CHAPTER FOUR

Quantum Nano-optics in the Electron Microscope

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1. INTRODUCTION

Quantum optics concerns optical phenomena that cannot be described without taking into account the wave-particle duality. As ironically stated by Lamb (1995) in an interesting discussion, there are only very few situations where using the concept of photon is relevant. One major exception happens when a system is sufficiently confined to exhibit a discrete number of electronic levels. If one considers only the fundamental and first excited states (see Fig. 1A), the system can be simplified as a two-level system (TLS). Such a

![Diagram A](image1)

![Diagram B](image2)

![Diagram C](image3)

![Diagram D](image4)

![Diagram E](image5)

**Fig. 1** Summary of the main concepts and tools tackled in this chapter. (A) A system with two electronic levels has the property of emitting only one photon at a time. Despite the simplicity of this assertion, emitting one photon at a time is a pure quantum property. (B) Detecting a single-photon source requires the measurement of the correlation function $g^{(2)}(\tau)$. (C) In this chapter, we describe CL experiments in a STEM. (D) Most generally, STEM-CL experiments concern the measurement of an optical spectrum at a given position of the electron beam. (E) A special type of interferometer, the Hanbury Brown and Twiss interferometer, has to be fitted to a STEM in the particular case of quantum nanooptics experiments.
system can emit only one photon at a time and is therefore an ideal single-photon emitter (SPE). SPEs are finding important applications in quantum cryptography. Typical realizations of SPEs are atoms, quantum dots, molecules, or point defects in semiconductors. The nitrogen vacancy (NV) discussed further is probably the most studied SPE.

Characterizing an emitter as being an SPE cannot be done by measuring the first-order properties of light, such as its spectrum. It requires the measurement of the statistical properties of the light coming out of the emitter. This can be done by measuring the second-order correlation function $g^{(2)}(\tau)$, as shown in Fig. 1B. The study and quest for new SPEs is a very fertile field in which most of the experimental studies relies on the use of photoluminescence (PL) to measure $g^{(2)}(\tau)$. This technique is obviously diffraction limited, while the SPEs are all very small compared to the wavelength of light they emit, as they rely on large electron–hole confinement. Therefore, subwavelength techniques are desirable. Cathodoluminescence (CL) in a scanning electron microscope (SEM; Edwards & Martin, 2011; Yacobi & Holt, 1990) and especially in a scanning transmission electron microscope (STEM; Kociak & Zagonel, 2017; Yamamoto, Araya, & de Abajo, 2001; Zagonel et al., 2011) (as depicted in Fig. 1C) has shown great success in mapping optical excitations at deep subwavelength resolution, by using spectral imaging (SI) techniques (Fig. 1D). It is thus tempting to fit the typical apparatus for $g^{(2)}(\tau)$ measurements, namely the Hanbury Brown and Twiss (HBT) intensity interferometer depicted in Fig. 1D, to a STEM–CL apparatus. This has been recently successfully done (Tizei & Kociak, 2013).

Quantum nanooptics with free-electron beams is therefore possible. However, at the time of writing, only our team has developed tools and methodology to perform these experiments, although promising developments are underway in other teams. It is therefore the aim of this chapter to guide electron microscopists into the fascinating realm of quantum nanooptics with the hope this will trigger new and exciting discoveries in this emerging field. With this aim, we first introduce the basics concepts and instrumentation necessary to apprehend quantum nanooptics in an EM. However, we assume the reader familiar with the basics of electron spectromicroscopy (Egerton, 1996; Kociak, Stéphan, Walls, & Colliex, 2011; Kociak & Zagonel, 2017). We then introduce the main electronic excitations and mechanisms responsible for CL emission, allowing a deeper understanding of the properties of $g^{(2)}(\tau)$, which are not always similar to the one measured in PL. We then review recent results on the detection of SPEs (Bourrellier et al., 2016; Tizei & Kociak, 2013), and the difference between
statistics of photons emitted through CL and PL (Meuret et al., 2015). Finally, this difference allows the determination of nanometer-sized emitters’ lifetime, and we describe this unexpected application of $g^{(2)}(\tau)$ measurements (Meuret et al., 2016).

2. QUANTUM OPTICS

There are many well-established texts on general quantum optics (Fox, 2006; Loudon, 2000). Our aim here is to give sufficient elements of quantum optics to allow the reader to follow the rest of the text. We will start by an introduction to correlation functions in Section 2.1. After that, we will discuss the use of the second-order correlation function, $g^{(2)}(\tau)$, to characterize different states of light, including classical chaotic (an atom discharge lamp), Poissonian (a laser beam), and number states (a single-photon beam). This will be followed by a description of how the $g^{(2)}(\tau)$ might be measured using a Hanbury Brown and Twiss interferometer (Section 2.2).

2.1 Correlation Functions

Correlation functions of signals in time give important information about their statistical properties. In quantum optics these functions allow one to distinguish light beams with different coherence and temporal properties. In general terms, they are the convolution (of different orders) of the electric field of a light field at different times (the correlation function might also include spatial dependences which we omit here). The normalized first-order correlation function of a light beam is defined as

$$g^{(1)}(\tau) = \frac{\langle E^\dagger(t) E(t + \tau) \rangle}{\langle E^\dagger(t) E(t) \rangle}$$

with $E(t)$ is the electric field at time $t$, $\tau$ is the delay and

$$\langle E^\dagger(t) E(t + \tau) \rangle = \frac{1}{T} \int_T E^\dagger(t) E(t + \tau) dt.$$  

This function measures the first-order coherence of the light field and gives information, for example, about classical interference effects (such as observed in a Michelson–Morley interferometer).

A correlation function which has more interest in this discussion is the normalized second-order correlation function, which is defined as:
\[ g^{(2)}(\tau) = \frac{\langle E^*(t)E^*(t+\tau)E(t+\tau)E(t) \rangle}{\langle E^*(t)E(t) \rangle^2} = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2}, \] (3)

taking \( I(t) = E^*(t)E(t) \). In simple terms, this function measures the degree of correlation between the intensity of a light beam measured at two different times separated by the delay \( \tau \).

One can gain insight into the physical meaning of this function by rewriting the intensity as \( I(t) = I + \Delta I(t) \), with \( I \) the temporal average of the intensity and \( \Delta I \) the fluctuation from the average at time \( t \) (with average 0):

\[
g^{(2)}(\tau) = \frac{\langle (I + \Delta I(t))(I + \Delta I(t + \tau)) \rangle}{\langle (I + \Delta I(t)) \rangle^2} = \frac{\langle I^2 + I\langle \Delta I(t) \rangle + I\langle \Delta I(t + \tau) \rangle + \langle \Delta I(t)\Delta I(t + \tau) \rangle \rangle}{I^2} \]
\[ = \frac{\langle I^2 + \langle \Delta I(t)\Delta I(t + \tau) \rangle \rangle}{I^2}, \] (4)
as \( \langle \Delta I(t) \rangle = 0 \). First of all, one expects that for large time delays (in fact, larger than the coherence time of the beam, \( \tau_c \)) the fluctuations from the average are uncorrelated \( \langle \Delta I(t)\Delta I(t + \tau) \rangle \rangle = 0 \). Therefore:

\[ g^{(2)}(\tau >> \tau_c) = \frac{I^2}{I^2} = 1. \] (5)

Moreover, it can be shown that for any classical \( I(t) \) the average of the square of the intensity, \( \langle I(t)^2 \rangle \), is larger or equal to the square of the average, \( \langle I(t) \rangle^2 \) (Fox, 2006). Hence

\[ g^{(2)}(\tau) \geq 1 \] (6)

and

\[ g^{(2)}(0) \geq g^{(2)}(\tau). \] (7)

A simple hands-waving argument to support Eqs. (6) and (7) is that for a time varying \( I(t) \) the fluctuations will have positive and negative values, which will add up when squared. Hence (6) must be true. As the correlation between the fluctuation decreases for increasing time delay, \( g^{(2)}(\tau) \) must also decrease, leading to inequality (7). In the next three subsections we will compute this function for three different light beams: a chaotic beam, a coherent beam, and a single-photon beam (number state).
2.1.1 Chaotic Beam: Classical Light

A classical light beam typically has a small coherence time. A prototypical example is an atom discharge lamp. The phase between the light emitted from a given atom is randomized by its collisions with other atoms in the gas. In this section we will calculate the expected $g^{(2)}(\tau)$ function, starting from the $g^{(1)}(\tau)$ function, for this light source and interpret its physical meaning following the description of Loudon (2000). The general behavior of all light sources we encounter routinely, with the exception of lasers, can be interpreted in view of this model.

The electric field emitted by an atom in this lamp is

$$E(t) = E_0 e^{-i(\omega_0 t - \phi(t))},$$

where $\phi(t)$ is a random phase that is added at each collision (which occurs at random times).

