Lecture: Emerging Paradigms in Quantum Light Spectroscopy

An Experimentalist's Perspective

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Abstract

This lecture bridges the gap between the formalism of open quantum systems and the reality of optical experiments. We explore how quantum light (squeezed states, entangled pairs) serves not merely as a perturbative input, but as a probe of material complexity. We categorize these methods into three paradigms: **Sensitivity** (beating shot noise), **Resource** (using entanglement to probe many-body correlations), and **Witness** (certifying coherence).

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1 Part A: The Classical Baseline

Goal: Define the standard limits (Shot Noise, Damage) that quantum light seeks to overcome.

Ultrafast optical spectroscopy that exploits the high temporal resolution offered by femtosecond lasers has played a pivotal role in unveiling early snapshots of many critical processes. These

include charge generation mechanistics that drive next-generation solar cells, rate limiting steps in photo-chemical reactions including in photosynthetic reaction centers and quantum dynamics in condensed phase. These experiments fundamentally involve the excitation of materials with multiple ultrashort pulses and optical measurement of the resultant nonlinear response.

The nonlinear material response in the presence of intense incident radiation is typically modeled using the electric dipole Hamiltonian and a perturbation theory **expansion** of the dipole operator ($\hat{\mu}$). For example, in pump-probe and four-wave mixing experiments, which are considered to involve *three* field interactions, the time-dependent nonlinear response is written as:

$$S^{(3)}(\tau_3, \tau_2, \tau_1) = \langle \hat{\mu}(\tau_3)[\hat{\mu}(\tau_2), [\hat{\mu}(\tau_1), [\hat{\mu}(0), \rho(-\infty)]]]\rangle, \tag{1}$$

where the times $0 < \tau_1 < \tau_2 < \tau_3$ define the sequence of the time-ordered interactions and $\rho(-\infty)$ is the unperturbed density matrix of the material system. It can be seen from Eq. 1 that:

1. The nonlinear response is **assumed** to be of the **third-order**.
2. The response is estimated to be a ensemble **average** ().

The third-order truncation is not strictly representative of the experimental response due to the presence of non-negligible contributions from the higher orders simply because of the high peak excitation intensities used in the experiment. The inability to perform nonlinear spectroscopy at low photon flux stems from the **shot-noise limited sensitivity of classical optical detection**. Fundamentally, such a detection methodology is based on the measurement of time-integrated light intensity in a photo-detector. Although this is well represented by the ensemble average in Eq. 1, such a detection scheme intrinsically lacks access to critical information regarding the statistical fluctuations that are driven either by system-bath interactions or intrinsic quantum noise. While such information may be indirectly accessible through rigorous analysis of the nonlinear spectral lineshapes, higher-order contributions impose substantial ambiguity in the derived quantities.

The vision in exploring quantum spectroscopy and QIS in chemical sensing is to enhance optical techniques through the systematic incorporation of quantum optical methods, with the overarching goals of enhancing the detection sensitivity, removing the higher-order contributions, and quantifying the intrinsic noise in the material response.

1.1 Linear and Nonlinear Polarization

1.1.1 The Maxwell-Bloch Framework

In the semi-classical approximation, we treat the matter degrees of freedom quantum mechanically while the electromagnetic field remains classical. This regime is sufficient to describe linear absorption, refraction, and classical nonlinear optics.

The total Hamiltonian for the material system is given by:

$$\hat{H} = \hat{H}_0 + \hat{H}_{int}(t) \tag{2}$$

where $\hat{H}_0$ describes the unperturbed eigenstates of the material (e.g., electronic states of a molecule), and the interaction term in the dipole approximation is:

$$\hat{H}_{int}(t) = -\hat{\mu} \cdot \mathbf{E}(t) \tag{3}$$

Here, $\mathbf{E}(t)$ is the macroscopic classical field and $\hat{\mu}$ is the electric dipole operator.

1.1.2 Polarization as the Radiating Source

A fundamental concept in spectroscopy is that the detector never measures "absorption" directly. It measures the field at a distant point. The connection between the microscopic quantum dynamics and the macroscopic field is the **Polarization Density**, $\mathbf{P}(t)$.

From Maxwell's equations, the propagation of the electric field in a non-magnetic medium is governed by the wave equation with a source term:

$$\nabla^2\mathbf{E} - \frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2} = \mu_0\frac{\partial^2\mathbf{P}}{\partial t^2} \tag{4}$$

The polarization $\mathbf{P}(t) = \mathrm{Tr}[\hat{\rho}(t)\hat{\mu}]$ acts as the **source** of a new electromagnetic wave. This effectively recasts the spectroscopic problem: the driving laser induces a quantum coherence in the sample, which in turn acts as an antenna radiating a secondary field.

1.1.3 Thermodynamics of Absorption: The Work Functional

Before analyzing the field at the detector, we must establish that energy is indeed transferred from the field to the material. The rate of work done by the classical field on the polarization density is:

$$\frac{dW}{dt} = \mathbf{E}(t)\cdot\frac{d\mathbf{P}}{dt} \tag{5}$$

Consider a monochromatic driving field $\mathbf{E}(t) = \mathbf{E}_0\cos(\omega t)$.

- **Reactive Response (Refraction):** If the induced polarization is in phase with the driving field ($\mathbf{P}\sim\cos(\omega t)$), then $\dot{\mathbf{P}}\sim-\sin(\omega t)$. The time-averaged work $\langle\mathbf{E}\cdot\dot{\mathbf{P}}\rangle$ over one cycle is zero. No net energy is absorbed.
- **Dissipative Response (Absorption):** For net work to be done, $\mathbf{P}(t)$ must have a component lagging the drive by $\pi/2$ ($\mathbf{P}\sim\sin(\omega t)$). In this case, $\dot{\mathbf{P}}\sim\cos(\omega t)$, and the product $\mathbf{E}\cdot\dot{\mathbf{P}}$ averages to a positive non-zero value.

Conclusion: Microscopic energy absorption necessitates a $\pi/2$ phase shift between the driving field and the induced polarization.

1.1.4 The Macroscopic Consequence: Destructive Interference

How does this local energy transfer manifest at the detector? Let the incident field be a scalar plane wave $E_{inc}(z,t) = \mathcal{E}_0 e^{i(kz-\omega t)}$. The total field at the detector is the superposition of the incident light and the light radiated by the induced polarization (E_{rad}):

$$E_{total} = E_{inc} + E_{rad} \tag{6}$$

Solving the wave equation in the slowly varying envelope approximation (SVEA) for a thin sample of length L, the radiated field is proportional to the time derivative of the polarization:

$$E_{rad}\propto i\omega P(\omega) \tag{7}$$

Crucially, because the absorptive component of the polarization is 90° phase-shifted relative to the driving field ($P\approx i\chi'' E_{inc}$), where χ'' is the imaginary part of the susceptibility of the material, the radiated field becomes:

$$E_{rad}\propto i(i\chi'')E_{inc} = -\chi'' E_{inc} \tag{8}$$

The factor of -1 indicates a π phase shift. The radiated field is **exactly out of phase** with the incident field.

