Fundamental limits of pulsed quantum light spectroscopy of a two-level atom

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We study the fundamental limits of the precision of estimating parameters of a quantum matter system when it is probed by a travelling pulse of quantum light. In particular, we focus on the estimation of the interaction strength between the pulse and a two-level atom, equivalent to the estimation of the dipole moment. Our analysis of single-photon pulses highlights the interplay between the information gained from the photon absorption by the atom, as measured in absorption spectroscopy, and the perturbation to the field temporal mode due to spontaneous emission. Beyond the single-photon regime, we introduce an approximate model to study more general states of light in the limit of short pulses, where spontaneous emission can be neglected. We also show that for a vast class of entangled biphoton states, quantum entanglement provides no fundamental advantage and the same precision can be obtained with a separable state. We conclude by studying the estimation of the electric dipole moment of a sodium atom using quantum light. Our work initiates a quantum information theoretic methodology for developing the theory and practice of quantum light spectroscopy.

I. INTRODUCTION

Spectroscopy seeks to estimate one or more parameters appearing in the model of a matter system by measuring the light that has interacted with it. Recent technological developments have made it possible to use quantum light in spectroscopy [1], e.g., few-photon Fock, squeezed or entangled states that exhibit nonclassical spatial or temporal correlations [2]. This resulted in sensing with sensitivity better than the classical shot noise limit [3–6], in obtaining different scaling of the spectroscopic signals [7] with incident light intensity, as well as in new spectroscopic techniques [8–10]. Despite many proposals to perform spectroscopy with pulses of quantum light, a rigorous and quantitative assessment of the best achievable precision, and of the potential advantage of using entangled light, remains absent.

In this paper, we start to uncover the fundamental limits of quantum light spectroscopy by employing the tools of quantum estimation theory underlying quantum metrology. Our aim is to understand the extent to which the intrinsic enhancements of quantum metrology [11, 12] are relevant under the particular circumstances of practical quantum light spectroscopy experiments [1, 13]. Specifically, we focus on a paradigmatic scenario that can be considered a minimal example of quantum spectroscopy: A pulse of quantum light is used to probe a single two-level atom, as illustrated in Fig. 1, with the objective of estimating the light-atom coupling parameter $\Gamma$, proportional to the change in the modal structure of pulsed light after the light-atom interaction, and the latter by the change in the modal structure of pulsed light after the light-atom interaction.

Our work chooses this simplest of matter systems to establish a quantum information theoretic methodology for analysing quantum light spectroscopy. Calculating the fundamental bounds set by quantum mechanics to the precision of estimating $\Gamma$ requires a full description of the quantum state of the light and all mathematically valid detection techniques. The former is made challenging by the change in the modal structure of pulsed light after the light-atom interaction, and the latter by the infinitude of possibilities. Nevertheless, for single-photon pulses for instance, we clearly identify two sources of information about the parameter $\Gamma$: A “classical” one, related to absorption spectroscopy [14], and a “quantum” one, related to fluorescence lifetime estimation [15] and fluorescence spectroscopy [16]. That our methodology can elucidate phenomena typically studied in separate frameworks speaks to its strength.

Our work thus stands in contrast to previous ones where quantum estimation theory has been applied to estimating the light-matter coupling parameter in cavity-based setups [17, 18], wherein only one discrete mode of the light field is involved. It also stands in contrast to the analysis of spectroscopic signals that rely on evaluating the expectation values of particular observables [16], different for various spectroscopic setups. Finally, our methodology

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relies on studying the exact dynamics of a pulse interacting with a single atom. This is in contrast to “conventional” approaches [1, 19] that relate the induced polarizations in ensembles to the measured signals or treat the matter “effectively” [20–22].

Our main results are as follows:

1. We derive the fundamental precision bounds for estimating $\Gamma$ with generic single-photon and entangled biphoton states (in the slowly-varying envelope approximation, assumed throughout the paper), in Eqs. (30) and (44) respectively.

2. We identify practically reasonable measurements that achieve the fundamental precision for single-photon pulses in Sec. III A 3.

3. We show that there is, in general, no quantitative relationship between the precision of estimating $\Gamma$ and the excitation probability using a certain pulse (see e.g., Fig. 2). However, the two quantities are related for Fock states in the short-pulse regime, as in Sec. IV C.

4. For single-photon pulses, we show that the probability of losing the photon from the original travelling pulse wavepacket contains a relevant portion of the total information about the parameter that would be available at the end of the experiment in the ideal case, i.e., where all the spontaneously emitted light can be measured optimally. The ratio becomes one half in the limit of short pulses (see e.g., Fig. 3).

5. In Sec. IV B we show that in the limit of short pulses and detection of the light shortly after the interaction (in units of the atom lifetime) the variance of estimating $\Gamma$ decreases as the inverse of the pulse duration and as $1/n$ if probed by $n$-photon Fock states.

6. In Sec. V A we show that for entangled biphoton probes with real-valued temporal envelopes, entanglement is not a fundamental resource to enhance the estimation precision, since there always exists an unentangled single-photon probe that performs at least as well.

All the results in this paper, apart from 1. above, are obtained under the assumption of no detuning between the pulse carrier frequency and the transition frequency of the atom.

The paper is structured as follows. In Sec. II we present our theoretical framework: The model of light-matter interaction and a summary of local quantum estimation theory. In Sec. III we present an extensive analysis of the limits of the precision of estimating $\Gamma$ using single-photon pulses. In Sec. IV we approximate the problem to a much simpler one in the regime of short pulses and present a general solution within this approximation. In Sec. V we extend the analysis to entangled biphoton pulses, investigating the potential advantage afforded by such states. In Sec. VI we apply our general results to the EDM estimation of a sodium atom. We conclude in Sec. VII with a brief discussion.

II. THEORETICAL FRAMEWORK

We begin with a theoretical model of light-atom interaction, followed by a description of the quantum states of a travelling pulse of light. We then provide a brief introduction to quantum estimation theory necessary to quantify the fundamental and achievable precision in parameter estimation.

A. Model

1. Atom, field, and their interaction

We consider a single two-level atom (the “atom” or A subsystem) fixed in space modelled by its free Hamiltonians $H^A$. The ground and excited states of the atom are denoted by $|g\rangle$ and $|e\rangle$ respectively. Setting the ground state energy to zero,

$$H^A = \hbar \omega_0 |e\rangle\langle e|,$$

(1)

where $\omega_0$ is the transition frequency.

We next consider a travelling pulse of quantized radiation field (the “pulse” or $P$ subsystem), which must be described by a continuum of frequencies. As is customary in spectroscopic setups, we assume the field to have a well-defined direction of propagation. This leads to the free field Hamiltonian [23]

$$H^P = \hbar \int_0^\infty d\omega \omega a^\dagger(\omega)a(\omega),$$

(2)

with the bosonic operators $[a(\omega), a^\dagger(\omega')] = \delta(\omega - \omega')$ labelled by a continuous frequency $\omega$. We further assume the field to be sufficiently narrowband around a carrier frequency $\bar{\omega}$, to invoke the so-called quasi-monochromatic or slowly varying envelope approximation. Then the positive-frequency part of the electric field operator (in the interaction picture with respect to $H^P$) is

$$E(t) = i\hbar e A(\bar{\omega}) \int_{-\infty}^\infty \frac{d\omega}{\sqrt{2\pi}} a(\omega) e^{-i\omega t},$$

(3)

where $e$ is a unit polarization vector, $A(\bar{\omega}) = \sqrt{\bar{\omega}/(2e_0cA\hbar)}$ and $A$ is the transverse quantisation area.

The interaction between the travelling pulse and the atom is schematically illustrated in Fig. 1. It is modelled by an interaction term $H_1$. As the atom is much smaller than typical optical wavelengths, the interaction is well described by the dipole approximation. Making next the rotating wave approximation, the interaction Hamiltonian in the interaction picture generated by the unitary
transformation \(e^{-i(H_A + H_P) t}\) takes the standard form \([24]\)

\[
H_{AP}^t = d(t) \cdot E^t + d^t(t) \cdot E(t),
\]

\[
= -\hbar \sqrt{\Gamma} (a(t) - a^t(t))
\]

(5)

where \(d(t) = \mu_{eg} \sigma_- e^{-i\omega_0 t}\) is the positive frequency part of the dipole operator, \(\mu_{eg} = -q_e e |r| g\) is the relevant dipole matrix element \((q_e\) is the charge of the electron), and \(\sigma_- = |g \rangle \langle e| = \sigma_-^t\). In Eq. (5) we have introduced the so-called “quantum white-noise” operators

\[
a(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\sqrt{2\pi}} a(\omega)e^{-i(\omega-\omega_0)t}
\]

(6)

satisfying \([a(t), a^t(t')] = \delta(t - t')\) and the constant \(\Gamma = (\mu_{eg} \cdot \epsilon)^2 A(\omega)^2\) proportional to the square of the dipole moment.

In addition to the bosonic mode \(a\) that describes the pulse degrees of freedom, an atom in free space interacts with an infinitude of other modes of the electromagnetic field. We account for this by introducing a coupling to an additional bosonic mode \(b\) with a free Hamiltonian analogous to Eq. (2), leading to the interaction-picture Hamiltonian

\[
H_{AP}^t = -\hbar \sigma_+ \left( \sqrt{\Gamma} a(t) + \sqrt{\Gamma}_b b(t) \right) + \text{h.c.},
\]

(7)

where the additional set of white noise operators \(b(t)\) satisfying \([b(t), b^t(t')] = \delta(t - t')\) represents a collective “environment” (E) subsystem coupled to the atom. For completeness, we show in Appendix A that this is equivalent to a more realistic model where the environment consists of a discrete set of infinitely many modes.

Our approach is to treat A, P and E, as distinct subsystems, of which P is the only one that can be measured experimentally. This will change slightly in Sec. V for entangled biphoton states: the signal (S) subsystem plays the role of P, but an additional idler (I) subsystem that does not interact with either A or E, is also assumed to be measurable. The atom-environment interaction in Eq. (7) seeks to capture an experimental scenario where light emitted into the environment is irreversibly lost. Mathematically, this means tracing out the subsystem E; the resulting reduced dynamics of the atom-pulse state is governed by a master equation in Lindblad form

\[
\frac{d \rho_{AP}(t)}{dt} = -\frac{i}{\hbar}[H_{AP}^t, \rho_{AP}(t)] + \Gamma_a D[a] \rho_{AP}(t),
\]

(8)

where we have introduced the superoperator \(D[a] \rho = \Delta aA^t - \frac{1}{2} \{aA^tA + A^tA\rho\}\). While a master equation treatment is very useful numerically, for single-photon pulses it will be easier to solve the full unitary dynamics. We take the latter approach in Sec. III.

Although the Hamiltonian in Eq. (7) is obtained in the white noise limit—a Markov approximation, this is not enough to have a reduced dynamics in Lindblad form for a generic initial state of the E subsystem. The Lindblad form is guaranteed because the initial state is the vacuum and thus temporally uncorrelated. On the contrary, nonclassical initial states of the field, such as Fock or squeezed states, have temporal correlations and induce a non-Markovian reduced dynamics of the atom \([29]\). This will be the case for the initial state of the pulse. However, the reduced dynamics of the atom can generally be described by hierarchies of master equations \([26, 30, 31]\) or by using a fictitious cavity with suitable time-dependent coupling \([32, 33]\), as we briefly summarize in Appendix B.

The interaction Hamiltonian in Eq. (7) can be used to describe light-matter interactions in different scenarios by assigning different relative magnitudes to the quantities \(\Gamma_a\) and \(\Gamma\). In a free-space configuration with the atom probed by paraxial light, there is usually a strong coupling with the environment and a weak coupling with the pulse, resulting in \(\Gamma_a \gg \Gamma\) \([34]\). Nonetheless, by matching the pulse spatial and polarization degrees of freedom to the dipole pattern of the atom, one could in principle obtain a perfect coupling \(\Gamma_a = 0\) even in free space \([35]\). However, the scenario \(\Gamma_a = 0\) is mostly employed to study two-level atoms in one-dimensional waveguides \([36, 37]\).

In this paper, we will not grapple with such model-dependent details and take the Hamiltonian in Eq. (7) as our starting point until Sec. VI. There we will apply our methods to estimating the dipole moment of the Sodium \(D_2\) transition using travelling pulses of quantum light. Furthermore, we will always assume that the atom is initially in the ground state, because we want to model light absorption and the corresponding excitation induced by the pulse. However, if we keep the same Hamiltonian but started the dynamics with the atom in the excited state and both P and E in the vacuum, the overall decay rate would be \(\Gamma_{tot} = \Gamma + \Gamma_a\) \([26, 28, 35, 38]\), and in free-space this corresponds to the standard rate obtained from Wigner-Weisskopf theory \(\Gamma_{tot} = \frac{\mu_{eg}^2 A^2}{3 \pi e^2 h^3}\).

