Time-Resolved Fluorescence Signals of Barium Monofluoride

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The image on the front page represents the time-evolution of fluorescence; it shows the rotation and decay of a dipole emission pattern in a magnetic field. It was produced using a two-dimensional implementation of the model described in the text.
1 Context of the research: measuring the eEDM with BaF

1.1 eEDM measurements

This Master’s research project was performed as part of the NL-eEDM collaboration, which aims to measure the electron’s electric dipole moment using the barium monofluoride molecule as described in [1].

An electric dipole moment of a fundamental particle is a measure of the asymmetry of its internal charge distribution. If the electron were to possess a nonzero eEDM, it could help to explain the matter-antimatter asymmetry (CP violation) present in the universe that is currently unexplained by the Standard Model [2]. Theories that postulate as of yet undetected matter and gauge fields as extensions of the Standard Model predict values for the eEDM that are much larger than the Standard Model prediction. This makes eEDM measurements a competitive means to search for physics beyond the Standard Model.

The current upper limit on the eEDM has been determined in an experiment using ThO [3] as $10^{-29} \, e \cdot cm$. Molecules are often used for these measurements as they cause an effective enhancement of the eEDM due to the large electric field near the heavy nuclei [4]. The experiment proposed by the NL-eEDM collaboration has a projected sensitivity to an eEDM of $5 \cdot 10^{-30} \, e \cdot cm$. The proposed measurement by the NL-eEDM collaboration using BaF will attain this sensitivity primarily by maximising the coherent interaction time by slowing down the BaF beam using Stark deceleration and laser cooling. An outline of the full experimental strategy for the measurement of the eEDM using BaF is shown in Fig. 1.1.
1.2 Supersonic BaF source

To test various aspects of the full experimental design, and to perform spectroscopy of BaF and develop the necessary skill in manipulating the BaF molecule, a supersonic source is being used [5, 6]. This source produces a fast internally cold supersonic molecular beam in vacuum conditions. The molecules are excited by resonant laser radiation downstream of the source in a detection chamber. Laser-induced fluorescence (LIF) is detected by a photomultiplier tube (PMT) with sub-nanosecond time resolution. The full setup is described in [5], and overview is given in Fig. 1.2.

The research described in this report contributed to a measurement of the excited state lifetime of BaF by quantifying the modulation of the fluorescence signal due to quantum beats. This measurement is described in [5].

Figure 1.1. An overview of the experimental strategy of the NL-eEDM collaboration to measure the electron-EDM using an intense, cold and slow beam of BaF molecules.
Figure 1.2. Schematic overview of the experimental setup. BaF molecules are produced in a supersonic source and pass through a skimmer into the interaction region. The light from a Ti:Sa laser is delivered to the molecular beam via a 50 m single-mode optical fibre where it interacts with the molecules. Fluorescence is detected by a photomultiplier tube.
2 Testing and applying NIR-absorbing surfaces to reduce stray light in a LIF detection setup

2.1 Introduction

To increase the signal-to-noise ratio of the fluorescence signal (Fig. 2.1) from the BaF supersonic source, two categories of improvement measures were proposed. The first entails changing the components and geometry of the light detection system and laser beam to increase the signal, i.e. the number of fluorescence photons that are counted by the PMT. The second comprises the reduction of the background (noise) by minimising the amount of stray light in the detection setup through the introduction of light absorbing surfaces. Candidate surfaces had to show high absorbance at the wavelength of the detection laser (860 nm), which is the most significant source of light in the detection setup. In addition, the surfaces had to be compatible with high vacuum, and needed to be easy to apply to the components in the detection setup.

The research described in this chapter concerns the testing and application of such surfaces. In short, this research thus has the following goals:

1. To choose a light-absorbing surface that can be applied in a LIF detection chamber to reduce stray light significantly.

2. To develop a method to assess the relative reflectance of candidate surfaces quantitatively.

3. To find the optimal way to apply and handle this surface such that the background of the LIF signal is minimised.
2.2 Measurement methods

In order to assess the relative reflectance of different materials at 860 nm, a measurement method was developed. This method uses a CCD camera that images a screen, onto which light reflected from the sample is projected (Fig. 2.2). This method was quick to realise in the lab, and facilitated very fast measurements of different samples.

2.2.1 Experimental setup

In the measurement setup, laser light from a laser diode at 860 ± 5 nm passes through a beamsplitter, where part of the light (≈ 1 mW) is split off and is incident on a power meter to measure the power output used. The rest of the light (≈ 3 mW) is incident on the sample, mounted to a holder such that the plane of incidence is normal to the sample surface. Part of the reflected light is projected onto the screen, which is a piece of white paper. It is assumed that the screen reflects all incident light diffusely, i.e. Lambertian. The screen is then photographed using a CCD camera, of which the pixels are assumed to each have a near-identical linear response. The geometry is such that the angle of incidence of the beam on the sample is around 22.5°. The
The distance between the screen and the sample is approximately 15 cm. The camera images a part of the screen of roughly 18 by 11 cm, which is more or less centred around the specular ray. The camera thus images the light reflected into a solid angle of approximately 1 sr centred around the specular ray as projected on a screen.

**Figure 2.2.** Diagram showing the experimental setup used to measure the reflectance of various surfaces. NIR light from a laser is incident on the sample, and is reflected onto a screen. A part of the screen of 18 by 11 cm is imaged using an IR sensitive CCD camera. The distance between the sample and the screen and the camera and the screen is approximately 15 cm.

### 2.2.2 Measurements, image processing, and variations

Samples were mounted in the beam and a photograph using an exposure time of 332.5 ms was made. The sample was then moved in the holder so that the laser beam was incident on a different point on the surface. For each sample, photographs using at least three different points on the surface were made to estimate intra-sample surface variations $\sigma$, which was determined as the largest discrepancy found between a measured value and the average. An image of the screen was recorded with the laser turned off to measure the background intensity.