1.1.5 Detection and the "Beer-Lambert" Origin

The photodetector measures the intensity $I \propto |E_{total}|^2$:

$$I_{det} \propto |E_{inc} + E_{rad}|^2 \approx |E_{inc}|^2 + 2\mathrm{Re}(E_{inc}^* E_{rad}) \tag{9}$$

Given the anti-phase nature derived above, the cross term is negative. The intensity reduction (absorption) arises from the **destructive interference** between the unperturbed beam and the field radiated by the sample. The "energy absorption" by the material is the mechanism that enforces the specific phase relationship required for this destructive interference to occur in the forward direction.

1.1.6 The Fluctuation-Dissipation Link

Finally, using first-order perturbation theory, we relate the macroscopic susceptibility $\chi(\omega)$ to the intrinsic quantum fluctuations of the system. This yields the Linear Response function:

$$\chi^{(1)}(\omega) = \frac{i}{\hbar} \int_0^\infty dt\, e^{i\omega t} \langle [\hat{\mu}(t), \hat{\mu}(0)] \rangle \tag{10}$$

This confirms that the linear absorption spectrum $A(\omega) \propto \mathrm{Im}[\chi^{(1)}(\omega)]$ is strictly determined by the Fourier transform of the dipole-dipole correlation function. The light source is merely a probe of the equilibrium dynamics of the material system. Classically, spectroscopy measures the macroscopic polarization $P(t)$ induced by a field $E(t)$.

1.1.7 Extending to Nonlinear Response

The Nonlinear Expansion

When the driving field is strong, the linear approximation breaks down. We expand the polarization as a power series in the field:

$$P(t) = P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t) + \dots \tag{11}$$

Each term $P^{(n)}(t)$ arises from the n-th order interaction with the field and is governed by the n-th order susceptibility $\chi^{(n)}$.

The Response Function Formalism

Just as the linear polarization $P^{(1)}$ is the convolution of the linear response function $S^{(1)}$ with the field, the nonlinear polarization is a multi-time convolution. For the third-order case (critical for 2D spectroscopy and four-wave mixing):

$$P^{(3)}(t) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 S^{(3)}(t_3, t_2, t_1) E(t - t_3) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1) \tag{12}$$

Here, the time variables t_1, t_2, t_3 represent the **intervals** between interaction events, not absolute times.

Connection to Correlation Functions

The response function $S^{(n)}$ contains the microscopic physics of the material's interaction with the incident field. It is expressed as a sum of multi-point correlation functions of the dipole operator $\hat{\mu}$. For the third-order response $S^{(3)}$, the Liouville pathway analysis yields terms of the form (reference here???):

$$S^{(3)}(t_3, t_2, t_1) \propto \left(\frac{i}{\hbar}\right)^3 \langle \hat{\mu}(t_3 + t_2 + t_1) [\hat{\mu}(t_2 + t_1), [\hat{\mu}(t_1), \hat{\mu}(0)]] \rangle \tag{13}$$

This nested commutator structure reflects the sequence of perturbations: the system interacts with the field at three distinct times, creating coherences and populations that evolve during the intervals t_i.

Physical Interpretation

- $S^{(1)}$ **(Linear):** Probes the 2-point correlation $\langle\mu(t)\mu(0)\rangle$. This tells us about the equilibrium fluctuations of the dipole.
- $S^{(3)}$ **(Nonlinear):** Probes the 4-point correlation $\langle\mu(t_3)\mu(t_2)\mu(t_1)\mu(0)\rangle$. This reveals higher-order correlations, such as anharmonicity, coupling between different modes, and dephasing dynamics that are hidden in the linear spectrum (e.g., distinguishing homogeneous vs. inhomogeneous broadening).

The experimental limitation is not usually χ, but the **Damage Threshold** of the sample. To increase the Signal-to-Noise Ratio (SNR), we typically increase photon flux $\dot{N}$, but this scales only as SNR $\propto \sqrt{\dot{N}}$ (Shot-Noise Limit).

2 Part B: What is Quantum Light? (Generation)

Goal: Elucidate the "Source" Hamiltonian and introduce the hardware.

2.1 The Experimental Challenge: Synthesizing Optical Pulses

In a modern spectroscopy lab, we rarely use the direct output of a laser oscillator. To probe molecular dynamics, we require pulses that are:

1. **Tunable:** Spanning UV to Mid-IR.
2. **Short:** Femtosecond duration ($\sim 10 - 100$ fs) for high time resolution.

To achieve this, experimentalists exploit **Parametric Processes** in crystals lacking inversion symmetry ($\chi^{(2)}$ materials like BBO, KTP, or Lithium Niobate). These processes do not rely on energy storage in the material (unlike a laser medium) but rather on the instantaneous mixing of fields.

2.1.1 Classical Nonlinear Optics: DFG (Difference Frequency Generation) and OPA (Optical Parametric Amplification)

The foundation of these sources is Three-Wave Mixing. Consider a strong **Pump** field at ω_p and two lower frequency fields, **Signal** (ω_s) and **Idler** (ω_i), satisfying energy conservation $\omega_p = \omega_s + \omega_i$.

The nonlinear polarization driving the system is:

$$P_i^{(2)}(t) = \epsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j(t) E_k(t) \tag{14}$$

2.1.2 The Coupled Wave Equations

In the Slowly Varying Envelope Approximation (SVEA), neglecting loss, the evolution of the field amplitudes A along the propagation axis z is given by [Lecture 9 slides]:

$$\frac{dA_s}{dz} = i\frac{\omega_s d_{\text{eff}}}{n_s c} A_p A_i^* e^{i\Delta k z} \tag{15}$$

$$\frac{dA_i}{dz} = i\frac{\omega_i d_{\text{eff}}}{n_i c} A_p A_s^* e^{i\Delta k z} \tag{16}$$

Here, $\Delta k = k_p - k_s - k_i$ is the **phase mismatch**. Efficient energy transfer requires $\Delta k = 0$ (Phase Matching), which experimentally dictates the angle of the crystal.

2.1.3 Two Regimes of Operation

1. **Difference Frequency Generation (DFG):**
   - *Input:* Strong Pump (A_p) + Strong Signal (A_s).
   - *Output:* A new Idler field generated at $\omega_i = \omega_p - \omega_s$.
   - *Use:* Generating Mid-IR pulses by mixing a Near-IR pump with a tunable output.
2. **Optical Parametric Amplification (OPA):**
   - *Input:* Strong Pump (A_p) + Weak Seed ($A_s(0)$).
   - *Dynamics:* The pump amplifies the seed exponentially. If $\Delta k = 0$ and A_p is undepleted:
     $$A_s(z) = A_s(0)\cosh(\Gamma z) \approx \frac{1}{2}A_s(0)e^{\Gamma z} \tag{17}$$
     where $\Gamma \propto d_{\text{eff}}|A_p|$ is the parametric gain coefficient.
   - *Crucial Observation:* In classical theory, if the seed $A_s(0) = 0$, then $dA_s/dz = 0$. **No light is generated from nothing.**

2.2 The Quantum Leap: Spontaneous Parametric Down-Conversion (SPDC)

Experimentally, if we block the seed in an OPA, we still see a faint cone of colorful light. This is **Superfluorescence** or SPDC. To explain this, we must quantize the field. The classical seed $A_s(0)$ is replaced by the vacuum operator $\hat{a}_s$, which has non-zero fluctuations.

To rigorously describe SPDC, we move to the Interaction Picture. We define the quantization axis along z (propagation direction) and assume a collinear Type-II configuration (Signal=Ordinary 'o', Idler=Extraordinary 'e').