2. Quantum states of the travelling pulse

To describe a pulse of light travelling in a well-defined direction quantum mechanically, we introduce the continuous Fock states \([23]\)

\[
|n \xi\rangle = \frac{1}{\sqrt{n!}} \left( \int_0^{\infty} d\omega \hat{\xi}(\omega) a^t(\omega) \right)^n |0rangle,
\]

(9)

where \(\hat{\xi}(\omega)\) is the single-photon spectral amplitude, a square-integrable normalised function describing the wavepacket. As mentioned before, we assume the light to be sufficiently narrowband around the carrier frequency \(\bar{\omega}\), which we further assume to equal the atomic transition
frequency. Thus, $\tilde{\omega} = \omega_0$. In this regime, we can extend the integral in Eq. (9) to the whole real line and introduce the temporal amplitude $\xi(t) = \int_{-\infty}^{\infty} \frac{d\omega}{\sqrt{2\pi}} \tilde{\xi}(\omega)e^{-i(\omega-\omega_0)t}$, i.e., an envelope that modulates oscillations at the carrier frequency, as depicted in Fig. 1. Then we can introduce the photon-wavepacket creation operator (satisfying $[A_\xi, A_\xi^\dagger] = 1$)

$$A_\xi^\dagger = \int_{-\infty}^{\infty} dt \xi(t)a^\dagger(t) = \int_{-\infty}^{\infty} d\omega \tilde{\xi}(\omega)a^\dagger(\omega)$$

(10)

where $a(t)$ are defined in Eq. (6). In general $\xi(t)$ can be considered as one element of a complete orthonormal basis of functions $\xi_j(t)$, known as temporal modes [39, 40] (e.g., Hermite-Gauss polynomials if $\xi(t)$ is Gaussian). The Hilbert space of the $P$ subsystem is thus the tensor product of the Fock spaces associated to each temporal mode and the most general pure state therein is written as $\sum_n \sum_{n,j} c_{n,j}[n\xi_j]\rangle$. Thus, even if the description of a travelling pulse needs an underlying continuous degree of freedom (i.e., $\omega$ or $t$), the initial state describing the incoming pulse is effectively single-mode using the photon-wavepacket operators. The Fock states in Eq. (9) can be reexpressed as $|n\xi\rangle = \frac{1}{\sqrt{m}}A_\xi^n|0\rangle$ and descriptions of other states such as coherent states

$$|\alpha\rangle = e^{\alpha A_\xi^\dagger - \alpha^* A_\xi}|0\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}|n\xi\rangle,$$

(11)

with average photon number $\int_{-\infty}^{\infty} dt \langle\alpha\rangle a^\dagger(t)a(t)|\alpha\rangle = |\alpha|^2$ and squeezed vacuum states [31, 40]

$$|s\rangle = e^{\frac{1}{2}(rA_\xi^2 - r^* A_\xi^2)}|0\rangle = \frac{1}{\sqrt{e}} \sum_{n=0}^{\infty} \frac{r^n}{\sqrt{(2n)!}} \frac{\sqrt{2n+1}}{n!}|2n\xi\rangle,$$

(12)

with average photon number $\int_{-\infty}^{\infty} dt \langle s\rangle a^\dagger(t)a(t)|s\rangle = \sinh^2|s|$ (where $r = |s|e^{i\phi}, c = \cosh r$ and $s = e^{i\phi}\sinh r$) follow.

The preceding is not the most general scenario, since generic quantum states of light are supported on multiple temporal modes [42], e.g., realistic single-beam squeezed states obtained from parametric downconversion [23, 43]. We leave the analysis of this more general case for future studies. Note, however, that the entangled biphoton states in Sec. V necessarily involve multiple temporal modes.

Finally, having defined $\xi(t)$ and $a(t)$ as Fourier transforms centered around $\omega_0$, for a detuning $\Delta = \omega_0 - \tilde{\omega} \neq 0$ the temporal amplitude $\xi(t)$ acquires a linear temporal phase$^2$ equivalent to a shift of the spectral amplitude [44]. Since a complex-valued temporal amplitude might effectively make the pulse not resonant, a real $\xi(t)$ is to some extent a “natural assumption on resonance” [45], a choice we will also make in the following. A detailed study of the effect of detuning on pulsed quantum light spectroscopy of a two-level atom will be presented in following publications [46, 47].

B. Local quantum estimation theory

Estimation theory quantifies the precision in estimating the value of a parameter $\Gamma$ from experimental observations $x$ distributed according to a probability distribution $p_{\Gamma}(x)$ belonging to a parametric family. Quantum mechanically, $p_{\Gamma}(x) = \text{Tr}(\rho_{\Gamma}\Pi_x)$—the probability distribution of the collected data is obtained from the Born rule. Here $\rho_{\Gamma}$ is a quantum state depending on the parameter $\Gamma$, $\Pi_x$ is an element of a positive operator-valued measure (POVM), which mathematically describes a quantum measurement [48], and $x$ labels the possible experimental outcomes. For example, in a photon counting measurement $x$ is the number of detected photons. In this paper, $\rho_{\Gamma}$ may correspond either to the joint state of the atom and light or to the reduced state of the light only.

Denoting by $\hat{\Gamma}$ an unbiased estimator of $\Gamma$, its variance satisfies the Cramér-Rao bound (CRB) [49]

$$\text{Var}[\hat{\Gamma}] \geq \frac{1}{M C(\rho_{\Gamma}, \Pi_x)},$$

(13)

where $M$ is the number of repetitions of the experiment and $C(\rho_{\Gamma}, \Pi_x)$ is the classical Fisher information (CFI)$^3$ defined as

$$C(\rho_{\Gamma}, \Pi_x) = \sum_x \frac{1}{p_{\Gamma}(x)} \left( \frac{\partial p_{\Gamma}(x)}{\partial \Gamma} \right)^2,$$

(14)

where the summation becomes an integral for continuous distributions. Since the inequality (13) can be saturated in the limit $M \rightarrow \infty$ [49], e.g., by the maximum likelihood estimator, the CRB encodes the maximal precision that can be extracted by the collecting data from the distribution $p_{\Gamma}(x)$.

To identify the fundamental quantum limit on the variance of the estimator, the CFI must be maximised over all possible POVMs, obtaining [50–53]

$$\max_{\{\Pi_x\}} C(\rho_{\Gamma}, \Pi_x) = Q(\rho_{\Gamma}),$$

(15)

where we introduced the quantum Fisher information (QFI), defined as

$$Q(\rho_{\Gamma}) = \text{Tr}[\rho_{\Gamma}L_{\Gamma}^2],$$

(16)

$^2$ Applying a temporal phase means modifying the temporal amplitude as $\xi(t)e^{i\phi(t)}$, preserving the distribution $|\xi(t)|^2$.

$^3$ Since the CFI depends only on the classical probability distribution $p_{\Gamma}(x)$, we will often use $C(p)$ to denote the CFI of a particular $\Gamma$-dependent distribution $p$, dropping the $\Gamma$ dependence too.
where $L_Γ$ is the symmetric logarithmic derivative (SLD), an Hermitian operator satisfying the Lyapunov equation

$$\frac{∂ρ_Γ}{∂Γ} = p_ΓL_Γ + L_Γρ_Γ.$$

The bounds on the estimation precision are thus

$$\text{Var}[\tilde{Γ}] \geq \frac{1}{M C(ρ_Γ,Π_Γ)} \geq \frac{1}{M Q(ρ_Γ)}.$$

The latter inequality is known as the quantum CRB on the variance. We assume that $M$ can be made sufficiently large, so that we can meaningfully focus on the CFI and QFI as the relevant figures of merit to quantify the estimation precision. This setting is known as local estimation, since the CFI and QFI are defined locally around the true value of the parameter ($ρ_Γ$ and $∂Γρ_Γ$ evaluated at the true value of $Γ$ in all the equations above). For small $M$, non-local approaches such as Bayesian or minimax estimation would be more suitable.

Note that the CFI and QFI are dimensional quantities if the parameter has physical dimensions. To ease the comparison for different parameter values, we will focus on the dimensionless QFI $Γ^2 Q(ρ_Γ)$ that captures the estimation precision relative to the true parameter value. It sets a fundamental upper bound on the relative estimation precision $Γ^2 / \text{Var}[Γ]$, formally the squared inverse coefficient of variation of the unbiased estimator. These quantities are sometimes referred to as the quantum and classical signal-to-noise ratio (SNR) [53]; we do not adopt this terminology to avoid confusion with homonymous experimental quantities.

While the QFI defined in Eq. (16) does not have a simple closed-form expression in general and must be evaluated by diagonalizing the density matrix [53, 54], in some cases more explicit formulas can be obtained. For a pure state $|Ψ_T⟩$

$$Q(|Ψ_T⟩) = 4 \langle \partial_ΓΨ_T | Ψ_T⟩^2.$$

Another case that will be relevant is the rank-2 mixed state $ρ_T = |ψ_e⟩⟨ψ_e| + |ψ_g⟩⟨ψ_g|$, obtained from tracing out the atomic degrees of freedom from a pure state of the form $|ψ_T⟩ = |e⟩⟨\tilde{ψ}_e| + |g⟩⟨\tilde{ψ}_g|$. The two vectors $|\tilde{ψ}_e⟩$ and $|\tilde{ψ}_g⟩$ describing the quantum states of the field are neither normalized nor mutually orthogonal, and generally infinite-dimensional. In this paper we will use the tilde to denote unnormalized state vectors. In this scenario, the QFI can be evaluated explicitly without rewriting $ρ_T$ on an orthonormal basis by solving Eq. (17) using non-orthogonal bases [55–57], as recently shown in the context of superresolution imaging. We use this technique in Sec. IV.

Another useful property of the QFI is the extended convexity [58, 59]

$$Q\left(\sum m p_{m,Γ}ρ_{m,Γ}\right) \leq C(p_{m,Γ}) + \sum_i p_{i,Γ}Q(ρ_{m,Γ}),$$

where $p_{m,Γ}$ is a (potentially parameter-dependent) probability distribution and $ρ_{m,Γ}$ are normalized quantum states. In words, the QFI of a generic mixture is upper bounded by the CFI of the mixing probability plus the average QFI of the states; this reduces to standard convexity when the mixing probability does not depend on the parameter. This equation can be understood as a consequence of the monotonicity of the QFI under completely positive, trace-preserving maps [60], since the right-hand side of Eq. (20) is the QFI of the state $∑_m p_{m,Γ}ρ_{m,Γ} ⊗ |m⟩⟨m|$ while the left-hand side is obtained via its partial trace, potentially losing information. In the context of probabilistic quantum metrology, a state in this form can be obtained by making a selection measurement on an initial state and storing the outcome in an ancillary system that acts as a classical register [61]. If the states $ρ_{m,Γ}$ have support in mutually orthogonal subspaces (at least in the neighbourhood of the true parameter value), then the information contained in the classical register $\{|m⟩⟨m|\}$ is formally redundant, and Eq. (20) is saturated with equality.

III. SINGLE-PHOTON PULSES

We now begin the presentation of our results on quantum light spectroscopy of a two-level atom using single-photon pulses. This is a simple, yet conceptually rewarding and practically relevant scenario of quantum light spectroscopy. The results of this section can be applied to arbitrary pulse shapes, but we present analytical expressions for a few paradigmatic ones studied in the literature [35], often focusing on a rectangular pulse for clarity. This is more than a mere theoretical exercise, since the realization of nontrivial single-photon wavepackets is a well-developed experimental field [44, 62–65].

We first present the general, analytical expression for the QFI for single-photon pulses. Then we evaluate the QFI for various pulse shapes when the atom is perfectly coupled to the incoming pulse, i.e, $Γ_0 = 0$. Finally, we present results for an atom that can also emit spontaneously into an environment, focusing in particular on the free-space case where $Γ_0 ≫ Γ$, where we elaborate on the relation to single-photon absorption spectroscopy.

A. General expressions

1. Unitary evolution of atom, pulse and environment

We start by assuming the atom to be in the ground state. Then, the global atom-pulse-environment state never contains more than one excitation due to the form of the interaction Hamiltonian in Eq. (7). This state is given by (omitting the explicit time dependence for
where again we have suppressed the explicit time dependence. In the long-time limit we obtain an incoherent mixture of the vacuum and the state defined in Eqs. (21)–(26) is normalized, as we show in Appendix D (see also Ref. [28, Appendix D]). Note also that the global probability distribution \( \rho_{\Gamma} \) of not losing a photon is partly given [36] (see also Ref. [28, Appendix D])

\[
\rho_{\Gamma} = \left| \psi_{\Gamma} \right|^2 + \left\langle \tilde{\psi}_g^E \left| \tilde{\psi}_g^E \right\rangle, \quad \left| \psi_{\Gamma} \right| = \left| \psi_g^P \right| / \sqrt{\left\langle \tilde{\psi}_g^E \left| \tilde{\psi}_g^E \right\rangle.} \tag{28}
\]

The QFI of \( \rho_{\Gamma} \) is then the CFI of the two-outcome probability distribution \( \{p_T, 1 - p_T\} \) plus the QFI of the pure single-photon state rescaled by the corresponding probability:

\[
\mathcal{Q}(\rho_T) = \frac{(\partial_T p_T)^2}{p_T(1 - p_T)} + (1 - p_T)\mathcal{Q}(\left| \psi_{\Gamma} \right\rangle) \tag{29}
\]

\[
\equiv \mathcal{C}(p_T) + \mathcal{Q}(\left| \psi_{\Gamma} \right\rangle). \tag{30}
\]

This QFI equals the right-hand side of (20), saturating the extended convexity bound, since the two pure states in the mixture are orthogonal and the vacuum contains no information on \( \Gamma \).

There are two contributions to the fundamental limit on the precision of estimating \( \Gamma \):

(i) The probability \( p_T \) of losing a photon from the pulse due to absorption by the atom, giving the CFI \( \mathcal{C}(p_T) \) which we call the classical contribution to the total QFI \( \mathcal{Q}(\rho_T) \), and

(ii) The perturbation to the temporal shape of the single-photon wavepacket due to spontaneous emission, giving the QFI of the pure single-photon state (rescaled by the corresponding probability of not losing a photon) \( \mathcal{Q}(\left| \psi_{\Gamma} \right\rangle) = (1 - p_T)\mathcal{Q}(\left| \psi_{\Gamma} \right\rangle) = 4(1 - p_T)\left(\partial_T \left| \psi_{\Gamma} \right\rangle \left(\partial_T \left| \psi_{\Gamma} \right\rangle - \left| \partial_T \left| \psi_{\Gamma} \right\rangle \right)^2\right), \) which we call the quantum contribution.

In Appendix D we report more explicit expressions for \( \xi(t) \in \mathbb{R} \) in terms of the normalized single photon state \( \left| \psi_g^E \right\rangle. \) These are more convenient in the calculations of the following sections.

3. Optimal measurements

We now discuss the means of attaining (i) and (ii) above.

