Fundamental Quantum Limit to the Multiphoton Absorption Rate for Monochromatic Light

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The local multiphoton absorption rate for an arbitrary quantum state of monochromatic light, taking into account the photon number, momentum, and polarization degrees of freedom, is shown to have an upper bound that can be reached by coherent fields. This surprising result rules out any quantum enhancement of the multiphoton absorption rate by momentum entanglement.

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The excitation of a sample by multiple photons has become an important tool in optical imaging [1]. Two-photon absorption was first predicted by Göppert-Mayer in 1931 [2], but because an intense optical source would be required to observe the phenomenon, it was only 30 years later, after the invention of lasers, that two-photon absorption was first experimentally demonstrated by Kaiser and Garrett [3]. The advent of mode-locked lasers has further increased the available optical intensity and contributed to the success of multiphoton microscopy in biological imaging [1,4]. The spatial resolution improvement by multiphoton absorption also allows a higher bit density to be recorded in optical data storage [5] and finer features to be written in lithography [6,7], the primary tool in integrated circuit and nanostructure fabrication. A particularly intriguing proposal of "quantum lithography" was put forth by Boto *et al.*, who suggest that N-photon absorption of N entangled photons can lead to an N-fold resolution enhancement over the Rayleigh-Abbe resolution limit [7]. A proof-of-concept experiment was performed by D'Angelo, Chekhova, and Shih [8], but current technology has not yet been able to produce the high flux of entangled photons required for practical applications.

The requirement of high intensity has motivated researchers to explore other methods to enhance the multiphoton absorption rate. In quantum optics, it has long been realized that the statistics of light can significantly affect the rate of multiphoton processes. For example, the N-photon absorption rate for thermal light is a factor of $N!$ higher than that for laser light with the same intensity [9], the two-photon absorption rate for weak squeezed light is proportional to the intensity instead of the intensity squared [10], and the multiphoton absorption rate of spectrally entangled photons can also depend on the intensity linearly [11]. These encouraging results have led Boto *et al.* to suggest that in addition to the resolution enhancement, the multiphoton absorption rate for N momentum-entangled photons can be enhanced as well and grows linearly with respect to the intensity, as the entanglement might constrain the photons to "arrive at the same place [7]." Unfortunately, it was later shown that the quantum effects in the spatial domain are different from those in the time domain [12,13]. Steuernagel first pointed out the problem with Boto *et al.*'s claim and studied the multiphoton absorption rate for four momentum-entangled photons [12], while Tsang showed that there is in general a trade-off between resolution enhancement and multiphoton absorption rate for quantum lithography [13].

In Ref. [13], Tsang also derived an upper bound of the peak N-photon absorption rate for N monochromatic, s-polarized photons in one transverse dimension. The upper bound is on the order of the classical maximum one-photon intensity raised to the power N, indicating that the nonclassical momentum correlation among N photons is unable to significantly enhance the N-photon absorption rate. This specific result is only applicable to the study of quantum lithography, and it remains an open but fundamental question whether photons in an arbitrary quantum state of light can really be constrained to arrive at the same place and enhance the multiphoton absorption rate.

In this Letter, using an electromagnetic-field quantization formalism that takes into account the photon number, momentum, and polarization degrees of freedom, it is shown that there exists a fundamental upper bound on the local multiphoton absorption rate for monochromatic light. The bound is reached by coherent fields as defined by Titulaer and Glauber [14], which contain only one excited optical mode and imply independent photons. Given the well-known rate enhancement effect by photons entangled in the spectral domain [11], this result is surprising, as it rules out any similar effect by momentum entanglement. The result set forth in this Letter thus sheds light on our understanding of the quantum nature of light, and has important implications for the use of quantum optics in multiphoton imaging applications.

