FINDING AND CHARACTERIZING NV CENTERS OPTICALLY USING AUTOMATED SOFTWARE

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Abstract

To boost the research on technologies using single photon emitters, software has been developed to automate the process of searching and characterizing nitrogen-vacancy centers. During this project the distinct properties of nitrogen-vacancy centers have been studied and using software controlling the optical setup been formed into routines. A rough search was done using a peak finder looking for local maxima and characterizing was done using spectrum, correlation, lifetime and power measurements. The written routines and characterisations were tested by comparing their outputs with the desired outputs and proved itself to be trustworthy enough to be used in upcoming experiments.

Contents

1 Introduction

Wouldn't it be striking to send information faster than light? Using quantum teleportation, a piece of quantum information can be transmitted from one location to another without it being transmitted through space. Or to build a quantum computer, to use the rules of quantum mechanics to solve computational problems more efficiently? Or to use quantum cryptography, to send secure data which cannot be intercepted without noticing?
Many of these applications use single photon emitters on their basis. A defect in diamond known as the nitrogen-vacancy (NV) center as shown in figure 1 is such an emitter and distinguishes itself by its stability, possibilities to manipulate its quantum state and measurability at room temperature. To strengthen the research of these new technologies, lots of NV centers are needed and their properties have to be determined.

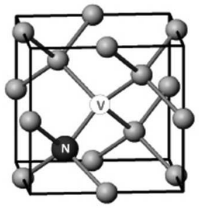


Figure 1: Nitrogen-Vacancy center as shown in [1]. a nitrogen atom (N) is substituded next to an empty lattice location (V).

The main goal of this project was to automate the process of finding and characterizing NV centers. To that purpose, new measurement software was developed to find single emitters, analyze them to determine whether or not NV centers and at the end characterize them.

2 Experimental method

The first step in the process of finding and characterizing NV center is a two dimensional (2D) confocal photoluminescence scan of the sample using a home built confocal microscope setup.

2.1 Optical setup

The sample is placed on a piezoelectric two-dimensional scanning unit (stage) which can move the sample. As seen in figure 2, the 532nm green laser comes in from the top, reflects on the beam splitter and enters the microscope objective. The objective can be moved parallel to the laser beam causing a change in the focus position on the sample. The focused excitation light hits the sample and thereby excites the NV-centers and its surroundings, causing them to emit fluorescent light back into the objective. This red light passes the beam splitter, reflects on the rotatable mirror, passes the pinhole and enters the photo detector. A rotatable mirror is used to align the incoming green laser with the red light emitted from the sample. A so called pinhole is used to filter light of the wrong focus depth. A beam focused on the sample will be focused on the pinhole and thus passes through while an unfocused beam will be unfocused at the pinhole and thus mostly hits the surroundings. The result is an optical

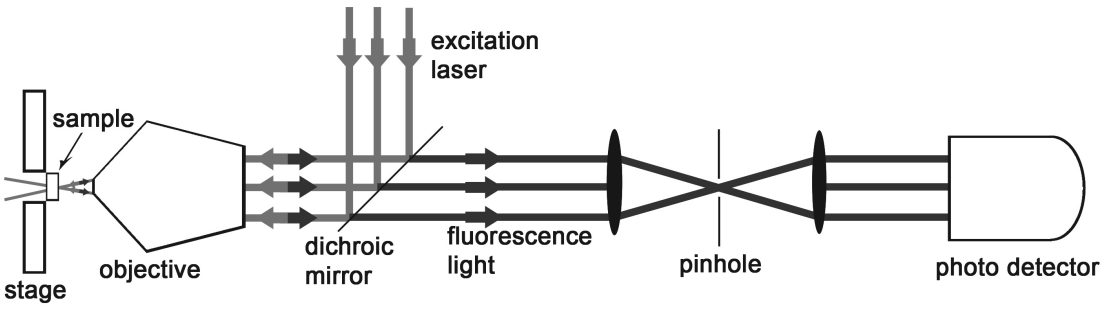


Figure 2: A simplified version of the experimental setup used to measure the fluorescent light. The laser (532 nm) is focused onto the sample. Fluorescence light is collected using the same objective, led through a pinhole and detected by a photo detector.

setup with variable focus able to scan the whole sample bit by bit and outputting its data as a two dimensional data array of intensity values. A visualization of this data can be seen in figure 3.

