Thermal Light Cannot Be Represented as a Statistical Mixture of Single Pulses

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We ask whether or not thermal light can be represented as a mixture of single broadband coherent pulses. We find that it *cannot*. Such a mixture is simply not rich enough to mimic thermal light; indeed, it cannot even reproduce the first-order correlation function. We show that it is possible to construct a modified mixture of single coherent pulses that *does* yield the correct first-order correlation function at equal space points. However, as we then demonstrate, such a mixture cannot reproduce the second-order correlation function.

Absorption of light by molecules can initiate fundamental photo-induced processes including photochemical reactions, photocatalysis, and solar energy conversion. While the photo-initiated dynamics can be resolved by using short laser pulses to populate and probe excited-state populations [1–4], the use of these techniques raises the question of whether or not the ultrafast pulses employed – which are significantly different from natural thermal light – lead to behaviour specific to those ultra-fast pulses. In particular, some researchers have recently questioned whether dynamics initiated by sunlight excitation might be different from those detected in femtosecond laser experiments performed on light-harvesting complexes [5–9]. This has opened a debate on how photo-excitation by natural light should be understood. For example, can sunlight be viewed as "a series of random ultrashort spikes with a duration as short as the bandwidth allows" [4]? Our work is inspired by femtosecond laser experiments, but rather than considering the relevance of these experiments to natural-light excitation, we focus on the relationship between sunlight and laser light.

Light from the sun indeed has an ultra-short coherence time of approximately 1.3 fs [10]; it has a spectrum close to that of black-body radiation at approximately 5777 K [11], characterized by thermal photon-number statistics [12]. In this paper we ask whether or not thermal light can be understood as a mixture of single broadband coherent pulses.

We find that it cannot. The first clue is given by considering a widely used class of pulses, where each pulse is defined by a linear phase relationship between its composing modes. The density matrix of a mixture of such pulses cannot represent thermal equilibrium, for any mixture of these individual pulses would exhibit off-diagonal elements in the density matrix when written in a spectral-Fock basis, whereas the density matrix representing thermal equilibrium is diagonal; see the Supple-

mental Material.

More generally, while the state of thermal light is represented by a density operator ρ^{th} with unit trace, we demonstrate that *no* unit-trace density operator ρ^{mix} consisting of a mixture of single pulses can equal ρ^{th}. Such a mixture cannot even give the correct result for the first-order correlation function. Nonetheless, it is possible to construct a *trace-improper* mixture ρ^{imp} that *does* yield a first-order correlation function at equal space points that matches that of thermal light. This has apparently not been demonstrated yet; we do it here.

To begin we build our pulses by quantizing the electromagnetic field in an infinite volume, with annihilation (creation) operators $a_{\mathbf{k}\lambda}$ ($a_{\mathbf{k}\lambda}^{\dagger}$), where the wave vector $\mathbf{k}$ ranges continuously and the helicity λ is positive or negative; these operators satisfy the commutation relations $\left[a_{\mathbf{k}\lambda}, a_{\mathbf{k}'\lambda'}^{\dagger}\right] = \delta(\mathbf{k} - \mathbf{k}')\delta_{\lambda\lambda'}$. A pulse is characterized by its nominal position $\mathbf{r}_{\mathrm{o}}$, a (complex) amplitude $\alpha_{\mathbf{r}_{\mathrm{o}}s}$, a spectral distribution $f_{\mathbf{r}_{\mathrm{o}}s;\mathbf{k}\lambda}$ – normalized so that $\sum_\lambda \int d\mathbf{k} \ |f_{\mathbf{r}_{\mathrm{o}}s;\mathbf{k}\lambda}|^2 = 1$, with $d\mathbf{k} = dk_x dk_y dk_z$ – and other parameters that we label collectively by s. From the spectral distribution we construct a creation operator

$$a_{\mathbf{r}_{\mathrm{o}}s}^{\dagger} = \sum_\lambda \int d\mathbf{k} \ f_{\mathbf{r}_{\mathrm{o}}s;\mathbf{k}\lambda} a_{\mathbf{k}\lambda}^{\dagger},$$

with $\left[a_{\mathbf{r}_{\mathrm{o}}s}, a_{\mathbf{r}_{\mathrm{o}}s}^{\dagger}\right] = 1$, and the pulse is described by the quantum state