Photos in the form of bitmap images ($1216 \times 1936$ 8-bit pixels) were processed using a Matlab script (see Appendix 5.1) to yield intensity profiles of the screen. The aforementioned background intensity was subtracted, and features due to noise and diffraction (speckle pattern) were subsequently mitigated by averaging over blocks of
pixels (25 × 25). Specifically, this was done by replacing the intensity of each pixel in the block by the average intensity over all pixels in the block. Projections onto height and width were made by summing all pixels in rows and columns respectively. Half widths at half maximum of these projections $w_{x,y}$ were calculated. The sum of all pixels $I_{\text{tot}}$ was also calculated and constitutes an estimate of the total relative reflectance.

### 2.3 Reflectance measurements

#### 2.3.1 Comparison of various materials

As an initial step towards finding a suitable surface, some readily available samples of different materials were tested. These included:

1. ‘Anodised Aluminium’: Black anodised aluminium
2. ‘CuO’: Various pieces of copper with a cupric oxide surface (CuO, as described in [7])
3. ‘Paint (OP)’: Various pieces of copper painted with MLS-85-SB paint [8]. The painting was performed in 2013, the pieces were never used in the experiment they were intended for (Old Paint)
4. ‘Black paper’: Black paper
5. ‘Velvet’: Velvet-like fabric

#### 2.3.1.1 Results & Discussion

The results of the measurements of the relative reflectance of the samples above using the measurement method described in Sec. 2.2 can be found in Fig. 2.3 and Table 2.1.

As can be seen in these results, the most reflected light was captured from the anodised aluminium, a material that is abundant in the LIF setup. The least reflected light was captured from the paper and the velvet, but neither material is compatible with high vacuum due to outgassing.

The total amount of captured light reflected from the paint is lower than that from both the anodised aluminium and cupric oxide. Not all reflected light is projected onto the screen, but light that is not captured does not contribute significantly to the
total reflectance for all samples. Specifically, it was seen in additional observations that the intensity of light reflected at angles much greater or smaller than the specular angle of reflection decreases monotonically with the distance from the maximum situated at the specular angle of reflection. In other words, at all angles of reflection not subtended by the screen, the intensity is lower than at angles that are subtended by the screen. Therefore, given the discrepancy in the amount of total captured light, and the solid angle that light was captured from, it can be concluded that the paint absorbs more light at 860 nm than the cupric oxide and the anodised aluminium.

In addition to the measurements described above, a measurement to estimate the absolute reflectance of anodised aluminium was made. This measurement was done by placing a power meter between the screen and the sample at a distance of several cm from the sample, centred on the specular ray. The geometry was such that the power meter collected light from a solid angle of roughly $\frac{1}{2}$ sr. The power meter thus measured the reflected light corresponding to at least the full width at half maximum of the reflected intensity distribution. This measurement showed that $\sim 10\%$ of the incident light was reflected into a beam centred around the specular ray.
<table>
<thead>
<tr>
<th>Intensity distribution</th>
<th>X-projection</th>
<th>Y-projection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anodised Aluminium</strong></td>
<td><img src="image1" alt="Intensity distribution" /></td>
<td><img src="image2" alt="X-projection" /></td>
</tr>
<tr>
<td>An. Alum.: I$<em>{\text{tot}}$ = 13, w$</em>{x,y}$ = (3.7, 3.3)</td>
<td><img src="image4" alt="An. Alum.: X-projection" /></td>
<td><img src="image5" alt="An. Alum.: Y-projection" /></td>
</tr>
<tr>
<td><strong>CuO</strong></td>
<td><img src="image6" alt="Intensity distribution" /></td>
<td><img src="image7" alt="X-projection" /></td>
</tr>
<tr>
<td>CuO: I$<em>{\text{tot}}$ = 4.2, w$</em>{x,y}$ = (0.82, 1.3)</td>
<td><img src="image9" alt="CuO: X-projection" /></td>
<td><img src="image10" alt="CuO: Y-projection" /></td>
</tr>
<tr>
<td><strong>'Old' Paint</strong></td>
<td><img src="image11" alt="Intensity distribution" /></td>
<td><img src="image12" alt="X-projection" /></td>
</tr>
<tr>
<td>'Old' Paint: I$<em>{\text{tot}}$ = 3.6, w$</em>{x,y}$ = (2.6, 2.1)</td>
<td><img src="image14" alt="'Old' Paint: X-projection" /></td>
<td><img src="image15" alt="'Old' Paint: Y-projection" /></td>
</tr>
<tr>
<td><strong>Paper</strong></td>
<td><img src="image16" alt="Intensity distribution" /></td>
<td><img src="image17" alt="X-projection" /></td>
</tr>
<tr>
<td>Paper: I$<em>{\text{tot}}$ = 3.4, w$</em>{x,y}$ = (4.4, 4.6)</td>
<td><img src="image19" alt="Paper: X-projection" /></td>
<td><img src="image20" alt="Paper: Y-projection" /></td>
</tr>
<tr>
<td><strong>Velvet</strong></td>
<td><img src="image21" alt="Intensity distribution" /></td>
<td><img src="image22" alt="X-projection" /></td>
</tr>
<tr>
<td>Velvet: I$<em>{\text{tot}}$ = 1, w$</em>{x,y}$ = (5.1, 4.8)</td>
<td><img src="image24" alt="Velvet: X-projection" /></td>
<td><img src="image25" alt="Velvet: Y-projection" /></td>
</tr>
</tbody>
</table>

**Figure 2.3.** Intensity profiles obtained for different samples are shown. The intensity distributions show the amount of captured light with respect to position on the screen. The X- and Y-projections were made by summing all pixels in rows and columns respectively.
2.3.2 Effects of surface roughness

As the painted samples described in Sect. 2.3 appeared glossy to the eye, and it was initially assumed that glossy surfaces reflect more light than matte ones, it was attempted to make the paint surface appear matte by changing its roughness. This was done by sanding it with sandpaper of different grit sizes.