2.2.1 The Biphoton Wavefunction

Unlike the single-mode approximation often seen in textbooks, we treat the fields as integrals over a continuum of frequency modes. The positive frequency component of the electric field operator is:

$$\hat{E}_j^{(+)}(z,t) = \int d\omega_j \mathcal{A}(\omega_j)\hat{a}_j(\omega_j)e^{i(k_j(\omega_j)z - \omega_j t)} \tag{18}$$

where $j \in \{p, o, e\}$ corresponds to Pump, Ordinary (Signal), and Extraordinary (Idler).

The interaction Hamiltonian in a $\chi^{(2)}$ medium is given by the volume integral of the polarization energy density(???). In the Rotating Wave Approximation (RWA), describing the annihilation of a pump photon and creation of an o-e pair:

$$\hat{H}_I(t) = \epsilon_0 \int_V d^3\mathbf{r}\, \chi^{(2)} \left[\hat{E}_p^{(+)}(\mathbf{r},t)\hat{E}_o^{(-)}(\mathbf{r},t)\hat{E}_e^{(-)}(\mathbf{r},t) + h.c.\right] \tag{19}$$

We treat the Pump field $\hat{E}_p^{(+)}$ as a classical field with a spectral envelope $\alpha(\omega_p)$:

$$E_p^{(+)}(z,t) \propto \int d\omega_p\, \alpha(\omega_p)e^{i(k_p(\omega_p)z - \omega_p t)} \tag{20}$$

The state vector evolves as $|\Psi(t)\rangle = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt' \hat{H}_I(t')\right]|\Psi_0\rangle$. Assuming a weak interaction (low conversion efficiency), we expand to first order:

$$|\Psi(t)\rangle \approx \left(\mathbb{I} - \frac{i}{\hbar}\int_{-\infty}^{\infty} dt' \hat{H}_I(t')\right)|vac\rangle \tag{21}$$

Substituting the field definitions into the Hamiltonian integral, the first-order term becomes:

$$\begin{aligned}\text{Term} \propto \int_{-\infty}^{\infty} dt' \int_{-L/2}^{L/2} dz \iiint d\omega_p d\omega_o d\omega_e \, \alpha(\omega_p)\, \hat{a}_o^\dagger(\omega_o)\hat{a}_e^\dagger(\omega_e) \\ \times \exp\left(-i\{[k_o + k_e - k_p]z - [\omega_o + \omega_e - \omega_p]t'\}\right)\end{aligned} \tag{22}$$

Note: The phase terms arise from $E^{(-)} \sim e^{+i(kz-\omega t)}$ and $E^{(+)} \sim e^{-i(kz-\omega t)}$ for the conjugates.

We perform the integrations to reveal the physics:

Step A: Time Integral (Energy Conservation) The time integral yields a delta function:

$$\int_{-\infty}^{\infty} dt' e^{i(\omega_p - \omega_o - \omega_e)t'} = 2\pi\delta(\omega_p - \omega_o - \omega_e) \tag{23}$$

This enforces $\omega_p = \omega_o + \omega_e$. We use this to integrate over $d\omega_p$, replacing $\alpha(\omega_p)$ with $\alpha(\omega_o + \omega_e)$.

Step B: Space Integral (Momentum Conservation) The spatial integral over the crystal length L defines the Phase Matching function:

$$\int_{-L/2}^{L/2} dz\, e^{-i(k_o + k_e - k_p)z} = L\,\text{sinc}\left(\frac{\Delta k L}{2}\right) \tag{24}$$

where the phase mismatch is $\Delta k = k_p(\omega_o + \omega_e) - k_o(\omega_o) - k_e(\omega_e)$.

The generated state is an entangled superposition of photon pairs:

$$|\Psi\rangle_{\text{SPDC}} = |vac\rangle + C\iint d\omega_o d\omega_e \underbrace{\alpha(\omega_o + \omega_e)}_{\text{Pump Envelope}} \underbrace{\Phi(\Delta k)}_{\text{Phase Matching}} \hat{a}_o^\dagger(\omega_o)\hat{a}_e^\dagger(\omega_e)|vac\rangle \tag{25}$$

2.2.2 Interpretation of the Joint Spectral Amplitude (JSA)

The function $f(\omega_o, \omega_e) = \alpha(\omega_o + \omega_e) \times \Phi(\Delta k)$ is the **Joint Spectral Amplitude**.

- $\alpha(\omega_o + \omega_e)$**:** Represents energy conservation. Since the pump pulse has a finite bandwidth, the sum of signal and idler frequencies is constrained to the pump width.
- $\Phi(\Delta k)$**:** Represents momentum conservation. The "Sinc" function imposes a band along the curve where indices of refraction match.

The intersection of these two functions determines the degree of frequency entanglement in the photon pair.

2.2.3 Implications for Spectroscopy

1. **Energy Entanglement:** The time integral enforces $\omega_s + \omega_i = \omega_p$. The pair is strictly correlated in energy.
2. **Momentum Bandwidth:** The $\text{sinc}(x)$ function has a width $\propto 1/L$.
   - A **long crystal** creates a narrow bandwidth (strict momentum conservation).
   - A **short crystal** creates a broad bandwidth (relaxed momentum conservation).
3. **Broadband Entanglement:** For spectroscopy, we often use short crystals to generate broad spectral bandwidths.

2.3 Squeezed State Generation

In the previous section, we treated the signal and idler as distinct modes. Now, we consider the **degenerate case** where $\omega_s = \omega_i = \omega$. To understand the nature of this light, we look at the Quadrature Operators, which are dimensionless analogues to position ($\hat{q}$) and momentum ($\hat{p}$):

$$\hat{X}_1 = \frac{1}{2}(\hat{a} + \hat{a}^\dagger) \quad \text{and} \quad \hat{X}_2 = \frac{1}{2i}(\hat{a} - \hat{a}^\dagger) \tag{26}$$

These operators obey the commutation relation $[\hat{X}_1, \hat{X}_2] = i/2$, leading to the Heisenberg Uncertainty Principle:

$$\Delta X_1 \Delta X_2 \geq \frac{1}{4} \tag{27}$$

- **Coherent State (Vacuum/Laser):** The noise is distributed equally: $(\Delta X_1)^2 = (\Delta X_2)^2 = 1/4$.
- **Squeezed State:** A state is "squeezed" if the variance in *one* quadrature is reduced below the vacuum limit (at the expense of the other):

$$(\Delta X_1)^2 < \frac{1}{4} \quad \text{or} \quad (\Delta X_2)^2 < \frac{1}{4} \tag{28}$$

Mathematically, a squeezed vacuum state $|\xi\rangle$ is generated by acting on the vacuum with the unitary **Squeeze Operator** $\hat{S}(\xi)$ [Gerry & Knight, Ch 7]:

$$\hat{S}(\xi) = \exp\left[\frac{1}{2}(\xi^* \hat{a}^2 - \xi \hat{a}^{\dagger 2})\right] \tag{29}$$

where $\xi = re^{i\theta}$ is the squeezing parameter (r is the degree of squeezing, θ is the angle).

Transformation of Operators: The operator $\hat{S}^\dagger(\xi)\hat{a}\hat{S}(\xi)$ performs a Bogoliubov transformation:

$$\hat{S}^\dagger(\xi)\hat{a}\hat{S}(\xi) = \hat{a}\cosh r - \hat{a}^\dagger e^{i\theta}\sinh r \tag{30}$$

This mixing of creation and annihilation operators is the hallmark of parametric amplification.