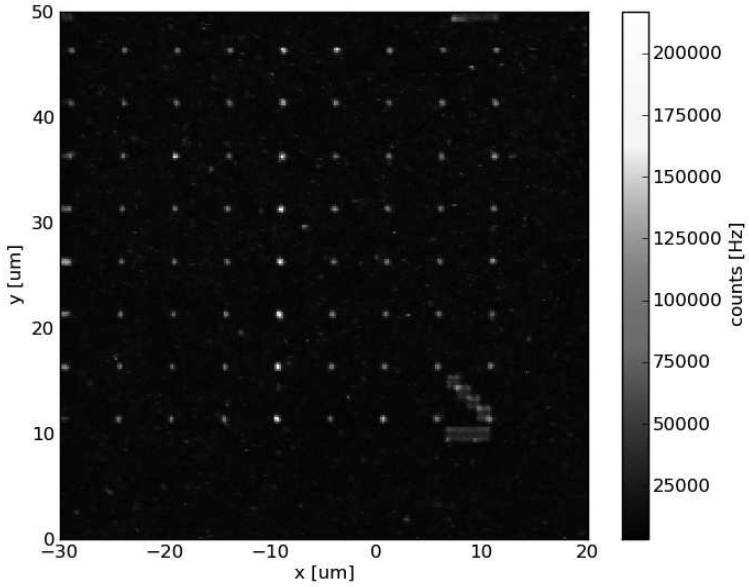


Figure 3: A 2D scan of a part of the crystal sample. The bright spots are golden structures used for indicating the coordinates on the sample.

