COMMENTARY

The path toward quantum advantage in optical spectroscopy of materials

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Quantum computers (1) are based on quantum bits (qubits), which are two-state quantum mechanical systems described by the wave function $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$, where the coefficients (amplitudes) are, in general, complex valued. Contrary to the classical bits, binary variables that can assume the value of zero or one, qubits are quantum superpositions of the $|0\rangle$ and $|1\rangle$ states, with the probabilities of measuring zero and one given by $|\alpha|^2$ and $|\beta|^2$, respectively. Multiple qubits can exhibit quantum entanglement (i.e., correlations between the results of measurements performed on individual qubits). An example is the maximally entangled (or Bell) two-qubit state, with wave function $|\Psi\rangle = 1/\sqrt{2}(|00\rangle + |11\rangle)$; measurement of a single qubit yields with equal likelihood either $|0\rangle$ or $|1\rangle$, but there is a perfect correlation between the results of the measurements on the first and the second qubits. Quantum computers aim to exploit the unique features of quantum superposition and entanglement to achieve the so-called quantum advantage (i.e., the capability to perform computations, based on quantum algorithms, which cannot be done with the existing bit-based classical computers in a reasonable amount of time). After several years of theoretical studies and laboratory-level experiments, quantum computing hardware is now maturing to be a technologically viable platform, with first demonstrations using either superconducting Josephson junctions (2) or quantum light sources (3). It is now expected that these advances will fuel interest in the exploration of the quantum advantage in other fields, such as sensing, communications, and simulations. Of particular promise is the area of quantum metrology, which aims to exploit the concepts of quantum superposition and entanglement to perform measurements with resolution and sensitivity superior to their classical counterparts.

Light is one of the most powerful tools in our hands to interrogate and understand the world around us. To a large extent, every novel optical metrology technique has redefined our comprehension of nature. Optical microscopy, absorption, photoluminescence and Raman spectroscopy, superresolution microscopy, ultrafast spectroscopy, and multiphoton imaging are just a few examples of experimental techniques that have revolutionized every field of natural sciences, from physics and chemistry to biology and medicine. In standard implementations of optical metrologies, following a semiclassical description of light–matter interactions, light is treated as an electromagnetic wave neglecting its quantum nature, and accordingly, only its intensity is measured. For example, absorption and luminescence spectroscopy measure the intensity of transmitted and emitted light, respectively, from the sample of interest. The presence of specific spectroscopic signatures, such as well-defined resonances, is typically interpreted as the evidence of excited states. Recently, however, a growing body of theoretical studies (4–6), followed by a still limited number of experimental proofs of concept, has demonstrated the unique advantages offered by the exploitation of quantum effects

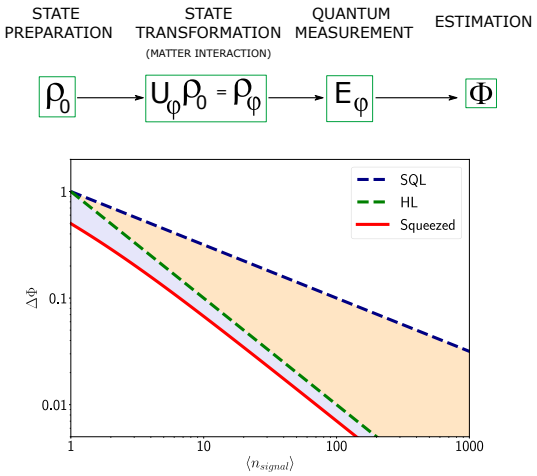

Fig. 1. (*Upper*) The general methodology behind quantum metrology. (*Lower*) Sensitivity limit of an optical measurement of the quantity of interest, Φ. Squeezed represents the Cramer–Rao bound with squeezed light. The limits are obtained using equations 9, 10, and 57 from ref. 11.

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in optical studies of matter. Noticeable examples are the linear scaling with the light intensity of the two-photon absorption rate for time-frequency entangled photons (7) and the use of quantum correlations to enhance nonlinear optical microscopy by pushing the sensitivity of stimulated Raman scattering below the shot-noise limit (8).