The classical term (i) in the QFI (30) is attained by any measurement that perfectly distinguishes the vacuum from the single-photon component. In principle, this is always possible and corresponds to a POVM with an element \( \Pi_0 = \left| \phi_0 \right\rangle \left\langle \phi_0 \right|, \) completed on the single photon subspace by a POVM with outcomes \( s \) (continuous or discrete) \( \Pi_{1,s} = \int d\tau d\tau' \Pi_{1,s}(\tau, \tau')a^\dagger(\tau)0^P(a(\tau')) \). This yields the joint probabilities \( p_0 = \text{Tr}[\rho_0 \Pi_0] = p_T \) and \( p_{s,1} = \text{Tr}[\rho_T \Pi_{1,s}] = (1 - p_T)\left| \psi_{\Gamma} \right\rangle \left| \psi_{\Gamma} \right\rangle, \) corresponding to the marginal and conditional probabilities \( p_1 = \int ds p_{s,1} = 1 - p_T \) and \( p_{s,1}/p_1 = \left| \psi_{\Gamma} \right\rangle \left| \psi_{\Gamma} \right\rangle, \) where we have used the overall CFI

\[
\rho^p = \left( \left| \psi_c \right|^2 + \left( \tilde{\psi}_g^E \left| \tilde{\psi}_g^E \right\rangle \right) \left| 0^P \right\rangle \left\langle 0^P \right| + \left| \tilde{\psi}_g^E \right\rangle \left\langle \tilde{\psi}_g^E \right|, \tag{27}
\]

where again we have suppressed the explicit time dependence. In the long-time limit \( t \to \infty \) the atom decays to the ground state and becomes disentangled from the light, but for \( \Gamma_1 > 0 \) the initial photon of the pulse is partly lost to the environment.
The first term of this expression is exactly the classical contribution (i) in Eq. (30), for any choice of the single-photon POVM $\Pi_{1,s}$. Physically, this is the information obtained by measuring the photon loss, as in single-photon absorption spectroscopy. Indeed, the CFI $C(p_T)$ represents all the information available when the measurement detects the presence of a photon but is insensitive to the shape of the wavepacket, i.e., a trivial single outcome POVM $\Pi_{1,s} = \delta(s - 1, \tau' - \tau')$ (formally the identity in the single-photon subspace such that $\langle \psi_T | \Pi_1 | \psi_T \rangle = 1$ for any $| \psi_T \rangle$).

The quantum term (ii) can be attained by choosing an appropriate single-photon POVM. A projection onto the output state $| \psi_T \rangle$ itself (more precisely the projection on a state $| \psi_{\tau'} \rangle$ in the limit $\Gamma' \rightarrow \Gamma$) saturates the QFI. This is an optimal measurement in local pure-state quantum estimation [67]. For completeness we show this explicitly in Appendix E. There are, however, infinitely many POVMs that saturate the QFI for pure states and they generally differ in how robust they are to imperfections in their practical implementation. The most robust POVM for which the CFI is least degraded by a worst-case small perturbation can be found exactly [68], and chosen in absence of other practical constraints.

Such formally optimal measurements may however be experimentally impractical. Consequently, we present two more measurements that are optimal for attaining (ii) when $\xi(t) \in \mathbb{R}$, an assumption that we will make for the explicit results in the next sections. The first is the POVM

$$\Pi_{1,s}(\tau, \tau') = \delta(s - \tau) \delta(\tau - \tau')$$

yielding the conditional probability density $p_{s|1} = |\psi_T(s)|^2$. For $\psi_T(s) \in \mathbb{R}$ and $\partial_T \psi_T(s) \in \mathbb{R}$ we have $\int ds |\partial_T \psi_T(s)|^2 = 0$ and the CFI of the probability distribution $p_{s|1} = \psi_T(x)^2$ equals the pure-state QFI, since $\int ds |\partial_T \psi_T(s)|^2 |\psi(s)|^2 = 4 \int d\tau |\partial_T \psi_T(s)|^2$.

The POVM in Eq. (31) operationally corresponds to measurement of photon arrival times, which can be accomplished using time-correlated single-photon counting (TCSPC) [69]. While TCSPC is ordinarily used in lifetime measurements using single-photon fluorescence spectroscopy, where the atom is assumed to be already excited and the excitation process itself is not modeled (TCSPC is, in fact, optimal for single exponential lifetime detection [15]), our proposal is somewhat different. The quantum term (ii) is saturated by the TCSPC measurement of the probability distribution $p_{s|1}$, which amounts to the measurement of the modulus-squared of the time-dependent envelope of the conditional single-photon state. However, to measure also the absorption probability and saturate the classical term (i), one should also know precisely the number $N_{inc}$ of photons incident on the two-level system, so that the probability can be estimated as $p_0 = 1 - N_{TCSPC}/N_{inc}$ for large $N_{inc}$, where $N_{TCSPC}$ is the total number of TCSPC counts. This is different from standard fluorescence detection, where one assumes the measured single-photon wavepacket to be a decaying exponential, and $N_{TCSPC}$ only acts as a normalization factor.

The second optimal measurement is to detect the light in a discrete orthonormal basis of temporal modes that includes the original pulse temporal mode, corresponding to a rank-1 projective POVM $\Pi_{1,s} = |\xi\rangle \langle \xi|$, where $|\xi\rangle = \int_{-\infty}^{\infty} d\tau \xi(\tau) a^\dagger(\tau) |0_T\rangle$. The optimality of temporal mode-resolved photodetection here has been studied in detail in Ref. [47] and will be presented in a follow-up paper [46].

Finally, we consider a suboptimal measurement that will be relevant in the following: Detecting photons only in the original unperturbed temporal mode of the pulse. For single photons, this corresponds to a two-outcome POVM with elements $\Pi_1 = |\xi\rangle \langle \xi| + \Pi_0 = 1 - \Pi_1$, where $|\xi\rangle = \int_{-\infty}^{\infty} d\tau \xi(\tau) a^\dagger(\tau) |0_T\rangle$ is the initial state of the single-photon pulse. The probability of such a detector clicking for the state in Eq. (27) is thus $p_{orig} = Tr[\Pi_1 \rho_T(t)] = |\langle \xi| \psi^g_T(t) \rangle|^2$. Clearly this measurement is suboptimal because it does not discriminate the vacuum from temporal modes orthogonal to $\xi$, which become populated due to the spontaneous emission of the atom. The performance of this measurement in attaining the quantum limit in Eq. (30) is addressed in the next section for some specific examples; we will see that this measurement is optimal or close to optimal when the effect of spontaneous emission is negligible.

### B. Perfect atom-pulse coupling

To further clarify our understanding of quantum light spectroscopy using single-photon pulses, we now focus on perfect atom-pulse coupling by setting $\Gamma = 0$. We study the effect of different pulse shapes by considering a few paradigmatic real-valued temporal amplitudes $\xi(t)$.

#### 1. Asymptotically long time

We start by studying the asymptotic case $t \rightarrow \infty$, when the final state of the pulse contains exactly one photon, and is pure and disentangled from the atom, i.e., $p_T = 0$. Then all the information about the parameter $\Gamma$ is encoded in the temporal shape of the wavepacket, which is perturbed due to the interaction.

In Fig. 2 we show the QFI of the asymptotic single-photon state as a function of pulse duration, for various pulse shapes. We define the pulse duration $T_\sigma$ as the standard deviation of the initial single-photon temporal distribution $\xi(t)^2$ to aid the comparison of different shapes; we will later use a different convention for rectangular
pulses, whose duration is unambiguously defined. The mathematical descriptions of the pulse shapes considered in Fig. 2 are provided in Appendix F, together with the available analytical expressions for the quantities of interest. Note that the dimensionless QFI depends solely on the dimensionless combination $\Gamma T_\sigma$.

Fig. 2 shows that the various pulse shapes display the same qualitative behaviour. The QFI increases linearly as the pulse duration increases from $T_\sigma = 0$. It reaches a maximum for a value around the fluorescence lifetime $\Gamma T_\sigma = 1$. Overall, there is a mild dependence on the particular shape. This behaviour is similar to that of the maximum excitation probability of the atom [35, 45], shown in the inset of Fig. 2. One might naively think that a higher excitation probability of the atom, which corresponds in some sense to a “better” interaction between the atom and the pulse, would correspond to a higher QFI of the outgoing pulse of light. Our results show otherwise. Firstly, the optimal pulse duration for a given pulse shape for the two quantities are different. Secondly, while a rising and a decaying exponential pulse of the same duration yield the same asymptotic QFI, i.e., overlapping curves in Fig. 2, the rising exponential is optimal to excite the atom [45, 70] (reaching one in the inset plot), while the decaying exponential performs much worse.

In Fig. 3, we show how much information can be extracted by detecting the photon in the original temporal mode compared to the information available in the asymptotic state by plotting the ratio between the CFI of this detection strategy $\mathcal{C}(\rho_{\text{orig}})$ (for $t \to \infty$) and the asymptotic QFI (already plotted on its own in Fig. 2). In the limit of short pulses $T_\sigma \to 0$ this ratio tends to the value 1/2; curiously it is always 1/2 for the rising and decaying exponentials. This has been proven exactly for all pulse shapes except for Gaussian pulses, for which all the quantities must be evaluated by solving the integrals numerically. We conjecture this to be a general feature of this metrological problem in the $T_\sigma \to 0$ limit, since the details of the pulse shape should be less relevant in this regime.

It is remarkable that for quantum light spectroscopy with single-photon pulses, this simple detection strategy yields a substantial fraction of the maximal information available, quantified by the asymptotic QFI, about the parameter. As we show in the next section, measuring the photon in the original temporal mode has the advantage that the information can be obtained rather rapidly after the interaction (about femto- or picoseconds for ultrafast pulses), without the need to wait for the atom to decay (timescale of nanoseconds in standard atomic and molecular systems). While this may be of limited appeal in spectroscopy, it may be exploited in quantum information processing.

Finally, one could in principle, optimize the pulse shape to maximise the estimation precision. Given the recent advances in the experimental shaping of single-photon wavepackets [44, 62, 64, 71], this could be of practical use.

2. Finite time

For finite $t$, the atom remains partially excited and the overall atom-pulse state entangled, so the classical contribution $\mathcal{C}(\rho_{\text{F}})$ in Eq. (30) now plays a role. While atom-pulse entanglement can in principle mean that not all the information is accessible by measuring the pulse subsystem only, at least for real-valued $\xi(t)$ and $\Gamma_\perp = 0$ this is not the case. In fact, there is no information about $\Gamma$ in the relative phase of the atom-pulse state $\psi_c(e)|0_{\rho}\rangle + |g\rangle\bar{\psi}_{\rho}^P$ and it is easy to verify that the QFI of this pure state is equal to the QFI of the reduced pulse state $\psi_c^2|0_{\rho}\rangle\langle0_{\rho}| + |\psi_{\rho}^P\rangle\langle\psi_{\rho}^P|$, i.e., in Eq. (27) for $\Gamma_\perp = 0$. [Image 55x608 to 298x740]
The classical contribution \( \lim_{t \to \infty} \) value line represents the information obtained by detecting the quantum contribution (ii) is relevant, as expected interplay of the two contributions and for large times only that the total QFI approaches its asymptotic value by an temporal mode. For a pulse of duration comparable to \( C \) Eq. (30) separately as a function of time, as well as the CFI \( \Gamma^2 \rho(\psi_T) \) (solid green, sum of the previous two), the dimensionless CFI \( \Gamma^2 C(\rho_{\text{orig}}) \) for photodetection in the original temporal mode (dot-dashed red) and the asymptotic value \( \lim_{t \to \infty} \Gamma^2 Q(\psi_T) \) (thin black line). The shaded purple region shows the pulse shape as a guide for the eye and it is not to scale on the vertical axis.

To highlight the qualitative features in this regime, we focus on a rectangular pulse \( \xi(t) = \sqrt{1/\Gamma T} \Theta(t) \Theta(T - t) \) supported on an interval of duration \( T^2 \), starting at \( t_0 = 0 \), where \( \Theta(x) \) is the Heaviside step function. This choice makes both analytical calculations possible and the identification of the beginning and the end of the pulse unambiguous.

In Fig. 4 we plot the two contributions to the QFI in Eq. (30) separately as a function of time, as well as the CFI \( \Gamma^2 \rho(\psi_T) \) obtained by measuring the absorption probability \( \rho(\psi_T) \). For simplicity, we let \( \Gamma = 10 \) and \( T = \frac{10}{\Gamma} \) for the previous section. In particular, for \( \Gamma_1 \) the quantum contribution due the perturbation of the photon wavepacket effected by spontaneous emission of the atom is less important and almost all the information can be retrieved by restricting measurements to the incoming temporal mode.

The choice \( \Gamma_1 / \Gamma = 10 \) is intended to capture a pulse interacting with an atom in free space, without particular geometries to enhance the coupling. It is comparable to that for the Na \( D_2 \) transition we consider in Sec. VI. In general, for \( \Gamma_1 \gg \Gamma \) the atom is coupled far more strongly with the vacuum environment than with the pulse and thus after the excitation it will spontaneously emit predominantly into the environmental modes.

In Fig. 6 we compare the total QFI (including both contributions in Eq. (30)) and the CFI of the original temporal mode for \( \Gamma_1 / \Gamma = 10 \) with that for the perfect-coupling case \( \Gamma_1 = 0 \) considered in the previous section. As expected, a larger \( \Gamma_1 \) decreases both the QFI and the CFI. However, in the region of short pulses (shown in the inset), the CFI \( C(\rho_{\text{orig}}) \) of the perfect coupling case

---

5 The duration parameter \( T \) is a multiple of the one used in Fig. (2), \( T_\sigma = T/\sqrt{1/2} \).
The information obtained during the interaction between the atom and the pulse is the same regardless of the presence of additional environment modes because the pulse is so short (i.e., $T \Gamma_{\text{tot}} \ll 1$) that the spontaneous emission terms can be neglected during this part of the dynamics. Moreover, in this limit all the information on $\Gamma$ is entirely retrieved by considering only the original temporal mode; this also motivates the next section where we introduce an effective single-mode model for the pulse-atom interaction. However, by waiting until the atom decays by spontaneous emission, additional information can be obtained if the emitted photon can be measured ($\Gamma_\perp = 0$) case) but nothing more if it decays almost completely into inaccessible modes ($\Gamma_\perp \gg \Gamma$).

**IV. SHORT TIME AND SHORT PULSE REGIME**

In this section we consider pulses with a real-valued temporal amplitude, which we rewrite as $\xi(t) = f(t)/\sqrt{T}$, where $f(x)$ is a scale-invariant shape function [28], dimensionless and squared-normalized $\int dx f(x)^2 = 1$. We have factored out the parameter $T$ that mathematically represents a dilation of $f(x)$ and it captures the pulse duration when $f(x)$ is well-localized around $x = 0$, as we assume in this paper; $t$ is a location parameter that essentially conveys the “time of arrival” of the pulse (such as the time of the peak of a unimodal temporal amplitude, e.g. the Gaussian wavepacket).