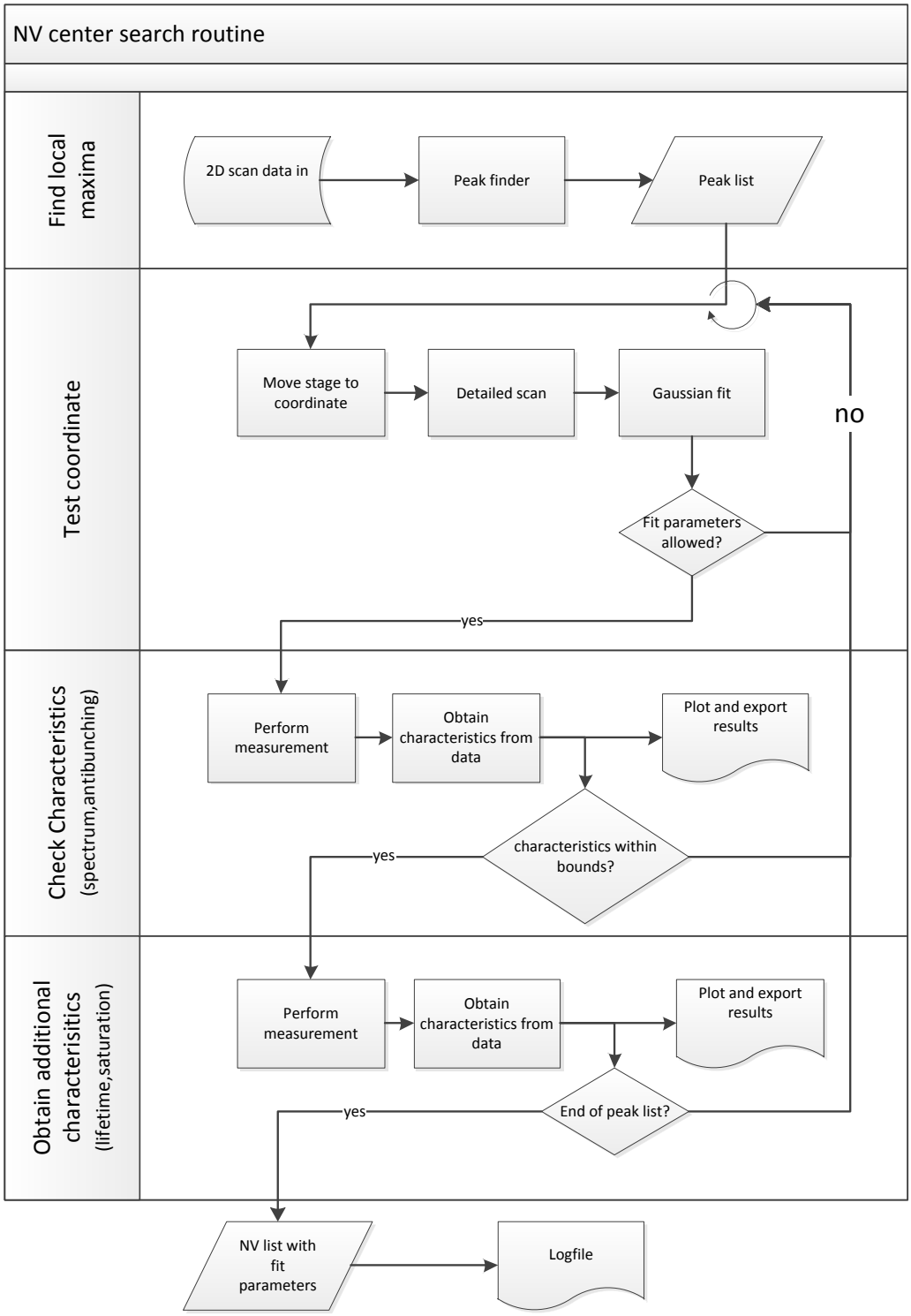


Figure 4: Flow diagram of the NV center search routine.

2.2 Routine

Once the two dimensional overview of the sample has been obtained, enough data is available for the software to start its routine. A graphical overview of this routine is shown in figure 4. The result of the two dimensional scan is analyzed by peak finder software resulting in a list of coordinates of possible NV centers. Then, the list is filtered by visiting the coordinates one by one and performing a detailed scan on its location. If the peak on that coordinate is still present and appears to be a NV center candidate, a spectrum measurement is done. The resulting spectrum then shows whether or not a NV center is present on the coordinate. Next, an antibunching measurement is done checking whether or not the coordinate contains only a single NV center. If indeed a single NV center is found, an additional lifetime and saturation measurement is done to fully characterize its optical properties.
The search for and characterization of the NV centers is done using measurement scripts controlling the individual measurements. These scripts are all modular, so new measurements can be added as desired. On top of that, all parameters the user would want to change are stored in an easy to reach settings variable. When for example the optical setup changes or other samples are used, one does not have to search the code, but suffices by changing these constants. These settings also include the measurements to be done, in which order and for what duration.
During the execution of the measurement and algorithms, everything is logged into log files and the measurement data and plots are saved. All is done using automated, intuitive naming containing time and date stamps so any information about the process is easy to retrieve. By studying the theory of the NV centers, one can know what to expect when measuring. This way it is known that photons leaving the emitter should do that one at a time (anti-bunched). On top of that, the NV-center is a special type of single photon emitter and has some specific characteristic values for its radiative lifetime, saturation power and spectrum of the photoluminescence. Using the software and its routines these values are automatically extracted from the measurement data and compared to the expected values for NV centers. The expected values are defined by the user as verification parameters. These parameters set the boundaries in which the measurement results should be to be counted as a NV center.

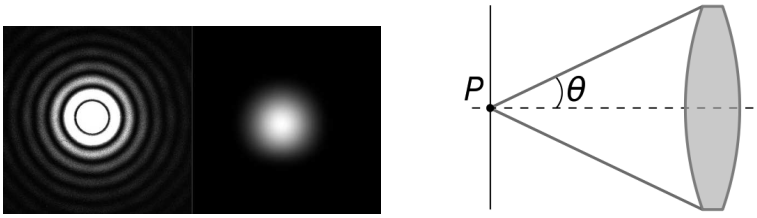
2.3 Sample

The samples used in this work are formed by putting a drop of nanocrystal resolved in water on a thin plate of glass (200 μm, SiO_2). After evaporation of the solvent, the nanocrystals remain and NV centers are randomly spread over the sample. On top is a thin layer of Sapphire (5 nm, Al_2O_3). Gold markers are used to indicate the coordinates of the found NV centers. The samples used in this project are actually of bad quality compared to samples using bulk diamond. So the measurement will have bad signal to background ratio's and the 2D scans like in figure 3 will not be very representative.

3 Point sources

The first step in the search for NV center is the search for point sources on the sample. As will be clear later, these point sources will not show up as single spots but rather a spread dot. Ideally, due to the higher fluorescence compared to its surrounding background, a NV center will stand out in the 2D scan.

3.1 Diffraction limit



(a) (b)

Figure 5: (a):Airy pattern left versus Gaussian pattern right, (b):Numerical aperture of a thin lens.