The following samples were tested:

1. 'Untreated (OP)': Untreated paint applied to a piece of copper (sample 3 in Sect. 2.3)
2. 'Polished (OP)': A part of the painted surface of the same piece of copper sanded with fine grit sandpaper (particle size $\sim 10^3$ nm)
3. 'Sanded (OP)': A part of the painted surface of the same piece of copper sanded with coarse grit sandpaper (particle size $\sim 10^5$ nm)

2.3.2.1 Results & Discussion

The results of the measurements of the samples above can be found in Fig. 2.4 and Table 2.1.

It can be seen that sanding with the fine grit sandpaper narrows the intensity profile, and sanding with coarse grit sandpaper broadens it. This is likely due to the fact that surface features after sanding with fine grit sandpaper are smaller than before sanding, and actually approach in size the wavelength of the incident light. Therefore, the interaction of the light with the surface more closely resembles that between light and a perfectly smooth surface compared to the interaction with the untreated surface. This means that the local variation of the surface normal of the rough surface causes less variation of the angle of reflection of incident rays than in the untreated case, leading to a narrower reflected beam centred around the specular ray [9, 10, 11]. This also explains the perceived increase in glossiness of the surface.

In addition, it can be seen that less reflected light is captured from the surface that was sanded with the coarse grit sandpaper than from both the 'polished' and 'untreated' surfaces. By the same arguments as in Sect. 2.3.1.1, it can therefore be concluded that the 'sanded' surface absorbs more of the incident light. This can be explained by the fact that the coarse grit sandpaper used introduces surface features that are much larger in size than the wavelength of the incident light. These features can then cause multiple interactions between the photons and the surface to occur, which leads to a higher probability of absorption [12, 13, 14].
2.3.3 Effects of handling and application of the paint

Although the manufacturer prescribes using an airbrush to apply the paint, use of a normal paintbrush was preferred. This is because the components used in the LIF setup have surfaces that are small or difficult to access, and use of a paintbrush requires less skill, time, and equipment. In addition, it was noticed previously that a procedure intended to clean the paint surface lead to a significantly higher reflectance. Therefore, to gain insight into the application and handling of the paint, new pieces of copper were painted, and were subsequently subjected to different treatments.

The following samples were tested:

1. ’Untreated (NP)’: a piece of copper painted for this experiment (New Paint) using a paintbrush, cured for two days at room temperature.

2. ’Wiping w/ paper (NP)’: a piece of copper painted for this experiment (New Paint) using a paintbrush, cured for two days at room temperature. The surface was subsequently wiped with a paper lens cleaning tissue.

3. ’Flushing w/ ethanol (NP)’: a piece of copper painted for this experiment (New Paint) using a paintbrush, cured for two days at room temperature. The surface was subsequently flushed with lab grade ethanol.

4. ’Wiping + flushing (NP)’: a piece of copper painted for this experiment (New Paint) using a paintbrush, cured for two days at room temperature. The surface was first flushed with lab grade ethanol, and subsequently wiped dry with a paper lens cleaning tissue.

5. ’Touching (NP)’: a piece of copper painted for this experiment (New Paint) using a paintbrush, cured for two days at room temperature. The surface was subsequently touched and rubbed extensively with bare fingers.

6. ’Heating (NP)’: a piece of copper painted for this experiment (New Paint) using a paintbrush, which was cured overnight in an oven at 150° C.

2.3.3.1 Results & Discussion

The results of the measurements of the samples above can be found in Figs. 2.5, 2.6 and Table 2.1. Note that all samples yielded significantly less captured reflected light than those tested previously, and the maximum of the intensity axis of the plots
below is therefore around an order of magnitude lower than that of the ones above. The colourbar has been rescaled correspondingly.

From the data it is apparent that heating, touching, and flushing the surface with ethanol have no significant effect on its reflectance. Wiping the surface using a paper lens cleaning tissue significantly increases its reflectance, and the effect is exacerbated by first flushing the surface with ethanol. This is likely due to the wiping actually polishing the surface similar to the fine grit sandpaper as described in Sect. 2.3.2.1, which also explains the perceived increase in glossiness. An explanation for the exacerbation of this effect when flushing with ethanol might be that the paint (which is an organic compound) is soluble in ethanol, and this causes more abrasion and hence more effective polishing of the surface. This seems to be supported by the fact that black residue was visible on the lens wipe after flushing and wiping the surface.

From the amount of captured light it can be concluded that all samples absorbed more light than those tested previously. This is because the paint surface of the old samples had degraded and been worn down over time. The paint is likely designed such that it has nanoscale surface features to increase the absorbance by causing photons to interact with the surface multiple times [15]. These surface features are delicate and damaging them increases the reflectance.

2.3.4 Uncertainty in the estimated total reflectance
Several effects contribute to the total uncertainty in the determination of the total reflected light. The sum of the intensity of all pixels in the CCD photographs $I_{\text{tot}}$ is an estimate of the total light reflected by the sample, but fails to take into account light not reflected onto the screen and saturation of the CCD chip. Uncertainty in the reflectance due to variations within the surface are accounted for by $\sigma_{I_{\text{tot}}}$.

The limited solid angle of reflection from which light is detected leads to an increase in the uncertainty but will not change the hierarchy of the estimated total reflectances for the different materials. This is because additional measurements revealed that the intensity of light reflected at angles not subtended by the screen decreases monotonically as a function of the magnitude of the angle of reflection. This means that light not reflected onto the screen contributes at most as the integral of the intensity seen at the edge of the screen integrated over the solid angle of reflection not subtended by the screen. In all cases, accounting for the light not
detected using the measurement method would not change the hierarchy of the estimated total reflectances for the different surfaces.