The approximate approach presented in this section will be applied to estimating the Na $D_2$ dipole moment in Sec. VI.

**A. Approximate interaction Hamiltonian with a single temporal mode**

For short times $t \ll 1/T_{\text{tot}}$ spontaneous emission, either back into the pulse or into the environment, can be
neglected. Considering also short pulses \( T \ll 1/\Gamma_{\text{tot}} \), the evolution of the atom-field state according to the master equation in Eq. (8) can be approximated by a unitary evolution obtained from a time-dependent Jaynes-Cummings (JC) interaction between the pulse temporal mode and the atom:

\[
H_{\text{JC}}(t) = i\hbar \sqrt{\Gamma} \xi(t) \left( A^\dagger \sigma_+ - A \sigma_- \right). \tag{33}
\]

This is the same approximate model introduced in Ref. [72] and investigated in Refs. [34, 38] for rectangular pulses, where its validity for paraxial beams propagating in free space was corroborated. The idea is that in this limit the temporal mode is not distorted and the dynamics can be approximated as a coherent interaction between the atom and a single temporal mode of the field.

Considering a complete basis of orthonormal temporal modes that satisfy \( \sum_k \xi_k(t)\xi_k(t') = \delta(t - t') \) we can formally express the white noise operators in the light-matter Hamiltonian in Eq. (5) as \( a(t) = \int dt' \sum_k \xi_k(t)\xi_k(t')a(t') = \sum_k \xi_k(t)A_k \). Fixing the zeroth temporal mode to be pulse temporal amplitude \( \xi_0(t) = \xi(t) \), all the other temporal modes are initially empty and our approximation is tantamount to saying that for short evolution times and short pulses they continue to remain practically empty. The dynamics is equivalent to that obtained by neglecting the terms \( k > 0 \) in the summation. We have numerically checked the validity of this approach by truncating the number of orthonormal modes and solving Scrödinger’s equation numerically [73].

We have also checked the validity of this approximation numerically using the methods of Refs. [32, 33] (also explained in Appendix B) that allow the study of the quantum state of a specific temporal mode of the light. Interestingly, this approach has recently been reformulated in Ref. [74] as an effective time-dependent JC interaction (as in Eq. (33)) between the atom and a fixed temporal mode, plus the interaction with a suitably defined additional orthogonal mode, for arbitrary evolution times and pulse durations. We have numerically checked that such an additional orthogonal mode also remains practically empty for short evolution times and short pulses. All the numerical checks have been performed for real temporal amplitudes \( \xi(t) \) and we restrict ourselves to this case for the rest of this section.

Since we are considering zero detuning, the time-dependence of the Hamiltonian in Eq. (33) is trivial and no-time ordering is needed; the solution is the same as for the standard JC model (describing a discrete cavity mode) with a redefined “time” variable \( \int_{t_0}^{t_f} \xi(t')dt' \equiv \xi T \), [72]. We assume that the pulse amplitude is localized at a time much later than \( t_0 \) so that formally we can set \( t_0 = -\infty \) when needed, as in Sec. III; we also assume that the integral \( \int_{t_0}^{\infty} \xi(t')dt' \), i.e., the total pulse-atom “interaction time” is finite. As in the previous sections, we also assume the atom to be initially in the ground state. For an arbitrary initial state of the pulse \( \vert \psi_0^P \rangle = \sum_{n=0}^{\infty} \psi_n \vert n \rangle \), where \( \vert n \rangle \) are the Fock states in the pulse temporal mode in Eq. (9), the atom-pulse initial state is thus \( \vert \psi_0^P \rangle = \sum_{n=0}^{\infty} \psi_n \vert n \rangle \). The evolved state is [75]

\[
\begin{align*}
\vert \psi^P(t) \rangle &= -i\epsilon \sum_{n=0}^{\infty} \sin(\sqrt{\Gamma} t n + 1) \vert n+1 \rangle \psi_n \vert n \rangle \\
&+ |g|^2 \sum_{n=0}^{\infty} \cos(\sqrt{\Gamma} t n) \vert n \rangle \psi_n \vert n \rangle \\
&\equiv |e| \langle \psi_e(t) \rangle + |g| \langle \psi_g(t) \rangle,
\end{align*}
\tag{34}
\]

where we have introduced two unnormalized field states that also appear in the rank-2 reduced state of the field

\[
\rho^P(t) = \text{Tr}_A [\vert \Psi^P(t) \rangle \langle \Psi^P(t) \vert] = \langle \psi_e(t) \vert \psi_e(t) \rangle + \langle \psi_g(t) \vert \psi_g(t) \rangle.
\tag{35}
\]

If \( \sqrt{\Gamma} | \xi_0 \rangle \) is large enough, this model predicts coherent Rabi oscillations between the two-level atom and a single temporal mode, a non-trivial result, given the intrinsic multimode nature of the problem. This behaviour was suggested by the atom’s reduced dynamics [26, 30] and it has been confirmed rigorously using quantum stochastic calculus in Ref. [27], reproducing the approximated model of Refs. [38, 72] that we also employ here.

### B. QFI expressions

The main advantage of this approximate model is that we can easily evaluate the QFI and apply existing results regarding the estimation of the coupling constant of the JC Hamiltonian [17]. Firstly, the overall atom-field QFI is proportional to the average number of photons \( \bar{n}_\xi \) in the pulse (since the atom is initially in the ground state); the time-dependent details of the problem enter only as a multiplicative factor:

\[
\mathcal{Q}(\langle \Psi^P(t) \rangle) = \frac{G_1^2}{\Gamma} \langle \psi_0^P \vert A^\dagger \xi A \vert \psi_0^P \rangle \equiv \frac{G_1^2}{\Gamma} \bar{n}_\xi.
\tag{36}
\]

For an arbitrary pulse shape \( \xi(t) = f(\frac{t}{T})/\sqrt{T} \), centered around \( \bar{t} = 0 \) without loss of generality, a change of variable gives \( G_1 = \sqrt{T} \int_{-T/2}^{T/2} dx f(x) \equiv \sqrt{T} F_1 \). This means that within this approximation the global atom-field QFI \( \mathcal{Q}(\langle \psi^P \rangle) \) is linear in the pulse duration \( T \), and different shapes only induce different proportionality constants.

Secondly, for the atom initially in the ground state and a Fock state wavepacket \( |n_\xi \rangle \), the QFI \( \mathcal{Q}(\rho^P) \) of the reduced field state in Eq. (35) after is equal to the pure-state QFI \( \mathcal{Q}(\langle \psi^P \rangle) \) of the composite field-atom system [17]. The same also holds for the reduced atomic state, but this is practically irrelevant as the atom cannot be measured directly. Moreover, the reduced state of the field is always diagonal in the Fock basis and photon counting is thus the optimal measurement that attains the QFI. Specifically, for an \( n \)-photon Fock pulse the QFI is

\[
\mathcal{Q}_{\text{Fock}} = \frac{nG_1^2}{\Gamma} = \frac{nTF_1^2}{\Gamma}.
\tag{37}
\]
We show in Appendix G that Eq. (37) for $n = 1$ is consistent with the short time and short pulse limit of the single-photon QFI of Sec. III; in particular the classical contribution is the only relevant one and coincides with the CFI of the probability $p_{\text{orig}}$ of finding the photon in the original temporal mode.

For other initial states of the pulse we need to evaluate the QFI $\mathcal{Q}(\rho^P)$ for the rank-2 density matrix in Eq. (35) employing Eq. (H7) in Appendix H, derived using the methods of Ref. [57]. Unlike Fock states, arbitrary states do not always saturate the inequality $\mathcal{Q}(\rho^P) \leq \bar{n}_G^2 / \Gamma$.

C. Linear absorption regime and connection to bosonic loss estimation

When the argument of the trigonometric functions in Eq. (34), i.e., the effective pulse-atom interaction, is small $\sqrt{T_T F} \sqrt{\bar{n}} \ll 1$ we can ignore saturation effects and the atom excitation probability is approximately $p_e(t) \approx n \Gamma G^2_T = n \Gamma T F^2_T$. This is linear in the number of photons, and we call this the linear absorption regime. Note that an absorption probability approximately linear in $T_T$ is a general feature in the short time and short pulse regime that holds also for more complex matter systems [28, Sec. IV]. Similarly, for states with an indefinite number of photons in this regime we obtain $p_e(t) \approx \bar{n}_G G^2_T / T$, showing that the details of the quantum state of the light are not important, as far as the excitation probability is concerned.

On the contrary, the QFI, i.e., the bound of the precision of the estimating the parameter of interest, is greatly influenced by the choice of the photonic probe state. While in this linear absorption regime the dimensionless QFI corresponds exactly to the excitation probability, for arbitrary photonic states with coherences it will not saturate the upper bound $\bar{n}_G G^2_T / T$ and thus they will be less effective as metrological probes. Indeed, we will see in Sec. VI that coherent and squeezed states with the same average number of photons perform much worse.

In this linear absorption regime the estimation problem is very closely connected to absorption spectroscopy [14], formally equivalent to loss estimation [76, 77]. The correspondence between the two problems is evident when considering the estimation of a small bosonic loss rate

$$0 < \gamma \ll 1$$

appearing in the Lindblad master equation describing the loss of excitations of a bosonic mode

$$\frac{d\rho}{dt} = \gamma (a \rho a^\dagger - 1/2 \{ a^\dagger a, \rho \}).$$

For $\gamma \to 0$, the leading-order term of the QFI for an initial Fock probe state $|n\rangle$, evolved for a time $t$, is $nt / \gamma$ [76, 77]. This is very similar to the QCRB obtained from the QFI in Eq. (37) for the atom-pulse coupling $\Gamma$, the difference being that the pulse duration $T$ acts as an effective interaction time instead of $t$ and there is an additional proportionality constant encoding the details of the pulse shape. Furthermore, for loss estimation, also measuring the environment into which the photons are lost gives no additional information about the loss parameter if Fock states (or other optimal probe states) are used [76, 77], just like for the estimation of the JC coupling parameter [17].

V. ENTEANGLED BIPHOTON PROBES

In this section, we consider the so-called linear biphoton setup, illustrated in Fig. 7, in which only one, labelled the signal (S), of the two macroscopically distinct modes, i.e., two beams, of an entangled biphoton state interacts with the atom, while the other mode, labelled the idler (I), evolves freely. This is the simplest instance of spectroscopy using entangled light—the archetypal instance of quantum light spectroscopy [1, 7, 19, 79, 80]. The biphoton setup (with coincidence detection at the end such that the idler photon serves as timing gate for signal photon) has been employed in absorption spectroscopy experiments [4, 5, 8], where improved SNR vis-à-vis spectroscopy using single mode detection was demonstrated. Our objective is to quantify the performance of entangled states in the simple spectroscopic setup of Fig. 7.

Theoretically, the statistics generated by a setup relying only on uncorrelated coincidence measurements can be reproduced exactly without the need of entanglement, as pointed out by Stefanov [81]. Moreover, since only one of the entangled photons interacts with the sample in Fig. 7, the setup is formally equivalent to the use of noiseless ancilla in quantum metrology. Therein, it is well-known that entanglement with ancilla is not advantageous in the case of noiseless unitary dynamics, but may be useful in presence of noise [82]. The exact conditions when noiseless ancilla improve the optimal achievable precision in quantum metrology, however, remain unknown [83]. For our problem, since the biphoton pulse becomes entangled with the atom, the dynamics of the field is not unitary and the initial entanglement between the signal and idler modes may be useful.

The most general biphoton state, entangled over the macroscopically distinct signal and idler modes, is written
where $\Phi(\omega_S, \omega_I)$ is the joint spectral amplitude (JSA) that codifies the spectral (or equivalently temporal) correlations of the biphoton state, and $\omega_S$ and $\omega_I$ denote the signal and idler frequencies respectively.

We first present an expression for the QFI without specifying a particular form for the JSA so as to preserve generality. Subsequently, in Sec. V A we make an additional assumption on the form of JSA that applies, for instance, to the specific example of entangled biphoton states produced as a result of type-II spontaneous parametric down-conversion (PDC) in birefringent $\chi^2$-nonlinear crystals in the weak downconversion limit [84–86]. In the PDC setting, the JSA is a product of the envelope of the pump field and a phase-matching function, which can be approximated using a Gaussian

$$\Phi(t) = \frac{1}{\sqrt{2\pi}} e^{-|a|^2},$$

Numerical results under this assumption will presented in Sec. VI.

Recent years have seen considerable experimental efforts devoted to developing methods to shape the JSA of biphoton states [88, 89]. PDC states with novel JSAs have been proposed or reported in experiments by domain-engineering the nonlinear crystal [90, 91], as well as fabricating multipole nonlinear crystals to generate $n$-mode frequency bin entanglement [92]. Time-frequency entangled states can also be produced using $\chi^3$-linear interaction of spontaneous four-wave mixing (FWM) [93] pulse shaping [94–99] or continuous-wave [100, 101] pumping in conventional optical fibres, photonic crystal fibres, and silicon on insulator (SOI) waveguides. Another curious source of correlated pairs is the biexciton-exciton cascade [102] that used to produced time-bin entangled states using quantum dot emitters [103]. It thus makes sense to optimize the JSA directly [104], or more practically the pump profile [105], for quantum information processing tasks. For our purposes, optimizing the JSA in order to obtain maximal QFI represents a quantum metrological recipe for source engineering the time-energy entangled states employed to estimate the $\Gamma$ parameter.

The JSA admits a Schmidt decomposition in terms of discrete Schmidt modes $\Phi(\omega_S, \omega_I) = \sum_k r_k \xi_k^S(\omega_S) \xi_k^I(\omega_I)$:

$$|\Phi_{\text{biph}}\rangle = \sum_k r_k A_k^\dagger B_k^\dagger |0^S\rangle |0^I\rangle = \sum_k r_k |\xi_k^S\rangle |\xi_k^I\rangle,$$

where $A_k^\dagger = \int d\omega_S \xi(\omega_S) a^\dagger(\omega_S)$ and $B_k^\dagger = \int d\omega_I \xi(\omega_I) b^\dagger(\omega_I)$ are photon-wavepacket creation operators for each Schmidt mode of the signal and idler photons respectively.