All optical setups have a resolution limit which comes up when focusing to objects smaller than the wavelength of the used light. When focusing a laser beam on a spot, the focus is never a single point but rather some sort of diffraction pattern as seen in figure 5(a). The other way around the same applies, so the light coming from a point source (opposite of focus) will reach the detector (to be seen as the opposite of a laser source) as a diffraction pattern. So the image of a distant point source, as formed by a converging lens, is never a point but rather some sort of finite sized spot. We are essentially collecting only a fraction of the incident wave front and therefore cannot hope to form a perfect image. When using circular lenses, the diffraction pattern is a circular spot known as the Airy disk. The central disk is surrounded by some ripples where the intensity is zero. In practice, this Airy disk is approximated as a Gaussian pattern by neglecting these ripples because they are small compared to the central disk.
The width of the central peak is equal to $d \approx 1.22\frac{f\lambda}{D}$ [3] where D is the aperture diameter; f is the focal length and λ is the wavelength of the used light. When trying to get the highest possible resolution, the width of the central peak should be as small as possible. Therefore the wavelength λ and focal length f should be small, and the aperture diameter D should be large. See figure 5(b). When writing d terms of the numerical aperture of the used objective using $NA = nsin(\alpha) \approx n\frac{D}{2f}$ with n the refractive index of the immersing medium and the angle, the width of the central peak is equal to

$$d \approx \frac{0.61\lambda}{NA}. \tag{1}$$

3.2 NV Center appearance

As seen above, the image as formed by a converging lens is not infinitesimal focused on a spot but is spread in a diffraction pattern. The NV-center cannot be seen as a point-source because it is in de order of Angstroms while the wavelength of the used light is in de order of microns. When scanning the sample, the stage will sweep underneath the laser. On every pixel, the stage waits a small amount of time to determine the number of photon counts per second of this location. For a point source, like the NV center, the resulting image of it is a Gaussian patternwith a width calculated by equation 1. In this experiment, the numerical aperture of the used objective is $NA = 0.95$, the wavelength of the used laser is 532 nm and thus the width is equal to 360 nm.

3.3 Algorithm for finding point sources

A peak finding algorithm is used to find local maxima in the data of the 2D scan of the sample. The algorithm first uses user-defined count-values for the minimum and maximum peak counts and background counts. The algorithm scans the data looking for local maxima that are within the boundary count values set by the user. For the sample in figure 3, the upper boundary is set to 6e4 to exclude the gold markers, and the lower boundary is set to 1e4 to exclude local maxima in the background. Next, the width of the peaks is tested. We saw that when obtaining the 2D map, point sources like NV-centers will show up as Gaussian spread dots. Knowing this, the algorithm now filters the peaks in its data that do not satisfy this property by fitting a Gaussian function to the peaks in both vertical and horizontal direction. A peak should be at least wider than the width of the Gaussian diffraction pattern calculated by equation 1 because it otherwise cannot come from a point source, but will rather be due to a measurement artifact or possibly a NV center which bleached while the laser swept over it.
A peak can neither be much wider that the width of the Gaussian diffraction pattern because it is surely no single NV center then. The algorithm uses the values for the minimum and maximum peak width defined by the user and compares these with the standard deviation of the Gaussian fit. The result is a list of peaks proven to be good enough to be extensively measured.

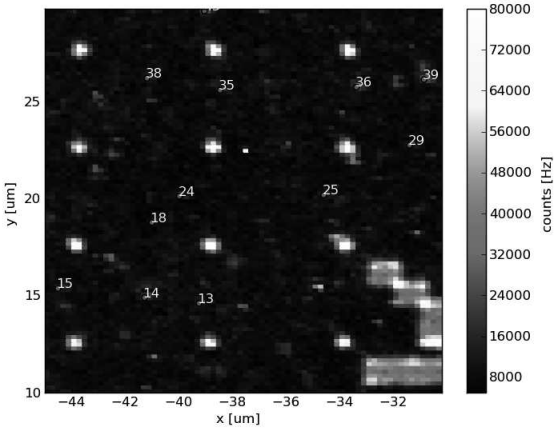


Figure 6: A small part of the sample analyzed using the peak finder algorithm. The marked peaks are still candidates for being a NV center. Later measurements made clear that only NV-14 and NV-36 were actual NV centers.

When this analysis is done, the list of coordinates is passed to another routine. This routine then moves the stage to that coordinate and tries to optimize its location around the peak. This is done by a short sweep scan in both x and y direction over the coordinate followed by a Gaussian fit. When the fit fails or has not all parameters such as the standard deviation within the boundaries, the peak is marked as not being a NV center and further measurements are skipped. There is also a change for the spot being a bleaching spot, meaning that it is becoming less active when excited by the laser and at the end not visible anymore. A bleaching spot will of course not fit the parameters and will thus be skipped. When the fit is successful, the fit parameters are within the set boundaries and the spot does not bleach, the next measurement is started.