Given a wider range of sensitivity of the CCD chip, the saturation that is present in some of the results could be eliminated. However, the saturation always occurs in the specular maximum of the reflected light, and surfaces that yield such a sharply peaked reflected intensity distribution are not suitable for use in the detection chamber as they would not reduce stray light effectively given the geometry of the chamber.
Figure 2.4. Intensity profiles obtained for different samples are shown. The intensity distributions show the amount of captured light with respect to position on the screen. The X- and Y-projections were made by summing all pixels in rows and columns respectively.
Figure 2.5. Intensity profiles obtained for different samples are shown. The intensity distributions show the amount of captured light with respect to position on the screen. The X- and Y-projections were made by summing all pixels in rows and columns respectively. Note that the maxima of the intensity axes of the plots are around an order of magnitude lower than before.
Figure 2.6. Intensity profiles obtained for different samples are shown. The intensity distributions show the amount of captured light with respect to position on the screen. The X- and Y-projections were made by summing all pixels in rows and columns respectively. Note that the maxima of the intensity axes of the plots are around an order of magnitude lower than before.
2.4 Conclusions

It has been shown that the MLS-85-SB paint absorbs more light than all other tested surfaces that are compatible with high vacuum (see Table 2.1). In addition, it was shown that the amount of light reflected from the paint is less than that reflected from anodised aluminium by an order of magnitude. Moreover, the paint is practical to apply to the components of the LIF setup, and is therefore the NIR-absorbing surface of choice for this experiment.

All newly painted samples appeared matte to the eye. It was assumed that the manufacturer has optimised the surface roughness of their product to yield the highest possible absorbance using nanoscale surface features, resulting in a matte appearance. The glossy appearance of the old sample was likely caused by the age and treatment of the surface in the past which have degraded these surface features. Therefore, no attempt is made to change the surface roughness of the paint surface of the components of the LIF setup, and care is taken to avoid damaging the paint surface.

2.4.1 Painting of the components

The components as manufactured by the workshop were painted using a paintbrush. Paint was applied to the inside of the beam dump by thinning the paint using acetone, pouring it into the beam dump, and shaking the part while covering the opening. All components were put in an oven at 150°C overnight to limit outgassing when placed in the vacuum. Pictures of the painted components can be found in Appendix 5.2.

2.4.2 Signal after improvements

With the new components, geometry, and light absorbing surfaces of the LIF setup (Fig. 2.7), the signal-to-noise ratio was vastly improved (see Fig. 2.8). Notably, the background count rate was reduced from 40 000 to 3 000 s⁻¹, and the selection and application of NIR-absorbing surfaces to reduce stray light can thus be deemed successful.
<table>
<thead>
<tr>
<th>Sample Preparation</th>
<th>$I_{\text{tot}}$ (arb. u.)</th>
<th>$\sigma_{I_{\text{tot}}}$</th>
<th>$w_x$ (cm)</th>
<th>$w_y$ (cm)</th>
<th>$\sigma_{w_{x,y}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial meas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anodised Aluminium</td>
<td>13</td>
<td>0.2</td>
<td>7.5</td>
<td>6.6</td>
<td>0.3</td>
</tr>
<tr>
<td>CuO</td>
<td>4.2</td>
<td>0.3</td>
<td>0.82</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Paint (OP)</td>
<td>3.6</td>
<td>0.3</td>
<td>2.6</td>
<td>2.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Paper</td>
<td>3.4</td>
<td>0.1</td>
<td>4.4</td>
<td>4.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Velvet</td>
<td>1.0</td>
<td>0.1</td>
<td>5.1</td>
<td>4.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Rough.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated (OP)</td>
<td>3.6</td>
<td>0.3</td>
<td>2.6</td>
<td>2.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Sanded (OP)</td>
<td>1.9</td>
<td>0.3</td>
<td>2.8</td>
<td>3.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Polished (OP)</td>
<td>3.3</td>
<td>0.3</td>
<td>1.2</td>
<td>0.69</td>
<td>0.3</td>
</tr>
<tr>
<td>Handl. &amp; appl.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated (NP)</td>
<td>0.53</td>
<td>0.2</td>
<td>5.7</td>
<td>4.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Wiping w/ paper (NP)</td>
<td>1.2</td>
<td>0.2</td>
<td>4.1</td>
<td>3.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Flushing w/ ethanol (NP)</td>
<td>0.50</td>
<td>0.2</td>
<td>5.6</td>
<td>4.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Wiping + flushing (NP)</td>
<td>1.7</td>
<td>0.2</td>
<td>3.3</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Touching (NP)</td>
<td>0.85</td>
<td>0.2</td>
<td>5.5</td>
<td>4.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Heating (NP)</td>
<td>0.64</td>
<td>0.2</td>
<td>5.8</td>
<td>4.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Table 2.1.** All calculated parameters that describe the measured intensity profiles for all the tested samples. $I_{\text{tot}}$ is the sum of all pixels, and $\sigma_{I_{\text{tot}}}$ is the uncertainty in $I_{\text{tot}}$ due to surface variations. $w_x$ and $w_y$ are the half widths at half maximum of the intensity profiles, and $\sigma_{w_{x,y}}$ is the uncertainty in $w_x$ or $w_y$ (whichever is largest) due to surface variations.
Figure 2.7. The new design of the detection chamber, seen along the BaF beam axis. The detection laser light enters the chamber from the left through the shown apertures and is mostly absorbed in the curved beam dump on the right, the end of which is indicated by a black triangle. Lenses are suspended over the interaction region to focus fluorescence onto the PMT at the top, which is not shown here. The anti-scatterer, shown in yellow at the bottom of the diagram, suppresses stray light from directly behind the interaction region. All components shown in colour in this diagram and the beam dump were painted with MLS-85-SB paint [8] (see Appendix 5.2), and in addition painted copper sheets were hung around the detection region to shield from stray light reflected off the vacuum chamber walls. The points at which the magnetic field was measured as described in Sec. 3.5.1.4 are indicated by red crosses.
Figure 2.8. A typical LIF signal as obtained after implementing the new detection optics and blackened surfaces. When compared to Fig. 2.1, it can be seen that the signal-to-noise ratio is vastly improved.
3 Modelling the effect of quantum beats in the time-resolved fluorescence spectroscopy of BaF

3.1 Introduction

The determination of the radiative lifetime of excited states of atoms and molecules within less than a percent requires excellent control of experimental parameters and quantitative knowledge of systematic effects. Time-resolved Laser Induced Fluorescence (LIF) detection using pulsed excitation can be used to measure the characteristic time constant of the radiative decay.