$$|\alpha_{\mathbf{r}_{\mathrm{o}}s} f_{\mathbf{r}_{\mathrm{o}}s}\rangle \equiv e^{\alpha_{\mathbf{r}_{\mathrm{o}}s} a_{\mathbf{r}_{\mathrm{o}}s}^{\dagger} - \alpha_{\mathbf{r}_{\mathrm{o}}s}^{*} a_{\mathbf{r}_{\mathrm{o}}s}} |vac\rangle,$$

where $|vac\rangle$ is the vacuum state and $\alpha_{\mathbf{r}_{\mathrm{o}}s}$ is a complex number; $\langle \alpha_{\mathbf{r}_{\mathrm{o}}s} f_{\mathbf{r}_{\mathrm{o}}s} | \alpha_{\mathbf{r}_{\mathrm{o}}s} f_{\mathbf{r}_{\mathrm{o}}s} \rangle = 1$. For the positive frequency part of the (Heisenberg) electric field operator,

$$\mathbf{E}^{(+)}(\mathbf{r}, t) = i \sum_\lambda \int d\mathbf{k} \ \sqrt{\frac{\hbar\omega_k}{16\pi^3\epsilon_0}} \mathbf{e}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\omega_k t} a_{\mathbf{k}\lambda}, \quad (1)$$

where $\omega_k = c\,|\mathbf{k}|$ and $\mathbf{e}_{\mathbf{k}\lambda}$ are the polarization vectors, we have the expectation value

$$\mathcal{E}^{(\mathbf{r}_\circ s)}(\mathbf{r}, t) \equiv \langle \alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s} | \mathbf{E}^{(+)}(\mathbf{r}, t) | \alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s} \rangle$$

given by (1) with the operator $a_{\mathbf{k}\lambda}$ replaced by the complex number $\alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s;\mathbf{k}\lambda}$. The state $|\alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s}\rangle$ is "coherent" in the sense that it factorizes correlation functions according to $G^{(n)(\mathbf{r}_\circ s)}(\mathbf{r}_1 t_1 \ldots \mathbf{r}_n t_n; \mathbf{r}_{n+1} t_{n+1} \ldots \mathbf{r}_{2n} t_{2n}) = \prod_j \left(\mathcal{E}^{(\mathbf{r}_\circ s)}(\mathbf{r}_j, t_j)\right)^* \mathcal{E}^{(\mathbf{r}_\circ s)}(\mathbf{r}_{j+n}, t_{j+n})$ for all orders of n [13]; here we use the superscript $(\mathbf{r}_\circ s)$ on G to identify the state $|\alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s}\rangle$, which is the quantum description of what might be called a "classical" pulse [13]. In particular, for such a state we have

$$\begin{aligned} G_{ij}^{(1)(\mathbf{r}_\circ s)}(\mathbf{r}t; \mathbf{r}'t') &\equiv \langle \alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s} | E_i^{(-)}(\mathbf{r}, t) E_j^{(+)}(\mathbf{r}', t') | \alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s} \rangle \\ &= \left(\mathcal{E}_i^{(\mathbf{r}_\circ s)}(\mathbf{r}, t)\right)^* \left(\mathcal{E}_j^{(\mathbf{r}_\circ s)}(\mathbf{r}', t')\right), \end{aligned}$$

where subscripts on field labels indicate Cartesian components, e.g. $E_j^{(+)}(\mathbf{r}, t) = \mathbf{E}^{(+)}(\mathbf{r}, t) \cdot \hat{\jmath}$.

We consider families of pulses such that for fixed parameters s the pulses only differ by their nominal positions $\mathbf{r}_\circ$. For such families of pulses we have

$$f_{\mathbf{r}_\circ s;\mathbf{k}\lambda} = K(s, \mathbf{k}\lambda)\, e^{-i\mathbf{k}\cdot\mathbf{r}_\circ}, \tag{2}$$

and the associated $\mathcal{E}^{(\mathbf{r}_\circ s)}(\mathbf{r}, t)$ depends on $\mathbf{r}$ and $\mathbf{r}_\circ$ only through its dependence on $(\mathbf{r} - \mathbf{r}_\circ)$; we will give particular examples of $K(s, \mathbf{k}\lambda)$ below. We assume that each member of the family is well localized in space at some initial time, $G_{ij}^{(1)(\mathbf{r}_\circ s)}(\mathbf{r}0; \mathbf{r}0) \to 0$ as $|\mathbf{r} - \mathbf{r}_\circ| \to \infty$, and that the integral of $G_{ij}^{(1)(\mathbf{r}_\circ s)}(\mathbf{r}0; \mathbf{r}0)$ over all space is finite. Then for fixed $\mathbf{r}$ the integral over all $\mathbf{r}_\circ$ of $G_{ij}^{(1)(\mathbf{r}_\circ s)}(\mathbf{r}0; \mathbf{r}0)$ will also be finite. It will be convenient below to work with a volume Ω centered at the origin,[1] and we define

$$\mu_i(\mathbf{r}, s, \Omega) \equiv \int_\Omega G_{ii}^{(1)(\mathbf{r}_\circ s)}(\mathbf{r}0; \mathbf{r}0)\, d\mathbf{r}_\circ. \tag{3}$$