To calculate the first-order correlation function, we need to compute the product

$$\langle E^*(t) E(t + \tau) \rangle = E_0^2 e^{-i\omega_0 t} \langle \left\{ e^{-i\phi_1(t)} + e^{-i\phi_2(t)} + \cdots + e^{-i\phi_N(t)} \right\} \times \left\{ e^{-i\phi_1(t + \tau)} + e^{-i\phi_2(t + \tau)} + \cdots + e^{-i\phi_N(t + \tau)} \right\} \rangle,$$

with $\phi_i(t)$ the random phase added to each atom $i$ at time $t$. The product of the phase terms from different atoms is uncorrelated and gives a zero average, so only the terms from the same atom contribute:

$$\langle E^*(t) E(t + \tau) \rangle = E_0^2 e^{-i\omega_0 t} \sum_{i=1}^{N} \langle e^{i(\phi_i(t + \tau) - \phi_i(t))} \rangle.$$

As the phase $\phi_i$ is a random value added at each atomic collision, only the field emitted between atomic collisions will contribute to the average in the last term above. Hence, the correlation will be proportional to the probability of observing an event after a delay $\tau$ between atomic collisions (Loudon, 2000):

$$\langle E^*(t) E_i(t + \tau) \rangle = E_0^2 e^{-i\omega_0 t} \int_\tau^\infty d\tau' p(\tau') (1),$$

with $p(\tau) d\tau = (1/\tau_c) e^{-\tau/\tau_c} d\tau$, $\tau_c$ the typical time between collisions, for positive values of $\tau$. For atom $i$:

$$\langle E^*_i(t) E_i(t + \tau) \rangle = E_0^2 e^{-i\omega_0 (\tau - \tau_c)}.$$
So the first-order correlation function for a collision broadened source:

\[ g^{(1)}(\tau) = e^{-i\omega_0 \tau} e^{-|\tau|/\tau_c}, \]  

(13)

using the fact that \( g^{(1)}(-\tau) = g^{(1)}(\tau)^* \). It can be shown that:

\[ g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 \]  

(14)

and therefore:

\[ g^{(2)}(\tau) = 1 + e^{-2|\tau|/\tau_c}. \]  

(15)

Using Eq. (15) we can check that \( \lim_{\tau \to \infty} g^{(2)}(\tau) = 1 \), \( g^{(2)}(\tau) > 1 \forall \tau \) and establish that \( g^{(2)}(0) = 2 \), a result valid for all classical light. The shape of this function is shown in Fig. 2. One can clearly see that a peak appears at low values of \( \tau \). The presence of intensity correlations indicates that there is a probability of detecting groups of photons larger than that expected from Poisson statistics. The observation of these correlations for light is called light *bunching* and is in strikes contrast with what we will discuss for single photons.

Before we continue, it is worth noting that the expected coherence time for classical light is of the order of femtoseconds. Therefore the width of bunching peak for this kind of light should be of the order of femtoseconds. This number should be kept in mind for the discussion in Section 6, where we will describe the observation of light bunching in CL experiments.

![Fig. 2](image_url)  

*Fig. 2* \( g^{(2)}(\tau) \) function for a collision broadened classical source, which follows Eq. (2). The time delay \( \tau \) was normalized by \( \tau_c \).
2.1.2 Coherence Beam: A Laser

An ideal laser is a monochromatic source of light fundamentally characterized by its long temporal coherence. The electric field of a laser beam can be modeled by a sine wave, $E_0 \sin(\kappa x - \omega t)$. This electric field has a constant average intensity over multiple optical cycles, $I_0$. For this reason, one can readily see that:

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} = \frac{I_0^2}{I_0^2} = 1,$$

for all $\tau$. This result can be seen also as the limit of equation (15) for infinitely long coherence times.

However, this is not equivalent to stating that an instantaneous measurement of the intensity (or the number of photons in the beam) always results in the same value. In fact, it can be shown that for a laser beam of constant intensity the probability of detecting $n$ photons follows the Poisson distribution. Hence the standard deviation of the average is $\Delta n = n^{\frac{1}{2}}$.

Eq. (16) is quite important for the normalization of the histograms measured in intensity interferometry experiments (Section 2.2). Fundamentally, we assume that at large time delays photon detections are uncorrelated and follow Poisson statistics. Therefore, a laser source can be used as a reference for $g^{(2)}(\tau)$ normalization (before or after the actual experiment).

2.1.3 Single-Photon Beam: Number State

A single-photon light beam is essentially different from the two types of light described previously. In simple terms, such a beam is constituted of individual photons separated by some time delay. In this case, at any time, no more than one photon can be detected in the beam. At first sight, one could envision using an attenuated laser as a source of single photons. However, this is fundamentally wrong, as even in the limit of extremely low intensities the probability of observing $n = 2$ is nonzero, given the Poisson statistics of the photon distribution in a laser beam. Therefore, a completely different approach is needed.

An alternative idea is to use a highly nonlinear system, which can only be excited once and that emits only one photon upon deexcitation (Fig. 3). Such a simple system will emit at most a photon once every excitation/deexcitation cycle, even if continuously excited. One possibility to realize this model in practice is to use the energy levels in individual atoms. The first experimental report of single-photon emission occurred in the late
1970s for a Na atoms being excited in resonance (Kimble, Dagenais, & Mandel, 1977).

In more precise terms a single-photon light beam is a number state with $n = 1$. That is, at any given time there will be exactly zero or one photon in a fixed time bin (typically the source lifetime or the excitation rate). In general terms, given a photon number state $|n\rangle$ one can calculate the expected $g^{(2)}(\tau)$. A detailed demonstration of the results summarized here can be found in other texts (Fox, 2006; Loudon, 2000).

For our discussion, we just need the result that a number state is an eigenvector of the number operator $\hat{n} = \hat{a}^\dagger \hat{a}$, with $\hat{a}^\dagger$ and $\hat{a}$, the annihilation and creation operators:

$$\hat{n} |n\rangle = n |n\rangle$$ \hspace{1cm} (17)

with $n$ the number of photons in the field. The expected value of $g^{(2)}(0)$ for a state $|n\rangle$ can be written in terms of the number operator:

$$g^{(2)}(0) = \frac{\langle \langle n|\hat{n}(\hat{n} - 1)|n\rangle \rangle}{\langle \langle n|\hat{n}|n\rangle^2} = \frac{n(n-1)}{n^2} = 1 - \frac{1}{n^2}$$ \hspace{1cm} (18)

With this, we see that the value at $\tau = 0$ is lower than that expected for a classical source. More generally, one can show that for a single emitter (Beveratos, 2002) $g^{(2)}(\tau)$ reads

$$g^{(2)}(\tau) = \frac{P(t + \tau|t)}{P(t)},$$ \hspace{1cm} (19)

where $P(t)$ is the probability of detection of a photon at time $t$ and $P(t + \tau|t)$ is the conditional probability of detection of a photon at time $t + \tau$ given that
one was detected at \( t \), which are proportional to the occupation of the excited state \( \sigma_e(t) \) (Beveratos, 2002). The population of the excited state is basically determined by the state lifetime, if the pumping rate is much smaller than the inverse of the lifetime. In this limit:

\[
g^{(2)}(\tau) = 1 - e^{(-\tau/\tau_e)}
\]  

(20)

The behavior of this function is shown in Fig. 4, and it shows that the probability to detect two photons at short-time delays is lower than that expected classically or for a coherent state. This behavior is called antibunching, and it is a clear signature of the observation of a single-photon source. Therefore, the objective in detecting single-photon sources is equivalent to observing light antibunching in \( g^{(2)}(\tau) \) measurements. In the next section we will describe how the \( g^{(2)}(\tau) \) can be deduced from the measurements within some approximations.

### 2.2 From Histograms to \( g^{(2)}(\tau) \)

As described before the \( g^{(2)}(\tau) \) can be interpreted as the probability of detecting a photon at time \( \tau \) in a light beam, given that one was detected at time 0 (start of the measurement). Although simplistic, this viewpoint allows one to devise an experimental setup to measure this quantity. At first sight, it would suffice to use a single-pixel detector to measure the arrival time of each photon and construct a histogram of the time delays between photons (Fig. 5).

![Fig. 4 \( g^{(2)}(\tau) \) function for single-photon source, where anticorrelation is observed at zero time delay \( g^{(2)}(0) = 0 \). The time delay \( \tau \) was normalized by \( \tau_c \).](image-url)
However, a technological problem prevents the realization of these measurements, at least for many systems of interest: detectors’ dead time in comparison with emitters’ lifetimes. Most of the single-photon sources studied have lifetimes between 1 and 100 ns. The reason behind this is practical: as high count rates are desired short lifetimes should be aimed for. This short lifetime means that our pixel detector in the proposed setup would need to detect and time tag photon detections at least with sub-nanosecond time resolution and dead time. Current state of the art detectors have the required time resolution (detection and discretization steps). However, their dead times are quite long: for the avalanche photodiode (APD) used in typical experiments (described in later sections) the dead time is 90 ns.

For this reason an alternative approach is needed. A possible solution to this issue was introduced by Hanbury and Twiss (1956) for a completely different application: to analyze the intensity correlation from light originated...
from stars at two separate points in space to determine their angular size. Basically, light from a source is collected and sent to two different arms. The intensity collected at each arm is measured by photomultiplier tubes and their amplitudes are correlated using electronics. However, as Hanbury and Twiss (1956) had already appreciated, this setup (sketch in Fig. 6) allows one to measure the coherence of a general light source. The intensity interferometer they proposed is usually referred to as Hanbury Brown and Twiss (HBT) interferometer. They demonstrated experimentally that the light from a single coherent source shows correlation as predicted by electrodynamic theory (Hanbury & Twiss, 1956). At that time, detectors did not allow the time resolution achievable today to measure the time dependence of the correlation, but only differences between correlated and uncorrelated sources.

With current technology, one can measure the arrival time photons with tens of picoseconds time resolution at about 1 MHz. Correlating signal from two such detectors allows a measurement of the $g^{(2)}(\tau)$.  

In greater detail, this experimental setup measures the temporal delay, $\tau$, between the arrival of a single photon on each detector: one of the detectors (arbitrary, but fixed) is used as the start of the clock, which is stopped upon detection of photon on the second detector (stop). This time delay is added to a histogram, which is an approximation to the $g^{(2)}(\tau)$ function. This fact is

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**Fig. 6** Sketch of a generic HBT interferometer. The key idea is that a photon beam is filtered in the desired wavelength range and then split into two beams. The photons in these beams are detected by two high quantum efficiency detectors, which work in start-stop configuration. The time delays between the arrival of a “start” and a “stop” photons are measured and recorded into a histogram. The basic components of the interferometer are two lenses, an optical filter, a beam splitter, IR filters, fast photodetectors, and correlation electronics.
true if the detection rate is low compared to the detectors’ dead time. Typically in an experiment count rates per detector are $10^5$ counts/s, so one event every 10 μs, far slower the detectors’ dead time of 90 ns. This ensures that time delays longer than the dead time are also probed.

In the next two sections we described the two intensity interferometers used in the experiments described in later sections.