2.3.1 Connection to SPDC (The Degenerate Case)

Recall our SPDC Hamiltonian derived in the previous lecture for the non-degenerate case:

$$\hat{H}_{SPDC} \propto i\hbar\chi^{(2)}(\hat{a}_p\hat{a}_s^\dagger\hat{a}_i^\dagger - h.c.) \tag{31}$$

If we operate in the **Degenerate** regime where signal and idler are indistinguishable ($\hat{a}_s = \hat{a}_i = \hat{a}$) and $\omega = \omega_p/2$:

- The pair creation term becomes $\hat{a}^\dagger\hat{a}^\dagger = (\hat{a}^\dagger)^2$.
- The pump is treated classically as a complex amplitude β.

The effective Hamiltonian becomes:

$$\hat{H}_{deg} = \frac{i\hbar\eta}{2}((\hat{a}^\dagger)^2 - \hat{a}^2) \tag{32}$$

where $\eta \propto \chi^{(2)}\beta$. The time evolution operator is $\hat{U}(t) = \exp\left[\frac{\eta t}{2}((\hat{a}^\dagger)^2 - \hat{a}^2)\right]$.

Comparing this to the definition of $\hat{S}(\xi)$, we see they are identical if $\xi = \eta t$. Thus, degenerate SPDC naturally implements the Squeeze Operator, generating a state with even-photon number statistics ($|0\rangle, |2\rangle, |4\rangle \dots$).

3 Part C: Photon Detection Methodologies

3.1 The Philosophy of Detection: Energy vs. Information

In classical spectroscopy, the central question is often: *"How much energy did the material absorb?"* We measure transmission or reflection to extract macroscopic parameters like the absorption coefficient $\alpha(\omega)$.

In quantum light spectroscopy, the question shifts: *"How much information did the material add to the photon's quantum state?"* To estimate this information, the source and detector must be treated as part of the same quantum system.

- **Classical Radio:** We detect the field amplitude $E(t)$ directly (e.g., inducing current in an antenna).
- **Optical Frequencies (10^{15} Hz):** The field oscillates too fast for electronics to follow. We cannot measure $E(t)$. Instead, we rely on **absorption events** (the photoelectric effect) to generate a signal.

3.2 Classical Detection Model

Classically, the probability of detection P_{det} is proportional to the accumulated energy (intensity) over the detector's integration time t:

$$P_{det} = \frac{D}{t} \int_0^t I(t')dt' \tag{33}$$

A realistic detector (like an Avalanche Photodiode or CCD) converts this energy into a photocurrent $i(t)$. However, this current is an average:

$$i(t) = \frac{D'}{t} \int_0^t I(t')dt' \tag{34}$$

The Limitation: This detector is a low-pass filter. It sees the "DC" intensity and slow fluctuations, but it averages out the rapid quantum fluctuations that carry the information we care about. To see quantum light, we need to count individual events.

3.3 Quantum Detection: Glauber's Theory

How do we describe a "click" quantum mechanically? Roy Glauber (Nobel Prize, 2005) formalized this by modeling the detector as an atom interacting with the field via the dipole transition $\hat{H}_{int} \propto \hat{\mu} \cdot \hat{E}$.

The Critical Question: Does the detector measure $\hat{E}^2$, $\hat{n}$, or something else?

1. **Absorption, not Emission:** Ideal photodetectors work by absorbing a photon (promoting an electron from valence to conduction band). Therefore, the detector couples to the **positive frequency part** of the field, $\hat{E}^{(+)}(\mathbf{r}, t)$, which contains the annihilation operator $\hat{a}$.
$$\hat{E}^{(+)}(\mathbf{r}, t) \propto \hat{a} e^{-i\omega t} \tag{35}$$
2. **The Transition Probability:** If the field is in state $|i\rangle$, the amplitude to transition to a final state $|f\rangle$ by absorbing a photon is $\langle f|\hat{E}^{(+)}|i\rangle$. The rate $w(t)$ is the sum over all possible final states (since we don't measure the field after the photon is gone):
$$w(t) \propto \sum_f |\langle f|\hat{E}^{(+)}|i\rangle|^2 = \langle i|\hat{E}^{(-)}\hat{E}^{(+)}|i\rangle \tag{36}$$

3.4 The Anatomy of Detection Efficiency

In quantum optics, the symbol η (efficiency) is often treated as a simple scalar between 0 and 1. However, experimentally, the **System Detection Efficiency (SDE)** is the product of three distinct physical probabilities:

$$\eta_{sys} = \eta_{coupling} \times \eta_{abs} \times \eta_{elec} \tag{37}$$

- **Coupling Efficiency ($\eta_{coupling}$):** The probability that a photon emitted from the source actually enters the active area of the detector (mode matching and fiber coupling losses).
- **Intrinsic Quantum Efficiency (η_{abs}):** The probability that a photon entering the active material is absorbed and generates a primary electron-hole pair. This depends on the material bandgap (Si vs. InGaAs) and the thickness of the depletion region.
- **Electronic/Threshold Efficiency (η_{elec}):** detectors produce a distribution of voltage pulses. To filter out electronic noise and "Dark Counts" (thermal false alarms), we set a **Discriminator Threshold**.
  - If the threshold is too high, we miss real photon events (lowering η).
  - If the threshold is too low, we count noise as photons (increasing Dark Count Rate).

3.5 The Hardware: Linear Mode vs. Geiger Mode

How do we turn a single electron-hole pair into a measurable macroscopic current?

3.5.1 Fast Photodiodes (Linear Mode)

Standard high-speed photodiodes (PIN) operate with a reverse bias below the breakdown voltage.

- **Mechanism:** One photon generates one electron-hole pair. There is no internal gain (or very low gain).
- **Output:** The photocurrent is directly proportional to the instantaneous intensity: $I(t) \propto \hat{E}^{(-)}\hat{E}^{(+)}$.
- **Limitation:** The signal from a *single* photon is buried deep beneath the thermal noise floor of the readout electronics. These are used for the detection of bright light, not at single photon levels.

3.5.2 Single Photon Avalanche Diodes (SPADs)

To detect single photons, we bias the diode **above the breakdown voltage** (Geiger Mode). The junction is in a metastable state.

- **Mechanism:** A single photo-electron is accelerated by the massive electric field, knocking loose other electrons (impact ionization). This creates a runaway "avalanche" of 10^5 - 10^6 electrons.
- **Output:** A macroscopic voltage spike (TTL pulse).
- **The "Binary" Nature:** The size of the avalanche is determined by the bias voltage, *not* by the number of photons.
  - 1 Photon $\rightarrow$ Avalanche (Click).
  - 2 Photons $\rightarrow$ Same Avalanche (Click).

  Therefore, a SPAD is **NOT Photon-Number Resolving (PNR)**. It effectively digitizes the field into "Vacuum" (0) or "Light" (≥ 1).