Using this method, the lifetime might be inferred by analysing the intensity distribution of detected fluorescence in time. The precise determination of the radiative lifetime from the time-resolved fluorescence signal requires a quantitative knowledge of all other effects that induce a time-dependence in the fluorescence.

3.1.1 The Hanle effect

An important phenomenon in the time-dependence of fluorescence is the Hanle effect. Broadly defined, the Hanle effect describes how a magnetic field affects a polarised signal from a quantum system. It was originally described by Hanle as the rotation of the plane of polarisation of atomic fluorescence in a magnetic field [16]. The Hanle effect has since been ubiquitously observed, and is relevant in a variety of other fields, such as astronomy [17] and condensed matter physics [18].

Hanle’s original observation was important in the development of quantum mechanics [19], and led to the introduction of the concept of coherent superposition states [20]. Fundamentally, the Hanle effect is a manifestation of the time-evolution of such coherent superposition states.
3.1.2 Time-evolution of coherent superpositions

Where the Hanle effect is usually referred to in the context of time-integrated signals, the time-resolved detection of fluorescence allows for a more direct observation of the time-evolution of coherence.

The excitation of atoms or molecules to a coherent superposition state leads to a rotation of the radiation pattern of fluorescence in space. Observing the fluorescence in a fixed direction then yield a signal that is modulated in time, and this modulation is referred to as quantum beats (see Fig. 3.1) [21, 22]. These quantum beats appear when the radiation couples the ground state to multiple excited angular momentum eigenstates, which is possible when the frequency bandwidth and polarisation of the laser pulse satisfies the selection rules for multiple transitions. The fluorescence emitted in the decay from this superposition state will then be modulated at a frequency that corresponds to the energy splitting between the different excited states [23, 24]. Quantum beats that are observed in time-resolved spectroscopy experiments tend to be closely spaced, such as low-field Zeeman or hyperfine states, as these can be coherently excited by laser fields and exhibit beats with periods comparable to the lifetimes [25].

Figure 3.1. An example of quantum beats between Zeeman substates observed in the time-resolved fluorescence signal from the pulsed excitation of Cadmium. [26]
3.1.3 Quantum beats in lifetime measurements

Quantum beats with periods comparable to the excited state lifetime can add a sinusoidal modulation to an exponential fluorescence decay signal that is not immediately apparent as such (see e.g. Fig. 3.2). An analysis of such signals that fails to take this modulation into account can therefore produce imprecise or false results. The extraction of excited state lifetimes from a fluorescence signal at a high precision therefore requires a quantitative understanding of the modulation induced by quantum beats.

The supersonic BaF source coupled to the LIF detection chamber described in Sec. 1.2 was used to measure the lifetime of excited states of BaF. The measured time-resolved fluorescence signal can be found in Fig. 3.3 and could contain a significant modulation due to Zeeman quantum beats (Fig. 3.1).

The goals of the research described in this chapter are thus:

1. To develop a quantitative understanding of the time-dependence and anisotropy of fluorescence in the framework of quantum optics.

Figure 3.2. Time-resolved emission decay traces of glyoxal. The corresponding real part of the Fourier-transform in the frequency domain reveal quantum beat modulation of the decay signal at frequencies equal to the Zeeman splitting of excited states. [27]
Figure 3.3. The measured time-resolved fluorescence signal of the $^2\Pi_{3/2}$ excited state of BaF [5].

2. To formulate a quantitative model that allows for the simulation of time-resolved fluorescence signals and implement this model numerically.

3. To apply this model to make a quantitative estimate of the contribution of quantum beats in a time-resolved fluorescence signal that was observed in an experiment.
3.2 Theory of angular transition amplitudes

In Sec. 3.2.1, the angular transition amplitude (ATA) for excitation as well as spontaneous and stimulated emission, is derived from perturbation theory. Thereafter, the time-dependence of this quantity is discussed. The derivations up to Eq. 3.13 follow the argumentation in [28] and [29].

3.2.1 Transition amplitudes for electric dipole transitions

3.2.1.1 Electric dipole Hamiltonian and perturbation theory

The interaction between the system and the electromagnetic field can be described by the electromagnetic vector potential $A$ in the Coulomb gauge: $\nabla \cdot A = 0$. The Hamiltonian $H$ of a bound electron in this electromagnetic field may then be written as [28]

$$H = \frac{p^2}{2m_e} + V(r) + \frac{eP \cdot A}{m_e} + \frac{e^2}{2m_e}A^2,$$

(3.1)

where $p$, $m_e$, $e$ are the electron’s momentum, mass, and charge respectively. $V(r)$ is the total potential energy of the electron not due to the applied electromagnetic field.

The field of a monochromatic plane wave can be written as

$$A(r,t) = \frac{E_0}{2\omega} \left( \epsilon e^{i(kr - \omega t)} + \epsilon^* e^{-i(kr - \omega t)} \right),$$

(3.2)

where $E_0$ is the amplitude of the wave, $\omega$ is the angular frequency, $\epsilon$ is the polarisation vector, and $k$ is the wavevector. If the wavelength is very large compared to the dimensions of the system, i.e. $k \cdot r \ll 1$, the vector potential can be expanded in $k \cdot r$ around 0:

$$A(r,t) = \frac{E_0}{2\omega} e^{i\omega t} (1 + ik \cdot r + \ldots) + \text{complex conjugate}$$

(3.3)

If only the zeroth order terms are retained, the field is effectively described as being constant over the volume of the system. This is called the electric dipole approximation.