### 2.2.1 HBT1—Visible

The first STEM-CL interferometer was built to detect light from NV$^0$ centers (Tizei & Kociak, 2012, 2013), which emit in a wavelength range from 575 nm to above 750 nm (phonon tail see Section 5). It was inspired by regular PL quantum optical setup. The key element in the setup is the detectors, which are required to have the highest quantum efficiency (to decrease the measurement time for a correlation function, as it scales with $I^2$) and with the smallest dead time. One of the best option at the time of the first HBT experiments in a STEM (Tizei & Kociak, 2013) was avalanche photo diodes (APDs), which are single-pixel detectors with an active surface 200 μm by 200 μm wide. Other than the small physical size, this detectors suffer from their sensitivity to high light input (above 1 M counts/s) when operational. The choice for detectors were τ-SPADs from Picoquant, which have a quantum efficiency of 70% at 670 nm, a dead time of 90 ns, a total time jitter of 350 ps (including the detection electronics). The detection electronics for timing and histogram integration was a PicoHarp 300, also from PicoQuant, which allows for acquisition of up to 65536 time delay channels, with time per channel between 4 and 512 ps. The optical part of the interferometer was built to image a single input fiber into the two detectors, after a beam splitter (Fig. 6). In this setup, one images the fiber onto the detectors. As the optical system has no demagnification, a single 200 μm-core fibers was chosen in relation to the limited size of the detectors. The fiber possesses an antireflection coating optimized to the 350–700 nm wavelength range and a numerical aperture of 0.2. Two lenses (also with antireflection coatings) were used to first produce a parallel light beam from the fiber input and then focus the light onto the detectors. Between the two lenses a single passband optical filter (570–720 nm) was used to limit the light detected to our range of interest. Finally a 50/50 beam splitter (Thorlabs with antireflection coating in the 350–700 nm wavelength range) was placed after the last lens to separate evenly the light between both detectors.
The detectors used have a known artifact: after the detection of a photon they have a nonzero probability of emitting an infrared photon (above 750 nm). This extra photon may be detected by the second detector, creating spurious correlated events (Fig. 7). To prevent these events, it is required to: (1) build the interferometer with a single last lens before the beam splitter and (2) use low-pass filters (<750 nm) in front of each detector. Point one ensures that light from one detector is not focused into the other detector.

2.2.2 HBT2—UV

This second interferometer was built to detect light from different III-Nitride compounds (Meuret et al., 2015) and hBN (Bourrellier et al., 2016), which emit in the near ultraviolet region (near-UV). Depending on the experiment, the operational range was modified by interchanging lenses coatings and optical filters. As in the previously described interferometer, the crucial element is the photodetector. To our knowledge, at the time of writing, the photodetector with the highest quantum efficiency and lowest dark noise in the near-UV range is photomultiplier tubes (PMT) from Hamamatsu: photon counting head H10682–210p. These detectors are fairly sensible to light even when not in operation (exposure to high intensities increases the dark noise). The correlation electronics used

![Graph showing number of events vs. time delay (ns).](image)

**Fig. 7** As described in the text, the PicoQuant τ-SPAD detectors have a nonzero probability of emitting IR photons when a visible photon is detected. The cross talk generated by these emitted photons is shown here, when light from a single diamond particle was detected. To avoid this cross talk, IR filters must be used.
was the same as the one used for the other interferometer (PicoHarp 300). The input the electronics accepts is a NIM (Nuclear Instrumentation Module) signal. The output of the PMT modules (which include a discriminator) is a TTL signal. The TTL needs to be converted into NIM using an electronic board. As the PMT physical detection surface (8 mm) is larger than that of the APD, an optical fiber with a larger core was used (600 μm) to facilitate alignment, without any antireflection coating. The optical path was essentially the same, using lenses and beam-splitters with antireflection coatings chosen for each desired wavelength range.

This setup can be upgraded to include an optical monochromator to filter light at shorter wavelength ranges on demand (at the cost of some losses in total intensity throughput).

### 2.2.3 Histogram Normalization

As described before, the time delay histogram measured by an HBT interferometer is an approximation to the second-order correlation function, \( g^{(2)}(\tau) \). One key point in the measurement is the normalization of the histogram (Beveratos, 2002). This is done in such a way that for a Poissonian source \( g^{(2)}(\tau) = 1 \) for all time delays. For a Poissonian source (such as a laser) the time delay between two photons in the beam is random and equally spaced in time. So, for count rates \( n_1 \) (counts per second) and \( n_2 \) in each detector there should be \( N^2 = T\Delta\tau N_1 N_2 \) counts in a delay window \( \Delta\tau \) (the experimental time bin size) integrated for time \( T \). Therefore, the normalized histogram is given by:

\[
C_{\text{Norm}}(\tau) = \frac{c(\tau)}{n_1 n_2 \Delta\tau T} = g^{(2)}(\tau) \tag{21}
\]

where \( c(\tau) \) is the measured histogram. This is strictly true only for a Poissonian source. As we discussed in previous sections, light beams with other temporal dependencies do not respect equation (21) for all \( \tau \). However, correlation effects in the \( g^{(2)}(\tau) \) function should always decrease for increasing \( \tau \). In this way, for \( \tau >> \tau_\text{c} \), with \( \tau_\text{c} \) some typical time of the system (i.e., a lifetime), the value of \( g^{(2)}(\tau) \) should tend to 1.

For the experiments described here, the normalization has been performed by assuming that for a long-time delay (typically at least five times the value of the emitter lifetime) \( g^{(2)}(\tau) = 1 \). This behavior has been checked using the interferometers described here to measure \( g^{(2)}(\tau) \) for a laser beam. In Fig. 8A we show a measurement of the photon-pair delay histogram for a
laser beam, integrated during $T = 50$ s. On the left ordinate axis of Fig. 8A the number of counts is shown. The count rates for this measurement were $N_1 = 1.7 \times 10^5$ counts/s and $N_2 = 9.2 \times 10^4$ counts/s. Using these values and the experimental time bin ($\Delta \tau = 512$ ps) we can normalize the histogram. This normalization is shown in the right ordinate axis of Fig. 8A. The average value of $g^{(2)}(\tau)$ in the window shown is 1.01. As the standard deviation is 0.04 in the same window, the discrepancy from 1 is statistical in nature. For long-time delays, the histogram is no longer a good approximation to $g^{(2)}(\tau)$ and the number of counts per time bin has not a constant behavior, contrary to what is expected for a Poissonian source (Fig. 8B and C).

To perform this measurements an attenuated laser can be used. As we stated before, the detectors used are quite sensitive to light. Typically, $1 \times 10^6$ photons/s is the operation limit for these detectors. This number of photons translates to a power of 0.3 pW for photons with wavelength 633 nm (Fox, 2006), which is far lower than the typical output power of diode laser (few mW). Therefore, to perform this measurement the beam from a diode laser was attenuated using optical densities before detection.
3. PRIMARY EXCITATIONS IN BULK AND QUANTUM-CONFINED MATERIALS

3.1 Introduction

In this section, we review the most important solid-state excitations relevant for the study of CL; mechanisms of light production under electron beam irradiation that totally depend on these excitations are described in the following section. The physics of basic excitations in semiconductors and the related emission have been introduced in many textbooks, among which Fox (2010) and Peter and Cardona (2010) have to be highlighted. Applications to CL and discussion of the electron–matter interaction have been tackled in the reference book of Yacobi and Holt (1990), and in more details in the case of the STEM-CL in a recent review (Kociak & Zagonel, 2017).

3.2 Electron–Holes Pairs

In a bulk semiconductor electronic states form bands. The most relevant bands for the study of luminescence are the valence and conduction bands (VB and CB) schematically drawn for a direct band gap semiconductor in Fig. 9A. In a real semiconductor, such as GaN extensively illustrated in this chapter, the band structure is more complex, with, for example, three (possibly degenerate) different types of valence (holes) bands (Peter & Cardona, 2010). However, these particularities will not affect the discussion on light

![Fig. 9](image-url)

**Fig. 9** (A) Simplified band structure for the valence (VB) and conduction band (CB). Possible donor’s and acceptor’s states are indicated. (B) Some of the possible transitions at room temperature. In this scheme, the effect of Coulomb interaction resulting in a lowering of the transition energy has not been indicated.
Basic excitations consist in electron–hole pairs (e–h pairs) excited above the band gap energy.

### 3.3 Doping and Gap States

In a real semiconductor, there are always defects or impurities. For the sake of this chapter, only point defects/impurities, namely atom vacancies or atomic dopants, are worth considering. Depending on their charge states, the defects can be classified as donors (if they bring additional electrons to the material) or acceptors (in the opposite case). This is presented in Fig. 9A.

The influence of these states on the possible excitations in the semiconductors is different depending how close in energy they are from the conduction band (for donors) or the valence band (for acceptors). The so-called shallow donors or acceptors have states close to the valence (resp. conduction) bands. The so-called deep donors or acceptors have states far from the valence (resp. conduction) bands. Therefore, shallow defects easily dope semiconductors at room temperature, giving rise to possible new electron–hole excitations with energies slightly smaller than the band gap energy of the pure semiconductor. The corresponding transitions are indicated in Fig. 9B, where the binding effect of the Coulomb interaction has not been taken into account. As these transitions have energies close to the band gap energy, they belong to the group of so-called near band edge (NBE) transitions. At the opposite end, deep defects are very unlikely to be ionized even at room temperature and therefore have transitions energies quite different from that of the band gap.

If a deep donor and a deep acceptor are sufficiently spatially close, they can bind through Coulombic interaction forming a donor–acceptor (DA) pair. They form, to first order, an hydrogenoid system. They are a very important class of excitations for the purpose of this chapter, as they are theoretically extremely similar to simple atoms with the ability to act as SPEs.