3.6 The Formalism: POVMs and the "Click"

Why POVMs?: Standard quantum mechanics textbooks describe measurement using *Projection Valued Measures* (PVMs), where operators project the system onto orthogonal eigenstates (e.g., $|\psi\rangle \to |n\rangle$). This assumes a perfect, noise-free measurement where outcomes are perfectly distinguishable. However, real experiments are messy. Detectors have finite efficiency ($\eta < 1$), dark counts, and often destroy the state upon measurement. To describe this, we generalize to **Positive Operator-Valued Measures (POVMs)**. A POVM is a set of operators $\{\hat{\Pi}_k\}$ describing the probabilities of experimental outcomes, satisfying $\sum_k \hat{\Pi}_k = \mathbb{I}$ and $\hat{\Pi}_k \geq 0$, but without requiring orthogonality ($\hat{\Pi}_i\hat{\Pi}_j \neq \delta_{ij}\hat{\Pi}_i$). This framework allows us to model "fuzzy" measurements where different quantum states might produce the same experimental "click."

3.6.1 Why SPADs are not Number Resolving

How do we derive the "Click / No-Click" operators for a detector with efficiency η? Imagine the detector is a perfect counter placed behind a beam splitter with transmission η.

1. Consider an input Fock state $|n\rangle$ containing n photons.
2. Each photon independently attempts to pass the beam splitter. It has a probability η of being transmitted (detected) and $(1-\eta)$ of being reflected (lost).
3. The detector registers a **"No Click"** outcome only if *zero* photons reach the active area.
4. This requires all n photons to fail the trial simultaneously. The probability of this joint event is the product of individual failure probabilities:

$$P(\text{No Click}|n) = \underbrace{(1-\eta) \times (1-\eta) \times \cdots \times (1-\eta)}_{n \text{ times}} = (1-\eta)^n \tag{38}$$

5. Translating this probability into an operator diagonal in the number basis, we obtain the No-Click POVM element:

$$\hat{\Pi}_0 = \sum_{n=0}^{\infty} (1-\eta)^n |n\rangle\langle n| \tag{39}$$

6. Finally, since the detector must either click or not click ($\hat{\Pi}_0 + \hat{\Pi}_{click} = \mathbb{I}$), the Click operator captures all other possibilities:

$$\hat{\Pi}_{click} = \mathbb{I} - \hat{\Pi}_0 = \sum_{n=1}^{\infty} [1 - (1-\eta)^n] |n\rangle\langle n| \tag{40}$$

This derivation highlights the utility of POVMs: we have successfully mapped a complex physical loss process into a single mathematical operator that can be applied to any arbitrary input state $\hat{\rho}$.

Physical Interpretation: The operator $\hat{\Pi}_{click}$ is a weighted sum of ALL number states $|1\rangle, |2\rangle, |3\rangle \ldots$.

- A "Click" does not project the state onto $|1\rangle$. It projects the state onto the subspace of "not vacuum."
- Consequently, a standard SPAD cannot distinguish a single photon state from a multi-photon squeezed state or a weak coherent state. We require statistical methods (like HBT / $g^{(2)}$) or advanced PNR detectors (like Transition Edge Sensors) to recover the photon number distribution.

3.7 POVMs for Photon Number Resolving (PNR) Detectors

While SPADs saturate at a single photon, advanced detectors like **Transition Edge Sensors (TES)** or **Superconducting Nanowire Single Photon Detectors (SNSPDs)** can distinguish between $n = 1, 2, 3...$ photons. However, they are not immune to loss.

To describe a realistic PNR detector, we model it as a **perfect counter** preceded by a **virtual beam splitter** with transmission η (representing the system efficiency).

The Physical Model (Binomial Loss)

If the incoming optical state has exactly m photons ($|m\rangle$), the loss mechanism (beam splitter) randomly deletes photons. The probability that exactly n photons survive to trigger the detector (where $n \leq m$) is governed by the Binomial Distribution:

$$P(n|m) = \binom{m}{n} \eta^n (1-\eta)^{m-n} \tag{41}$$

- η^n: Probability that n photons are transmitted.
- $(1-\eta)^{m-n}$: Probability that the remaining $m-n$ photons are lost.
- $\binom{m}{n}$: The number of ways to choose which photons survive.

The POVM element $\hat{\Pi}_n$ corresponds to the measurement outcome "The detector registered n photons." This operator is constructed by summing over all possible input states $|m\rangle$ that *could* have generated this outcome, weighted by the binomial probability:

$$\hat{\Pi}_n(\eta) = \sum_{m=n}^{\infty} \binom{m}{n} \eta^n (1-\eta)^{m-n} |m\rangle\langle m| \tag{42}$$

Key Observations:

1. **Diagonal in Number Basis:** Like the SPAD, this operator destroys phase information ($\langle n|\hat{\Pi}|k\rangle = 0$ for $n \neq k$). It purely measures intensity statistics.
2. **The Ideal Limit ($\eta \to 1$):** If the efficiency is 100%, the term $(1-\eta)^{m-n}$ vanishes unless $m = n$. The sum collapses to a single term:

   $$\hat{\Pi}_n(1) = |n\rangle\langle n|$$

   This recovers the standard Projective Measurement.
3. **The Reconstruction Problem:** Experimentalists measure the probability distribution of outcomes $P_{meas}(n) = \mathrm{Tr}[\hat{\rho}\hat{\Pi}_n]$. However, because of loss, $P_{meas}(n)$ is a "smeared" version of the true photon statistics $P_{true}(m)$. Recovering the true statistics often requires Maximum Likelihood Estimation (MLE) algorithms.

Example: Detecting a Two-Photon State

Consider a pure 2-photon Fock state $|\psi\rangle = |2\rangle$ incident on a PNR detector with $\eta = 50\%$.

- **Outcome $n = 2$:** Both photons survive.

$$P(2) = \langle 2|\hat{\Pi}_2|2\rangle = \binom{2}{2}(0.5)^2(0.5)^0 = 0.25$$

- **Outcome** $n = 1$**:** One is lost, one survives.

$$P(1) = \langle 2|\hat{\Pi}_1|2\rangle = \binom{2}{1}(0.5)^1(0.5)^1 = 0.50$$

- **Outcome** $n = 0$**:** Both are lost.

$$P(0) = \langle 2|\hat{\Pi}_0|2\rangle = \binom{2}{0}(0.5)^0(0.5)^2 = 0.25$$

Even though the input was a perfect $|2\rangle$ state, the detector registers a single photon 50% of the time. This illustrates why rigorous POVM modeling is essential for interpreting quantum light experiments.

Goal: Translate operators $\hat{n}$ into voltage pulses.

4 Linking the Photocurrent $i(t)$ to POVMs

4.1 The Conceptual Gap

We have previously defined $i(t)$ as a continuous current observable, while POVMs $\{\hat{\Pi}_n\}$ were defined as discrete probability operators. The physical link between them is the **Integration Window** and the **Readout Electronics**.

4.2 The Current Operator and Accumulated Charge

The photocurrent operator $\hat{i}(t)$ is proportional to the photon flux. In the Heisenberg picture, for a detector with gain G and elementary charge e:

$$\hat{i}(t) = Ge\eta\hat{a}^\dagger(t)\hat{a}(t) + \hat{i}_{noise}(t) \tag{43}$$

Real electronics do not measure instantaneous current; they measure the total charge Q accumulated over a response time τ:

$$\hat{Q}(\tau) = \int_0^\tau \hat{i}(t')dt' = Ge\hat{m} \tag{44}$$

Here, $\hat{m}$ is the operator for the **number of detected photoelectrons**.

4.3 POVMs as Spectral Decomposition

The POVMs $\{\hat{\Pi}_n\}$ describe the statistics of this integrated observable $\hat{m}$.