Since each $G_{ii}^{(1)(\mathbf{r}_\circ s)}(\mathbf{r}0; \mathbf{r}0)$ is real and positive, $\mu_i(\mathbf{r}, s, \Omega)$ will be finite and positive for all $\mathbf{r}$ and Ω, increasing as Ω increases and with a well-defined limit $\mu_i(\mathbf{r}, s, \infty)$; here and except when explicitly mentioned otherwise we assume the amplitudes $\alpha_{\mathbf{r}_\circ s}$ and parameters s used to characterize the pulses are held fixed and independent of Ω.

To attempt to describe thermal light in a volume Ω by a mixture of single pulses, we would write

$$\rho^{\mathrm{mix}} = \int ds \int_\Omega d\mathbf{r}_\circ \frac{\mathfrak{p}(s)}{\Omega} |\alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s}\rangle \langle \alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s}|, \tag{4}$$

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[1] Note that Ω is different from the quantization volume that is always taken infinite in this Letter

where pulses are included with equal density about each central position $\mathbf{r}_\circ$ in the volume, and $\mathfrak{p}(s) \geq 0$ with

$$\int ds\, \mathfrak{p}(s) = 1, \tag{5}$$

where here and in (4) the variables constituting s are to be integrated or summed over as required; the condition (5) guarantees that $\mathrm{Tr}(\rho^{\mathrm{mix}}) = 1$. Because correlation functions describe the interaction of light with matter, they form a practical tool to compare different radiation states [13]. For thermal light filling all space [10, 12]

$$\begin{aligned} G_{ij}^{(1)\mathrm{th}}(\mathbf{r}t; \mathbf{r}(t + \tau)) &= \mathrm{Tr}\left(\rho^{\mathrm{th}} E_i^{(-)}(\mathbf{r}, t) E_j^{(+)}(\mathbf{r}, t + \tau)\right) \\ &= \delta_{ij} \int_0^\infty \frac{\hbar c k^3}{6\pi^2 \epsilon_0} \frac{e^{-ick\tau}}{e^{\beta\hbar ck} - 1} dk, \quad (6) \end{aligned}$$

and while near the edge of the volume Ω we would not expect (4) to give a correct representation of thermal equilibrium, we would demand that it does so near the origin.

We now prove that we cannot choose the pulses so that $\rho^{\mathrm{mix}} = \rho^{\mathrm{th}}$ as $\Omega \to \infty$. For

$$\begin{aligned} G_{ii}^{(1)\mathrm{mix}}(\mathbf{00}; \mathbf{00}) &= \mathrm{Tr}\left(\rho^{\mathrm{mix}} E_i^{(-)}(\mathbf{0}, 0) E_i^{(+)}(\mathbf{0}, 0)\right) \\ &= \int ds \int_\Omega d\mathbf{r}_\circ \frac{\mathfrak{p}(s)}{\Omega} G_{ii}^{(1)(\mathbf{r}_\circ s)}(\mathbf{00}; \mathbf{00}) \\ &= \frac{1}{\Omega} \int ds\, \mathfrak{p}(s) \mu_i(\mathbf{0}, s, \Omega), \end{aligned}$$

and since $G_{ii}^{(1)\mathrm{mix}}(\mathbf{00}; \mathbf{00})$ is clearly finite for any Ω, the integral of $\mathfrak{p}(s)\mu_i(\mathbf{0}, s, \Omega)$ over s must be finite for any Ω. As $\mathfrak{p}(s)\mu_i(\mathbf{0}, s, \Omega) > 0$ for all s and is an increasing function of Ω with a well-defined limit $\mathfrak{p}(s)\mu_i(\mathbf{0}, s, \infty)$ as $\Omega \to \infty$, we see that $G_{ii}^{(1)\mathrm{mix}}(\mathbf{00}; \mathbf{00}) \to 0$ as $\Omega \to \infty$. But from (6) it is clear that $G_{ii}^{(1)\mathrm{th}}(\mathbf{00}; \mathbf{00}) \neq 0$. Thus we cannot represent thermal equilibrium by a unit-trace density operator describing a mixture of single pulses. Such a mixture is simply not rich enough to describe thermal light.

