymmetry of the initial state. The asymmetric part of the JSA gains stronger expression in the ultrafast regime, and become negligible for a narrowband [11, 29]. Therefore, the signal corresponding to the protocols in Eqs. 11a−11d are calculated using an ultrafast pump with σp = 0.9meV and depicted in Fig. 5b−e respectively. The Schmidt number κθ for the above parameters and a L = 0.4mm, varies between 1−5 (depending on θ). Figs. 5b−e present the TPR pathway, where we observe Fano-like resonances [28] located along the diagonal lines in which ωa + ωb = ωf, where such that ωa/b = ωc/g1, ωb/a = ωf, where Note that the transition ωf, where ωc/g1 is 2eV is not resolved in TPR yet it appears in RRP, this stems from the antisymmetric nature of the JSA Φ (ωa, ωb) which vanishes when ωa = ωb. While ITPR is symmetric to the exchange, RRP is antisymmetric and thus fully resolved. Nonetheless, different choices of cycling may resolve this transition (see Sec. S5 of the SM and Fig. 5a for such example). Figs. 5d−e depict the RP pathway, scanning the single exciton energy manifold from which all transitions ωc, g1 are visible. Finally, one can verify that the information in panel (a) of Fig. 5 is composed of a combination of panels (b) and (d), excluding the degenerate transitions in which ωa = ωb.

C. Comparison with classical wave-mixing

Nonlinear spectroscopic signals are usually described semiclassically using a sequence of temporally-separated bright classical pulses (containing many photons), that trigger matter dynamics and result in a single photon [30]. The generated photon is modulated by m light-matter interactions, resulting in m + 1 order correlation function (m+1 wave-mixing). This nonlinear response is given by the expectation value of the integrated change of the electric field intensity I = ∫ dt ⟨I⟩ [31]. The intensity is a single photon quantity, related to the electric field operator I = E† E. Quantum sources can reach superior signal-to-noise ratio scaling (Heisenberg limit) [32–36], enabling reduced radiation exposure for comparable measurement certainty. Particularly, to improve
the resolution of sensitive samples, limited by radiation dose constraints [37]. One way to benefit from the quantum properties of the EM field, is via direct coupling of quantum-light with to the sample (e.g. entangled photons, squeezed states). Sample stimuli using such sources has shown to yield remarkable control over population dynamics and pathway selection [25, 38, 39]. Alternatively, as done here, one can probe quantum effects of the emitted radiation directly via multiple photons counting (e.g. antibunching [40], supersresolved imaging [41–44]).

Following this reasoning, are interested in multiple photon-detection. The resulting wave-mixing is denoted \((n + m)\)-WM corresponding to the application of \(m\) fields and detection of the \(n\) photons. While \((m + 1)\)-WM depend on several pathways, \((n + m)\)-WM are naturally restricted to lower number of diagrams and may not be written in the form of amplitude-square. Specifically to the above setup, coincidence counting eliminates the single photon diagram depicted in Fig. 6 denoted \(S\). This occurs since only one photon is populated in final state. This cancellation yields significant change in the observed physics compared to single-photon (intensity) signal. Intensity observable generated from nonlinear processes, are generated from anharmonicities in signal. Intensity observables generated from nonlinear states. This cancellation yields significant change in the observed physics compared to single-photon (intensity) signal. Intensity observables generated from nonlinear processes, are generated from anharmonicities in signal. Intensity observable generated from nonlinear processes, are generated from anharmonicities in signal. Intensity observables generated from nonlinear processes, are generated from anharmonicities in signal.

The second detection protocol, involves frequency-locking the central frequency of the pair-\(S\)WM also give rise to different intensity-coupling-signal scaling relations. For example, double excitation signals induced by entangled pairs are known to scale linearly (rather than quadratically) with the pump intensity \(I_p\) [45–47]. This unique effect permits studying doubly excited manifold with smaller probability of ground-state bleaching, thus potentially reduce sample damage.