In a report in PNAS, Dorfman et al. (9) have generalized this to the context of nonlinear optical spectroscopy of materials, where they achieved superior precision and accuracy in comparison with the classical analogs. Most material systems are composed of manifolds of excited states, whose dynamics following photoexcitation determine their photophysical properties. Coherent nonlinear optical spectroscopy aims at the measurement of various characteristics of the excited states, including their population decay rates and the interactions with the environment that lead to dephasing, as well as quantum correlations between different states. On a fundamental level, this is accomplished by photoexciting the sample with a sequence of time-ordered light fields (10). Multiple interactions with the incident fields induce a nonlinear polarization in the material, which emits coherent radiation along specific directions determined by the so-called phase-matching conditions. In the common case of a third-order [$\chi^{(3)}$] nonlinear response, interaction with three light fields gives rise to the emission of a fourth field, resulting in the so-called four-wave mixing (FWM) signals.

The amplitude and phase (or generally, the spectral intensity) of these nonlinear signals carry the desired information on the excited-state dynamics and correlations. This approach has proven to be very powerful but presents two main challenges: 1) the low intensity of the nonlinear signal, whose detection is limited by the intrinsic noise associated with the granular nature of light, and 2) the lack of simultaneous access to high spectral and temporal resolution. Quantum metrologies may offer new resources to overcome these outstanding challenges in the field of nonlinear optical spectroscopy.

In general, a quantum optical measurement in its most generic form may be described as the sequence of events sketched in Fig. 1 (12). An appropriate photon state is first selected and prepared as a probe state. This can be a single-photon state, an entangled state, or a classical coherent state. The state, defined by its density matrix ρ_0, is prepared such that it is sensitive to a specific physical quantity of interest, say the phase of the optical response ϕ. Interaction of the probe state with matter results in a unitary transformation U_ϕ of the probe state, leading to a transformed state ρ_ϕ with encoded phase information. The transformation is quantified through a specific quantum measurement, E_ϕ. A series of measurements are statistically analyzed to obtain an estimate Φ of the quantity of interest. This methodology holds true for quantum optical spectroscopy as well.

Optical measurements are performed using photodetectors, which deliver an electrical signal following light absorption in a semiconductor. Even in the ideal case of 100% photon detection efficiency, there is a fundamental limit set to the detection sensitivity or the precision in the estimate of Φ due to the stochastic nature of each absorption event and the absence of any correlation between the events. This fundamental limit, often referred to as the standard quantum limit (SQL) or the shot-noise limit, states that the detection accuracy increases as $1/\sqrt{\langle n_{sig}\rangle}$, where $\langle n_{sig}\rangle$ is the number of signal photons. This limit can be overcome by inducing correlations between the photons through quantum entanglement, which suppresses the statistical variance between the photodetection events. It has been demonstrated (11, 12) that this dramatically improves the measurement sensitivity toward the Heisenberg limit (HL) that scales as $1/\langle n_{sig}\rangle$. Both SQL and HL are estimated within the framework of a semiclassical treatment of photon detection, with additional quantum elements associated with the input probe state (11). These limits can be further pushed through the full quantum treatment of photodetection as pioneered by Glauber (13) and Sudarshan (14).

In this context, it is convenient to represent the photon quantum state in the Wigner space, in which it is decomposed into orthogonal amplitude and phase, which are analogous to the real and imaginary components of the classical electromagnetic field. It can be shown that the amplitude and phase quadratures of the photon state do not commute or, in simpler words, that it is impossible to simultaneously measure both the amplitude and phase of the quantum optical field with unlimited precision, with the limit set by the Heisenberg uncertainty principle. A classical light field emitted by a laser, known as coherent optical state, equally spreads the uncertainty between amplitude and phase, thereby limiting the precision of the measurement. However, there exist other kinds of quantum light, which provide ways to overcome these limitations.