4 Spectrum

On the coordinates which are likely to contain a NV center, a spectrum measurement is performed. This measurement gives a strong indication whether or not a NV center is present, but takes some time to complete depending on the setup, sample and other influences. The spectrum of the photoluminescence can be used to identify a NV center because these have a characteristic emission. A two level model is used to explain the emission spectrum of a NV center.

4.1 The NV center spectrum

This two level model considers the structure of the NV center as if it has only a ground and an excited state as seen in figure 7. Actually it is a structure containing five levels, but the two level model does its job well enough to be used.

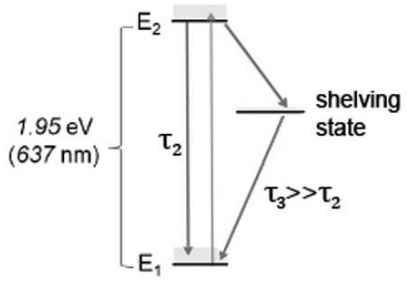


Figure 7: Two level model of NV center (with additional shelving state for explaining anti-bunching later) with the vibronic levels in grey. During the transition from E_2 to E_1 a photon is emitted while from the shelving state to E_1 is not. These transitions occur with a lifetime of τ_2 and τ_3 respectively.

The energy difference of the two levels is in such a way that when an electron falls from the excited state to the ground state, a photon is emitted with a energy of 1.95 eV corresponding to a wavelength of 637 nanometers. In the photoluminescence spectrum, this accounts for the so called 'zero-phonon line' peak, where zero-phonon is another way of saying that the energy was unaltered. In figure 7, this is a transition between the two bold lines. Besides this peak, the spectrum contains a broad side band, due to the vibrational degrees of freedom of the NV center [4]. To understand the spectrum graph, one should understand the Franck-Condon principle. The Franck-Condon principle explains the intensities of the transitions, which are changes in electrons and vibrational energie in the molecule due to the absorption or emission of a photon with a corresponding energy. The principle poses that a transition is more probable if the wavefunctions of their states overlap. Transitions with a high probablity occur more often and thus give a higher intensity in the measurement.

4.2 Spectrum analysis

The script initiates the spectrum measurement for a default time of 30 seconds and analyses the data afterwards.
Figure 8 shows the spectrum of a typical NV Center together with the spectrum random background. Notice the zero phonon line around a wavelength of 640 nm on the first plot.

This peak on a hill differentiates the NV center spectrum from the background spectrum and can thus be used to determine the presence of a NV center. The data around the local peak is fit with a Gaussian on a slope having a formula equal to

$$h + ax + Ae^{-\frac{(x-\mu)}{\sigma^2}} \tag{2}$$

Where a is the slope of the hill, σ is the standard deviation of the Gaussian and μ the location of the center of the peak. Checking whether or not the fitted data is on an ascending hill by checking the slope value to be positive, the standard deviation is within a normal range and μ is around 640 nm, gives the verdict of spectrum being from a NV center or not.

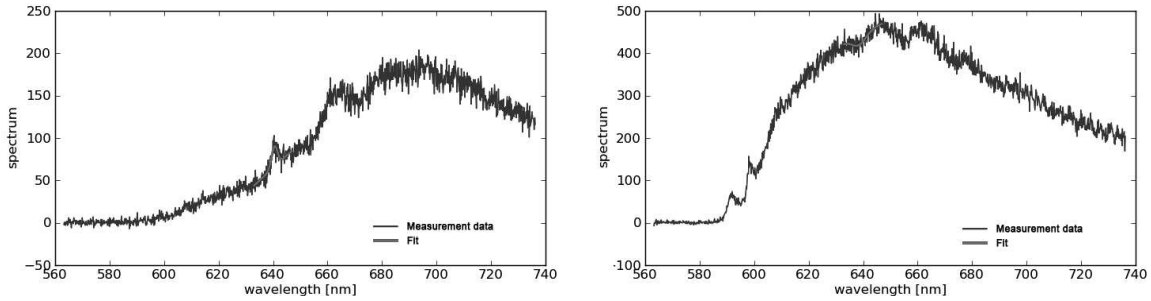


Figure 8: Plots of two spectrum measurements. Left, a NV center is measured with its zero phonon line on 640 nm and a standard deviation of its Gaussian fit of 1.1. Right, a gold marker is measured, which does not contain a zero phonon line and will thus not be included as a NV center.

5 Antibunching

With the spectrum measurement done, we accept the spot as a NV center. But it is still unclear whether it is only one as desired. Therefore an antibunching measurement is done using the Hanbury Brown-Twiss experiment. When the single photon emitter is really only emitting a single photon at a time, the fluorescent photon stream should be antibunched. To check this, the principle of the Hanbury Brown-Twiss (HBT) experiment is used [2].