### 3.4 NV$^0$ in Diamonds

NV centers in diamond nanoparticles are constituted of a substitutional nitrogen atom in the carbon lattice next to a carbon vacancy as shown in Fig. 10. Although not formally a DA, it is a very similar form of hydrogenoid system. This defect has a quite well-established energy-level structure (Doherty et al., 2013). It appears with two charge states: neutral (NV$^0$) and charged (NV$^-$). These two states have zero-phonon lines (ZPL) at 575
and 637 nm. The first one has a singlet fundamental state, while the second one has a triplet state (Doherty et al., 2013). Both centers are known to be single-photon sources from HBT experiments in confocal microscopes using laser excitation (Beveratos, Broui, Poizat, & Grangier, 2001; Gruber et al., 1997; Jelezko & Wrachtrup, 2006). The neutral state (NV$^0$) is almost always observed in CL experiments (Burton, Steeds, Meaden, Shreter, & Butler, 1995; Tizei & Kociak, 2012; Zaitsev, 2001), contrary to the NV$^-$ state. In this chapter, we will describe the detection of a single-photon beam emitted from a single NV$^0$ center in a diamond nanoparticle. The experiments have been performed with the interferometer optimized to the visible range described in Section 2.2.1 using APD detectors.

3.5 Phonons

Vibrational excitations in solids can couple to electronic excitations. The way they interact with the electronic excitations can be complicated to describe in the general case. However, it leads eventually to the appearance of phonon replicas. A simplified and heuristic model of phonon-dependent luminescent spectra is given in Section 4.4.

3.6 Excitons

In the preceding sections, except for the DA pairs or NV defects, electrons, and holes were supposed to be independent. This is generally not the case. Due to the Coulombic interaction, electrons and holes close to the band

![Structure of the NV center in diamond.](image-url)
edges will interact to form hydrogenic-like systems, much like DA pairs do. However, in semiconductors, the Coulombic interaction is usually strongly screened, and the binding is small. Typical binding energies $E_b$ are 20 meV for GaN (Sieber, 2016). In the materials (GaN) considered here, the binding energy is larger than the temperature of liquid nitrogen divided by the Boltzmann constant. This ensures that even in the bulk materials, excitons may exist (see the case of quantum-confined system later in Section 3.8) at these temperatures. At temperatures higher than $E_b/k_B T$, the exciton gets ionized, and we are left with unbound $e^–h$ pairs. We note that different excitons correspond to the different electron–hole transitions described in Fig. 9B. For example, the exciton formed by an electron in the conduction band and an hole in the valence band will be called free-exciton; its energy will be that of the band gap minored by the binding energy. Other forms of excitons that interact with donors or acceptors may exist. They usually have even smaller energies than the free-exciton or the equivalent unbound NBE transitions.

3.7 Plasmons

3.7.1 Bulk Plasmons

In a finer description of the excitations of solid-state materials, a special sort of excitation has to be discussed. In addition to the aforementioned excitations, bulk plasmons do exist. Bulk plasmons are well known in metals, where they are described as collective longitudinal acoustic-like waves of the free-electron gas. This type of excitations also exists in semiconductors as collective oscillations of the $e^–h$ pairs close to the bottom of the conduction band and the top of the valence band. Typical plasmons energies are much above the visible range—typically 20–30 eV. Also, their longitudinal character prevents them to couple to light in the far-field. However, we will see that they play a crucial role for the CL mechanisms.

3.7.2 Surface Plasmons

Surface plasmons are the surface equivalent of bulk plasmon waves. In several metals (silver, gold, etc.) they display interesting physics and promising applications. One of the great success of the CL in the past 20 years has been the mapping of these waves at deep subwavelength resolution within metal nanoparticles (Das, Chini, & Pond, 2012; Losquin et al., 2015; Vesseur, de Waele, Kuttge, & Polman, 2007; Yamamoto et al., 2001).
However, the typical lifetimes of the surface plasmons in nanoparticles are sub-picoseconds, so that with the instrumentation described here accessing their temporal behavior is impossible. Interested readers may refer to Losquin and Lummen (2017) for a description of alternative techniques to tackle this issue.

### 3.8 Confinement

An important phenomenon in nanoscience and their application is the confinement of electrons and holes. This is schematized in Fig. 11. When a semiconductor of band gap energy $E_{g<}$ is embedded in a semiconductor of higher band gap energy $E_{g>}$, then potential wells for electrons and holes may form. Depending on the band alignment scheme, different scenario may occur, but for the sake of the simplicity we will assume in the following that the confinement is of type I, namely the smallest band gap lies entirely within the larger one (see Fig. 11). In such a case, when the size of the material with the smallest band gap becomes smaller than the de Broglie wavelength, the excitations get confined. Energy becomes discretized along the confinement direction. The higher the confinement, the larger the energy distance between energy levels.

![Fig. 11 Effect of confinement and quantum-confined Stark effect. Left: A material of relatively smaller band gap is embedded in a material of relatively larger band gap. Depending on the relative band alignment, energy ($E$) wells can form at the smaller band gap material (here localized along an arbitrary direction $X$). States of different energies form. The thinner the well, the higher the energy states separation. In the presence of an electric field, bands are bent. Middle: for large confinement (thin wells), the energy separation between the closest e–h states is barely affected. The situation changes (right) for thick wells.](image-url)
3.8.1 Quantum-Confined Stark Effect
In the presence of an electrical field, the energy bands of a material bend as schematically shown in Fig. 11, middle. If the bending is relatively small and the confinement high, the (quantified) electron and hole states are not essentially modified. However, when the field is high, the energy levels start to be affected. The effect can be strong enough so that the energy differences between the closest e–h states becomes smaller than the band gap of the bulk material. Moreover, electron and hole states become localized on opposite sides of the wells, largely decreasing their wavefunctions overlap. This effect is called quantum-confined Stark effect (QCSE) (Miller et al., 1984). Although not ubiquitous, this effect is determinant to the understanding of the utmost technologically interesting materials made up of AlGaInN alloys, because it can change the energy and intensity of the emission by several orders of magnitude (Kalliakos et al., 2004; Lefebvre, Homma, & Finnie, 2003; Lefebvre & Gayral, 2008). In these materials, the field, which can be as high as 10 MV/cm, arises from the pyro- and piezoelectric effects when the material is grown along its polar direction.

3.8.2 Two-Dimensional Confinement
An important class of quantum-confined materials are quantum wells (QW), where the confinement takes place along one dimension only. An important consequence of bidimensional confinement is the increase of excitonic binding energy (theoretically a factor of 4). In GaN for example, this leads to very robust excitonic states.

Such QWs are objects of choice for CL experiments. We report in Fig. 12 an example of GaN Qdiscs (which essentially behave as QW) embedded in AlN to form a nanowire. STEM-CL allows to isolate individual Qdiscs emissions (Kociak & Zagonel, 2017; Meuret et al., 2016; Zagonel et al., 2011) that can be attributed to specific quantum disks (Fig. 12A and B). The quantum disk thickness can be measured in a TEM with almost monolayer accuracy (one monolayer is around 0.28 nm in GaN). It is then possible to plot the relation between the Qdiscs energy and their thickness, reproducing the expected increase in energy as the thickness decreases. Note also how the QCSE manifests itself at larger thickness (larger than 4 nm typically).
3.8.3 Three-Dimensional Confinement

Systems confined in three dimensions are of particular interest for quantum optics applications, as they naturally form SPEs. Indeed, the 3D confinement leads to a series of discrete states, much like an hydrogenic system. Transitions from the closest energy states leads to a strong luminescence line, whose energy depends on the confined size. Recently, individual QDots have been studied by STEM-CL (Mahfoud et al., 2013). Unfortunately, we are not aware of SPE detection by CL yet, although these systems are very appealing (see Fig. 13).

3.8.4 Estimation of the Lifetime

The way an excited state relaxes to the fundamental one can be complicated, involving emission of photons, electrons, phonons, trapping in other states, etc. However, since monitoring light emission is of prime importance, one classifies these phenomena as radiative or nonradiative. In the most simple cases, the probability to transit from one state to the other decreases exponentially with a time constant equal to the total lifetime \( \tau \). This lifetime is
related to the radiative $\tau_R$ and nonradiative $\tau_{NR}$ lifetimes through $1/\tau = 1/\tau_R + 1/\tau_{NR}$. For the sake of brevity, we will not discuss the expression of $\tau_{NR}$ and oversimplifying the expression $\tau_R$ by noting that in the two main cases of interest here (quantum-confined systems and SPEs):

$$1/\tau_R \approx \int d\vec{r} \Phi_e(\vec{r})\Phi_h(\vec{r})^2$$

where $\Phi_e(\vec{r})$ and $\Phi_h(\vec{r})$ are symbolic expressions for the electron and hole wavefunctions (for example, in reality, the envelope wavefunctions should be used for quantum-confined systems). The main consequence of this expression is that the lifetime is increasing with decreasing spatial overlap of the two wavefunctions involved in the transition.

There is a large scattering of values for the radiative lifetimes. For NVs, the nitrogen and vacancy being spatially separated, the overlap is reduced and relatively long lifetimes are expected (typically 1–100 ns in NV centers for example). In the case of QW influenced by the QCSE, the lifetimes will change on several orders of magnitude with the size of the structure, which determines the electron–hole wavefunctions overlap (Lefebvre & Gayral, 2008, see Fig. 14).
4. CL PHENOMENON

4.1 Introduction

For the sake of simplicity, we will start by discussing the case of the STEM-CL. More details on the STEM-CL can be found in Kociak and Zagonel (2017). The frontier between STEM and SEM is arbitrary, and therefore the following has to be interpreted with care. In the following, we will describe the SEM cases as experiments where the acceleration voltage is relatively small (typically few keV, and anyway less than 30 kV), and sample essentially infinitely thick (in the sense of penetration depth, see Section 4.3). On the other hand, the STEM-CL case concerns situations where the high voltage is relatively high (from 60 to 200 kV, 60 kV being more typical), and is considered as very thin (in the sense of the mean-free path \( \lambda_e \), see Section 4.2).