The proof would fail if we allowed the amplitudes of the pulses to change as Ω changed. In fact, we will see below that we *can* mimic the first-order correlation function of thermal light at equal-space points by that of unit-trace mixture of single pulses if we allow the square of the amplitudes of the pulses to scale as Ω. While such a scaling could be entertained for finite Ω, the pulses would acquire infinite energy as $\Omega \to \infty$. If we return to our assumption of fixed amplitudes and properties regardless of Ω, the scaling of $G_{ij}^{(1)\mathrm{mix}}(\mathbf{00}; \mathbf{00})$ as $1/\Omega$ suggests a different strategy, i.e., the consideration of *trace-improper* density operators, of the form

$$\rho^{\mathrm{imp}} = \int ds \int_\Omega d\mathbf{r}_\circ\, \bar{p}(s) |\alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s}\rangle \langle \alpha_{\mathbf{r}_\circ s} f_{\mathbf{r}_\circ s}|, \tag{7}$$

where $\bar{p}(s) \geq 0$ and

$$\int ds \, \bar{p}(s) = \frac{1}{\mathcal{V}},$$

where $\mathcal{V}$ is a constant with units of a volume $[\Omega]$. The probability distribution $\bar{p}$ has units of $[\Omega^{-1} V_s^{-1}]$, where V_s is the volume of the integration space of the parameters s. Importantly, $\mathrm{Tr}(\rho^{\mathrm{imp}}) = \Omega/\mathcal{V}$ scales as Ω, and so certainly $\rho^{\mathrm{imp}} \neq \rho^{\mathrm{th}}$, since $\mathrm{Tr}(\rho^{\mathrm{th}}) = 1$, independent of the volume. Yet one might hope that the trace-improper mixture could lead to a correct representation of *some* of the properties of thermal light, if $\bar{p}(s)$ and the spectral functions $f_{\mathbf{r}_o s}$ and amplitudes $\alpha_{\mathbf{r}_o s}$ are chosen correctly. We next show that this is possible for the first-order correlation function (6). Here we let the volume $\Omega \to \infty$ in (7) at the start, and show that with a correct choice of $\bar{p}(s)$, $f_{\mathbf{r}_o s}$, and $\alpha_{\mathbf{r}_o s}$ we can find

$$G_{ij}^{(1)\mathrm{imp}}(\mathbf{r}t; \mathbf{r}(t+\tau)) \equiv \mathrm{Tr}\left(\rho^{\mathrm{imp}} E_i^{(-)}(\mathbf{r}, t) E_j^{(+)}(\mathbf{r}, t+\tau)\right)$$
$$= \int ds \int d\mathbf{r}_o \, \bar{p}(s) \left(\mathcal{E}_i^{(\mathbf{r}_o s)}(\mathbf{r}, t)\right)^* \mathcal{E}_j^{(\mathbf{r}_o s)}(\mathbf{r}, t+\tau),$$

where the integral of $\mathbf{r}_o$ now ranges over all space, such that

$$G_{ij}^{(1)\mathrm{imp}}(\mathbf{r}t; \mathbf{r}(t+\tau)) = G_{ij}^{(1)\mathrm{th}}(\mathbf{r}t; \mathbf{r}(t+\tau)). \qquad (8)$$

As a first example we take s to include a central wave vector $\mathbf{k}_o = k_o \hat{\mathbf{m}}$ of the pulse, with the unit vector $\hat{\mathbf{m}}$ identifying the main polarization direction, and a unit vector $\hat{\mathbf{n}}$ that characterizes the polarization as described below; thus $s = \{k_o, \hat{\mathbf{m}}, \hat{\mathbf{n}}\}$, V_s has units of inverse volume, and $\bar{p}(s)$ is dimensionless. We characterize pulses of this type by

$$K(s, \mathbf{k}\lambda) = \mathcal{N} \, L(\mathbf{k}, \mathbf{k}_o) \, (\mathbf{e}_{\mathbf{k}\lambda}^*) \cdot (\mathbf{k} \times \hat{\mathbf{n}}),$$