5.1 Hanbury Brown-Twiss experiment

In the HBT experiment, the fluorescence is first led through a 50:50 beam splitter. A photon reaching this beam splitter has a 50% change of entering the first channel and a 50% change of entering the second channel, always enters one and never enters two of them. One of the channels is a bit longer which gives us a known time interval comparing the ends of both channels. At the end of the channels the photon will be detected by one of the two detectors. A photon hitting the first detector will start a counter. When another photon hits the first detector the counter stops and the time interval is noted. This way a graph is made showing how much each time interval occurred. When two photons enter the beam splitter at exact the same time, because they are from the same source, they are counted on the time interval known from the difference in length of the channels. So when in the correlation graph a dip emerges in the data on that time interval, it is known that there are less photons coming in

exactly at the same time. The dip will never reach zero because there are always photon pairs coming in at the same time from background fluorescence.

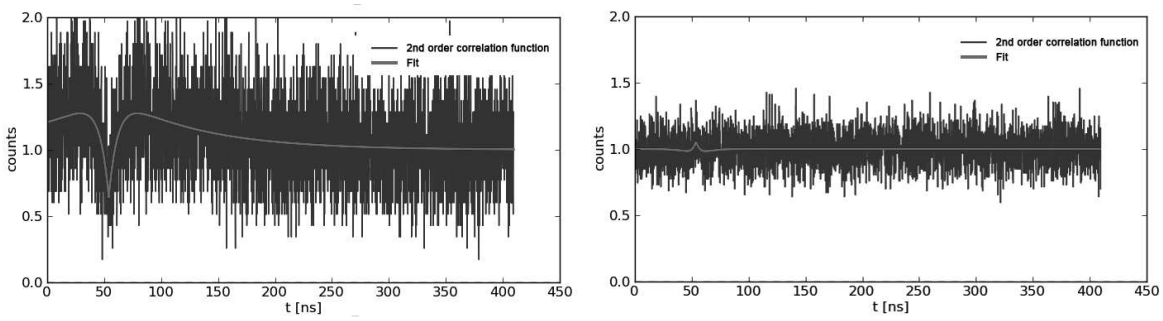


Figure 9: second order correlation functions of a NV center (left) and a gold marker (right) fitted with exponential functions resulting in a dip depth of 0.36 for the NV center. The dip at t=50ns actually is at a time difference of zero due to the on purpose difference of optical fiber lengths.

The count value is set at longer time delays to be equal to one by normalizing the data. At long time delays, there is a high probability that the shelving state has been reached. Once in the shelving stage, the NV center needs some time to fall back into the ground state. This transition has a lifetime τ_3 that is much longer than the transition from E_2 to E_1 and besides that, no photon is emitted. The result is a lower number of counted photons.
At time delays around 50 ns (and thus an actual time delay of 0 ns because of the length difference in the optical fibers), the probability is somewhat higher than one. This is because at these time delays the probability that the shelving state (see figure 7) was reached is low and thus more photons where emitted and thus counted by the measurement.

5.2 Analysis of the second order correlation function

The data is fitted with a second order correlation function of the form

$$A\left[1 + c_2 e^{-\frac{|x-x_0|}{\tau_2}} + c_3 e^{-\frac{|x-x_0|}{\tau_3}}\right] \tag{3}$$

As used in [5]. Here, A is the normalization factor to let the correlation equal one at both ends. From the fit parameters, the measured dip can be calculated as

$$dip = 1 - (1 + c_2 e^0 + c_3 e^0) = c_2 + c_3. \tag{4}$$

As noticed above, this dip is the measured dip and not the actual dip because of background fluorescence. To account for this background fluorescence, the signal to background ratio of the two detectors is determined with a saturation measurement. As in chapter 7, the saturation curves of both the NV contribution and the background are measured and fitted. Dividing the two gives the signal to background curve as seen in figure 9. Only thing that remains is checking the power at which the anti-bunching measurement is taking place and get the signal to background value from the curve. This is done for both detectors and results in two values between zero and one: α_1 and α_2 .It has been showed [1] that the actual zero without background is equal to

$$correction = 1 - \frac{\alpha_1 \alpha_2}{(1+\alpha_1)(1+\alpha_2)}. \tag{5}$$

The actual dip depth is eventually calculated by dividing the measured dip with the background correction.

$$depth = dip/correction \tag{6}$$

To determine whether or not a measurement was from a NV center, the depth of the fit is checked. This depth should be higher than 0.05 to count.