4.2 Interaction: STEM Case

4.2.1 Primary Excitations Creation

Contrary to PL, where the incoming photon directly creates one electron–hole pair, the process of e–h pair creation is less straightforward in CL. When a fast electron impinges on a thin material, it interacts elastically and inelastically. Per definition, only the later interaction is susceptible to transfer
energy to the material. This energy transfer is, however, usually not large. As depicted on the EELS spectrum shown in Fig. 15, in a thin sample most of the electrons do not lose energy—see the contribution to the zero-loss peak (ZLP). When they lose energy, this is essentially in the so-called low-loss energy region (between 1 and 100 eV), the core-loss energy region having vanishingly small contributions. The low-loss region itself is dominated by the bulk plasmon described in Section 3.7.1. Apart from bulk plasmons, of course other excitations like excitons are created, but they will negligibly be part of the further processes compared to the larger bulk plasmon cross section. Once created, the bulk plasmon deexcites in a matter of few femtoseconds due to its highly dissipative character. It will deexcite in the form of a limited number of hot e–h pairs—obviously at most equal to that permitted by energy conservation, namely less than $E_p/E_g$, where $E_g$ is the band gap energy and $E_p$ the bulk plasmon energy. Typically, $E_p/E_g \approx 5$ for GaN.

The probability to create N plasmons is a Poissonian process with mean equal to $t/\lambda_c$, where $t$ is the thickness of the sample and $\lambda_c$ the inelastic mean-free path. Since $\lambda_c$ increases with voltage (Drouin et al., 2007; Egerton, 1996), the interaction decreases with voltage. For example for GaAs (Tanuma, Powell, & Penn, 2011), at 100 kV, $\lambda_c \approx 100$ nm. It is therefore common in TEM to work mostly in regimes where $t/\lambda_c \leq 1$. In such a case, the probability for the electron to create plasmons, and therefore hot electron hole pairs, is small. When $t/\lambda_c$ increases, another description is necessary which will be given in Section 4.3.
4.2.2 Thermalization and Diffusion

Once created, the e–h pairs thermalize in a ps second range to their local energy minima (Sieber, 2016).

At this time, the e–h pairs (which may be bound in the form of excitons) start to diffuse until they deexcite radiatively or nonradiatively. Different types of diffusion are given in Yacobi and Holt (1990). An important consequence of the diffusion is that STEM– (and SEM–) CL can be seen as excitation spectromicroscopy: the optical information gained when the beam is at a particular position comes from all positions around the beam (where radiative events have taken place). This results in a smoothed imaging, the typical smoothing extension being the diffusion length. This diffusion length will decrease depending on the presence of nonradiative and radiative recombination centers. Although in high purity materials it can be very large (e.g., excitons in diamond, Barjon et al., 2011), this is fortunately not the case for many nanoscale structures. Indeed, in quantum-confined systems, the potential wells themselves often act as effective e–h traps; also, surfaces (always present at least in the direction perpendicular to the electron beam in the case of STEM–CL) may act as efficient nonradiative centers, etc. This allows a relatively high spatial resolution in CL, although largely dependent on the material of interest and its nanostructuration. This is exemplified in the case GaN Qdiscs (where the resolution can be better than 5 nm, Zagonel, Rigutti, Jacopin, Songmuang, & Kociak, 2012) or in the case of NV centers in nanodiamonds (80 nm full width at half maximum, FWHM, Fig. 16, Tizei & Kociak, 2013).

4.3 Interaction: SEM Case

The case of SEM–CL has been discussed in many books (Sieber, 2016; Yacobi & Holt, 1990). In this thick sample/low voltage regime, the above description is no longer valid. Of course, the main source of e–h is the excitation of hot e–h pairs through multiple bulk plasmons creation. However, in addition to inelastic scattering, the incoming electrons suffer from strong elastic interaction. Even for arbitrarily small incoming beam diameters, the electrons will spread over a large volume, known as the interaction pear. The radius of such a pear can be as large as few microns at kV accelerating voltages. The incoming electron will lose all its energy while being scattered in the material and eventually stopped, so that the most relevant length in this case is not the mean-free path but rather the penetration length (Yacobi & Holt, 1990). All the other mechanisms of thermalization and diffusion are
also valid in this case. We, however, note that the interaction pair typical radius can be much larger than a typical diffusion length, so that the resolution is rather limited by this in SEM–CL than by the diffusion length. Besides the loss of resolution, two issues come with the strong interaction in the SEM case. Firstly, all the initial energy of electron is lost, and transferred in part in the form of heat, strongly heating the sample. Also, the number of e–h created per incoming electron is usually \(\text{Yacobi & Holt, 1990}\) given as \(E_0/3E_g\) where \(E_0\) is the incoming beam energy. This number can be very large so that at high incoming currents, saturation, and nonlinear effects could be experienced.

These effects are supposed to be lowered in the so-called \textit{low injection} regime, where the density of minority charge carriers injected through e-beam excitation is much lower than the equilibrium density of majority carriers at a given temperature \(\text{Sieber, 2016; Yacobi & Holt, 1990}\). We will stick to this regime for the sake of simplicity.

Such nomenclature relying on volume density may not be relevant to understand the effect of a beam on an SPE such as an NV center in diamond. However, the basic interest of sticking to the low injection regime is to avoid inducing nonlinearities due to saturation of states occupation. In the case of a NV, which is in a first approximation a TLS, saturation arises as soon as the NV is excited twice in between two recombinations events. A current \(I\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{(A) ADF (annular dark field) image of a diamond nanoparticle. (B) Intensity map of the NV\(^0\) center over the particle shown in (A) extracted from a full spectrum image. A very localized spot, with FWHM of about 80 nm was observed. \textit{After Tizei, L. H. G., & Kociak, M. (2012). Spectrally and spatially resolved cathodoluminescence of nanodiamonds: Local variations of the NV(0) emission properties. Nanotechnology, 23 (17), 175702. http://www.ncbi.nlm.nih.gov/pubmed/22481219. http://dx.doi.org/10.1088/0957-4484/23/17/175702, reprint with permission.}}
\end{figure}
corresponds to the production of \( N = \frac{t}{\lambda_e} \alpha I \tau / e \) e–h pairs, where \( \alpha \) is the number of e–h pairs created by plasmon, and \( e \) is the magnitude of the electron charge. This is of course neglecting the exponentially decreasing number of e–h reaching the NV when it is away from the injection position. A moderate \( I = 10 \mu A \) creates during a lifetime \( \tau = 1 \) ns. With a typical thickness to mean-free path ratio of 0.1, \( N \approx 0.1 \times 5 \times 10^{-11} \times 10^{-9} / (1.6 \times 10^{-19}) \approx 0.03 \) e–h pairs as an upper estimate. This is a very rough estimate as it totally neglects the effect of diffusion which will lower this number extremely rapidly. This explains that saturation of individual NV or other individual point defect has never been reported to the best of our knowledge in STEM-CL.

### 4.4 Deexcitations Mechanisms and CL Emission

In Section 3.8.4, we have dealt with the evaluation of the radiative lifetime, which essentially follows from the Fermi golden rule. Nonradiative events can also take place, to which a nonradiative lifetime is attached, so that the total lifetime \( 1/\tau = 1/\tau_R + 1/\tau_{NR} \). Radiative recombination events can be either unbound e–h pair recombinations or excitonic recombinations. The two processes are different—in the unbound case, the minority carrier can recombine with any other majority carrier; in the excitonic case, the initial e–h pair has to recombine together. However, in the low injection regime, the two phenomena cannot be distinguished on the CL intensity. In the two cases, the CL intensity reads (Sieber, 2016; Yacobi & Holt, 1990):

\[
I_{\text{CL}} \propto \frac{n}{\tau_R} \tag{23}
\]

with \( n \) being either the density of excess minority carriers or the density of excess excitons. We note that \( I_{\text{CL}} \) is inversely proportional to the radiative lifetime, which is not surprising as it is a radiative technique. The former formula is valid in the stationary regime. However, if one follows the time evolution of the CL intensity after a pulse excitation, then we should write:

\[
I_{\text{CL}}(t) \propto \frac{n(t)}{\tau_R} = n_0 e^{-t/\tau} / \tau_R \tag{24}
\]

with \( n_0 \) being the density of charge carriers at time 0. The CL intensity therefore decays exponentially with time, with a time constant equal to the total lifetime. Otherwise speaking, the CL emission rate (the CL intensity) is inversely proportional to the radiative lifetime for a given density of charge carrier, but decays with a time constant equal to the total lifetime. Therefore, all the techniques in this chapter, for which the absolute value of \( I_{\text{CL}} \) is irrelevant, are measuring the total lifetime and not the radiative one.
Finally, as mentioned earlier, it is interesting to discuss a toy model taking the role of phonons into account for the case of a DA pair or other point defects such as NVs, because the influence of phonon replicas cannot be neglected in this case. It will help to understand later how a spectrally broad emission can nevertheless lead to single-photon emission.

In Fig. 17, we present a schematic energy diagram for a bound e–h pair with separation $R$ and presenting two possible electronic states (the fundamental and an excited one). Each state has a vibrational substructure (here simplified has a constant energy difference harmonic oscillator distribution of states). In addition, the first excited state has a larger $R$ value, just like the $2p$ state of the hydrogen atom compared to the $1s$ one. Therefore, during the transition from the fundamental to the first excited state, the mean distance changes. Due to the Fermi golden rule, transitions occur when the overlap of the vibrational states are maximal. Let us assume for the sake of simplicity that the excited state has only the lowest vibrational state occupied (see Fig. 17). In the absence of an $R$ change, one would expect a maximum transition to the corresponding vibrational ground state of the electronic ground state.
state, which maximize the overlap integral. In the present case, the overlap is maximal for another transition (see Fig. 17). The system can therefore emit a photon while making a transition between two vibrational states with maximum overlap and then will emit several phonon to reach its fundamental vibrational state. The excitation then can relax nonradiatively to the minimum vibrational energy state of the fundamental electronic state by emitting several phonons. This appears as a peak in the spectra and therefore is called a phonon replica (note the inversed energy scale on the spectrum in the right of Fig. 17). Exception is made for the higher energy transition involving the transition from both fundamental vibrational states, called the ZPL as it does not involved the emission of a phonon.