Consider the problem of multiphoton absorption depicted in Fig. 1. An M-photon absorber, such as an atom, a molecule, a quantum dot, or a nanoparticle, is illuminated by light, with a certain quantum state $|\Psi\rangle$, in free space. Since such an absorber is usually much smaller than the characteristic length scales of light, it can be assumed to be infinitesimally small and interact with the local field at a certain point in space. The light is assumed to be approximately monochromatic, which enables one to study the spatial quantum effects separate from the temporal effects studied in Ref. [11]. In most multiphoton absorption ex-

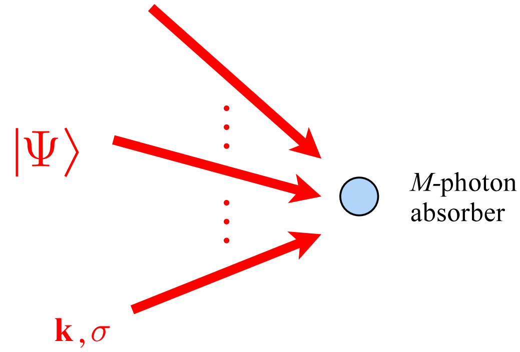

FIG. 1 (color online). An infinitesimally small M-photon absorber is illuminated by an arbitrary quantum state of monochromatic light, given by $|\Psi\rangle$.

periments, the absorber is weakly coupled to the electric field of light, so that the electromagnetic fields can be quantized using the free-space formalism, as in conventional quantum-optical detection theory [15,16].

In this case, the positive-frequency electric field operator is given by [15]

$$\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}t) = \frac{i}{(2\pi)^{3/2}}\sum_{\sigma}\int dk_x dk_y dk_z \left(\frac{\hbar\omega}{2\epsilon_0}\right)^{1/2} \times \hat{a}(\boldsymbol{k}\sigma)\varepsilon(\boldsymbol{k}\sigma)e^{i\boldsymbol{k}\cdot\boldsymbol{r}-i\omega t}, \tag{1}$$

where $\boldsymbol{k} \equiv k_x\hat{\boldsymbol{x}} + k_y\hat{\boldsymbol{y}} + k_z\hat{\boldsymbol{z}}$ is the wave vector, $\omega = ck = c(k_x^2 + k_y^2 + k_z^2)^{1/2}$ is the optical frequency, σ denotes the two polarizations transverse to the wave vector, ε is the unit polarization vector, and $\hat{a}(\boldsymbol{k}\sigma)$ is the photon annihilation operator with the commutation relation $[\hat{a}(\boldsymbol{k}\sigma), \hat{a}^\dagger(\boldsymbol{k}'\sigma')] = \delta^3(\boldsymbol{k} - \boldsymbol{k}')\delta_{\sigma\sigma'}$.

To conform with classical optics conventions, it is desirable to change the independent optical mode variables from $(k_xk_yk_z\sigma)$ to $(k_xk_y\omega\gamma\sigma)$, where $\gamma = -1, 1$ indicates the sign of k_z and accounts for both forward and backward propagating modes, so that $k_z = \gamma(k^2 - k_x^2 - k_y^2)^{1/2}$. The electric field can then be expressed in terms of propagation modes [13,17]:

$$\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}t) = \frac{i}{(2\pi)^{3/2}}\sum_{\gamma\sigma}\int_0^\infty d\omega \int_{k_x^2+k_y^2\le k^2} dk_x dk_y \left(\frac{\hbar\omega}{2\epsilon_0}\right)^{1/2} \times \left(\frac{\omega}{c^2|k_z|}\right)^{1/2}\hat{a}(k_xk_y\omega\gamma\sigma)\varepsilon(k_xk_y\omega\gamma\sigma) \times e^{i\boldsymbol{k}\cdot\boldsymbol{r}-i\omega t}. \tag{2}$$

To make the monochromatic approximation, I follow Blow *et al.* [18] and perform the substitutions $\int_0^\infty d\omega \to 2\pi/T$, $\hat{a}(k_xk_y\omega\gamma\sigma) \to \hat{a}(k_xk_y\gamma\sigma)[T/(2\pi)]^{1/2}$, and $\hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r}t) = \hat{\boldsymbol{E}}^{(+)}(\boldsymbol{r})e^{-i\omega t}$, where T is the characteristic pulse width, resulting in

$$\hat{\mathbf{E}}^{(+)}(\mathbf{r}) = \frac{i}{(2\pi)^2}\left(\frac{\hbar\omega}{2\epsilon_0 cT}\right)^{1/2}\sum_{\gamma\sigma}\int_{k_x^2+k_y^2\le k^2} dk_x dk_y \left(\frac{k}{|k_z|}\right)^{1/2} \times \hat{a}(k_xk_y\gamma\sigma)\varepsilon(k_xk_y\gamma\sigma)e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{3}$$