6 The validity of approximating the sinc phase-matching function as a Gaussian was studied by experimentally measuring joint temporal intensities using time-resolved femtosecond upconversion [87]. Both the sinc and Gaussian phase-matching function were in rough agreement with experimental values.
the QFI saturates the upper bound in Eq. (20) and is composed of a classical and a quantum contribution
\[ Q(\rho_{SI}) = C(pr) + prQ\left(\rho_{T}^{(0)}\right) + (1-pr)Q\left(\rho_{T}^{(1)}\right), \] (44)
where the classical is \( C(pr) = (dp_r/d\Gamma)^2/[p_r(1-p_r)] \) and the quantum is \( Q = prQ(\rho_0) + (1-pr)Q(\psi_1) \). Eq. (44) is similar to Eq. (30) for single-photon pulses, the main difference being that \( \rho^{(0)}_0 \) can now carry information on the parameter due to the entanglement with idler modes, while in the single-photon case one would have just the vacuum, which carries no information.

If we neglect the emission into environment modes (by setting \( \Gamma \rightarrow 0 \)), the mixed state in Eq. (41) becomes rank 2 and we can take evaluate the QFI using Eq. (H8) in Appendix H, obtaining \( Q(\rho_{SI}) = 4 \sum_k |r_k|^2 \left( |\partial_t \psi_{e,k}|^2 + \langle \partial_t \tilde{\psi}_{g,k}^S | \partial_t \tilde{\psi}_{g,k}^S \rangle + \text{Im}[\psi_{e,k}^* \partial_t \psi_{e,k} + \langle \tilde{\psi}_{g,k}^S | \partial_t \tilde{\psi}_{g,k}^S \rangle] \right) \).

### A. No advantage from entanglement for real-valued joint temporal amplitudes

In this section, we limit ourselves to the case of perfect coupling (\( \Gamma \rightarrow 0 \)), but the argument will apply to \( \Gamma > 0 \) for short times when spontaneous emission can be neglected.

We also assume that the temporal amplitudes of the Schmidt modes are of the form \( e^{i\varphi_k} \xi^S_k(t_s) \) with real \( \xi^S_k(t_s) \) and \( \varphi_k \) (i.e., they have no temporal phases). The Hermite-Gaussian modes obtained as Schmidt basis functions of a two-dimensional Gaussian JSA have, for instance, this form. More generally, this is also true when the time-domain envelope \( \Phi(t_s, t_1) \) is real-valued:

\[ \sum_n r_n \xi^S_n(t_s) \xi^S_n(t_1) = \sum_n r_n \xi^S_n(t_s) \xi^S_n(t_1) \]
\[ \Rightarrow \xi^S_n(t_s)^* \xi^S_n(t_1)^* = \rho \xi^S_n^2(t_s), \xi^S_n(t_1)^* = \rho \xi^S_n^2(t_1), \quad p = \pm 1, \] (45)
i.e., the Schmidt signal and idler functions are either both real, or completely imaginary. In either case, this implies a lack of a relative temporal phase for the signal Schmidt modes, which are of interest here. Since the overall phases \( \varphi_k \) do not depend on time, they will also factor out of \( \psi_{e,k}(t) \) and \( \psi_{g,k}^S \) and since it does not depend on the parameter \( \Gamma \) it will also factor out when taking the derivatives.

Under these assumptions, we can show that
\[ Q(U^{ASI}|g\rangle\langle \Phi_{biph}) = \sum_k |r_k|^2 Q\left(\psi_{e,k}|0^S\rangle + |g\rangle|\tilde{\psi}_{g,k}^S\right) \] (46)
\[ = \sum_k |r_k|^2 Q\left(\psi_{e,k}|0^S\rangle + |g\rangle|\tilde{\psi}_{g,k}^S\right) \] (47)
\[ = \sum_k |r_k|^2 Q\left(\psi_{e,k}^*|0^S\rangle + |g\rangle|\tilde{\psi}_{g,k}^S\right) \] (48)
\[ = Q\left(\sum_k |r_k|^2 \left[|\psi_{e,k}|0^S\rangle + |\tilde{\psi}_{g,k}^S\right] \right) \] (49)

The first equality holds because all the components in the superposition live in mutually orthogonal subspaces, thanks to the idler modes, and because the normalized pure states \( \psi_{e,k}|0^S\rangle + |g\rangle|\tilde{\psi}_{g,k}^S \) are orthogonal to their \( \Gamma \)-derivatives thanks to the assumption on the absence of temporal phases for the Schmidt modes. This assumption justifies also the second equality, together with the fact that we are considering single-photon wavepackets of the signal beam. Physically, it means that for each single-photon wavepacket the information on \( \Gamma \) is fully available in the reduced state of the field subsystem. In the final equality, we have stressed that the QFI obtained in the previous line corresponds to the QFI of an initial classically correlated state \( \sum_k \rho_k^2 \xi^S_k^2 \xi^S_k^2 \) \( \xi^S_k \) \( \xi^S_k \) instead of an entangled state.

Eqs. (46)–(48) mean that using a biphon probe state whose Schmidt temporal modes have no temporal phases is equivalent to probing the atom with randomly chosen single photon states \( \xi^S_k \) with probability \( |r_k|^2 \), but retaining the knowledge on each value \( k \), e.g., by detecting the idler photons in the Schmidt modes to perform heralded state preparation of single-photon wavepackets in the signal mode. If the knowledge on the values \( k \) is not available we are left with the mixed single-photon state \( \sum_k \rho_k^2 \xi^S_k^2 \xi^S_k^2 \) obtained by tracing over the idler mode. Such a mixed single-photon state yields in general less information on \( \Gamma \) as shown by the convexity property of the QFI in Eq. (20).

Since the QFI in Eq. (46) is a convex sum of the QFI of the different Schmidt-modes, it is, in principle, always better to deterministically prepare the single-photon wavepacket in the mode \( \xi^S_k \) with the largest QFI \( \max_k Q\left(\psi_{e,k}|0^S\rangle + |\tilde{\psi}_{g,k}^S\right) \). This clearly shows that entanglement is not a fundamental resource, since there is always a single-photon wavepacket that gives at least as high a precision. However, we note that it could be more practical to implement entangled-state strategies rather than some theoretically superior non-entangled one. More specifically, in the next section we show that for a realistic Gaussian joint spectral density coming from PDC, the additional entanglement actually decreases the short-time QFI and it is better to employ a Gaussian single-photon wavepacket.

\[7\] A real \( \Phi(t_s, t_1) \) only constitutes a sufficient condition, and it is possible to construct more general JSAs whose Schmidt bases do not have a temporal phase.
B. Short-time and short signal photons regime

The idler and signal photons being entangled in time, the temporal properties of one of the two subsystems cannot be defined unambiguously. However, we can get a sense of the relevant time scales from the arrival-time distribution of the signal photon \( p(t_S) = \sum_k |r_k|^2 |\xi_S^k(t_S)|^2 \) (where the idler beam is traced out), since this distribution will have a well-defined temporal width. We can write each Schmidt temporal mode in term of scale-invariant orthonormal functions as \( \xi_S^k(t_S) = \int_{-\infty}^{\infty} f_k^S(t_S/T) / \sqrt{T} \), introducing an overall scale parameter \( T \) for the whole basis of functions. Even if being a complete basis implies that the functions \( \xi_S^k(t_S) \) will eventually spread over the whole real axis, we can still think of the parameter \( T \) as a duration when there is moderate entanglement, so that a limited number of Schmidt modes are sufficient to describe the state and all of them have a temporal duration still captured by \( T \).

Making these assumptions, when \( \Gamma t \ll 1 \) and \( \Gamma T \ll 1 \) we see that, just like in the single-photon case, the excitation probability is linear in \( \Gamma T \): 

\[
p_e(t) = \sum_k |r_k|^2 |\psi_{e,k}(t)|^2 = \Gamma T \sum_k |r_k|^2 |F_{t,k}|^2
\]

where \( F_{t,k} = \int_{-\infty}^{\infty} dx f_k^S(x) \) and thus also very small. There is approximately no perturbation to the shape of each Schmidt temporal mode, and in this limit all the information is contained in the classical term so that the QFI reads

\[
Q(\rho_{\text{St}}) \approx C(p_T) \approx \frac{p_e(t)}{\Gamma^2} = \frac{T \sum_k |r_k|^2 |F_{t,k}|^2}{\Gamma}.
\]  

(49)

This expression will be used in the next section, as its predictions match the results obtained from solving Schrödinger equation numerically [73] for the relevant time-scale.

VI. DIPOLE MOMENT ESTIMATION OF A SODIUM ATOM IN FREE SPACE

In this section we rephrase estimation of \( \Gamma \) as the more physical problem of estimating the EDM \( \mu = \mu_{eg} \cdot \epsilon \). For simplicity, we further assume that \( \mu_{eg} \) and \( \epsilon \) are parallel. Then the EDM is related to the parameter we have considered in previous sections as \( \Gamma = \mu^2 A(\bar{\omega})^2 \), where we assume that the constant \( A(\bar{\omega}) = \sqrt{\bar{\omega}/(4\pi\hbar c A)} \) of the propagating field is known perfectly, so that estimating \( \Gamma \) or \( \mu \) are formally equivalent problems. Such a parameterization entails the relation \( Q_\mu = (d\Gamma/d\mu)^2 Q_\Gamma = 4\mu^2 A(\bar{\omega})^4 Q_\Gamma \) between the QFI for the two different parameters (and analogously for any CFI of particular measurements).

To obtain concrete numbers, we use the experimental data reported in Ref. [109] for the \( D_2 \) transition of a sodium atom. Specifically, we set the dipole moment \( \mu = 2.988 \times 10^{-29} \text{C} \cdot \text{m} = 1.868 \times 10^{-8} \text{e} \cdot \text{cm} \), the transition frequency \( \omega_0 = 2\pi \times 508.333 \text{THz} \) (also equal to the carrier frequency of the pulse) and the decay constant \( \Gamma_{\text{tot}} = 61.542 \times 10^6 \text{s}^{-1} \) corresponding to a lifetime \( 1/\Gamma_{\text{tot}} = 16.249 \text{ns} \). We compute the value of \( A(\bar{\omega}) \) by considering the transverse quantisation area \( A \) to be equal to the effective scattering of the light \( \sigma = \lambda_0^2/2\pi \), with \( \lambda_0 = 2\pi c/\bar{\omega}_0 \) the central wavelength of the light. With these parameter values, we obtain the ratio \( \Gamma_{\text{tot}}/\Gamma = 11.56 \), similar to the value previously considered in Sec. III; the decay rate into the perpendicular modes is obtained by subtracting the decay rate into the propagating pulse modes from the total free-space decay rate \( \Gamma_{\text{tot}} = \Gamma_{\text{tot}} - \Gamma \).

We fix the pulse shape to be an ultrashort Gaussian of duration \( T = 1/\sigma_p = 0.15 \text{ps} \) and we consider different single-temporal-mode states: Single-photon Fock (denoted as “1-photon \( \sigma_p \)’’ in Figs. 8 and 9), coherent and squeezed vacuum as defined in Sec. II A. These parameters put us well into the short-pulse regime defined previously: \( \Gamma_{\text{tot}} T = 9.2313 \times 10^{-6} \) and \( \Gamma T = 7.34995 \times 10^{-7} \) and we can thus neglect all spontaneous emission effects by considering the dynamics of the system up to shortly after the interaction. If we considered a regime where spontaneous emission is not negligible the fact that \( \Gamma_{\text{tot}} \) is also proportional to \( \mu^2 \) would also need to be accounted for, making the problem different from the one studied in previous sections.

We also consider entangled biphoton states obtained with a Gaussian pump pulse with spectral width \( \sigma_p = 1/T \) and with a Gaussian phase-matching function, so that the overall JSA is a bivariate Gaussian and the Schmidt modes are Hermite-Gauss polynomials. We fix the entanglement time \( T_{\text{ent}} = 2.09 \text{ps} \). See Appendix I for the definition of \( T_{\text{ent}} \) and other details of the PDC process. This corresponds to an entanglement entropy \( S = 0.62 \). Notice that we are fixing the pump to have the same
temporal profile as the temporal mode considered for the unentangled probe states. However, the scale parameter of the family of signal Schmidt modes, as introduced in Sec. V B, is not the pump pulse duration $T$, but the parameter $1/k_S$ introduced in Eq. (I11) in Appendix I, which depends on the details of the PDC process. For this reason we also consider a single-photon state having a Gaussian shape corresponding to the 0-th Schmidt mode of the entangled state (denoted as “1-photon $H_0$” in Figs. 8 and 9).

With this choice of parameters we are safely in the regime of validity of the approximation presented in Sec. IV. Since we will not consider intense pulses with high photon numbers, we are also working in the linear absorption regime. For entangled biphoton probes we can evaluate the QFI using Eq. (49).

The comparison of these states is shown in Fig. 8, where the coherent and squeezed vacuum pulses have a mean photon number $\bar{n}_\xi = 1$. We remark that in this short-pulse and linear absorption regime, the excitation probability for the single-photon, Fock and squeezed states are essentially identical, since they depend only on the average photon number and on the shape of the temporal mode. Most importantly, Fig. 8 shows that single-photon probes perform better than states with an indefinite photon number and coherences in the Fock-basis. This is confirmed more generally for other parameter configurations for which the approximate model is valid. This is consistent with the conclusion of Sec. IV C, which draws connection to estimation of an optical loss rate, for which fixed photon number states are indeed optimal.

In Fig. 8 we see that the 0-th HG mode alone carries more information than the entire biphoton state. This behaviour is confirmed more generally in Fig. 9, where we show the QFI for a fixed pump pulse duration $T = 0.15\text{ps}$, identical to the previous figure, but now varying the entanglement time. Notice that in this regime, the amount of entanglement in the biphoton state has the same qualitative behaviour as the entanglement time $T_{\text{ent}}$. In this figure we also show the QFI of a single photon state with the same Gaussian shape as the pump and the QFI of 0-th Schmidt mode single-photon states for the different values of $T_{\text{ent}}$. In the plotted region we see that considering just a single-photon state prepare in the 0-th Schmid modes always outperforms the corresponding entangled state. This is consistent with the argument in Sec. V A on the suboptimality of entangled biphoton probes, for real-valued joint temporal amplitudes (such as the Gaussian considered in this section).