In describing the interaction of the system with the electromagnetic wave, another approximation can be made: the term in the Hamiltonian (Eq. (3.1)) proportional to $A^2$ can be neglected, provided $\omega \gg E_0$, which is the case in most laser spectroscopy.
experiments [28]. The part of the Hamiltonian that describes the interaction with the electromagnetic wave is then

\[ H_{EM} = \frac{eE_0}{2m_e\omega} \mathbf{p} \cdot \mathbf{E} + c.c. \]  

(3.4)

For weak electric fields required for resonant excitation, this interaction energy is a small perturbation of the total Hamiltonian. Using time dependent perturbation theory, the transition amplitude, i.e. the probability amplitude \( c_b(t) \) to find the system in state \( \psi_b \), can be shown to be equal to

\[ c_b(t) = -\frac{i}{\hbar} \int_0^t \langle \psi_b | H_{EM} | \psi_a \rangle e^{i\omega_{ab}t'} dt'. \]  

(3.5)

where \( \omega_{ab} = (E_b - E_a)/\hbar \). [28, 29, 30]

3.2.1.2 Angular matrix elements and transition amplitudes

Substituting Eq. (3.4) into Eq. (3.5) and using commutation relations, it can be shown that the transition amplitude is proportional to the matrix element:

\[ \mathcal{M} = \langle \psi_b | \mathbf{E} \cdot \mathbf{r} | \psi_a \rangle, \]  

(3.6)

which can also be written in terms of the transition dipole moment \( \mathbf{d}_{ab} \) [30]

\[ \mathcal{M} = \frac{1}{e} \mathbf{E} \cdot \mathbf{d}_{ab}. \]  

(3.7)

In addition to properties intrinsic to the initial and final states \( |\psi_a\rangle, |\psi_b\rangle \) and the magnitude of the electric field, the probability amplitude for a dipole transition therefore depends on the relative orientation of the transition dipole moment and the electric field [30]. The full angular dependence of the dipole transition amplitude is contained in \( \mathcal{M} \), and can be isolated by first decomposing the wavefunctions into products of angular and radial parts,

\[ \mathcal{M} = \int R_a^*(r)Y_a^*(\mathbf{r})\mathbf{E} \cdot \mathbf{r}R_b(r)Y_b(r)d^3\mathbf{r}. \]  

(3.8)

The angular parts of the wavefunction \( Y \) are eigenfunctions of angular momentum, and can thus be identified as the spherical harmonics of degree \( l \) (the angular momentum quantum number) and order \( m \) (the angular momentum projection quantum number).
number with respect to the quantisation axis) \( Y_l^m \). For superpositions of different angular momentum eigenstates, \( Y \) is given by a corresponding linear combination of spherical harmonics. Extracting only the part of \( M \) that gives the angular dependence, and switching to spherical coordinates gives the angular matrix element

\[
M_{\text{ang}} = \int Y_{l_a}^{m_a*}(\phi, \theta) (\mathbf{e} \cdot \mathbf{r}) Y_{l_b}^{m_b}(\phi, \theta) d\Omega. \quad (3.9)
\]

The anisotropy of the interaction of the light with the system can be further elucidated by switching to the spherical basis:

\[
\hat{u}_{+1} = \frac{1}{\sqrt{2}} (\hat{x} + i\hat{y}), \quad \hat{u}_{-1} = \frac{-1}{\sqrt{2}} (\hat{x} - i\hat{y}), \quad \hat{u}_0 = \hat{z}. \quad (3.10)
\]

The \( \mathbf{r} \) vector can be decomposed in this basis as \(^1\) [29]:

\[
\mathbf{r} = \sqrt{\frac{4\pi}{3}} (Y_1^1(\phi, \theta)\hat{u}_{+1} + Y_1^{-1}(\phi, \theta)\hat{u}_{-1} + Y_0^0(\phi, \theta)\hat{u}_0), \quad (3.11)
\]

The polarisation of the light \( \mathbf{e} \) is naturally expressed in this basis as a linear combination of helicity eigenstates:

\[
\mathbf{e} = c_{+1}\hat{u}_{+1} + c_{-1}\hat{u}_{-1} + c_0\hat{u}_0. \quad (3.12)
\]

Switching to spherical coordinates, and plugging the new expression for \( \mathbf{e} \cdot \mathbf{r} \) into Eq. 3.9, the angular matrix element \( M \) becomes

\[
M_{\text{ang}} = \int Y_{l_a}^{m_a*} \left[ c_{+1} Y_1^1(\phi, \theta) + c_{-1} Y_1^{-1}(\phi, \theta) + c_0 Y_0^0(\phi, \theta) \right] Y_{l_b}^{m_b} d\Omega. \quad (3.13)
\]

In practice, the polarisation of the light can be well controlled, such that a state might be obtained for which the coefficients in Eq. (3.12) can be chosen at will.

The integrand in Eq. 3.13 can be interpreted as the angular transition amplitude per unit solid angle

\[
A_{a\rightarrow b}(\phi, \theta) = Y_{l_a}^{m_a*} Y_1^1 Y_{l_b}^{m_b}, \quad (3.14)
\]

such that

\[
M_{\text{ang}} = \int Y_{l_a}^{m_a*} Y_1^1 Y_{l_b}^{m_b} d\Omega = \int A_{a\rightarrow b}(\phi, \theta) d\Omega, \quad (3.15)
\]

\(^1\)This can be verified by taking \( \mathbf{u} \cdot \mathbf{r} \) with \( \mathbf{r} = \sin(\theta) \cos(\phi) \hat{x} + \sin(\theta) \sin(\phi) \hat{y} + \cos(\theta) \hat{z} \).
in which $Y_1^M$ is shorthand for the linear combination of spherical harmonics that describes the polarisation of the light that drives the transition, where $M = \pm 1, 0$. The transition probability or equivalently the absorption or emission intensity $I(\phi, \theta)$ per unit solid angle for the transition $|l_a, m_a \rangle \rightarrow |l_b, m_b \rangle$ is proportional to the absolute square of the angular transition amplitude:

$$I(\phi, \theta) \propto |A_{a \rightarrow b}(\phi, \theta)|^2 = \left| Y_{l_a}^{m_a} Y_1^M Y_{l_b}^{m_b} \right|^2. \quad (3.16)$$

$A_{a \rightarrow b}(\phi, \theta)$ thus fully describes the angular dependence of the transition probability, i.e. the anisotropy of absorption and emission of photons by the molecule, due to the quantisation of angular momentum in space. Therefore, $A_{a \rightarrow b}(\phi, \theta)$, given by the product of three spherical harmonics (Eq. 3.14), referred to henceforth as the angular transition amplitude (ATA) will be used in the model described in section 3.3.