In Eq. (3), the integration in the transverse momentum space is inside a circle, which calls for the use of cylindrical coordinates as defined by $k_x = k\alpha\cos\beta$, $k_y = k\alpha\sin\beta$, $kx = \rho\cos\phi$, $ky = \rho\sin\phi$, and $kz = \zeta$. The electric field becomes

$$\hat{\boldsymbol{E}}^{(+)}(\rho\phi\zeta) = \frac{i}{2\pi}\left(\frac{\eta_0 I_0}{2}\right)^{1/2}\sum_{\gamma\sigma}\int_0^1 d\alpha \int_0^{2\pi} d\beta \left(\frac{\alpha^2}{1-\alpha^2}\right)^{1/4} \times \hat{a}(\alpha\beta\gamma\sigma)\varepsilon(\alpha\beta\gamma\sigma) \times e^{i\alpha\rho\cos(\beta-\phi)+i\gamma(1-\alpha^2)^{1/2}\zeta}, \tag{4}$$

where $\eta_0 \equiv (\mu_0/\epsilon_0)^{1/2}$ is the free-space impedance and I_0 is defined as $I_0 \equiv \hbar\omega/(T\lambda^2)$, which is on the order of the optical intensity of one photon with pulse width T focused onto an area of λ^2. The annihilation operator satisfies the commutation relation $[\hat{a}(\alpha\beta\gamma\sigma), \hat{a}^\dagger(\alpha'\beta'\gamma'\sigma')] = \delta(\alpha - \alpha')\delta(\beta - \beta')\delta_{\gamma\gamma'}\delta_{\sigma\sigma'}$, and the s and p polarization vectors are $\varepsilon(\alpha\beta\gamma s) = -\sin(\beta-\phi)\hat{\boldsymbol{\rho}} + \cos(\beta-\phi)\hat{\boldsymbol{\phi}}$ and $\varepsilon(\alpha\beta\gamma p) = -\gamma(1-\alpha^2)^{1/2}[\cos(\beta-\phi)\hat{\boldsymbol{\rho}} + \sin(\beta-\phi)\hat{\boldsymbol{\phi}}] + \alpha\hat{\boldsymbol{\zeta}}$, respectively.

An N-photon momentum eigenstate can be written as [15]

$$|\alpha_1\beta_1\gamma_1\sigma_1,\ldots,\alpha_N\beta_N\gamma_N\sigma_N\rangle = \frac{1}{\sqrt{N!}}\hat{a}^\dagger(\alpha_1\beta_1\gamma_1\sigma_1)\ldots \times \hat{a}^\dagger(\alpha_N\beta_N\gamma_N\sigma_N)|0\rangle, \tag{5}$$

so that a Fock state $|N\rangle$ with a total photon number N can be expressed in terms of a momentum-space probability amplitude ϕ_N:

$$\phi_N(\alpha_1\beta_1\gamma_1\sigma_1,\ldots,\alpha_N\beta_N\gamma_N\sigma_N) \equiv \langle\alpha_1\beta_1\gamma_1\sigma_1,\ldots,\alpha_N\beta_N\gamma_N\sigma_N|N\rangle, \tag{6}$$

$$|N\rangle = \sum_{\gamma_1\sigma_1\ldots\gamma_N\sigma_N}\int d\alpha_1 d\beta_1\ldots d\alpha_N d\beta_N \phi_N(\alpha_1\beta_1\gamma_1\sigma_1,\ldots,\alpha_N\beta_N\gamma_N\sigma_N)|\alpha_1\beta_1\gamma_1\sigma_1,\ldots,\alpha_N\beta_N\gamma_N\sigma_N\rangle. \tag{7}$$

In the specific case of $N = 2$, ϕ_2 becomes the well-known biphoton amplitude, which has been widely used to describe the entanglement of photon pairs generated by spontaneous parametric down-conversion [19]. A general quantum state of light is then given by a superposition of Fock states:

$$|\Psi\rangle = \sum_{N=0}^{\infty} C_N |N\rangle, \tag{8}$$

which completes the description of the quantum state of monochromatic light in free space.