- The **Observable** is $\hat{m} = \sum n\hat{\Pi}_n$.
- The **Probability** of measuring charge $Q = Gen$ is $P(n) = \mathrm{Tr}[\hat{\rho}\hat{\Pi}_n]$.

Thus, $i(t)$ provides the raw dynamics, while the POVMs describe the statistics of the integrated signal.

4.3.1 Special Case: SPADs (Thresholding)

For a Geiger-mode SPAD, the electronics apply a non-linear threshold function Θ. The output current is binary:

$$i_{out}(t) = \begin{cases} I_{pulse} & \text{if } \int_0^\tau \hat{i}_{in}(t')dt' > 0 \quad (\text{Outcome } \hat{\Pi}_{click}) \\ 0 & \text{if } \int_0^\tau \hat{i}_{in}(t')dt' = 0 \quad (\text{Outcome } \hat{\Pi}_0) \end{cases} \tag{45}$$

5 Noise in Light

When measuring $i(t)$, we observe fluctuations. We classify optical noise into a hierarchy: When we measure a laser beam on a photodetector, the current $i(t)$ fluctuates. We can classify this noise into three distinct regimes based on their origin:

1. **Technical Noise (Classical):** Caused by vibrations, laser driver instability, or $1/f$ noise in electronics. *Remedy:* Better feedback loops, vibration isolation. This noise can theoretically be reduced to zero.

2. **Shot Noise (The Particle Limit):** Even a perfectly stable laser has random photon arrival times (Poissonian statistics).

$$(\Delta n)^2 = \langle n \rangle \tag{46}$$

   In the frequency domain, this appears as "white noise." This is the **Standard Quantum Limit (SQL)** for classical spectroscopy.

3. **Quantum Noise (The Wave Limit):** This is the vacuum fluctuation entering the open port of the experiment. In a Coherent State (laser), the Quantum Noise is exactly equal to the Shot Noise. In a **Squeezed State**, the noise in one quadrature is suppressed *below* this limit.

5.1 The Measurement Problem

Why can't we measure squeezing with a standard photodiode? A single photodiode measures the photon number operator $\hat{n} = \hat{a}^\dagger \hat{a}$.

- For a Squeezed Vacuum state, $\langle \hat{n} \rangle = \sinh^2(r)$ (very small).
- A direct detector just sees a very faint, slightly noisy signal. It cannot access the phase-dependent correlations ($\langle \hat{X}^2 \rangle$ vs $\langle \hat{P}^2 \rangle$) where the "squeezing" actually resides.

To measure quadratures, we need a reference frame. We use **Balanced Homodyne Detection**.

5.2 Balanced Homodyne Detection

The standard method to detect continuous variable quantum information. We mix the weak quantum signal ($\hat{a}_s$) with a strong, classical "Local Oscillator" (LO, α_{LO}) on a 50:50 beam splitter.

5.2.1 The Beam Splitter Transformation

The beam splitter mixes the modes. The fields at detectors D_1 and D_2 are:

$$\hat{a}_1 = \frac{1}{\sqrt{2}}(\hat{a}_s + \hat{a}_{LO}) \tag{47}$$

$$\hat{a}_2 = \frac{1}{\sqrt{2}}(\hat{a}_s - \hat{a}_{LO}) \tag{48}$$

(Note the minus sign from the phase shift upon reflection).

5.2.2 The Difference Current

The detectors measure intensity $\hat{n}_1$ and $\hat{n}_2$. We electronically subtract the photocurrents:

$$\hat{I}_- \propto \hat{n}_1 - \hat{n}_2 = \hat{a}_1^\dagger \hat{a}_1 - \hat{a}_2^\dagger \hat{a}_2 \tag{49}$$

Substituting the beam splitter equations:

$$\hat{I}_- \propto \frac{1}{2}[(\hat{a}_s^\dagger + \alpha_{LO}^*)(\hat{a}_s + \alpha_{LO}) - (\hat{a}_s^\dagger - \alpha_{LO}^*)(\hat{a}_s - \alpha_{LO})] \tag{50}$$

Expanding this, the $|\alpha_{LO}|^2$ terms cancel (common mode rejection) and the $|\hat{a}_s|^2$ terms cancel. We are left with the interference terms:

$$\hat{I}_- \propto \alpha_{LO}^* \hat{a}_s + \alpha_{LO} \hat{a}_s^\dagger \tag{51}$$

Let the Local Oscillator have a phase θ: $\alpha_{LO} = |\alpha| e^{-i\theta}$.

$$\hat{I}_- \propto |\alpha|(\hat{a}_s e^{-i\theta} + \hat{a}_s^\dagger e^{i\theta}) = 2|\alpha| \hat{X}_\theta \tag{52}$$

Conclusion: The difference photocurrent is directly proportional to the **Quadrature Operator** $\hat{X}_\theta$ of the signal field. By scanning the LO phase θ (using a piezo mirror), we can map out the "shape" of the quantum state in phase space.

5.3 Experimental Signature of Squeezing

How do we know we have squeezed light?

1. **Calibration (The Shot Noise Level):** First, block the signal port (input = Vacuum $|0\rangle$). The Homodyne detector measures the vacuum fluctuations of the empty port beating against the LO. This establishes the **Shot Noise Limit (SNL)** or 0 dB reference.
2. **Measurement:** Unblock the Squeezed Vacuum. Scan the LO phase θ.
3. **The Trace:** Display the noise power (variance of $\hat{I}_-$) on a Spectrum Analyzer.
   - At $\theta = 0$ (Squeezed axis): The noise drops **below** the SNL (e.g., -3 dB). This is non-classical.
   - At $\theta = \pi/2$ (Anti-Squeezed axis): The noise rises **above** the SNL (e.g., +3 dB).

Experimental Realities:

- **Mode Matching:** The Signal and LO must overlap perfectly spatially. Any mismatch acts like a loss channel, mixing in regular vacuum and destroying the squeezing.
- **Common Mode Rejection Ratio (CMRR):** The subtraction must be perfect to cancel the classical noise of the LO.

6 Intensity Correlations and Photon Statistics

While Homodyne detection measures the wave nature (quadratures), we use **Intensity Interferometry** to probe the particle nature of light. The central quantity is the second-order coherence function, $g^{(2)}(\tau)$.

6.1 The Hanbury Brown-Twiss (HBT) Setup

To measure correlations, we cannot simply use one detector, as it has a "dead time" after a detection event. Instead, we use the HBT configuration:

1. The input field $\hat{a}$ impinges on a 50:50 Beam Splitter.
2. The light is split into two arms, monitored by detectors D_1 and D_2.
3. We measure the **Coincidence Rate** $R_{12}(\tau)$: the rate of simultaneous "clicks" (with time delay τ).

6.2 Deriving $g^{(2)}$ from POVMs

Standard textbooks define $g^{(2)}$ in terms of intensity operators $\hat{n}$. However, real experiments use SPADs, which are "Click/No-Click" devices. Let us rigorously derive the connection.