VII. DISCUSSION AND CONCLUSIONS

We have introduced a quantum information theoretic methodology for analysing and understanding spectroscopy with pulses of quantum light. Focusing on the simplest quantum matter system and employing a fully quantum model of light-matter interaction, we have elucidated that origins of the classical and quantum information that lead to precision spectroscopy. Along the way, we have recognized connections to existing spectroscopic techniques.

Our first step towards the understanding of spectroscopy with pulsed quantum light can serve as the foundation for numerous explorations. Evident theoretical questions on the utility of non-resonant pulses [46, 47] in the spectroscopy of simple and more complex matter systems such as those affected by a phononic bath [28] remain open. More importantly, we hope that our work will clear a path towards tangible quantum advantages in spectroscopy experiments with pulsed quantum light.

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8 A fuller discussion of the tradeoffs in the precision of estimation between the pump pulse and crystal parameters in the PDC process will be provided in following publications [46, 47].
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Appendix A: Equivalence between spontaneous emission into many modes or a single mode for the reduced dynamics

In this Appendix we show that the field modes orthogonal to the pulse mode (and thus initially empty) that represent a photonic environment can be effectively described as a single collective mode that interacts with the atom, as mentioned after Eq. (7) in Sec. II A.

A two-level atom in free space can be described as interacting with a discrete set of infinitely many modes of the
electromagnetic field. With the usual dipole and Markovian approximations (explained in the main text in Sec. II A) the interaction-picture Hamiltonian is

\[ H(t) = -i\sqrt{\Gamma_{\text{tot}}\eta_P}(\sigma_- a(t)^\dagger - \sigma_+ a^\dagger(t)) - i \sum_j \sqrt{\Gamma_{\text{tot}}\eta_j}(\sigma_- a_j(t) - \sigma_+ a_j^\dagger(t)). \] (A1)

In this expression \( \Gamma_{\text{tot}} \) is the standard Wigner-Weisskopf spontaneous-emission rate in free space, which could be suitably modified to model emission of radiation in a different propagating medium, while the parameters \( \eta_i > 0 \) are geometric factors that determine the coupling of the atom with the mode \( l \), see for instance Ref. [28] for a more in-depth discussion. In particular, we have separated the term corresponding to the interaction with the travelling pulse mode, which we assume to be the only experimentally accessible one. The others modes are initially in the vacuum and we treat them as an inaccessible, i.e. environmental degrees of freedom. For this reason, it is more convenient to treat them as a single collective mode, defined as

\[ b(t) = \sum_j \sqrt{\frac{\eta_j}{\sum_j \eta_j}} a_j(t), \] (A2)

and satisfying \([b(t), b^\dagger(t')] = \delta(t - t')\) so that we can rewrite the Hamiltonian (7) used in the main text with \( \Gamma = \Gamma_{\text{tot}}\eta_P \) and \( \Gamma_\perp = \Gamma_{\text{tot}}\sum_j \eta_j \).

**Appendix B: Dynamics of the state in the travelling pulse temporal mode**

In this Appendix we briefly summarize the framework of Refs. [32, 33] that is mentioned in Sec. II A and that has been used to validate the approximation explained in Sec. IV and the results of Ref. VI.

When \( \Gamma_\perp = 0 \) the Schrödinger equation for the joint pulse-atom system can be formally solved for input pulses containing a finite number of photons, as shown in Ref. [36], but the integrals become intractable rapidly as the number of photons increase. However, to the best of our knowledge there is no general approach to obtain the field state analytically for arbitrary \( \Gamma \) and \( \Gamma_\perp \). The main difficulty is that the interaction does not only transform the input quantum state, initially defined in a single temporal model only through the operators \( A^\dagger \) introduced in Eq. (10), but also changes the temporal mode structure due to the spontaneous emission of the atom, as schematically depicted in Fig. 1.

It is more tractable to focus on the output state of the light in a particular temporal mode, i.e., the reduced state obtained by tracing out all the other field temporal modes. In this way, we only take into account the effect that the interaction with the atom has onto the quantum state of the travelling pulse, without taking into account the modifications to the temporal wavepacket due to spontaneous emission.

A powerful formalism to treat this scenario was recently introduced by Kiilerich and Mølmer [32, 33]. Without delving fully into the details, the physical system, i.e., the atom interacting with a travelling pulse of radiation, can be mapped to the atom interacting with two fictitious optical cavities \( u \) and \( v \), corresponding to the bosonic annihilation operators \( a_u \) and \( a_v \), with a time-dependent coupling. The quantum states of the cavity \( u \) and \( v \) correspond to states of the incoming and outgoing pulse, respectively. The whole dynamics of the composite system can be described by a time-dependent Lindblad equation:

\[ \dot{\rho}(t) = -\frac{i}{\hbar}[H(t), \rho(t)] + \Gamma_\perp \mathcal{D}[\sigma_-]\rho(t) + \mathcal{D}[L(t)]\rho(t), \] (B1)

where the Hamiltonian reads

\[ H(t) = \frac{i\hbar}{2}(\sqrt{\Gamma}g_u(t)a_u^\dagger\sigma_- + \sqrt{\Gamma}g_v^*(t)a_v\sigma_+ + g_u(t)g_v^*(t)a_u^\dagger a_v - \text{h.c.}), \] (B2)

the time-dependent couplings depend on the shape of the chosen temporal mode as follows

\[ g_u(t) = \frac{\xi^*(t)}{\sqrt{1 - \int_0^t dt' |\xi(t')|^2}}, \quad g_v(t) = -\frac{\xi^*(t)}{\sqrt{\int_0^t dt' |\xi(t')|^2}}, \] (B3)

and the collapse operator is

\[ L(t) = \sqrt{\Gamma} \sigma_- + g_u(t)a_u + g_v(t)a_v. \] (B4)
Crucially, in Eq. (B1) excitations can only go from the cavity $u$ to the atom and from the atom to the cavity $v$ [32]. Since we are focusing on the quantum state of the light in the same temporal mode as the input pulse, the function $\xi(t)$ appears in both couplings (B3), however in general they could be different. In a spectroscopy setting we can only measure the output light scattered by the two-level atom and thus we consider the reduced state of the cavity $v$, i.e. $\rho_v(t) = \text{Tr}_{u,s} \rho(t)$.

**Appendix C: Explicit check of single photon states normalization**

In this Appendix we show explicitly that the state given by Eqs. (24), (25) and (26) of Sec. IIIA1 is normalized to unity. We only consider the case $\Gamma_\perp = 0$ for simplicity.

The amplitude of the excited atomic state is

$$\psi_e(t) = -\sqrt{\Gamma} \int_{-\infty}^{t} dt' e^{-\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi(t')$$

(C1)

and the corresponding probability is

$$|\psi_e(t)|^2 = \Gamma \left| \int_{-\infty}^{t} dt' e^{-\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi(t') \right|^2 = \Gamma e^{-\Gamma t} \left| \int_{-\infty}^{t} dt' e^{\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi(t') \right|^2.$$  

(C2)

The pulse component is

$$|\tilde{\psi}_g^P(t)| = \int_{-\infty}^{\infty} d\tau \left( \xi(\tau) + \sqrt{\Gamma} \Theta(t-\tau) \psi_e(\tau) \right) a^\dagger(\tau) |0^P\rangle$$

(C3)

with modulus squared

$$\langle \tilde{\psi}_g^P(t) | \tilde{\psi}_g^P(t) \rangle = \int_{-\infty}^{\infty} d\tau \left| \xi(\tau) + \sqrt{\Gamma} \Theta(t-\tau) \psi_e(\tau) \right|^2$$

$$= \int_{-\infty}^{\infty} d\tau |\xi(\tau)|^2 + \int_{-\infty}^{t} d\tau \left( \Gamma |\psi_e(\tau)|^2 + 2\sqrt{\Gamma} \text{Re}[\psi_e(\tau)\xi^*(\tau)] \right)$$

$$= 1 + \Gamma^2 \int_{-\infty}^{t} d\tau e^{-\Gamma \tau} \left| \int_{-\infty}^{\tau} dt' e^{\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi(t') \right|^2 - 2\Gamma \int_{-\infty}^{t} d\tau e^{-\Gamma \tau} \text{Re} \left[ \int_{-\infty}^{\tau} dt' e^{\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi^*(\tau) \right].$$

(C4)

Since we are assuming that the atom is initially in the ground state, i.e. $|\psi_e(-\infty)|^2 = 0$ we can rewrite the excitation probability as

$$|\psi_e(t)|^2 = \Gamma e^{-\Gamma t} \left| \int_{-\infty}^{t} dt' e^{\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi(t') \right|^2 = \Gamma \int_{-\infty}^{t} d\tau \frac{d}{d\tau} \left[ e^{-\Gamma \tau} \left| \int_{-\infty}^{\tau} dt' e^{\frac{i}{\hbar} \tilde{\xi}(t-t')} \xi(t') \right|^2 \right],$$

(C5)

explicitly computing the derivative inside the integral one can recognize the last two terms of Eq. (C4) with an overall opposite sign and verify that $|\psi_e(t)|^2 + \langle \tilde{\psi}_g^P(t) | \tilde{\psi}_g^P(t) \rangle = 1$. The reasoning when $\Gamma_\perp > 0$ is analogous.

**Appendix D: Single-photon QFI for real-valued wavepackets**

For $\xi(t) \in \mathbb{R}$ all the temporal amplitudes remain real and we can rewrite the QFI in terms of the unnormalized state $|\tilde{\psi}_T\rangle = \sqrt{1-p_T}|\psi_T\rangle$, satisfying $\langle \tilde{\psi}_T | \tilde{\psi}_T \rangle = 1 - p_T$ and $|\partial_T \tilde{\psi}_T\rangle = \frac{1}{\sqrt{1-p_T}} |\partial_T \psi_T\rangle + \frac{\partial_T p_T}{2(1-p_T)} |\tilde{\psi}_T\rangle$ and substituting this expression in the second term of Eq. (30) we obtain an alternative expression for the QFI

$$Q(p_T) = \langle \partial_T p_T \rangle^2 / p_T + 4 \langle \partial_T \tilde{\psi}_T | \partial_T \tilde{\psi}_T \rangle.$$  

(D1)

This is because

$$\langle \partial_T \tilde{\psi}_T | \partial_T \tilde{\psi}_T \rangle = (1 - p_T) \langle \partial_T \psi_T | \partial_T \psi_T \rangle + \frac{(\partial_T p_T)^2}{4(1-p_T)}.$$  

(D2)
The form in Eq. (D1) is particularly convenient, since we can immediately use the unnormalized state in Eq. (25) without renormalizing it first. These identities hold because we have \( \langle \psi | \partial_\tau \psi \rangle = 0 \), in accordance with Eq. (H8), where the second terms in the summation vanish.

The terms appearing in (D1) can be evaluated more explicitly as follows (denoting \( \|v\|^2 = \langle v|v \rangle \))

\[
\begin{align*}
pr(t) &= \psi_c(t)^2 + \|\psi_g^E(t)\|^2 \\
\psi_c(t)^2 &= \Gamma \left( \int_{-\infty}^{t} dt' e^{-\frac{\Gamma t'}{2}} (t-t') \xi(t') \right)^2 \\
\|\psi_g^E(t)\|^2 &= \Gamma \int_{-\infty}^{t} dt' \left( \int_{-\infty}^{t} dt'' e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right)^2 \\
\partial_\tau pr(t) &= \left( \int_{-\infty}^{t} dt' e^{-\frac{\Gamma t'}{2}} (t-t') \xi(t') \right)^2 + 2\Gamma \left( \int_{-\infty}^{t} dt' e^{-\frac{\Gamma t'}{2}} (t-t') \xi(t') \right) \left( \int_{-\infty}^{t} dt'' \frac{\Gamma t''}{2} e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right) \\
&+ \Gamma \int_{-\infty}^{t} dt' \left( \int_{-\infty}^{t} dt'' e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right)^2 \\
&+ 2\Gamma \int_{-\infty}^{t} dt' \left( \int_{-\infty}^{t} dt'' e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right) \left( \int_{-\infty}^{t} dt'' \frac{\Gamma t''}{2} e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right)^2 \\
&+ 2\Gamma \int_{-\infty}^{t} dt' \left( \int_{-\infty}^{t} dt'' e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right)^2 \left( \int_{-\infty}^{t} dt'' \frac{\Gamma t''}{2} e^{-\frac{\Gamma (t-t'')}{2}} \xi(t'') \right).
\end{align*}
\]

We also report the probability of the asymptotic single-photon component to be in the pulse temporal mode

\[
\begin{align*}
p_{\text{orig}}(t) &= \langle \psi_g^P(t) \rangle^2 \\
\langle \psi_g^P(t) \rangle &= 1 + \sqrt{\Gamma} \int_{-\infty}^{t} d\tau \psi_c(\tau) \xi(\tau) = 1 - \Gamma \int_{-\infty}^{t} d\tau \left( e^{-\frac{\Gamma \tau}{2}} \xi(\tau) \int_{-\infty}^{t} dt' e^{-\frac{\Gamma t'}{2}} \xi(t') \right).
\end{align*}
\]

Appendix E: Optimality of projecting on the probe state for pure-state local quantum estimation

In this Appendix we show explicitly that a projection on the state itself saturates the pure state QFI as stated in Sec. III A 3.