The corresponding spectrum in Fig. 17 shows the effect of phonon replicas. Contrary to what we would expect from a TLS such as a DAP pair, the spectrum becomes very large, with all the replicas potentially overlapping and which eventually lead to broad bands (Robins, Cook, Farabaugh, & Feldman, 1989). How can single-photon emission happen in that conditions that naively has been defined as arising from the transition from only one pair of state at a time? The contradiction is only apparent. At any time, whatever excited and fundamental substates are considered, the states are populated by at most one e–h pair, at least under a moderate excitation. Even if the energy of the emitted photon is not necessarily the same at any time, there is always at most one photon in the photon beam, and SPE can therefore be measured.

5. SINGLE-PHOTON DETECTION IN THE ELECTRON MICROSCOPE

Having described some key points of the interaction between electrons and mater and also general CL experiments, in this section we discuss some experimental results demonstrating the detection of single-photon sources (SPE) using a fast electron beam as the excitation source. As described in previous sections, laser beams in confocal optical microscopes are typically used for SPE detection. Our motivation to start using electrons is their reduced wavelength (3.7 pm at 100 keV kinetic energy), which allows the realization of nanometer-wide beams even in not too complex machines. To begin, we will describe the use of the HBT interferometer described in Section 2.2.1 to identify neutral nitrogen vacancy (NV0) centers in diamond nanoparticles.
To start with, CL spectroscopy of diamond nanoparticles shows that localized emission spots with the NV$^0$ spectral signature can be detected (Fig. 16). These spots have spatial widths of the order of 80 nm ($1/e$ intensity drop). This indicates that these particles may contain individual emitters. Moreover, particles containing two distinct NV$^0$ emissions can also be found. For example, in Fig. 16 one can see that two emission regions between which small shifts of the ZPL and changes in the ZPL to photon band intensity ratio are observed. These observations point to the existence of two emitters in the nanoparticle. Of course, the spots observed in Fig. 18 are only indirect evidence of single-photon emission and a measure of $g^{(2)}(\tau)$ is needed to confirm this hypothesis.

In Fig. 19, we present the first measurements of antibunching measured by STEM-CL (Tizei & Kociak, 2013). Measurements were performed in individual particles with photon emission rate of the order of $4 \times 10^4$ (Tizei & Kociak, 2013). The $g^{(2)}(0)$ value is 0.46. Any value below 0.5 is the signature of a single-photon source. Values above 0 are associated with background noise due to the nanoparticle. Given the emission rate, typical acquisition times for a $g^{(2)}(\tau)$ is a few minutes. The $g^{(2)}(0)$ value is extracted by fitting the following model to the experimental curve:

$$g^{(2)}(\tau) = \begin{cases} 1 - g e^{-\tau/\tau_{tot}}, & \text{if } \tau \geq 0 \\ 1 - g e^{\tau/\tau_{tot}}, & \text{if } \tau < 0 \end{cases}$$

(25)

**Fig. 18** (A) ADF image of a diamond nanoparticle containing two emission maxima. (B) Two distinct ZPL are seen for this nanoparticle. (C) A map of the NV$^0$ total intensity shows that two spatially maxima are observed. (D) A projection of the spectral information along the line connecting the two emission maxima shows that the ZPL suffers a shift between the two maxima. (E and F) Multiple linear square fit components using the two spectra in (D) as input. Two distinct emission regions are observed.
where $\tau_{\text{tot}}$ is the total lifetime (radiative and nonradiative) of the excited state of the NV$^0$. Note that from the antibunching curve one can measure the lifetime of the center being excited.

Such an individual center detection could also have been performed using laser excitation in a confocal optical microscope. Here, the benefit of an electron microscope is the selective excitation of different positions in a sample with high spatial resolution.

For example, in Fig. 19 we show the measurement of the $g^{(2)}(\tau)$ at two different positions in the same nanoparticle (marked by red and blue rectangles). We observe that the dip of the $g^{(2)}(\tau)$ function at $\tau = 0$ changes from 0.46 to 0.73. The first value indicates a single-photon source with some background. The second indicates two different possibilities: (1) two centers with the same previous background or (2) one center with larger background. In any case, this experiment demonstrates the higher spatial resolution available with the use of a focused fast electron beam.
The two experiments described as examples demonstrate the possibility to detect single-photon sources at high spatial resolution using a focused beam of fast electrons.

### 5.1 Background Subtraction in Experiments With Electron Excitation

Eq. (3) shows that \( g^{(2)}(\tau) \) is a correlation at different times of the total intensity of a light beam. Therefore, if a light beam is originated from \( n \) sources, with intensities \( I_n \), the \( g^{(2)}(\tau) \) will be

\[
g^{(2)}(\tau) = \frac{\left\langle \sum_n I_n(t) \sum_n I_n(t+\tau) \right\rangle}{\left\langle \sum_n I_n(t) \right\rangle^2}. \tag{26}
\]

For this reason, if a light beam with intensity \( S(t) \) from a single-photon source is detected in the presence of a Poissonian background of intensity \( B(t) \) the measured \( g^{(2)}(\tau) \) will include contributions from both light beams. The presence of a background has been already considered for experiments using laser excitation (Beveratos, 2002). We follow this treatment here. We assume that the total light intensity is the sum of a single-photon beam \( S(t) \) and a Poissonian background \( B(t) \), \( I(t) = S(t) + B(t) \), when the single-photon source is excited. Moreover, we suppose that \( B(t) \) can be measured exactly by placing the beam next to the single-photon source. This translates to the hypothesis that the background is homogeneous around the analyzed region. If this is true:

\[
g^{(2)}(\tau) = \frac{\left\langle (S(t)+B(t))(S(t+\tau)+B(t+\tau)) \right\rangle}{\left\langle (S(t)+B(t)) \right\rangle^2}
= \frac{\left\langle (S(t)+S(t+\tau)) \right\rangle + \left\langle (S(t)+B(t+\tau)) \right\rangle + \left\langle (B(t)+S(t+\tau)) \right\rangle + \left\langle (B(t)+B(t+\tau)) \right\rangle}{\left\langle (S(t)+B(t)) \right\rangle^2}.
\tag{27}
\]

Taking into account that \( S(t) \) and \( B(t) \) are uncorrelated and defining \( \rho = S/(S+B) \), with \( S = \langle S(t) \rangle \) and \( B = \langle B(t) \rangle \):

\[
g^{(2)}(\tau) = \frac{\langle S(t)S(t+\tau) \rangle}{\langle (S(t)+B(t)) \rangle^2} + 1 - \rho^2. \tag{28}
\]
The quantity we want to measure is $g^{(2)}_{\text{SPE}}(\tau) = \langle S(t)S(t+\tau) \rangle / \langle S(t) \rangle^2$. This corrected $g^{(2)}_{\text{SPE}}(\tau)$ can be extracted from the experimental $g^{(2)}(\tau)$ if $B(t)$ is known:

$$g^{(2)}_{\text{SPE}}(\tau) = \frac{\langle S(t)S(t+\tau) \rangle}{\langle (S(t)+B(t)) \rangle^2 \rho^2} = \frac{g^{(2)}(\tau) - 1 + \rho^2}{\rho^2}. \tag{29}$$

This same operation can be performed with CL data, given that the excitation current is sufficiently high to avoid bunching effects (Section 6).

As an example of application to CL data, we will show how the background contribution from H3 centers can be subtracted to obtain the $g^{(2)}(\tau)$ function from NV$^0$ centers in diamond (Tizei et al., 2013). One of the great benefits of using a focused beam of fast electrons is the high spatial resolution available, which allows the acquisition of spectrum images. Specifically for CL data, spectrum images allow one to follow in detail the spatial distribution of different signals. For our discussion of the H3 background on the NV$^0$ signal, our interest is to obtain the spatial distribution of these two emissions, see Eq. (20).

Typically, in the diamond nanoparticles used in Tizei and Kociak (2012) both H3 and NV$^0$ emissions are observed. The typical emission spectrum is shown in Fig. 20A, where a first set of peaks due to H3 centers is observed starting at 500 nm and second set associated to NV$^0$ above 575 nm (ZPL position). The background created by the H3 center can be measured at each position by fitting an exponential model, which was validated by fits to spectra containing only the H3 emission.

For the NV$^0$ experiments the interest is concentrated in the wavelength range between 575 and 725 nm (defined by optical filters in the interferometer). We can define a signal to background ratio as (which is the same as $\rho$ previously defined):

$$\text{SBR} = \rho = \frac{I_{\text{NV}^0}}{I_{\text{NV}^0} + I_{\text{H3}}}. \tag{30}$$

which is a measure of the ratio between the signal of interest (from the NV$^0$ center) and the total intensity. The intensity spatial distribution of the two emissions are not the same, as we see in Fig. 20D and E given rise to changes
in the SBR value. The NV$^0$ emission appears mostly concentrated in one spot in the nanoparticle.

Measuring $g^{(2)}(\tau)$ at the NV$^0$ emission maximum we obtain the curve shown in Fig. 21. The measured antibunching dip is $g^{(2)}(0) = 0.90$. From the spectrum measured at the same position (Fig. 20A) we can estimate the SBR to be 0.74. This value is expected to be in the [0.69, 0.78] interval with
high confidence. From these values, using Eq. (29), we can see that the actual $g^{(2)}(0)$ value should be 0.81 and within the interval of confidence [0.78, 0.83].

Before continuing with another application of CL-STEM toward the detection of single-photon source, we should stress the high spatial resolution available in experiments using a focused electron probe allows for an increased SBR, as a smaller volume of the material is excited. Moreover, the spectrum image capabilities permit the determination of the background intensity with greater accuracy.

Finally, due to the physics of the electron matter interaction bunching of light may be observed, as described in Section 6. This introduces possible errors in the background subtraction procedure. To avoid this problem, CL-STEM experiment should be performed at sufficiently high current, as described in Section 6.