For ϕ_N to be a representation of the N-photon quantum state, ϕ_N must satisfy the normalization condition:

$$\sum_{\gamma_1\sigma_1\ldots\gamma_N\sigma_N} \int d\alpha_1 d\beta_1 \ldots d\alpha_N d\beta_N |\phi_N(\alpha_1\beta_1\gamma_1\sigma_1, \ldots, \alpha_N\beta_N\gamma_N\sigma_N)|^2 = 1, \tag{9}$$

and the bosonic symmetrization condition:

$$\phi_N(\ldots, \alpha_n\beta_n\gamma_n\sigma_n, \ldots, \alpha_m\beta_m\gamma_m\sigma_m, \ldots) = \phi_N(\ldots, \alpha_m\beta_m\gamma_m\sigma_m, \ldots, \alpha_n\beta_n\gamma_n\sigma_n, \ldots) \text{for any } n \text{ and } m. \tag{10}$$

In particular, a coherent field is defined as a quantum state of light in which ϕ_N is factorizable for all N [14]:

$$\phi_N(\alpha_1\beta_1\gamma_1\sigma_1, \ldots, \alpha_N\beta_N\gamma_N\sigma_N) = \prod_{n=1}^{N} f(\alpha_n\beta_n\gamma_n\sigma_n). \tag{11}$$

A coherent field is created by exciting only one optical mode, and implies photons with independent statistics.

The M-photon absorption rate for an infinitesimally small absorber situated at (ρ, ϕ, ζ) in the weak coupling regime is proportional to

$$\langle :\hat{I}_p^M(\rho\phi\zeta): \rangle = \left\langle :\left\{\frac{1}{\eta_0}[\boldsymbol{p}^* \cdot \hat{\boldsymbol{E}}^{(-)}(\rho\phi\zeta)][\boldsymbol{p} \cdot \hat{\boldsymbol{E}}^{(+)}(\rho\phi\zeta)]\right\}^M : \right\rangle, \tag{12}$$

where $\hat{I}_p$ is the optical intensity operator for the electric field measured along a certain direction with unit vector $\boldsymbol{p}$. Equation (12) also gives the spatial pattern produced by many independent M-photon absorbers. For a coherent field, the M-photon absorption pattern $\langle :\hat{I}_p^M(\rho\phi\zeta): \rangle$ is factorizable and proportional to $\langle \hat{I}_p(\rho\phi\zeta)\rangle^M$, and thus agrees with the classical prediction of the multiphoton absorption pattern [14]. As such, one can define entanglement for N photons as a condition in which ϕ_N is not factorizable, so that the multiphoton absorption pattern deviates from the classical theory, as in the case of quantum lithography [7].

As the Fock states are eigenstates of the multiphoton absorption operator, one can study the absorption rate for each Fock state and take the average of the rates at the end of the analysis. Without loss of generality, assume that the absorber is at the origin. Using Eqs. (4) and (7), one can write the M-photon absorption rate for an N-photon state explicitly in terms of ϕ_N:

$$\begin{aligned}\langle N|:\hat{I}_p^M:|N\rangle = &\left(\frac{I_0}{8\pi^2}\right)^M \frac{N!}{(N-M)!} \sum_{\gamma_{M+1}\sigma_{M+1}\ldots\gamma_N\sigma_N} \int d\alpha_{M+1} d\beta_{M+1} \ldots d\alpha_N d\beta_N \\ &\times \left| \sum_{\gamma_1\sigma_1\ldots\gamma_M\sigma_M} \int d\alpha_1 d\beta_1 \ldots d\alpha_M d\beta_M \left[\prod_{n=1}^{M} \left(\frac{\alpha_n^2}{1-\alpha_n^2}\right)^{1/4} \boldsymbol{p}\cdot\varepsilon(\alpha_n\beta_n\gamma_n\sigma_n)\right] \phi_N(\alpha_1\beta_1\gamma_1\sigma_1, \ldots, \alpha_N\beta_N\gamma_N\sigma_N) \right|^2.\end{aligned} \tag{13}$$