The state of the system is \( |\psi_T\rangle \) and we consider a projective measurement \( \Pi_1 = |\psi_T\rangle \langle \psi_T| \) and \( \Pi_0 = \mathbb{1} - \Pi_1 \), so that \( p_1 = \langle \psi_T|\psi_T\rangle \) and \( p_0 = 1 - p_1 \) and \( \partial_\tau p_1 = -\partial_\tau p_0 = 2\text{Re}(\langle \psi_T|\psi_T\rangle \langle \psi_T|\partial_\tau \psi_T\rangle) \). We aim to take the limit \( \Gamma' \to \Gamma \) for which \( \text{lim}_{\Gamma' \to \Gamma} \langle \psi_T|\psi_T\rangle = 1 \) and \( \text{lim}_{\Gamma' \to \Gamma} \text{Re}(\langle \psi_T|\partial_\tau \psi_T\rangle) = 0 \), and \( \text{lim}_{\Gamma' \to \Gamma} \partial_\tau p_1 = 0 \). The CFI of such a two-outcome measurement is \( C(p_1) = \frac{(\partial_\tau p_1)^2}{p_1(1-p_1)} \) and becomes a 0/0 indeterminate form in the limit \( \Gamma' \to \Gamma \). Using L'Hôpital’s rule we obtain

\[
\begin{align*}
\text{lim}_{\Gamma' \to \Gamma} C(p_1) &= \text{lim}_{\Gamma' \to \Gamma} \frac{(\partial_\tau p_1)^2}{p_1(1-p_1)} = \text{lim}_{\Gamma' \to \Gamma} \frac{2\partial_\tau p_1 \partial_\tau^2 p_1}{\partial_\tau p_1 (1-2p_1)} = -2\partial_\tau^2 p_1 |_{\Gamma'=\Gamma} = -4 \left( \text{Re}(\langle \psi_T|\partial_\tau^2 \psi_T\rangle) + |\langle \psi_T|\partial_\tau \psi_T\rangle|^2 \right). \\
\end{align*}
\]

Differentiating the equality \( \langle \psi_T|\partial_\tau \psi_T\rangle + \langle \partial_\tau \psi_T|\psi_T\rangle = 0 \) we obtain \( \text{Re}(\langle \psi_T|\partial_\tau^2 \psi_T\rangle) = -\langle \partial_\tau \psi_T|\partial_\tau \psi_T\rangle \) and thus \( \text{lim}_{\Gamma' \to \Gamma} C(p_1) = Q(|\psi_T\rangle) \) according to Eq. (19).

Appendix F: Single-photon wavepackets details

In Table I we report details for all the pulse shapes mentioned in Figs. 2 and 3 of Sec. III B, including their definition, the excitation probability, the (dimensionless) QFI and the (dimensionless) CFI corresponding to a measurement in the original temporal mode; as mentioned in the main text the only relevant parameter for these quantities is the dimensionless product \( \Gamma T \). For the Gaussian pulse analytical expressions for the QFI and CFI are not available. The arrival time of all the pulses corresponds to their peak, except for the rectangular pulse for which it corresponds to the beginning of the region with a nonzero photon density.
Table I. Pulse shapes used in the main text. The arrival of all the pulses is at $t = 0$. $\Theta$ is the Heaviside step function.

| Shape                  | $\xi(t)$ | $T_\sigma$ | $p_c(t)$ | $\Gamma^2 Q(\rho^\infty)$ | $\Gamma^2 \mathcal{C}(p_{\text{orig}})$ |
|------------------------|----------|------------|----------|-----------------------------|------------------------------------------|
| Rectangular            | $\frac{\Theta(t)\Theta(T-t)}{\sqrt{T}}$ | $\frac{2}{\sqrt{12}}$ | $0$ | $t \leq 0$ | $2\left(\frac{2e^{-t/T}(T+2)}{T}\right)$ |
| |                      |          | $4e^{-t/T}(e^{-t/T} - 1)^2$ | $0 < t < T$ | $s\left(2e^{-t/T}(T+2)\right)$ | $2\left(\frac{2e^{-t/T}(T+2)}{T}\right)$ |
| |                      |          | $4e^{-t/T}(e^{-t/T} - 1)^2$ | $t \geq T$ | | |
| Rising Exp             | $\frac{1}{\sqrt{12}}e^{rac{4}{T}t} \Theta(-t)$ | $T$ | $t \leq 0$ | $4\Gamma T e^{-t/T}(1 - 1)^2 \Theta(t)$ | $4\Gamma T e^{-t/T}(1 - 1)^2$ |
| |                      |          | $4\Gamma T e^{-t/T}(1 - 1)^2$ | $t > 0$ | $8\Gamma T e^{-t/T}(1 - 1)^2$ | $4\Gamma T e^{-t/T}(1 - 1)^2$ |
| Decaying Exp           | $\frac{1}{\sqrt{T}}e^{-\frac{4}{T}t} \Theta(t)$ | $T$ | $t \leq 0$ | $4\Gamma T e^{-t/T}(1 - 1)^2 \Theta(t)$ | $4\Gamma T e^{-t/T}(1 - 1)^2$ |
| |                      |          | $4\Gamma T e^{-t/T}(1 - 1)^2$ | $t > 0$ | $64\Gamma T e^{-t/T}(1 - 1)^2$ | $64\Gamma T e^{-t/T}(1 - 1)^2$ |
| Symmetric Exp          | $\frac{1}{\sqrt{12}}e^{-\frac{4}{T}t} \Theta(t)$ | $T$ | $t \leq 0$ | $4\Gamma T e^{-t/T}(1 - 1)^2 \Theta(t)$ | $4\Gamma T e^{-t/T}(1 - 1)^2$ |
| |                      |          | $4\Gamma T e^{-t/T}(1 - 1)^2$ | $t > 0$ | $64\Gamma T e^{-t/T}(1 - 1)^2$ | $64\Gamma T e^{-t/T}(1 - 1)^2$ |
| Gaussian               | $\frac{1}{\sqrt{T}(2\pi)^{1/4}} e^{-\frac{1}{2T}t^2}$ | $T$ | | | |

Appendix G: Short-time regime for short single photon pulses

In this Appendix we show that the QFI in Eq. (37) derived for the approximated time-dependent JC model of Sec. IV for the case a single-photon pulse corresponds to the result obtained from the exact expressions derived in Sec. III.

We consider times much shorter than the lifetime, i.e., $t,t_0 \ll 1/\Gamma_{\text{tot}}$. While $t_0$ is the "start of the experiment" and is assumed to be in the past, i.e., $t_0 < t$ for the final time at which detection happens, we can actually think that the only relevant $t_0$ in the experiment is related to the region where the pulse $\xi(t)$ is non-zero (justifying then the substitution $t_0 \to -\infty$ in the integrals in the main text). For simplicity and without loss of generality we always assume the peak (or the "arrival time") of the pulse to be at $t = 0$, so that $t_0$ is always negative. It follows that for short pulses with $\Gamma_{\text{tot}} T \ll 1$, $t_0$ can be assumed to be $|t_0| \ll 1/\Gamma_{\text{tot}}$ so that we can neglect the exponentials also for $t < 0$.

In this regime, spontaneous emission is negligible and the corresponding exponential factors can be omitted from Eq. (24), obtaining

$$\psi_c(t) = -\sqrt{T} \int_{t_0}^{t} dt' \xi(t') = -\sqrt{T T} \int_{t_0}^{t/T} dx f(x),$$

$$\langle \psi^P_g(t) | \xi \rangle = 1 - \Gamma \int_{t_0}^{t/T} dx f(x) \int_{t_0}^{t/T} dx' f^*(x'),$$

where we have used the scale-invariant pulse shape $f(x)$ defined as $\xi(t) = f(t/T)/\sqrt{T}$, satisfying $\int_{-\infty}^{\infty} |f(x)|^2 dx = 1$. For a short pulse satisfying $\Gamma T \ll 1$ we can expand $p_{\text{orig}}$ to first order in $\Gamma T$ and obtain

$$p_{\text{orig}} = \left| \langle \psi^P_g(t) | \xi \rangle \right|^2 \approx 1 - \Gamma T \int_{t_0}^{t/T} dx \left( \langle \xi(x) | \int_{t_0}^{T} dx' f^*(x') \rangle + \int_{t_0}^{t/T} dx \langle \xi(x) | \int_{t_0}^{T} dx' f^*(x') \rangle \right),$$

$$\int_{t_0}^{t/T} dx f(x) \int_{t_0}^{t/T} dx' f^*(x') = 1 - |\psi_c(t)|^2,$$

where the equality between the first and second line can be obtained as simply an integration by parts $\int_{t_0}^{t/T} dx f(x) \int_{t_0}^{t/T} dx' f^*(x') = \int_{t_0}^{t/T} dx f(x) \int_{t_0}^{t/T} dx' f^*(x').$

This calculation shows that, to first order in $\Gamma T$, the small probability of not detecting a photon in the pulse temporal mode after the interaction with the atom is only due to the atom absorption and not because other temporal modes become populated (recall that $\psi^P_g(t)$ is not a normalized state). This, in turn, means that we only have the classical contribution to the QFI, which becomes

$$\frac{[\partial_t p_c(t)]^2}{p_c(t)[1 - p_c(t)]} \approx \frac{[\partial_t p_c(t)]^2}{p_c(t)} = \frac{p_c(t)}{\Gamma^2} = \frac{T}{\Gamma} \int_{t_0}^{t/T} f(x) dx \int_{t_0}^{t/T} f(x) dx = \frac{TF^2}{\Gamma},$$

for
where the first approximate equality holds for \( \Gamma T \ll 1 \) because \( p_e(t) = |\psi_e(t)|^2 = \Gamma T \int_{t_0}^{t/T} dx f(x) \) is also a very small quantity. We have also used that \( \partial_T p_e(t) = p_e(t)/T \). This expression in Eq. (G4) corresponds to the Fock state QFI in Eq. (37) obtained from the approximate time-dependent JC model, for \( n = 1 \).

At the same time, we can show that the quantum contribution \( Q(\psi_T) \) vanishes faster than the \( C(p_{\text{orig}}) \) in the limit of short times \( t - t_0 \ll 1/\Gamma_{\text{tot}} \). In order to show this, we first note the following expression for QFI of the normalized state \( |\psi\rangle_T \) in terms of the overlaps of unnormalized wavepacket \( |\psi^P_T\rangle \):

\[
Q(\psi_T) = 4 \frac{\langle \partial_T \psi_T^P | \partial_T \psi_T^P \rangle}{\langle \psi_T^P | \psi_T^P \rangle} - 4 \left( \frac{\langle \partial_T \psi_T^P | \partial_T \psi_T^P \rangle}{\langle \psi_T^P | \psi_T^P \rangle} \right)^2
\]

(G5)

where we have employed the earlier assumption that \( \psi_T, \partial_T \psi_T \in \mathbb{R} \). The first term in the above expression can be expressed as the following power series of pulse duration \( T \) from which we can extract the leading term (in keeping with the assumption of short pulses so that \( \Gamma T \ll 1 \)):

\[
\frac{\langle \partial_T \psi_T^P | \partial_T \psi_T^P \rangle}{\langle \psi_T^P | \psi_T^P \rangle} = \frac{T \int_{t_0}^{t} d\tau F^2_\tau}{1 - \Gamma T F^2_t} = T \int_{t_0}^{t} d\tau F^2_\tau + \Gamma T^2 F^2_t \int_{t_0}^{t} d\tau F^2_\tau + \cdots \approx T \int_{t_0}^{t} d\tau F^2_\tau
\]

(G6)

Similarly, the (square root of) the second term is, to leading power in \( T \):

\[
\frac{\langle \psi_T^P | \partial_T \psi_T^P \rangle}{\langle \psi_T^P | \psi_T^P \rangle} \approx T \left[ \int_{t_0}^{t/T} dx \left( \int_{x/T}^{x} dx' f(x') \right) \left( \Gamma T \int_{t_0/T}^{x} dx' f(x' - f(x)) \right) \right]
\]

(G7)

Using the mean value theorem for definite integrals to approximate \( F_\tau = \frac{t-t_0}{T} f(\frac{t-t_0}{T}) \) s.t. \( t_0 < t_1 < t \), the quantum contribution \( Q(\psi_T) \) obeys the following bound:

\[
Q(\psi_T) \leq 4 T^2 \left( \frac{t-t_0}{T} \right)^2 f \left( \frac{t_1 - t_0}{T} \right)^2 - 4 T^2 \left( \frac{t-t_0}{T} \right)^4 \left[ \frac{\Gamma T}{3} \int_{t_0/T}^{x} dx' f(x' - f(x)) \right]^2 - \frac{1}{2} f \left( \frac{t_3 - t_0}{T} \right)^2 \leq 4 T^2 \left( \frac{t-t_0}{T} \right)^2 f \left( \frac{t_1 - t_0}{T} \right)^2 - \frac{1}{2} f \left( \frac{t_3 - t_0}{T} \right)^2, \quad t_0 < t_1, t_2, t_3 < t
\]

(G8)

meaning that \( Q(\psi_T) \) scales as \( O((t - t_0)^3) \), whereas the classical contribution in Eq. (G4) scales as \( O((t - t_0)^2) \). Therefore, as \( \Gamma_{\text{tot}} (t - t_0) \to 0 \), the quantum contribution vanishes faster, leaving only \( C(p_{\text{orig}}) \).

**Appendix H: QFI of a rank-2 state**

In this Appendix we evaluate the QFI of a rank-2 density matrix, written as a mixture of two non-orthogonal pure states. This is employed in the main paper for the state in Eq. (35) obtained in the approximate time-dependent JC model introduced in Sec. IV, in particular it is applied to coherent and squeezed states in Sec. VI. However, more generally, the reduced state of the field is described by rank-2 density matrix whenever \( \Gamma_\perp = 0 \) and \( t < \infty \), i.e., when the quantum state of the pulse is mixed only for being entangled with the two-level atom.

We consider the rank-2 density matrix

\[
\rho_T = |\tilde{\psi}_e\rangle\langle \tilde{\psi}_e | + |\tilde{\psi}_g\rangle\langle \tilde{\psi}_g |
\]

(H1)

such as the one in Eq. (35) for the reduced state of the field. We denote with \( B \) the (generally nonorthogonal) basis formed by these two vectors and their derivatives with respect to the parameter of interest \( \Gamma \)

\[
B = \left\{ |\tilde{\psi}_e\rangle, |\tilde{\psi}_g\rangle, |\partial_T \tilde{\psi}_e\rangle, |\partial_T \tilde{\psi}_g\rangle \right\}
\]

(H2)

with the Gramian matrix

\[
G^B = \begin{bmatrix}
\langle \tilde{\psi}_e | \tilde{\psi}_e \rangle & \langle \tilde{\psi}_e | \tilde{\psi}_g \rangle & \langle \tilde{\psi}_g | \partial_T \tilde{\psi}_e \rangle & \langle \partial_T \tilde{\psi}_e | \partial_T \tilde{\psi}_g \rangle \\
\langle \tilde{\psi}_g | \tilde{\psi}_e \rangle & \langle \tilde{\psi}_g | \tilde{\psi}_g \rangle & \langle \tilde{\psi}_g | \partial_T \tilde{\psi}_e \rangle & \langle \partial_T \tilde{\psi}_e | \partial_T \tilde{\psi}_g \rangle \\
\langle \partial_T \tilde{\psi}_e | \tilde{\psi}_e \rangle & \langle \partial_T \tilde{\psi}_e | \tilde{\psi}_g \rangle & \langle \partial_T \tilde{\psi}_g | \partial_T \tilde{\psi}_e \rangle & \langle \partial_T \tilde{\psi}_e | \partial_T \tilde{\psi}_g \rangle \\
\langle \partial_T \tilde{\psi}_g | \tilde{\psi}_e \rangle & \langle \partial_T \tilde{\psi}_g | \tilde{\psi}_g \rangle & \langle \partial_T \tilde{\psi}_g | \partial_T \tilde{\psi}_e \rangle & \langle \partial_T \tilde{\psi}_g | \partial_T \tilde{\psi}_g \rangle
\end{bmatrix}
\]

(H3)
Assuming that $\mathcal{B}$ is a basis means that the vectors must be linearly independent and thus $G^\mathcal{B}$ invertible. While the linear independence of $|\psi_e\rangle$ and $|\psi_g\rangle$ is implied by the assumption that $\rho_T$ is rank-2, the linear independence of the whole basis $\mathcal{B}$ is as an extra assumption in this derivation, but it is valid for the applications considered in this paper.