(recall Eq. 2) where $\mathcal{N}$ is a normalization constant chosen so the normalization of $f_{\mathbf{r}_o s; \mathbf{k}\lambda}$ is satisfied, and $L(\mathbf{k}, \mathbf{k}_o)$ is a real function. The expectation value of $\mathbf{E}^{(+)}(\mathbf{r}) \equiv \mathbf{E}^{(+)}(\mathbf{r}, 0)$ in the state $|\alpha_{\mathbf{r}_o s} f_{\mathbf{r}_o s}\rangle$ is given by

$$\mathcal{E}^{(\mathbf{r}_o s)}(\mathbf{r}) = i\mathcal{N}\alpha_{\mathbf{r}_o s} \int d\mathbf{k} \, \sqrt{\frac{\hbar\omega_k}{16\pi^3\epsilon_0}} (\mathbf{k} \times \hat{\mathbf{n}}) L(\mathbf{k}, \mathbf{k}_o) e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}_o)}.$$

This allows the representation of very general forms of pulses in free space; $\mathcal{E}^{(\mathbf{r}_o s)}(\mathbf{r})$ will typically be centered at $\mathbf{r}_o$, and its polarization is characterized by having *no* component in the $\hat{\mathbf{n}}$ direction, $\hat{\mathbf{n}} \cdot \mathcal{E}^{(\mathbf{r}_o s)}(\mathbf{r}) = 0$. In specifying $\bar{p}(s)$ we assume a uniform distribution over pulse directions $\hat{\mathbf{m}}$; for a given $\hat{\mathbf{m}}$ only $\hat{\mathbf{n}}$ perpendicular to $\hat{\mathbf{m}}$ are chosen, but the distribution over such $\hat{\mathbf{n}}$ is also uniform. Choosing a fixed direction in the plane perpendicular to $\hat{\mathbf{m}}$ for each $\hat{\mathbf{m}}$, and denoting the angle that $\hat{\mathbf{n}}$ makes from this direction by Ψ, we have

$$\int ds \, \bar{p}(s) \to \int_0^\infty dk_o \, p(k_o) \int d\hat{\mathbf{m}} \int_0^{2\pi} d\Psi,$$

where the remaining dependence $p(k_o)$ is on the magnitude of the central wave vector of the pulse, $k_o = |\mathbf{k}_o|$.

For any proposed $L(\mathbf{k}, \mathbf{k}_o)$ our task is then to see if $p(k_o)$ can be chosen so that our condition (8) is guaranteed. We begin by considering pulses of a Gaussian form;

$$L(\mathbf{k}, \mathbf{k}_o) = e^{-\frac{|\mathbf{k}-\mathbf{k}_o|^2}{2\sigma^2}}. \qquad (9)$$

For thermal radiation at $T = 5777$ K we find that the condition (8) can be guaranteed only if σ is chosen so that the pulse has a bandwidth on the order of THz or smaller, describing pulses that are on the order of picoseconds in length or longer [15]. Interestingly, no physical solution can be found for femtosecond pulses with a bandwidth as broad as the thermal spectrum. The problem is that the Gaussian shape (9) differs too much from the shape required to guarantee that the norm of the integrand of (6) is reproduced. Thus the only way that we can satisfy (8) is to choose σ so small that, compared with the thermal spectrum, $L(\mathbf{k}, \mathbf{k}_o)$ is essentially proportional to a Dirac delta function; then $p(k_o)$ itself is relied on to capture the shape of that integrand.

To satisfy (8) with broadband pulses we can work instead with a set of parameters s that includes only a nominal direction of propagation of the pulse $\hat{\mathbf{m}}$, as well as a polarization vector $\hat{\mathbf{n}}$ as before, $s = \{\hat{\mathbf{m}}, \hat{\mathbf{n}}\}$. Note now that V_s is dimensionless whereas $\bar{p}(s)$ has dimension of Ω^{-1}. We take our pulses (2) to be specified by

$$K(s, \mathbf{k}\lambda) = \mathcal{N} \, l(k) \, \upsilon(\hat{\mathbf{k}} \cdot \hat{\mathbf{m}}) \, (\mathbf{e}_{\mathbf{k}\lambda}^*) \cdot (\mathbf{k} \times \hat{\mathbf{n}}), \qquad (10)$$

where the function $\upsilon(x)$ is chosen to characterize the spread in the direction of wave vectors in the pulse and should be peaked at $x = 1$ for $\hat{\mathbf{m}}$ to indicate the nominal direction of propagation of the pulse; the function $l(k)$ is now relied on to help capture the shape of the norm of the integrand of (6). For $\bar{p}(s)$ we assume that the $\hat{\mathbf{m}}$ are distributed isotropically and, for each $\hat{\mathbf{m}}$, all $\hat{\mathbf{n}}$ perpendicular to $\hat{\mathbf{m}}$ are equally distributed,