To derive an upper bound on this quantity, I observe that the M-dimensional integral in Eq. (13) can be regarded as an inner product between the expression in square brackets and ϕ_N^*. Applying Schwarz's inequality and the normalization condition in Eq. (9), I obtain

$$\begin{aligned}\langle N|:\hat{I}_p^M:|N\rangle \le &\left(\frac{I_0}{8\pi^2}\right)^M \frac{N!}{(N-M)!} \sum_{\gamma_{M+1}\sigma_{M+1}\ldots\gamma_N\sigma_N} \int d\alpha_{M+1} d\beta_{M+1} \ldots d\alpha_N d\beta_N \\ &\times \sum_{\gamma_1\sigma_1\ldots\gamma_M\sigma_M} \int d\alpha_1 d\beta_1 \ldots d\alpha_M d\beta_M |\phi_N(\alpha_1\beta_1\gamma_1\sigma_1, \ldots, \alpha_N\beta_N\gamma_N\sigma_N)|^2 \\ &\times \sum_{\gamma_1\sigma_1\ldots\gamma_M\sigma_M} \int d\alpha_1 d\beta_1 \ldots d\alpha_M d\beta_M \left| \prod_{n=1}^{M} \left(\frac{\alpha_n^2}{1-\alpha_n^2}\right)^{1/4} \boldsymbol{p}\cdot\varepsilon(\alpha_n\beta_n\gamma_n\sigma_n) \right|^2 \\ = &\left(\frac{I_0}{8\pi^2}\right)^M \frac{N!}{(N-M)!} \left[\sum_{\gamma\sigma} \int_0^1 d\alpha \int_0^{2\pi} d\beta \left(\frac{\alpha^2}{1-\alpha^2}\right)^{1/2} |\boldsymbol{p}\cdot\varepsilon(\alpha\beta\gamma\sigma)|^2\right]^M = \left(\frac{I_0}{3\pi}\right)^M \frac{N!}{(N-M)!}.\end{aligned} \tag{14}$$

This bound does not depend on $\boldsymbol{p}$, the direction along which the electric field is measured, and is therefore applicable to the isotropic multiphoton absorption measurement $\langle :\hat{I}^M: \rangle = \langle :[\hat{\boldsymbol{E}}^{(-)} \cdot \hat{\boldsymbol{E}}^{(+)}]^M: \rangle$. Hence, for an arbitrary quantum state, the M-photon absorption rate is bounded by the following:

$$\langle :\hat{I}^M: \rangle \leq \left(\frac{I_0}{3\pi}\right)^M \sum_{N \geq M} |C_N|^2 \frac{N!}{(N-M)!}. \tag{15}$$

Equation (15) is the central result of this Letter. Although this bound is derived for one absorber, it is also equivalent to a bound on the peak absorption rate for many independent absorbers. The factor $\sum_N |C_N|^2 N!/(N-M)!$ depends only on the statistics of total photon number and accounts for the effect of photon-number fluctuations on the multiphoton absorption rate, as investigated in Refs. [9,10]. This factor, however, does not depend on the structure of ϕ_N, which governs the momentum correlations of photons. The dependence of the bound on the Mth power of I_0, on the other hand, agrees with classical multiphoton absorption theory, and suggests that a coherent field can reach this upper bound. To prove this, recall the fact that the Schwarz upper bound is reached when the two functions in the inner product are linearly dependent. One possible quantum state with a ϕ_N^* linearly dependent on the square-bracketed expression in Eq. (13) is given by

$$\phi_N \propto \prod_{n=1}^{N} \left(\frac{\alpha_n^2}{1-\alpha_n^2}\right)^{1/4} \boldsymbol{p}^* \cdot \varepsilon^*(\alpha_n \beta_n \gamma_n \sigma_n), \tag{16}$$

which is factorizable and thus a coherent field by definition.

In conclusion, the quantum limit to the multiphoton absorption rate derived above demonstrates that, heuristically speaking, it is impossible for monochromatic photons to arrive at the same specific location in free space more often than do independent photons focused onto an area of λ^2. While this result is applicable to most multiphoton imaging experiments and suggests that spatial quantum effects are not useful in enhancing the multiphoton absorption rate for those applications, it is possible to generalize the theory to more complex and exotic situations, such as the use of polychromatic light, cavity confinement, and strong coupling between light and the absorbers. Such generalizations will lead to the study of multimode cavity quantum electrodynamics, which should exhibit more complex and interesting phenomena than the case studied here and may ultimately benefit nonlinear optics applications.

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