5.2 Single-Photons From hBN Flakes

One of the main interests of using fast electrons is the broadband characteristics of the excitation mechanism. This is true for different reasons, depending if the excitation is coherent or incoherent (Kociak & Zagonel, 2017). For the coherent mechanism, such as for plasmons, the electromagnetic field of the electron directly creates the excitation. As this field spans a large frequencies range, broadband excitation is possible (Kociak & Zagonel, 2017). For incoherent mechanism, such as electron–hole pairs creation in semiconductors, the reason is subtler. Typically, a bulk plasmon is excited by the fast electron beam, which then decays into electron–hole pairs above the band gap of the material with a given distribution in energy. These pairs will decay toward the band gap and they may create excitation at different energy levels (for example, different point defects at distinct energies). This leads again to a broadband emission excitation, as previously described.

In many cases, this broadband excitation can be quite helpful. It allows one to search a large spectral range in one experiment. Moreover, as it extends into the ultraviolet range, it allows for experiments which may be complicated with optics (either because lasers are technologically complicated or inexistent or because of light absorption in the UV range).

New single-photon sources are actively sought for due to possible applications such as quantum computing and quantum metrology. In the past, most known single-photon sources were point defects in bulk matrices (NV in diamond) or confined semiconductors, such as GaN
(Holmes, Choi, Kako, Arita, & Arakawa, 2014; Kako et al., 2006) or InAs (Moreau et al., 2001). Recently, there have been many reports of single-photon sources observed in layered materials, such as WSe$_2$ (Koperski et al., 2015) and hBN (Bourrellier et al., 2016; Tran, Bray, Ford, Toth, & Aharonovich, 2016).

In this section, we describe how new single-photon source in hBN has been identified using CL-STEM experiments. These have been performed with the HBT interferometer described in Section 2.2.2. hBN is a van der Vaals crystal with a band gap of around 6.5 eV. It has a lamellar crystal structure similar to that of graphite, which allows its exfoliation into monolayers, similarly to graphene. Each layer is constituted by two triangular lattices of B and N. A pure monocrystal of hBN is transparent, due to its large band gap. The optical response of the perfect crystal is dominated by an exciton, which appears at 210 nm (5.9 eV) (Watanabe, Taniguchi, & Kanda, 2004).

The inclusion of defects into the hBN structure creates energy levels which, upon excitation, give rise to light emission in the near-UV to visible range. Recently, a large research activity has lead to the report of many distinct emission centers in the literature. Most of these emission centers microstructure, if not all, are still unknown.

The emission properties of hBN have been explored using CL-STEM. It was observed that a specific emission, around 4.1 eV (Fig. 22), appears in localized spots with a spatial distribution of about 80 nm and is constitute of three peaks at 3.73, 3.91, and 4.09 eV. This specific spectral signature was already known in the literature (Taniguchi & Watanabe, 2007). Its microstructure is still unknown, but EPR (Taniguchi & Watanabe, 2007) and SIMS experiments (Katzir, Suss, Zunger, & Halperin, 1975) point to a carbon-related defect. A broadband emission is observed in the same spectral range as the localized spots. This band is not spatially correlated to the spots. Moreover, its intensity increases as a function of electron dose, indicating that it is probably related to electron damage. It is known that the most common defect created by a fast electron beam in hBN is boron vacancies (Zobelli, Gloter, Ewels, Seifert, & Colliex, 2007). Museur, Feldbach, and Kanaev (2008) have shown that this emission lifetime varies in the 22–200 ns range, with multiple decay behavior, indicating that its microstructure might be that of a donor–acceptor pair.

The high spatial localization of the emission spots indicates that these are possibly individual defects, which may work as single-photon sources,
similarly to what is observed with the NV centers in diamond. To test this hypothesis, we have measured the $g^{(2)}(\tau)$ function in region containing small densities of these emission spots. In Fig. 23 we show the measurement for one of these spots. Initially, for this spot, $g^{(2)}(0) = 0.43$ without background subtraction (due to the broadband appearing in the same spectral range and mentioned previously). The emission rate observed was $6 \times 10^{4}$ photons/s per detector. This count rate is unusually high (at least four times higher than typical NV$^0$ experiments, taking into account the detectors quantum efficiency). The total exposure time was 6 s. Using the method described in

**Fig. 22** (A) ADF image of an hBN flake. The brighter parts of the image are the lacey carbon support film. (B) CL spectra at three different positions on the flake showing all emission components observed in this energy range: three emission peaks at 3.73, 3.91, and 4.09 eV and a broadband emission. Maps of the broadband emission (C) show that it is spatially uncorrelated to the three emission peaks (D and E), while these three are correlated. The three emission peaks appear in localized spots with an FWHM of about 80 nm. Adapted with permission from Bourrellier, R., Meuret, S., Tararan, A., Stéphan, O., Kociak, M., Tizei, L. H. G., & Zobelli, A. (2016). Bright UV single photon emission at point defects in h-BN. Nano Letters, 16 (7), 4317–4321 (PMID: 27299915). [http://dx.doi.org/10.1021/acs.nanolett.6b01368](http://dx.doi.org/10.1021/acs.nanolett.6b01368).
Section 5.1 we have subtracted the broadband contribution obtaining $g(2)(0) = 0.2$. Both values are below the 0.5 threshold, demonstrating a single-photon source.

A second measurement was performed on the same emission spot. The spectrum observed shows the previously observed three peaks with similar intensity. However, the broadband shows a higher emission intensity (Fig. 23D). With the higher background we measured $g(2)(0) = 0.58$. However, once again, after background subtraction $g(2)(0) = 0.2$ (Fig. 23F). These results give support to the fact that the 3-peak emission stems from a single-photon source, possibly a point defect.

The detection of a new single-photon source using CL-STEM experiments demonstrates that standard quantum optics experiments may benefit from the high spatial resolution and broadband excitation available in electron microscopes.
6. LIGHT BUNCHING IN CL

In a first approximation, the physics of excitation creation in semiconductor and wide-band gap materials by fast electron beam is fairly similar to that of off-resonance laser excitation. Therefore CL spectral signature is equivalent to that of off-resonance PL (Mahfoud et al., 2013). However, the exact details of electron–hole pair creation are not the same. In particular, the decay of bulk plasmons may lead to the creation of more than one electron–hole pair, what allows the excitation of different emission centers in finite temporal windows (centers which will be the source of the light detected in experiments). The impact of this particularity is the topic of this section.

As already described in Section 3, most inelastic scattering events of a fast electron in matter create a bulk plasmon (Egerton, 1996), which are collective excitations valence band electrons (Egerton, 1996) and have a typical energy between 10 and 30 eV in semiconductors. These high energy excitation may decay through different channels, including electron–hole pairs with energy close to the band gap energy. As the band gap energy is incidentally smaller than that of the bulk plasmon (3.5 eV in GaN, for example), many electron–hole pair may be created upon a single decay. This fact was already considered in the past, with models predicting different total number of pairs (Klein, 1968). In any case, the key fact is the creation of more than one electron–hole pair per bulk plasmon decay (and also electron–material inelastic scattering).

At this point, it is important to note the typical times involved in the complete scattering/decay/light emission process. The transit time of a fast electron (speed a fraction of the speed of light) during which it interacts with the material is of the order of a few femtoseconds. The created bulk plasmon will eventually decay, possibly creating electron–hole pairs. The decay process takes place in time scales of the order of femtoseconds. The electron–hole pairs created will diffuse until their decay, which might occur while transferring energy to a possible light emission center (such as a NV$^0$ center). This process occurs in a picosecond time scale. Finally, the excited centers will decay emitting photons in a time scale dictated by their lifetimes (from picoseconds to microseconds).

If centers with long lifetimes (compared with the whole excitation process time) are probed, within a good approximation they can be said to be excited synchronously by the decay of a bulk plasmon. In this case, the photons emitted will all exit the sample in a light packet (or bunch) in a time window of the
order of the lifetime. Therefore, if a group of identical emission centers are excited in this way, one would expect to observe the emission of a light bunch for each bulk plasmon created in the material or, within a good approximation, for each inelastic scattering (as most create bulk plasmons).

These packets of photons can be interpreted in a different fashion: for each detected photon, there is a large probability of detecting a second photon for short-time delays (that is, the intensity will show temporal correlations). That is, we should observe light bunching. We should note that this bunching effect is a purely classical effect, due to the creation of multiple electron–hole pairs for each incident electron. This is a particularity of experiments with fast electrons.

The HBT intensity interferometer is an experiment well adapted to observe this temporal correlation. As a large number of photons are available within the bunch, one would expect to find a large number of detection events with small delay times, \( \tau \). This translates to the observation of a bunching peak around \( \tau = 0 \) in the \( g^{(2)}(\tau) \) function.

This bunching peak was first observed in diamond nanoparticles containing a large number of NV\(^0\) centers (Meuret et al., 2015). The bunching peak is shown in Fig. 24A. To be sure that the observed effect was linked to the excitation using electrons, we performed on the same sample an intensity interferometry experiment using a confocal optical microscope with a laser excitation (532 nm). We observed a flat \( g^{(2)}(\tau) \) curve, as expected for an ensemble of identical emitters (Fig. 24B).

It was observed that the bunching peak amplitude with respect to the Poissonian background (uncorrelated) depends on the electron current present in the beam: the amplitude decreases with increasing current (Fig. 24A). This seemingly puzzling observation can easily be explained in view of the process described above. The strong correlation occurs due to the observation of multiple photons stemming from a single electron excitation. However, as different electrons in the excitation beam do not have a phase relation, it is expected that bunches of photons stemming from distinct electrons should also be uncorrelated. That is, as current increases a greater number of uncorrelated photon bunches will be emitted in shorter time scales, leading to a greater number of events with no correlation and, consequently, smaller bunching amplitude. This is in perfect agreement with observations.

The validity of this interpretation was confirmed by a Monte Carlo model, which includes all the elements in the excitation and deexcitation chain described above (Meuret et al., 2015). The key elements of the model are the emission centers’ lifetime, the electron current, electron energy, sample thickness and the number of electron–hole pairs created by each incident
The probability of interaction between electron–hole pairs and the localized also enters the equation, although with smaller influence (Meuret et al., 2015). We should note that the electron current values at which bunching is observed are from a few to tens of pA. For larger currents, this effects should be harder to detect for thick samples.