$$\int ds \, \bar{p}(s) \to p \int d\hat{\mathbf{m}} \int_0^{2\pi} d\Psi,$$

where p is now a constant with units of $[\Omega^{-1}]$, $d\hat{\mathbf{m}}$ indicates an integration over solid angle, and Ψ denotes the angle $\hat{\mathbf{n}}$ makes from a fixed direction in the plane perpendicular to $\hat{\mathbf{m}}$. Such a trace-improper mixture can lead to (8) by choosing

$$l(k) = \frac{1}{k\sqrt{e^{\beta\hbar ck} - 1}} \text{ and } p|\alpha|^2 = \frac{4\zeta(3)}{\pi^4(\beta c\hbar)^3}, \qquad (11)$$

where ζ is the Riemann-zeta function [15]. By comparing (6) and (11), it is clear that the bandwidth of the pulse helps capture that of the thermal radiation.

The requirement of a fixed product $p|\alpha|^2$ illustrates that the need for improper behavior as $\Omega \to \infty$ can be
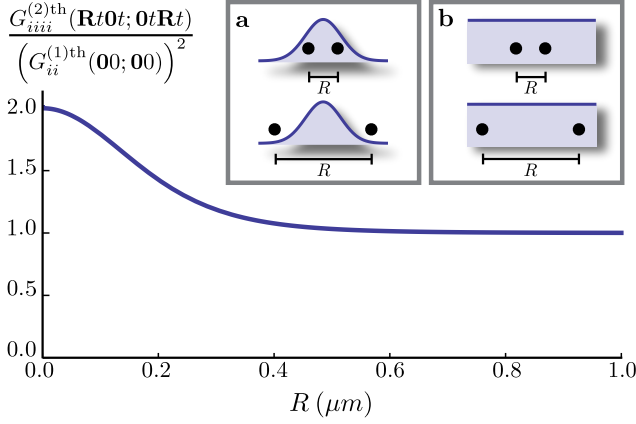
FIG. 1: Normalized second-order correlation function for thermal light as a function of the distance $R\hat{\imath}$. Note that it is non-zero for all values of R. Inset: Schematic depicting two detectors (e.g. atoms with a broad absorption band) within (a) the field of a localized pulse and (b) thermal radiation. As the distance between the two atoms increases, the probability that both absorb a photon from any localized pulse tends to zero.

met either by the trace or by the pulses. In the example of a density operator ρ^{imp} we have been considering, any finite p will lead to an infinite trace for $\Omega \to \infty$. Alternately, we could repeat the derivation sketched here insisting on a density operator of unit trace; then we would find that p would vanish as $\Omega \to \infty$, and the condition (11) would demand that $|\alpha|^2$ diverge in that limit. The latter option would only make physical sense for a finite volume of observation Ω; we put it aside for now, but return to it again below.

The preceding two examples show that although a trace-improper mixture of single pulses is not described by the same density operator as thermal light, such a mixture can be constructed to reproduce the first-order correlation function of thermal light. As we look at higher-order correlation functions we will necessarily find that such a mixture fails to reproduce the properties of thermal light, since $\rho^{\mathrm{imp}} \neq \rho^{\mathrm{th}}$. But can such a mixture capture the second-order correlation function? This is defined by $G^{(2)}_{i_1 i_2 i_3 i_4}(\mathbf{r}_1 t_1 \mathbf{r}_2 t_2; \mathbf{r}_3 t_3 \mathbf{r}_4 t_4) = \langle E^{(-)}_{i_1}(\mathbf{r}_1 t_1) E^{(-)}_{i_2}(\mathbf{r}_2 t_2) E^{(+)}_{i_3}(\mathbf{r}_3 t_3) E^{(+)}_{i_4}(\mathbf{r}_4 t_4)\rangle$. Choosing all times identical along with $\mathbf{r}_1 = \mathbf{r}_4$ and $\mathbf{r}_2 = \mathbf{r}_3$, this expression represents two simultaneous absorption events at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively [13]. For thermal light at $T = 5777$ K, the second-order correlation function $G^{(2)\mathrm{th}}_{iiii}(\mathbf{R}t0t; 0t\mathbf{R}t)$ (no sum over i) is shown in Fig. 1 [18] as a function of the distance $\mathbf{R} \equiv \mathbf{r}_2 - \mathbf{r}_1$ we imagine separating two broadband detectors; we take the direction of $\mathbf{R}$ to lie along the Cartesian axis i. Importantly, beyond a distance that corresponds to the coherence length, i.e. of about 0.39 μm for $T = 5777$ K, the second-order correlation function is independent of both