Expanding the the spherical harmonics in the angular matrix element (Eq. 3.15) as the product of a complex phase and an associated Legendre polynomial,

$$\mathcal{M}_{\text{ang}} = \int e^{-im_a \phi} e^{iM \phi} e^{im_b \phi} d\phi \times$$

$$\int P_{l_a}^{m_a}(\cos(\theta)) P_1^M(\cos(\theta)) P_{l_b}^{m_b}(\cos(\theta)) d\cos(\theta), \quad (3.17)$$

allows the angular momentum selection rules to be derived. These selection rules constrain the angular transition amplitude. By symmetry arguments, the integral over $\theta$ is only nonzero when

$$l_b = l_a \pm 1, \quad \text{or} \quad \Delta l = \pm 1, \quad (3.18)$$

and the integral in $\phi$ will only be nonzero if

$$m_b = m_a - M, \quad \text{or} \quad \Delta m = 0, \pm 1. \quad (3.19)$$

This means both the total and the projection of the angular momentum must be conserved to allow the transition, given that one unit of angular momentum might be transferred between the field and the system (through the spin-1 photon).

When these selection rules (Eqs. 3.18, 3.19) are obeyed, $A_{a \rightarrow b}(\phi, \theta)$ will be positive and real for any $\theta, \phi$. This allows the angular transition amplitude to be represented by a closed three-dimensional surface as described in Sec. 3.3.
3.2.2 Time-dependence of the transition amplitude

3.2.2.1 Quantum Beats

The anisotropy of the transition rate is at the basis of time-dependent modulation of the emission into a certain direction. Such a time-dependent modulation occurs when individual atoms or molecules are excited to coherent superposition states of different substates with different energy eigenvalues. Here, the example of Zeeman substates is given, following [30].

The angular part of the wavefunction describing radiation that is linearly polarised perpendicular to the magnetic field can be described as $Y^M_l = \frac{1}{\sqrt{2}} (Y^1_l + Y^{-1}_l)$. Such radiation satisfies $\Delta m = \pm 1$ selection rules, which allows for the excitation to a coherent superposition of $|j,(m+1)\rangle$ and $|j,(m-1)\rangle$ states.

Each of the excited substates $|\psi_m\rangle$ in a superposition state evolves according to the time-evolution operator:

$$ |\psi_m(t)\rangle = \exp\left(-i\frac{H}{\hbar}t\right) |\psi_m(t=0)\rangle. \quad (3.20) $$

This time dependence can be factored out in the case that these excited substates are degenerate in energy. In the presence of a magnetic field $B$ this degeneracy is lifted, and the time evolution factor of each Zeeman substate is given by

$$ \exp\left(-i\frac{mg \mu_B B}{\hbar}t\right) = e^{-i\omega_m t}, \quad (3.21) $$

where $g$ is the Landé factor, $\mu_B$ is the Bohr magneton, and $\omega_m$ is the Zeeman shift (in angular frequency) of a substate with magnetic quantum number $m$.

A time-dependent superposition state composed equally of $m = \pm 1$ substates is then given by

$$ |\psi_e(t)\rangle = \frac{1}{\sqrt{2}} \left( e^{-i\omega_{+1} t} |+1\rangle + e^{-i\omega_{-1} t} |-1\rangle \right) \quad (3.22) $$

The transition amplitude for transitions between such a state and the ground state will therefore be proportional to a factor

$$ c_g(t) \propto e^{-i\omega_{+1} t} + e^{-i\omega_{-1} t}, \quad (3.23) $$

which, as can be seen by taking the absolute square, induces a harmonic modulation of the decay probability with a frequency

$$ \omega_{+1} - \omega_{-1} = 2\omega_L, \quad (3.24) $$

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where $\omega_L$ is the Larmor frequency. Thus,

$$I(\phi, \theta, t) \propto 1 + \cos (2\omega_L t).$$  \hspace{1cm} (3.25)

This modulation is referred to as the quantum beat, as its frequency is equal to the
difference of the Bohr frequencies of the two superposed parts of the wavefunction.
This mechanism is the same for any transition involving coherently superposed
substates with a different energy eigenvalue.

Zeeman quantum beats can be equivalently described as the Larmor preces-
sion of the transition dipole moment, and corresponding precession of the angular
transition amplitudes, of the superposed transitions [25]. This precession entails
a time-dependent anisotropy of the transition probability, which manifests as the
modulation of the emission and absorption rate in space and time. This is essentially
an interference phenomenon between the different transitions analogous to Young’s
double slit experiment. To observe this modulation in time, detection must occur in
a specific direction (i.e. light must be collected from a solid angle less than $4\pi$ sr)
and in such a way that the transitions can not be distinguished [31].

3.2.2.2 Radiative decay

Since the transition dipole moment does not depend explicitly on time, the intensity
of spontaneous emission after excitation decays exponentially over time, with a
time constant that is referred to as the lifetime $\tau$. Zeeman and hyperfine substates
exhibit the same lifetime [28]. Therefore, the decay of the total transition rate in any
direction can be described by an exponential factor, and thus

$$I(\phi, \theta, t) \propto \exp \left( -\frac{t}{\tau} \right),$$  \hspace{1cm} (3.26)

where $t = 0$ is the time of excitation.

3.2.2.3 The Hanle effect

The Hanle effect describes the dependence of a time-integrated fluorescence signal
on an applied magnetic field [32, 33, 28]. Taking the intensity of spontaneous
emission $I(\phi, \theta)$ (integrated over a limited solid angle) as the fluorescence signal, this
dependence can be found by combining the time-dependence induced by quantum
beats (Eq. 3.25) and spontaneous decay (Eq. 3.26)

$$I(t) \propto \exp \left( -\frac{t}{\tau} \right) \left[ 1 + \cos (2\omega_L t) \right].$$  \hspace{1cm} (3.27)
Figure 3.4. A typical Hanle effect signal of Ca atoms [34]. The time-integrated fluorescence signal is plotted for different values of the magnetic field. The dependence of the fluorescence on the magnetic field is a Lorentzian function (Eq. 3.28).