As the name suggests, squeezed light refers to the photon state in which the precision for one of the quadratures is increased at the expense of the precision for the other (11, 15). The measurements of relative amplitude and phase of a stream of photons are subject to statistical fluctuations because of elements of stochastic nature in photon generation, propagation, and detection. While it is not possible to precisely measure both the amplitude and phase simultaneously, at least one of them can be estimated with enhanced precision by sacrificing the other, effectively pushing the accuracy limit of the measurement. The variable that gains precision is said to be squeezed since the spreading of the photon state in the Wigner space reduces along that particular coordinate. For example, if the uncertainty in the amplitude measurement is increased, then the correlations between the photon-counting events will increase. This can be experimentally observed through the second-order coherence function, i.e., the time-correlation of the light intensity, and the phenomenon is referred to as photon antibunching. We can now estimate the so-called Cramer–Rao bound for the precision in the phase measurement with squeezed light, shown in Fig. 1, which is lower in comparison with the semiclassical SQL and HL bounds.

In order to generate squeezed light, one needs to decrease the uncertainty on one of the quadratures while increasing it on the other. Nonlinear interactions in materials provide effective tools to achieve this squeezing. To understand how squeezing works, let us consider optical parametric amplification (OPA), which is a three-wave mixing process in a nonlinear crystal characterized by a second-order susceptibility $\chi^{(2)}$. In an OPA, an intense light field at the pump frequency is incident on the nonlinear crystal. The rest of the photon modes at all the other frequencies are not populated and thus, are considered to be in the so-called vacuum state, which consists of random noise photons whose relative amplitude and phase components are statistically fluctuating around zero. The pump field generates a nonlinear polarization in the crystal, which consequently drives the vacuum field between regions of high and low polarization within the crystal. This results in the reduction of the randomness in the amplitude fluctuations of the vacuum state, which now acquires a degree of certainty in its amplitude that mirrors the pump field. This is a typical example of an amplitude squeezed vacuum state. While this state is still not populated by any photons yet, a squeezed photon state can be generated by seeding the OPA with another coherent, low-intensity signal field with a well-defined spectrum instead of the noise photons. Control

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of the relative phase between the pump and signal fields enables either amplitude or phase squeezing, as discussed extensively elsewhere (11, 12, 16). $\chi^{(2)}$ processes are widely used to generate amplitude and phase squeezing of light for ultrasensitive measurements, including in the new generation of gravitational wave detectors (17).

Amplitude squeezing can also be achieved by FWM in dense atomic vapors, which have large $\chi^{(3)}$ (18). A dense vapor phase of ^{85}Rb atoms is composed of two correlated ground states and two excited states, which enable the so-called double-Λ excitation scheme. The FWM experiment involves two incident photon fields, a strong coherent pump field, and a weak probe field. The pump field generates atomic coherences between pairs of ground and excited states in the ^{85}Rb atoms, which decay through the emission of two photons, one in the direction of the probe field and the other in the complementary, phase-matched direction, referred to as the conjugate beam. Given that the probe and conjugate beams are quantum correlated, the noise in their relative intensities can be reduced below the SQL by their simultaneous counting and measurement of the differential signal. Moreover, the double-Λ scheme further reduces the generation of noise photons via spontaneous decay, thus improving the squeezing efficiency.

The paper by Dorfman et al. (9) produces squeezed light from ^{85}Rb vapors, but it puts a twist on nonlinear spectroscopy with quantum light; instead of generating the quantum light and using it to probe the properties of a material, the authors exploit the process of squeezed light generation itself to retrieve information on the nonlinear optical response of the material. By comparing the classical and the quantum squeezed signals for both probe and conjugate beams, the authors make two observations: 1) The quantum signal shows robustness against external noise perturbations and achieves sensitivity below the SQL; 2) by showing extra peaks in the nonlinear response, the quantum signal provides additional information with respect to the classical one and opens an additional observation window on the $\chi^{(3)}$ of the studied system.

The paper by Dorfman et al. (9) represents another important milestone along the road to the full exploitation of the quantum advantage in nonlinear optical spectroscopy. In this field, theory is well ahead of experiments, and a lot of schemes still remain to be demonstrated and applied to a variety of fields ranging from biology to solid-state physics. The recent push toward the development of experimental tool kits for quantum technologies (including sources and detectors), also fueled by large-scale initiatives such as the European Quantum Flagship (19) (https://qt.eu/) and the Quantum Leap efforts from the US NSF (20), allows us to foresee a bright future for quantum-enhanced optical spectroscopies.

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