the distance $\mathbf{R}$ and the orientation of that vector with respect to the Cartesian axis i,

$$G^{(2)\mathrm{th}}_{iiii}(\mathbf{R}t0t; 0t\mathbf{R}t) \xrightarrow[R\to\infty]{} \left(\frac{\pi^2}{90\epsilon_0 \beta^4 (\hbar c)^3}\right)^2. \quad (12)$$

Clearly, in the presence of thermal light there is a non-zero probability of simultaneous broadband detection events occurring regardless of the distance between the two detectors.

We have not been able to evaluate the second-order correlation function for ρ^{imp} analytically. However, since each member of our family of pulses is localized in space, each individual pulse is not able to simultaneously excite two detectors if they are well separated. Although our mixture is trace-improper, it is composed of an incoherent mixture of individual, localized pulses (cf. Eq. 7). Therefore the total probability should equal the sum of the individual realizations, and we expect our argument to apply to the mixture as well. Hence such a mixture can never capture the result (12).

Returning to a finite observation volume Ω and the use of a unit-trace density operator representing a mixture of single pulses with $|\alpha_{\mathbf{r}_o s}|^2$ proportional to Ω, from the arguments above we see that such a density operator would have no chance of describing the second-order correlation function properly if the observation volume were significantly larger than the size of the pulses. For if it were, the chance of any pulse in the mixture exciting two detectors at different ends of the observation volume would be negligible. Now at $T = 5777$ K the size of the pulses (10) is about 0.4 μm [15], as might be expected from the characteristic length scale of Fig. 1. Hence even if we employed a unit-trace mixture of single pulses with the square of their amplitudes proportional to the observation volume, for observation volumes larger than a few cubic microns such mixtures would necessarily describe the second-order correlation function incorrectly.

In summary, we have shown that no mixture of single coherent pulses can represent thermal radiation. Allowing the mixture to be trace-improper, or allowing the square of the amplitudes of the pulses to scale with the observation volume, we can reproduce the first-order correlation function of thermal light at equal space points. If Gaussian pulses are used, pulses with a surprisingly narrow bandwidth are required. Alternately, broadband pulses with a lineshape mirroring the thermal spectrum can be used. The mixtures are schematically represented in Fig. 2. Nonetheless, these mixtures, and indeed any (proper or improper) mixture of well-localized pulses, fail to reproduce even the second-order correlation function of thermal light. The difficulties suggest that one should look instead for a representation of thermal light as mixture of *sets* of pulses, where each set contains more than one pulse.
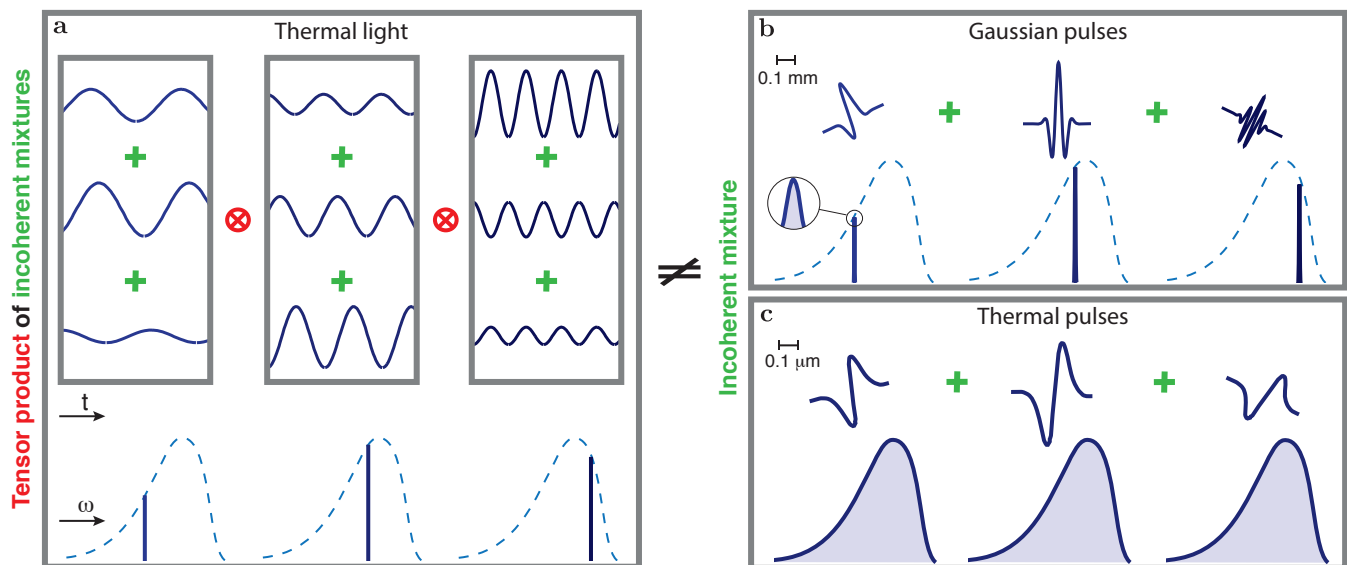
FIG. 2: Schematics illustrating the richness of thermal light as a tensor product over an infinity of modes. The green "+" indicates an *incoherent* sum; the red "⊗" a direct product. (a) Thermal light is built from a tensor product of mixed states, each composed by a mixture of monochromatic coherent states (represented by continuous waves in the insets) with various amplitudes and phases. (b;c) The trace-improper mixture of single pulses with (b) Gaussian or (c) thermal lineshape can only reproduce the first-order correlation function (see details in the text).