For the NV$^0$ centers in diamond nanoparticles the lifetime measured is between 10 and 20 ns, in agreement with PL experiments. The predictions of the Monte Carlo model are represented by continuous curves in Fig. 24 in perfect agreement with the experimental data as a function of current. However, for the diamond nanoparticles, the sample thickness could not be measured, as the particle was too thick for low-loss EELS relative thickness measurements (Egerton, 1996). The thickness was estimated from the 2D projection of the nanoparticles and assuming it is roughly symmetric.

To check the model against a more robust dataset, experiments in thin layers of hBN (Fig. 24C) containing a large number of the centers associated
with the single-photon source previously described have been performed. The thickness of the layers was measured using low-loss EELS. Using this information and the previously described measured quantities, the expected $g^{(2)}(\tau)$ can be calculated, which are in agreement with the measured curves.

These two experiments and the associated mode give support to the interpretation provided for the observation of bunching in light emitted from materials excited by fast electrons.

7. LIFETIME MEASUREMENTS AT THE NANOMETER SCALE

An interesting aspect of the light bunching effect described in the previous section is that if only one type of emitter is excited, its associated lifetime can be measured with high spatial resolution. This is true, because the decay of the bunching peak at zero time delay can be approximated by an exponential decay (Meuret et al., 2016, 2015). This can already be seen from the proposed model and from a comparison between the bunching peaks in NV$^0$ experiments with literature time-resolved PL (TR-PL) experiments (Liaugaudas, Davies, Suhling, Khan, & Evans, 2012). We should note that time-resolved CL experiments also allow lifetime measurements (Merano et al., 2005). However, a direct comparison between CL and PL is necessary. Experiments in GaN quantum disks in AlN nanowires comparing these techniques will be described in the next section.

7.1 GaN Quantum Disks: PL vs CL

To demonstrate the equivalence of CL bunching measurements and TR-PL to measure lifetimes a series of experiments in AlN nanowires containing single GaN quantum disks has been performed. The reason to use individual QDisks is that TR-CL do not provide sufficient spatial resolution to distinguish multiple quantum disks inside the same nanowire. These experiments have been performed using the HBT interferometer described in Section 2.2.2 for CL experiments and a confocal microscope also with an HBT interferometer for spatially resolved TR-PL experiments. For the fully optical experiment the spatial resolution was of the order of 1 $\mu$m.

To allow experiments in transmission in the electron microscope and in a confocal optical microscope, the nanowires were dispersed on Si chips containing 100 $\times$ 100 $\mu$m$^2$ holes covered by a 15 nm thick Si$_3$N$_4$ film.
In principle, the experiments should have been performed in the same nanowires, starting with the CL experiments to prevent any electron beam-induced damage. However, during TR-PL experiments, it has been realized that the sample would drift by large distances when nanowires on the thin membrane were excited by the laser beam. This drift was probably a result of thermal dilatation induced by sample heating.

As a result experiments were performed on two sets of nanowires, both on the same Si$_3$N$_4$ grid. The lifetime measurements plotted against the quantum disks emission energy for both techniques are shown in Fig. 25. As one can see, the data points disperse around a line—due to the QCSE, showing that both datasets agree statistically. This demonstrates that light bunching in CL experiments measures the same quantity as TR-PL.

In the next section we will show how the bunching effect can be used to measure lifetimes with nanometer spatial resolution.

### 7.2 GaN Quantum Disks: Spatial Resolution

The lifetime of objects separated by large distances (greater than at least 1 $\mu$m) can be measured by all-optical techniques, such as TR-PL. However, for objects more closely packed, techniques with greater spatial resolution. One solution is the use of time-resolved cathodoluminescence (TR-CL),

![Fig. 25](image_url) **Fig. 25** Lifetime measurements for single GaN QDisks in AlN nanowires using TR-PL (orange diamonds) and bunching in CL (purple circles). The dependence of lifetime with emission energy is the expected one. The statistical agreement between measurements shows that bunching in CL indeed measures lifetimes. *Adapted with permission from Meuret, S., Tizei, L. H. G., Auzelle, T., Songmuang, R., Daudin, B., Gayral, B., & Kociak, M. (2016). Lifetime measurements well below the optical diffraction limit. ACS Photonics, 3(7), 1157–1163. http://dx.doi.org/10.1021/acsphotonics.6b00212.*
such as the experiments described by Merano et al. (2005). In these experiments, so far performed in scanning electron microscopes (SEM) with thick semiconductor samples have demonstrated spatial resolution as good as 50 nm.

To show what can be done with our bunching technique, experiments in stacks of 8 quantum disks separated by 15 nm of AlN in AlN nanowires have been performed (image in Fig. 26A). As previously demonstrated (Zagonel et al., 2011), CL-STEM allows the mapping of the emission energy of similar systems with spatial resolution down to 5 nm. CL-STEM spectrum image in the described system shows that the emission energy of each quantum disk can easily be discerned (Fig. 26B).

In addition to the spectral mapping, the bunching effect can be used to measure the lifetime of each quantum disk. This is shown in Fig. 26C. The measured lifetimes are between 0.5 and 2.3 ns. As expected, higher emission energy is correlated with shorter lifetimes. However, this observation is not true for all experiments reported in Meuret et al. (2016), as deviations from this tendency were seen in different nanowires. This is probably linked to heterogeneities between nanowires, as is commonly the case for these systems.

Fig. 26 (A) ADF image of a NW containing 8 GaN QDisks separated by 15 nm of AlN. (B) Color-coded image of the emission energy at the peak intensity as a function of position. (C) Projected spectrum image (abscissa axis is a spatial direction along the NW axis and the ordinate is energy) showing emission energy as a function of position. The numbers in the colored rectangles show the lifetime measured in ns at each position. Scale bar in (A) measures 10 nm. Adapted with permission from Meuret, S., Tizei, L. H. G., Auzelle, T., Songmuang, R., Daudin, B., Gayral, B., & Kociak, M. (2016). Lifetime measurements well below the optical diffraction limit. ACS Photonics, 3(7), 1157–1163. http://dx.doi.org/10.1021/acsphotonics.6b00212.
8. PERSPECTIVES

The developments described in this text concern the use of the high resolution of a free-electron beam in conjunction with the statistical and quantum properties of light to explore new physics at reduced dimensions. This is a small contribution in a very active field aimed at the active control of electron beams (possibly in conjunction with a light beam) to probe new physical effects. The vast range of new developments, which have large fundamental interest by themselves, might be efficiently coupled to experiments such as those described here to dive deeper in quantum nanooptics.

For example, pulsed guns technology, should they be applied to SEM (Fu et al., 2014; Grundmann, Christen, Bimberg, Fischer-Colbrie, & Hull, 1989; Merano et al., 2005) or to TEM (Barwick, Flannigan, & Zewail, 2009) are progressing quickly, with typical pulses times duration ranging from sub-picoseconds to nanoseconds. There is, therefore, room for applying the power of PL techniques relying on time resolution to CL (Meuret et al., 2017). In addition, it has recently been demonstrated that quantum optical experiments with the free-electron beam of a TEM could be performed (Feist et al., 2015). In other words, it is possible to evidence the quantum nature of the free-electron beam through the creation of quantum superpositions of free-electron states. Combining the full quantum properties of the incoming electron, the material of interest and the electromagnetic field is a totally new and exciting field of investigation. Finally, the wave behavior of the free-electron beam is at the basis of many imaging techniques in EM (high resolution, holography and all their derivatives). However, only very recently it has been possible to manipulate the phase of the free electrons with the flexibility that is ordinary in optical physics. This has first been demonstrated to form exotic forms of waves such as vortex electron beams (Verbeeck, Tian, & Schattschneider, 2010). Phase-shaped beams can be now created with theoretically any symmetry. Symmetry engineering has been proved to be extremely efficient to study surface plasmons symmetry (Guzzinati et al., 2016) in the visible range. We can guess that such symmetry engineering would be quite useful to the study of quantum nanooptical systems.

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REFERENCES

Barjon, J., Tillocher, T., Habka, N., Brinza, O., Achard, J., Issaoui, R., … Bergonzo, P.
(2011). Boron acceptor concentration in diamond from excitonic recombination inten-


Beveratos, A. (2002). Réalisation expérimentale d’une source de photons uniques par fluorescence de
centres colorés dans le diamant. Application à la cryptographie quantique. (PhD thesis).
Université Paris XI.

from single NV color centers in diamond. In P. Tombesi & O. Hirota (Eds.), Quantum
communication, computing, and measurement 3. New York: Springer.

Bourrellier, R., Meuret, S., Tararan, A., Stéphan, O., Kociak, M., Tizei, L. H. G., &
Zobelli, A. (2016). Bright UV single photon emission at point defects in h-BN. Nano
6b01368.

variation in grains of CVD diamond film. Diamond and Related Materials, 4(10),

Das, P., Chini, T. K., & Pond, J. (2012). Probing higher order surface plasmon modes on
individual truncated tetrahedral gold nanoparticle using cathodoluminescence imaging
and spectroscopy combined with FDTD simulations. Journal of Physical Chemistry C,

org/10.1016/j.physrep.2013.02.001.

V2.42: A fast and easy-to-use modeling tool for scanning electron microscopy and

Edwards, P. R., & Martin, R. W. (2011). Cathodoluminescence nano-characterization of
semiconductors. Semiconductor Science and Technology, 26(6), 064005.


Quantum coherent optical phase modulation in an ultrafast transmission electron micro-


Fu, X., Jacobin, G., Shahmohammadi, M., Liu, R., Benamer, M., Ganiere, J.-D., … Yu, D.
(2014). Exciton drift in semiconductors under uniform strain gradients: Application to

(1997). Scanning confocal optical microscopy and magnetic resonance on single defect cen-