While single photon detection events scale linearly with the pump \(\propto I_p\), the two-photon signal scales quadratically \(\propto I_p^2\) maintaining the double excitation probability linear with the pump. This allows application of lower intensities per desired detection gain, improving signal to noise ratio [48–50]. This principle can be generalized to \(n\) photon population detection in a straightforward manner.

III. DISCUSSION

The measurement of a fixed number of photons using coincidence detection narrows down the observed physics of the sample. Only microscopic pathways which are terminated with a certain final-state contribute. In contrast, nonlinear signals observed with classical light are not sensitive to the last state of the matter. Specifically, two-photon coincidence of weakly-coupled entangled pair to a sample generates a unique \((2+2)\) wave-mixing, eliminating some microscopic pathways. Like four-wave-mixing \((4\text{-WM})\), the signal depends on a four point dipole correlation function of matter. The difference is that the elaborate detection does not single out one field, as the \(4\text{-WM}\) signal, but two fields are detected. We can thus view the process as a generalized \(4\text{-WM}\). To Avoid confusion we simply refer to it as \((2+2)\) WM, corresponding to the number of applied and detected fields.

In the first detection scheme, we have considered the total photon coincidence-count in the absence of spectral and temporal resolutions. The two-natural control-parameters of the setup depicted in Fig. 1 are the HOM relative delay \(T\), and the central frequency of the pair-generating pump \(\omega_p\). A fascinating effect occurs when considering a degenerate phase-matching condition with a symmetric narrowband JSA \((\theta = 0)\); such that the photon-pair are distributed sharply around half the pump frequency \(\omega_p/2\). The TPR pathways vanish and the only RP pathway that survives is diagram \(D_3\) (Fig. 3). This generates the following dynamics: (1) the density matrix of the sample is excited then de-excited back to the initial band (here, ground) (2) Green’s function of the system at time \(T\) is measured. Since \(T\) is controlled with arbitrary precision, the intraband dephasing dynamics can be reconstructed temporally as shown in Fig. 4a-c. This provides a potential platform to characterize the system’s coupling to its environment. Small \(T\) expansion can reveal moments of the sample Hamiltonian \((H_s)\) and provided in Sec. S2 of the SM. This provides a compelling direction for future study aligned with the great efforts invested in studying decoherence and energy leaks in current quantum technologies.

The second detection protocol, involves frequency-
resolve coincidence-counting. By cycling values of $T$ and the entangled pair exchange-phase $\theta$ we are able to discriminate between TPR and RP pathways. Known pathway-selection-protocols typically generate destructive interference to suppress certain populations [25], or induce distinct scaling of each process with the intensity [38]. Here, we select pathways by projecting the high-dimensional signal to process-specific data, without reducing the event probability of other processes. Moreover, by combining signals with different $\theta$ and $T (\omega_a - \omega_p)$ (phase cycling), we demonstrate the ability to obtain the phase of four-point matter correlation-function in Fig. 5b-e. This implies that temporal reconstruction is possible by straightforward Fourier transform. Interestingly, the cycling protocols related to the real part of the correlator require an asymmetric JSA for exchange, inherited from the pump in the ultrafast pumping regime. This suggests that obtaining temporal behavior of the correlator necessitates an ultrashort generating pump – which is compatible with temporal resolution – despite that the measurement is conducted in frequency domain. An ultrashort pump generate a spontaneous pair that carry an identity-revealing spectral information [15]. The resulting distinguishability renders a “which-pathway?” information available. The relation between the JSA asymmetry and the temporal resolution upper-bound merit further study, since the temporal and frequency control parameters are not conjugate quantities. Notably, these effects occur specifically at low entanglement values and steered by the variable effective exchange phase.