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[1] G. Fleming, *Chemical Applications of Ultrafast Spectroscopy*, *International Series of Monographs on Chemistry* (Oxford University Press, 1986).

[2] A. H. Zewail, "Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond," J. Phys. Chem. A **104**, 5660 (2000).

[3] R. van Grondelle and V. I. Novoderezhkin, "Energy transfer in photosynthesis: experimental insights and quantitative models," Phys. Chem. Chem. Phys. **8**, 793 (2006).

[4] Y.-C. Cheng and G. R. Fleming, "Dynamics of Light Harvesting in Photosynthesis," Annu. Rev. Phys. Chem. **60**, 241 (2009).

[5] X.-P. Jiang and P. Brumer, "Creation and dynamics of molecular states prepared with coherent vs partially coherent pulsed light," J. Chem. Phys. **94**, 5833 (1991).

[6] T. Mančal and L. Valkunas, "Exciton dynamics in photosynthetic complexes: excitation by coherent and incoherent light," New Journal of Physics **12**, 065044 (2010).

[7] K. Hoki and P. Brumer, "Excitation of biomolecules by coherent vs. incoherent light: Model rhodopsin photoisomerization," in *Procedia Chemistry*, **3**, 122 (2011).

[8] P. Brumer and M. Shapiro, "Molecular response in one-photon absorption via natural thermal light vs. pulsed laser excitation," Proc. Nat. Am. Soc. **109**, 19575 (2012).

[9] I. Kassal, J. Yuen-Zhou, and S. Rahimi-Keshari, "Does Coherence Enhance Transport in Photosynthesis?," J. Phys. Chem. L. **4**, 362 (2013).

[10] Y. Kano and E. Wolf, "Temporal coherence of black body radiation," Proc. Phys. Soc. **80**, 1273 (1962).

[11] M. Iqbal, *An Introduction to Solar Radiation* (Academic Press, 1983).

[12] L. Mandel and E. Wolf, *Optical coherence and quantum Optics* (Cambridge university press, 1995), Chap. 13.

[13] R. J. Glauber, "Coherent and incoherent states of the radiation field," Phys. Rev. **131**, 2766 (1963).

[14] R. Loudon, *The Quantum Theory of Light*, 3rd ed. (Oxford University Press, Oxford, 2000), Chap. 1.

[15] A. Chenu, A. M. Brańczyk, and J. E. Sipe, "First-order decomposition of thermal light in terms of a statistical mixture of pulses," *in preparation*.

[16] D. G. Bradley and G. H. C. New, "Ultrashort pulse measurement," in *IEEE*, **72**, 313 (1974).

[17] C. L. Mehta and E. Wolf, "Coherence Properties of Blackbody Radiation. II. Correlation tensors of the quantized field," Phys. Rev. **134**, 1149 (1964).

[18] A. M. Brańczyk, A. Chenu, and J. E. Sipe, "Second-order correlation function of thermal light," *in preparation*.