6 Lifetime

Now that the local maximum is for sure a NV center and, on top of that, a single one, more information is desired. For that reason the radiative lifetime is determined from a measurement using a pulsed laser.

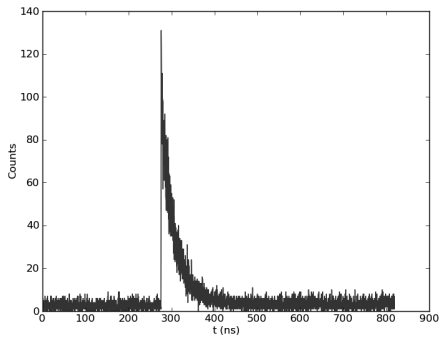


Figure 10: Plot of a lifetime measurement of a NV center. At t=280ns the pulse was send and at that point the number of counts falls off exponentially.

A single photon emitter will, when excited into its higher state by a laser, fall back into its ground state and thereby emit a photon. After being excited the photon is not emitted immediately, but rather after some radiative time specified by the inverse of the Einstein coefficient [2]. This coefficient governs the rate at which spontaneous emission occurs; the process by which an electron in an upper level drops down to a lower level. The change of the occurrence of this emission is an exponential decay function with a decay constant equal to the radiative lifetime. The value of the radiative lifetime for a transition can range from about a nanosecond to several milliseconds, according to the type of radiative process that occurs. For a typical NV center in nanocrystals, the lifetime has been reported as 22ns [5].
To measure the lifetime, a pulsed laser was used producing short pules of excitation light with a duration of around 100 pico seconds. After the pulse is fired, the photo diode waits for the emitted photon to arrive and stores the duration. This is done many times and the result is data as in figure 10.

6.1 Analysis of lifetime

Fitting this data with an exponential decay function of the following form

$$h + Ae^{-\frac{(x-x_0)}{\tau}} \tag{7}$$

leads to the value of the lifetime τ for this measurement. Here h is the offset of the exponential decay, x_0 is the time at which the pulse is fired and A a normalization constant. Figure 11 shows the exponential fit of the lifetime measurement together with its error. When not a NV center, but for example a gold marker or some random background is measured, the result will be a lifetime of around zero.

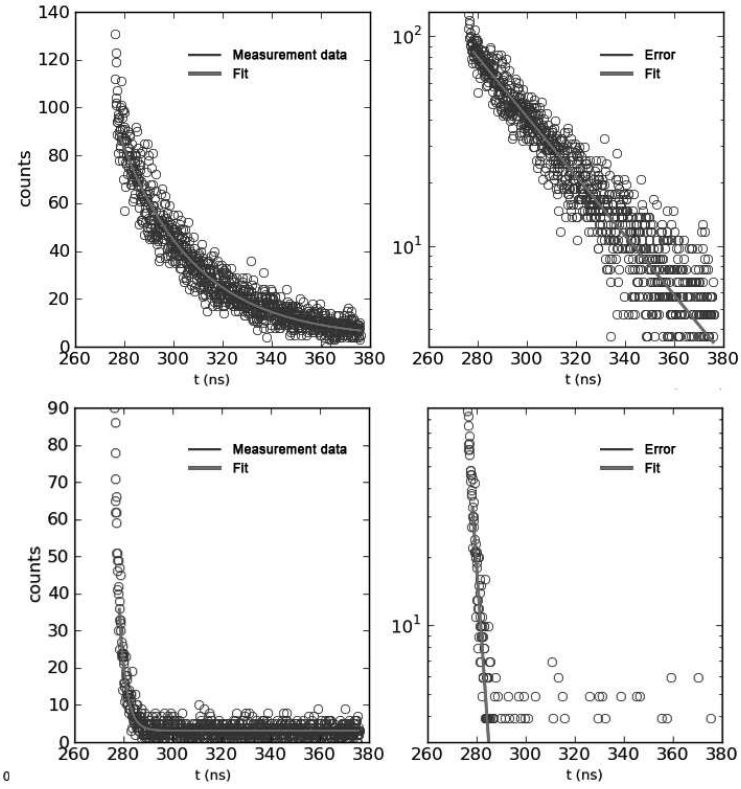


Figure 11: The left subplots show the fit of the lifetime measurement of a NV center (above) and gold marker (below) resulting in a lifetime of $\tau = 30.6$ ns and $\tau = 3.1$ ns respectively. The data is fitted with an exponential decay function. The right subplots show the errors of the fit.