In addition to the benefits listed above, matter-induced field nonlinearities may also improve the frequency resolution [35, 36]. Correlation-based detection techniques – such as coincidence – can reveal such electromagnetic field nonlinearities. These correlations are signatures matter-induced photon-photon coupling [51], free-electrons coupling [52] and thus carry matter information that is imprinted in the post-interaction counting-statistics. Characterization of the ‘reading’ process that access this information, is one of the central goals of interferometric-spectroscopy.

IV. MATERIALS AND METHODS

Schmidt number calculation

The Schmidt number is a function of the (single photon) reduced density matrix. It enables to represent the JSA in the following way

$$\Phi_{\theta} (\omega_a, \omega_p) = \sum_n \sqrt{p(n|\theta)} \psi_n(\omega_a) \phi_n(\omega_p).$$

(12)

Here $\{\psi_n, \phi_n\}$ are single photon eigenfunctions and their weights $p(n|\theta)$. To obtain this representation we solve $p(n|\theta) \psi_n (\omega) = \int d\omega' K_1 (\omega, \omega') \psi_n (\omega')$ and $p(n|\theta) \phi_n (\omega) = \int d\omega' K_2 (\omega, \omega') \phi_n (\omega')$. These kernels are found from the reductions $K_1 (\omega, \omega') = \int d\omega'' \Phi_{\theta} (\omega, \omega'') \Phi_{\theta}^* (\omega', \omega'')$ tracing the second frequency variable, and $K_2 (\omega, \omega') = \int d\omega'' \Phi_{\theta} (\omega'', \omega) \Phi_{\theta}^* (\omega'', \omega')$. They can be interpreted as single-photon correlation functions [14]. To obtain the Schmidt spectrum and characterize the degree of entanglement, we discretize the kernels and numerically solve the integral eigenvalue equations. We have used a $900 \times 900$ kernel discretization grid and calculated separately for each $\theta$. The Schmidt number which is a measure of the effective Hilbert space dimensionality is obtained by

$$\kappa_{\theta} = \frac{1}{\sum_n p^2 (n|\theta)}.$$  

(13)

Intraband dephasing signal computation

Eq. 7 reveals the intraband dephasing in time-domain using solely the HOM relative delay $T$ as scanning time-variable. We express the correlation functions using the dipole lowering operator $V = \sum_{i,j} \mu_{ij} |j\rangle \langle i|$ and its complex conjugate, where $(i, j)$ label energy eigenstates of the exciton system corresponding to $|g_f\rangle, |e_q\rangle$ and $|f_i\rangle$. The expectation value in Eq. 7 is requires Green’s function of the sample in frequency domain $G(\omega) = (\omega - H + i\epsilon)^{-1}$, where $H$ is the Hamiltonian of the sample. With these definitions, we obtain the coincidence counting for our model system

$$C[\Lambda] \propto \sum_{e,e',g} \frac{1}{\frac{\pi}{2} - \omega_{e'E'} - i\gamma_{g'g}} \frac{1}{\frac{\pi}{2} - \omega_{eg} + i\gamma_{eg}} \langle g' | [1 - iT (T)] | g' \rangle$$

used in the calculations presented in Fig. 4. The short-lived excited-states of the first excited manifold serve as a prefactor to the relaxation process of the ground state manifold. The calculation of Eq. 8 in Fig. 4 where obtained on a discretized grid by scanning $10^4$ frequency, and $10^4$ points corresponding to $\omega_p$ and $T$ respectively.

2D spectra calculation

The results for the section were obtained by direct implementation of Eqs. S22–S25 in Sec. S4 of the SM. The JSA was discretized within the shown interval in Fig. 5 in a $200 \times 200 \times 200 \times 200$ corresponding to $\omega_a, \omega_p, \omega_p$ and the implementation of the numerical integration. The signal shown Fig. 5 is obtained by integration over $\omega_p$. The ultrashort pump induces large exchange asymmetry in addition to its broad frequency range coverage.

SUPPLEMENTARY MATERIALS

Supplementary material for this article are attached.
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