Using the notation of Ref. [57] we can represent operators as matrices expressed on the basis $\mathcal{B}$ and Eq. (17) becomes

$$2\partial_T\rho^\mathcal{B} = L_T^\mathcal{B}G_T^\mathcal{B}\rho^\mathcal{B} + \rho_T^\mathcal{B}G_T^\mathcal{B}L_T^\mathcal{B}.$$ \hspace{1cm} (H4)

This equation can be solved efficiently by using block vectorization [56, 57]. Once a solution is found, the QFI can be evaluated as

$$Q(\rho_T) = \text{Tr}[L_T^\mathcal{B}G^\mathcal{B}\partial_T\rho_T^\mathcal{B}G^\mathcal{B}]$$ \hspace{1cm} (H5)

For the rank-2 model in (H1) the density matrix and its derivative have a very simple form in the basis $\mathcal{B}$:

$$\rho^\mathcal{B} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \quad \partial_T\rho^\mathcal{B} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$ \hspace{1cm} (H6)

and the Lyapunov equation can be solved analytically to obtain an explicit, albeit complicated, expression for the QFI that depends only on the matrix elements of $G^\mathcal{B}$.

$$Q(\rho_T) = \frac{-4}{\Delta(G_{11} + G_{22})} \left\{ \Delta \left[ (\text{Im} \, G_{13} - \text{Im} \, G_{24})^2 + (\text{Im} \, G_{14} + \text{Im} \, G_{23})^2 \right] \\
+ 4\Delta G_{11}(\text{Im} \, G_{33} + \text{Im} \, G_{44}) + 4\Delta G_{22}(\text{Im} \, G_{33} + \text{Im} \, G_{44}) \\
- 4(\text{Im} \, G_{13})^2 G_{22}^2 + 8 \text{Im} \, G_{13} \text{Re} \, G_{12} G_{23}(\text{Im} \, G_{14} + \text{Im} \, G_{23}) + 8 \text{Im} \, G_{13} \text{Im} \, G_{12} G_{23}(\text{Re} \, G_{23} - \text{Re} \, G_{14}) \\
- 4G_{11} G_{22} \left[ 2 \text{Im} \, G_{13} \text{Im} \, G_{24} + (\text{Re} \, G_{14} - \text{Re} \, G_{23})^2 \right] + 8 \text{Im} \, G_{12} \text{Re} \, G_{12} \text{Im} \, G_{14} + \text{Im} \, G_{23})(\text{Re} \, G_{14} - \text{Re} \, G_{23}) \\
+ 8 \text{Im} \, G_{24} \text{Re} \, G_{12} G_{11}(\text{Im} \, G_{14} + \text{Im} \, G_{23}) \\
- 4(\text{Re} \, G_{12})^2 (\text{Im} \, G_{14} + \text{Im} \, G_{23} + \text{Re} \, G_{14} - \text{Re} \, G_{23})(\text{Im} \, G_{14} + \text{Im} \, G_{23} - \text{Re} \, G_{14} + \text{Re} \, G_{23}) \\
+ 8 \text{Im} \, G_{12} \text{Im} \, G_{24} G_{11}(\text{Re} \, G_{23} - \text{Re} \, G_{14}) - 4(\text{Im} \, G_{24})^2 G_{11}^2 \right\},$$ \hspace{1cm} (H7)

where $\Delta = G_{11} G_{22} - |G_{12}|^2 > 0$ is the determinant of the first diagonal block of $G^\mathcal{B}$ and the superscript $\mathcal{B}$ has been suppressed for compactness.

A much simpler expression can be obtained when the two parameter-dependent rank-1 states live in orthogonal subspaces, i.e. $\langle \tilde{\psi}_e | \tilde{\psi}_g \rangle = 0$, $\langle \tilde{\psi}_e | \partial_T \tilde{\psi}_g \rangle = 0$ and $\langle \tilde{\psi}_g | \partial_T \tilde{\psi}_e \rangle = 0$:

$$Q(\rho_T) = \sum_{x=e,g} 4(\partial_T \tilde{\psi}_x | \partial_T \tilde{\psi}_x)^2 + \text{Im} \left( \frac{\langle \tilde{\psi}_x | \partial_T \tilde{\psi}_x \rangle^2}{\langle \tilde{\psi}_x | \tilde{\psi}_x \rangle} \right),$$ \hspace{1cm} (H8)

which makes the computation easier by avoiding a renormalization of the two orthogonal states. However, since the two states in the mixture are orthogonal, this QFI can also be obtained from the standard formulas based on the eigendecomposition of the density matrix [53, 54].

**Appendix I: Description of Parametric Down Converted (PDC) State**

The biphoton state generated at the end of low-gain type-II PDC interaction in birefringent crystals (such as BBO or KTP crystals) that converts the classical pump photon into (signal and idler) daughter photons is obtained as the first order perturbation term,

$$|\Phi_{\text{PDC}}\rangle = \frac{1}{\sqrt{N}} \left( |0\rangle + \int d\omega_S \int d\omega_I f_{\text{PDC}}(\omega_S, \omega_I) a^\dagger(\omega_S) b^\dagger(\omega_I) |0\rangle \right),$$ \hspace{1cm} (I1)
where $N$ is the normalization factor which ensures that $|\Phi_{\text{PDC}}\rangle$ is well normalized. For a more complete description of the PDC process, including in the high-gain regime, see Ref. [86].

The bivariate JSA $f_{\text{PDC}}(\omega_S, \omega_I)$ is the following product of the classical pump pulse envelope (which is assumed to be Gaussian with spectral width given by $\sigma_p$), and the sinc phase-matching function for collinear setups,

$$f_{\text{PDC}}(\omega_S, \omega_I) = -\frac{i\alpha_{\text{pump}}}{\hbar} \operatorname{sinc}\left(\frac{\Delta k(\omega_S, \omega_I)L}{2}\right) \frac{1}{\sqrt{2\pi\sigma_p^2}} e^{-\frac{(\omega_S + \omega_I - \omega_p)^2}{2\sigma_p^2}},$$  \hspace{1cm} (I2)

where $\alpha_{\text{pump}}/\hbar$ depends on the crystal properties (such as crystal length $L$, and the second-order – as PDC is a three-wave mixing process – non-linear susceptibility $\chi^{(2)}$), as well as beam properties (chief amongst them being the beam width that fixes the area of quantization in the paraxial description). For simplicity, we bunch these experimental parameters together into the efficiency of the downconversion process [16].

The phase-matching function $\Delta k(\omega_S, \omega_I)$ can be related to the different group velocities and times of arrival of the two photons, by Taylor expanding the signal/idler wavevectors around their respective central frequencies (for which conservation of energy dictates $\omega_S + \omega_I = \omega_p$),

$$k(\omega_X) = \tilde{k}_X + \left. \frac{\partial k}{\partial \omega_X} \right|_{\omega_S = \omega_x} (\omega_X - \bar{\omega}_X) + \ldots, \quad X = S, I.$$  \hspace{1cm} (I3)

The first-order coefficient can be identified as the inverse of the wavepacket group velocity $1/v_X = \partial k/\partial \omega_X|_{\omega_S = \bar{\omega}_X}$. Keeping then only the linear terms in the Taylor expansion, the phase-matching function is

$$\Delta k(\omega_S, \omega_I)L = \left(\frac{1}{v_p} - \frac{1}{v_S}\right) L(\omega_S - \bar{\omega}_S) + \left(\frac{1}{v_p} - \frac{1}{v_I}\right) L(\omega_I - \bar{\omega}_I) = T_S (\omega_S - \bar{\omega}_S) + T_I (\omega_I - \bar{\omega}_I),$$  \hspace{1cm} (I4)

where $T_S = (1/v_p - 1/v_S)L$ is the time difference between the arrival of the wavepacket travelling at the group velocity of the pump versus that of the first photon, and similarly for $T_I$. The time delay between the arrival of the two photons is captured by the quantity $T_{\text{ent}} = T_S - T_I$, henceforth referred to as the entanglement time. In the main text we only study two-photon states with frequency anti-correlations ($T_S > 0, T_I > 0$), with the specific choice of $T_S = 0.12 T_{\text{ent}}$ and $T_I = 1.12 T_{\text{ent}}$. The entanglement time $T_{\text{ent}}$ itself is varied in Fig. 9 between 0.25 ps and 3.5 ps and fixed to $T_{\text{ent}} = 2.09\text{ps}$ for the biphoto curve in Fig. 8.

Finally, the sinc function can be approximated as a Gaussian [84, 86, 87] ignoring their minor maxima, as

$$\operatorname{sinc}\left(\frac{\Delta k(\omega_S, \omega_I)L}{2}\right) \approx \exp\left(-\gamma(\Delta k(\omega_S, \omega_I)L)^2\right), \quad \gamma = 0.04822.$$

yielding a JSA that is now proportional to a two-dimensional Gaussian function,

$$f_{\text{PDC}}(\omega_S, \omega_S) \approx -\frac{i\alpha_{\text{pump}}}{\hbar} \frac{1}{\sqrt{2\pi\sigma_p^2}} \exp\left(-a(\omega_S - \bar{\omega}_S)^2 + 2b(\omega_S - \bar{\omega}_S)(\omega_I - \bar{\omega}_I) - c(\omega_I - \bar{\omega}_I)^2\right)$$  \hspace{1cm} (I6)

where

$$a = \frac{1}{2\sigma_p^2} + \gamma T_S^2, \quad b = \frac{1}{2\sigma_p^2} + \gamma T_S T_I, \quad c = \frac{1}{2\sigma_p^2} + \gamma T_I^2.$$

$$\sum_{n=0}^{\infty} \frac{w^n H_n(x) H_n(y)}{2^n n!} = \frac{1}{\sqrt{1-w^2}} \exp\left[\frac{2wxy - w^2(x^2 + y^2)}{1-w^2}\right],$$  \hspace{1cm} (I9)

where $H_n(x)$ is the $n$-th order Hermite polynomial. Then, using Mehler’s Hermite polynomial formula [110],
we can express the two-dimensional Gaussian JSA as the following sum of products of univariate functions,

\[ f_{PDC}(\omega_S, \omega_I) \approx \sum_{n=0}^{\infty} r_{n,PDC} h_n(k_S(\omega_S - \bar{\omega}_S)) h_n(k_I(\omega_I - \bar{\omega}_I)), r_{n,PDC} = -\frac{\alpha_{pump}}{h} \sqrt{\frac{1 + w^2}{4\sqrt{ac\sigma_p^2}}} w^n, \]  

(110)

where \( k_S \) and \( k_I \) are the projections of the elliptical JSA onto the \( \omega_S \)- and \( \omega_I \)-axes respectively,

\[ k_S = \sqrt{\frac{2a(1 - w^2)}{(1 + w^2)}}, \quad k_I = \sqrt{\frac{2c(1 - w^2)}{(1 + w^2)}}, \]  

(111)

de the Schmidt weight factor \( w \) is obtained using the quadratic formula,

\[ w = -\sqrt{ac + \sqrt{ac - b^2}} \]  

(112)

Defining mode creation operators for signal and idler modes as

\[ A_n^\dagger = \int d\omega_S h_n(k_S(\omega_S - \bar{\omega}_S)) a^\dagger(\omega_S), \quad B_n^\dagger = \int d\omega_I h_n(k_I(\omega_I - \bar{\omega}_I)) b^\dagger(\omega_I), \]  

(113)

so the bosonic commutation relations \([A_m, A_n^\dagger] = \delta_{mn}, [B_m, B_n^\dagger] = \delta_{mn}\) hold, the approximate PDC state then has the following Schmidt form

\[ |\Phi_{PDC}\rangle \approx \frac{1}{\sqrt{N}} \left( |0\rangle + \sum_{n=0}^{\infty} r_{n,PDC} A_n^\dagger B_n^\dagger |0\rangle \right) \approx \frac{1}{\sqrt{N}} \left( |0\rangle + \sum_{n=0}^{\infty} r_{n,PDC} |\xi_{n}^S\rangle |\xi_{n}^I\rangle \right) \]  

(114)

where \(|\xi_{n}^S\rangle = A_n^\dagger |0\rangle \) (\(|\xi_{n}^I\rangle = B_n^\dagger |0\rangle \)) are \( n \)-mode Schmidt basis kets for the signal (idler) photons. Finally, if we post-select for only successful detections of the two-photon state, the biphoton PDC state becomes

\[ |\Phi_{biph}\rangle = \sum_{n=0}^{\infty} r_{n,biph} |\xi_{n}^S\rangle |\xi_{n}^I\rangle, \quad r_{n,biph} = \frac{r_{n,PDC}}{\sqrt{\sum_{n=0}^{\infty}|r_{n,PDC}|^2}} = -i w^n \sqrt{1 - w^2}, \]  

(115)

which has the same form as Eq. (39). Notice that this is equivalent to renormalizing \( f_{PDC}(\omega_S, \omega_I) \) to be treated as a proper wavefunction, thus the efficiency parameter \( \alpha_{pump} \) does not enter explicitly in the description of the post-selected state.