7 Saturation

7.1 Photoluminescence

When exciting a single photon emitter with increasing power, it eventually gets saturated. At low power, at some moments the emitter is not excited and will thus not emit a fluorescent photon until it gets excited and falls back to its ground state again. With increasing power,

the change of the emitter getting excited by the laser photons approaches one and will be excited almost any time. Then every lifetime, a photon is emitted by the emitter, but never more than that. The number of photons emitted per second, photoluminescence (PL), as a function of incoming laser power is of the form

$$I = I_\infty \frac{P}{P_{sat} + P}. \tag{8}$$

P_{sat} is the power at which the PL saturates, and thus the rate at which the emitter excites is no longer depending on the laser power, but rather on its lifetime. A rough way of determining the saturation power is to check at which power the fluorescence counts are half of the fluorescence counts at high power. In the case of this optical setup, the typical value for the saturation power is 0.4 milliwatt, but this will differ for other setups.
The background around the single photon emitter however will not be saturated with increasing incoming laser power. Because the background consists of many different types of photoluminescence, the signal of the background will just increase linearly with excitation power. So increasing the laser power will not only increase the number of counts from the single photon emitter, but also from the background. Using the highest possible excitation power is therefore not the best option. By calculating the signal to background ratio, the power value at which the single photon emitter is most distinct from its background can be found.

7.2 Analysis of saturation measurement

The algorithm uses the PL data of the total, NV-Center contribution and background. It then fits the total and NV center data with the function of formula 8 and the background with a linear function. A plot shows the result with the corresponding fit values like figure 12.

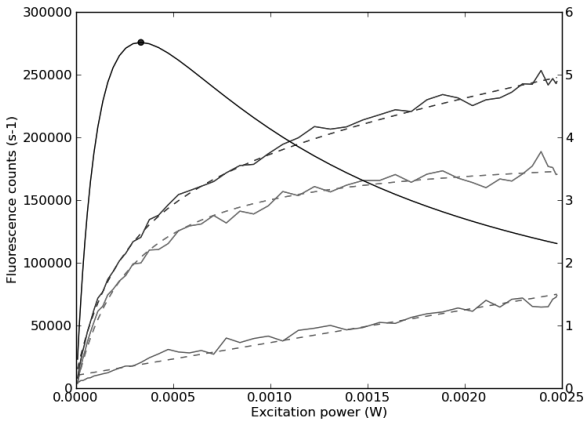


Figure 12: The number of photons emitted per second versus the excitation power of the incoming laser of the background, NV and total contribution in green, red and blue respectively with their fits dashed. The result was a saturation power of 0.4 mW. In black, the signal to background ratio is plotted with its maximum on 0.34 mW. note: this data was measured using a different numerical aperture causing the high fluorescence counts.

Data obtained while aiming on a single photon emitter is shown in blue. The red line shows the signal data minus the background data and thus the fluorescence of only the single photon emitter. Data obtained while not aiming on a single photon source is shown in green. Then, by dividing the fit values of the NV-Center data on the fit values of the background data the signal to background values are calculated. The algorithm then searches within these values for the maximum values and shows that in the plot like figure 12.

8 Performance and Conclusions

The performance of the measurement script was tested on a nanocrystal sample with known NV center location. First, a list of 20 known NV centers of good quality was used as input. The result was them all being marked as indeed being a NV center. Next, using the peak finder, the sample was scanned and analyzed and an extended list was found containing some non-NV centers. None of the non-NV centers were marked as if they were NV centers. Some of the NV centers in the list where marked as not being one. In 70% of the cases this was due to a fit of the spectrum resulting in parameters trespassing the set verification parameters. In the rest of the cases this was due to the optimization of the peak not working because of the bad signal to background ratio on that location. Another advantage of this is that only NV centers of good quality will be found.
The samples used during this project did not lead to very good optical measurements. The signal to background ratio has a maximum of 5.5 where one usually expects 20. For testing the performance of the measurement scripts, this bad quality has actually an advantage. A script working on a sample of low quality, will only work better on a high quality sample like bulk diamonds. And besides that, the low quality NV centers which are unwanted will be removed from the data resulting in a list of only good, usable and stable NV centers.
As an improvement to this work, one can perform a electron spin resonance measurement instead of the spectrum measurment for a more confident list of NV centers. Moreover, by adding additional software controlling the routines in this project, it is possible to measure the whole sample automatically instead of only the current range. And when using a bulk diamond as sample, additional software could be added to measure on different focus depth automatically.

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