6.2.1 The Joint POVM

A coincidence event means D_1 clicks **AND** D_2 clicks. The measurement operator for this joint event acting on the state exiting the beam splitter is:

$$\hat{\Pi}_{coinc} = \hat{\Pi}^{(1)}_{click} \otimes \hat{\Pi}^{(2)}_{click} \tag{53}$$

Recall from Part C that for a SPAD with efficiency η:

$$\hat{\Pi}_{click} = \mathbb{I} - \sum_{n=0}^{\infty} (1-\eta)^n |n\rangle\langle n| \tag{54}$$

6.2.2 The Weak Field Approximation (Linear Regime)

In a typical quantum spectroscopy experiment, the light intensity is low (single photon regime, $\langle n \rangle \ll 1$). We can Taylor expand the term $(1-\eta)^n$:

$$(1-\eta)^n \approx 1 - n\eta + \mathcal{O}(\eta^2)$$

Substituting this into the expansion of the identity $\mathbb{I} = \sum |n\rangle\langle n|$:

$$\hat{\Pi}_{click} \approx \sum_{n=0}^{\infty} [1 - (1-n\eta)]|n\rangle\langle n| = \eta \sum_{n=0}^{\infty} n|n\rangle\langle n| = \eta\hat{n} \tag{55}$$

Crucial Result: In the low-flux limit, the discrete "Click" operator becomes proportional to the continuous Number operator $\hat{n}$.

6.2.3 Back-Propagating to the Source

The coincidence rate is $R_{12} \propto \langle \hat{\Pi}^{(1)}_{click} \hat{\Pi}^{(2)}_{click} \rangle \approx \eta^2 \langle \hat{n}_1 \hat{n}_2 \rangle$. Using the beam splitter relations for input mode $\hat{a}$ and vacuum input $\hat{v}$:

$$\hat{a}_1 = \frac{\hat{a} + \hat{v}}{\sqrt{2}}, \quad \hat{a}_2 = \frac{\hat{a} - \hat{v}}{\sqrt{2}}$$

The term $\hat{n}_1\hat{n}_2 = \hat{a}_1^\dagger \hat{a}_1 \hat{a}_2^\dagger \hat{a}_2$. Dropping vacuum terms (which average to zero in Normal Ordering):

$$\langle : \hat{n}_1 \hat{n}_2 : \rangle \propto \langle \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a} \rangle \tag{56}$$

Thus, the probability of a coincidence count is proportional to the **Normally Ordered Intensity Correlation**:

$$g^{(2)}(\tau) = \frac{\langle \hat{a}^\dagger(t)\hat{a}^\dagger(t+\tau)\hat{a}(t+\tau)\hat{a}(t) \rangle}{\langle \hat{a}^\dagger(t)\hat{a}(t) \rangle^2} \tag{57}$$

6.3 The Physics of $g^{(2)}(0)$

We look at the zero-delay value ($\tau = 0$) to categorize the light source.

6.3.1 Classical Light (Bunching/Random)

Classically, $g^{(2)}(0) = \langle I^2 \rangle / \langle I \rangle^2$. By Cauchy-Schwarz, $\langle I^2 \rangle \geq \langle I \rangle^2$, so $g^{(2)}(0) \geq 1$.

- **Coherent State (Laser):** The detection events are uncorrelated (Poissonian). $g^{(2)}(0) = 1$.
- **Thermal Light (Chaotic):** The intensity fluctuates wildly. Photons prefer to arrive in "bunches" (Bose-Einstein statistics). $g^{(2)}(0) = 2$.

6.3.2 Quantum Light (Antibunching)

For a single photon Fock state $|1\rangle$:

$$\langle 1|\hat{a}^\dagger \hat{a}^\dagger \hat{a}\hat{a}|1\rangle = 0 \tag{58}$$

(The first annihilation lowers state to $|0\rangle$, the second kills it).

$$g^{(2)}(0) = 0 \tag{59}$$

Interpretation: A single photon cannot split at a beam splitter. It goes either to D_1 OR D_2. Coincidences are impossible.

- $g^{(2)}(0) < 1$ is the **Non-Classicality Criterion**. It implies the field cannot be described by a classical probability distribution of intensities.

6.4 Experimental Reality: The Heralded $g^{(2)}$

In our SPDC experiments, we often use **Heralding**. We generate pairs (Signal + Idler).

1. We detect the Idler photon (The "Herald") at detector D_H.
2. This projects the Signal arm into a single-photon state $|1\rangle_s$.
3. We perform the HBT test on the Signal arm *conditioned* on a click at D_H.

This "Heralded $g^{(2)}_{cond}$" is the standard metric for the purity of single-photon sources. A value of $g^{(2)}_{cond}(0) < 0.05$ is considered a high-quality source.

7 Wave-Particle Duality in Detection

We have now introduced two very different ways to detect "Quantumness." It is crucial to understand that these probe complementary aspects of light.

7.1 The Two Faces of Non-Classicality

7.2 Is the "Wave" Measurement Truly Quantum?

Students often ask: *"If Homodyne detection measures electric field waves, isn't that classical?"* The answer lies in the **Noise**.

- A **Classical Wave** $E(t) = E_0 \cos(\omega t)$ has a precise amplitude and phase. If we measure it carefully, the noise is zero (limited only by technical imperfections).

Aspect	Particle Nature (Discrete Variable)	Wave Nature (Continuous Variable
Observable	Photon Number $\hat{n}$	Field Quadrature $\hat{X}, \hat{P}$
Detector	SPAD / HBT Interferometer	Balanced Homodyne Detector
Key Metric	$g^{(2)}(0)$ (Intensity Correlation)	ΔX^2 (Noise Variance)
Classical Limit	$g^{(2)}(0) \geq 1$	$\Delta X^2 \geq$ Shot Noise (Vacuum)
Quantum Signature	**Antibunching:** $g^{(2)}(0) < 1$	**Squeezing:** $\Delta X^2 <$ Vacuum
Interpretation	"Photons arrive one by one"	"Field is quieter than vacuum"

Table 1: Comparison of Discrete vs. Continuous Variable Quantum Optics

- A **Quantum Field** is an operator. Even in the vacuum state $|0\rangle$, it fluctuates due to the non-commutativity $[\hat{X}, \hat{P}] = i/2$.

Squeezing is a Quantum Phenomenon because: To create a squeezed state, we must correlate pairs of photons so strongly that their quantum fluctuations destructively interfere in one quadrature.

- *Classical view:* You can't have "negative" noise or noise "below zero."
- *Quantum view:* The "Zero" level is the Vacuum. Squeezing dips **below** this fundamental floor. This is impossible for any classical statistical distribution of waves (formally, the Glauber-Sudarshan P-function becomes singular).

7.3 Visualizing the Difference

- **Direct Detection ($g^{(2)}$):** Imagine standing in the rain. You count individual drops hitting your skin. If the drops arrive perfectly regularly (like a ticking clock), that is **Antibunching**. Rain doesn't naturally do that; it requires a "Quantum Cloud."
- **Homodyne Detection (Squeezing):** Imagine looking at the ocean surface. It is never perfectly flat; there are always ripples (Vacuum fluctuations). **Squeezing** is like using a magical device to calm the ripples until the surface is smoother than physically allowed by nature, at the cost of making the waves much taller (Anti-squeezing) elsewhere.

8 Entanglement Entropy as a Probe of Material Complexity

We have established how to generate entangled states (Part B) and how to detect them (Parts C & D). Now, we arrive at the frontier of Quantum Light Spectroscopy: using the **change** in photon entanglement to diagnose **many-body interactions** inside a material.

Based on our recent theoretical developments [Bittner et al. JCP 2020, Dambal et al. 2025], we move beyond simple absorption measurements. We view the material not as a "bucket" that absorbs photons, but as a **Quantum Channel** that processes the information encoded in the biphoton wavefunction.

8.1 1. The Formalism: Spectral Entanglement Entropy

The Joint Spectral Amplitude (JSA), $\Phi(\omega_s, \omega_i)$, contains all the correlations between the signal and idler photons. To quantify the entanglement, we perform a **Schmidt Decomposition** (Singular Value Decomposition in the continuum limit).

8.1.1 The Schmidt Decomposition

Any bipartite pure state can be written in a diagonal basis:

$$\Phi(\omega_s, \omega_i) = \sum_k \sqrt{\lambda_k} u_k(\omega_s) v_k(\omega_i) \tag{60}$$

- $\{u_k(\omega_s)\}$ and $\{v_k(\omega_i)\}$ are the orthonormal **Schmidt Modes** (eigenfunctions of the reduced density matrices).
- $\{\lambda_k\}$ are the **Schmidt Coefficients**, satisfying $\sum \lambda_k = 1$.
- λ_k represents the probability that the photon pair is found in the k-th mode.

8.1.2 The Von Neumann Entropy

The spectral entanglement entropy S is the Shannon entropy of the Schmidt coefficients:

$$S = -\sum_k \lambda_k \ln(\lambda_k) \tag{61}$$

- $S \to 0$**:** The state is separable (Factorizable product state).
- S **is large:** The state is highly entangled (Many active modes).

8.2 Input-Output Theory: The Material as a Processor

In a spectroscopy experiment, we prepare an initial entangled state $|\Psi_{in}\rangle$ via SPDC. This state scatters off a material sample. We detect the output state $|\Psi_{out}\rangle$.

The central hypothesis of this paradigm is:

$$S(\Psi_{out}) \neq S(\Psi_{in}) \iff \text{Material Many-Body Interactions} \tag{62}$$

8.2.1 The Scattering Matrix Approach

As detailed in [Piryatinski et al. 2025], the transformation is governed by the scattering matrix $\hat{\mathcal{S}}$. The input and output operators are linked via the material's Green's Function. In the weak coupling limit, the output JSA is a convolution of the input JSA and the material response function R:

$$\Phi_{out}(\omega_s, \omega_i) \approx \iint d\omega_s' d\omega_i' R(\omega_s, \omega_i; \omega_s', \omega_i') \Phi_{in}(\omega_s', \omega_i') \tag{63}$$

Consider a material modeled as a set of excitons.

1. **Non-Interacting Excitons ($\Delta = 0$):** If the excitons are simple harmonic oscillators (independent bosons), the scattering is linear. The Schmidt modes $\{u_k, v_k\}$ might rotate (unitary transformation), but the distribution of weights $\{\lambda_k\}$ remains largely invariant (assuming no loss).
$$\Delta S \approx 0$$
2. **Interacting Excitons ($\Delta \neq 0$):** If excitons interact (e.g., via Coulomb repulsion or Pauli blocking), the system is anharmonic. The scattering event mixes the Schmidt modes non-trivially. This redistributes the Schmidt weights λ_k, altering the entropy.
$$\Delta S \propto f(\text{Interaction Strength})$$

Conclusion: A measurement of ΔS serves as a **Witness** for many-body correlations. We can detect exciton-exciton scattering without needing high-intensity pump pulses (which characterize classical nonlinear spectroscopy).

Lyapunov-Based Dynamics for Polaritons In recent work [Dambal et al. 2025], we extended this to cavity-polariton systems where light and matter hybridize strongly. Calculating the full wavefunction evolution is computationally expensive. Instead, we use the **Gaussian State Formalism**.

Since the SPDC state is Gaussian, and linear polariton interactions preserve Gaussianity, we can track the **Covariance Matrix** σ rather than the full Hilbert space.

The Covariance Evolution The dynamics of the system (Photons + Excitons) are governed by the Lyapunov equation:

$$\frac{d\sigma}{dt} = A\sigma + \sigma A^T + D \tag{64}$$

where A captures the drift (Hamiltonian dynamics + Decay) and D captures the diffusion (Noise/Fluctuations).

Entanglement in Phase Space From the final covariance matrix σ_{out}, we can compute the Symplectic Eigenvalues $\{\nu_k\}$. The entropy is determined directly from these eigenvalues:

$$S = \sum_k \left(\frac{\nu_k + 1}{2} \ln \frac{\nu_k + 1}{2} - \frac{\nu_k - 1}{2} \ln \frac{\nu_k - 1}{2} \right) \tag{65}$$

Key Result from Dambal et al.: When the biphoton is resonant with the Lower Polariton (LP) or Upper Polariton (UP) branches, we observe distinct spikes in the output entanglement entropy. These features are sensitive to the **hop-hop scattering** and cavity dissipation rates, providing a fingerprint of the polariton dynamics that is invisible in linear transmission spectra.

8.3 Experimental Reconstruction

How do we measure this entropy in the lab? (Based on Moretti et al. JCP 2023).

We cannot measure the wavefunction Φ directly. We measure the **Joint Spectral Intensity (JSI)**:

$$|\Phi(\omega_s, \omega_i)|^2 = \text{Coincidence Rates}$$

The Phase Problem: The entropy depends on the amplitude Φ, which includes phase. However, for highly entangled states generated by SPDC, the Schmidt modes are often well-approximated by Hermite-Gauss functions.

1. Measure JSI via scanning monochromators or time-of-flight.
2. Perform SVD on the square root of the JSI (assuming flat phase, or using reference phase information).
3. Compute λ_k and S.

While strictly a lower bound, this "Intensity Entropy" has been shown to capture the essential qualitative changes in material interactions.

The entanglement entropy can be estimated through the measurement of the JSA of a spectrally entangled state.

9 Part D: The Spectroscopic Link (Three Paradigms)

The core of the lecture: applying quantum light to chemical systems.

9.1 Paradigm 1: Sensitivity (Enhanced Precision)

Using squeezed light to lower the noise floor below the Shot Noise Limit.

- **Application:** Quantum-Enhanced Stimulated Raman Scattering (SRS).
- **Benefit:** Imaging biological samples at powers below the photodamage threshold.

9.2 Paradigm 2: Light as a Resource (Probe of Complexity)

Using the quantum state itself (entanglement) to probe matter.

- **Entangled Two-Photon Absorption (ETPA):**
  - *Theory:* "Packetized" photons should scale linearly (N) rather than quadratically (N^2).
  - *Controversy:* Discrepancies between theory and recent experimental bounds. - show that this is not possible.
- **Entropy Spectroscopy:**
  - Measure the entropy increase ΔS of the photon state after interaction.
  - ΔS correlates with the scrambling of information by the many-body system.

9.3 Paradigm 3: Light as a Witness (Coherence Judge)

Using interference to certify quantum coherence in the sample.

- **Hong-Ou-Mandel (HOM) Spectroscopy:**
- **Mechanism:** Indistinguishable photons bunch (dip in coincidences).
- **Interpretation:** If the material induces dephasing (which-path information), the photons become distinguishable, and the dip vanishes.
- **Observable:** Visibility V.

Summary Table: From Observable to Theory

Paradigm	Exp. Observable	Theoretical Quantity
Sensitivity	Noise Variance ΔI^2 (Homodyne)	Squeezing Parameter ξ
Resource	Coincidence Rate ($g^{(2)}$), Entropy ΔS	Mutual Info $I(S:E)$
Witness	HOM Visibility V	Dephasing Rate γ_{ph}

References