Integration of these terms from \( t = 0 \) to infinity gives

\[
\int_0^\infty \exp\left(-\frac{t}{\tau}\right) \left[ 1 + \cos(2\omega_L t) \right] dt = 1 + \frac{(\frac{1}{\tau})}{\left(\frac{1}{\tau}\right)^2 + 4\omega_L^2}.
\] (3.28)

This characteristic term describes a Lorentzian function of \( \omega_L(B) \) with a half width at half maximum at \( 2\omega_L = 1/\tau \) (see Fig. 3.4).
3.3 Numerical model for time-resolved fluorescence signals

To quantify the contribution of quantum beats to a fluorescence signal, a numerical model was developed. This numerical model is a computational tool that calculates angular transition amplitudes (Eq. 3.14) per unit solid angle and their time evolution as

\[ A(\phi, \theta, t)_{a \rightarrow b} \propto e^{-\frac{t^2}{\tau}} \cdot e^{-i\omega_r t} \left[ Y_{m_a}^* Y_{1}^M Y_{m_b}^l \right], \]  

(3.29)

where \( \omega_r \) is the precession frequency of the angular transition amplitude (see Sec. 3.2.2). The numerical model can calculate weighted sums of different angular transition amplitudes and take the square of the sum of these different amplitudes to find the intensity of absorption or emission. As described in Sec. 3.2, the absolute square of the angular transition amplitude is directly proportional to the probability of a transition between states \(|a\rangle\) and \(|b\rangle\) in which a photon of specified polarisation is absorbed, spontaneously emitted, or stimulates emission in a direction \((\phi, \theta)\). In the current implementation, the model is used to simulate the time-dependence of a fluorescence signal (due to spontaneous emission) according to Eq. 3.20 after excitation by radiation of known frequency and polarisation. The numerical model currently consists of several Matlab scripts (see Appendix 5.3).

3.3.1 Determination of transition strengths

To simulate an experimental fluorescence signal, the angular transition amplitudes for all transitions to the ground states must be added together. Therefore, the transitions that can occur and their relative strength need to be determined first. The frequency and polarisation of the excitation radiation in an experiment determines the population of the excited states, and thus also determines which transitions to the ground state can occur and what the relative strength of those transitions is. These experimental conditions need to be translated into the corresponding model parameters, after which these parameters can be input into the model. The parameters used in the model are described in Fig. 3.5.

In the model, all transitions that are possible given the bandwidth of the excitation radiation in the experiment must be selected manually. The polarisation, which is elliptical in general, must be input by providing the parameters \( \varepsilon, \beta, \) and \( \eta \). \( \varepsilon \) is
the ratio of the semi-major to the semi-minor axis, $\beta$ is the angle between the semi-major axis and the quantisation axis, and $\eta$ is the angle between the propagation vector of the excitation radiation and the magnetic field. From these parameters, the polarisation content of the excitation radiation in terms of spherical harmonics (see Sec. 3.2, Eq. 3.12) is determined by the model by decomposition of the polarisation ellipse into the spherical basis with respect to the quantisation axis.

From this decomposition and given the power spectral density of the radiation, the relative transition strengths of the different allowed transitions are determined. The transition strengths are computed as the product of the relative intensity of the frequency and polarisation components of the excitation radiation. Crucially, the relative transition strength of transitions to coherent superposition states is quantified. As explained in Sec. 3.2, transitions from superposition states to the ground state are responsible for the appearance of quantum beats.

### 3.3.2 Computation of angular transition amplitude surfaces

Having identified all occurring transitions and their relative strength, the model then calculates the angular transition amplitude for every allowed transitions and multiplies it by its relative transition strength to yield a weighted angular transition amplitude for every transition. The angular transition amplitudes are computed as products of (linear combinations of) spherical harmonics, where the order and degree are determined by the angular momenta of the initial and final states. The spherical harmonics are computed using Matlab’s built-in `legendre` function.

In the model, $A(\phi, \theta)$ is represented by a surface in 3D space (e.g. Figs. 3.6a and 3.6b). The length of a vector that connects the origin and a point on the surface is the transition amplitude for a direction in space that corresponds to the orientation of the vector. The absolute square of the amplitude integrated over the full solid angle gives the transition strength.

The weighted sum of all angular transition amplitudes squared is normalised such that integration over the full $4\pi$ sr yields unity. This weighted sum of different angular transition amplitudes constitutes a quantitative description of the intensity of spontaneous emission in space for the given properties of the system and the excitation radiation, and can be visualised as in e.g. Fig. 3.7.
Figure 3.5. Coordinate system and parameters used in the numerical model. The z-axis is defined as the quantisation axis due to the magnetic field $B$. $\phi$ and $\theta$ are the azimuthal and polar angle with respect to this z-axis respectively, where $\phi = 0$ is defined as the azimuthal angle of the semi-major axis of the polarisation ellipse. $\beta$ is the angle between the magnetic field and the semi-major axis of the polarisation ellipse. $\epsilon$ (not shown in the diagram) is the ratio of the major axis to the minor axis of the ellipse. $\eta$ (not shown in the diagram) is the angle between the direction of propagation of the excitation radiation and the magnetic field. $\gamma$ and $\delta$ are the azimuthal and polar angle of the fluorescence detection respectively.
Figure 3.6. Angular transition amplitude surfaces for transitions from (a) a non-superposition state and (b) a $m = \pm 1$ superposition state. Spontaneously emitted light from these transitions will be linearly polarised parallel or perpendicular to the magnetic field respectively as indicated by the $E$ vector. These transitions can be driven in either direction most efficiently by laser radiation with this same polarisation. The mutually orthogonal geometry for excitation and detection is shown here, where $B = z$ is the magnetic field direction, excitation happens along the $x$-axis and fluorescence is detected in the $y$-direction. The colour of the surface indicates the distance from the origin.
Figure 3.7. The surface represents the weighted sum of angular transition amplitudes for the transitions $\frac{1}{\sqrt{2}}(|1, -1\rangle + |1, +1\rangle) \rightarrow |0, 0\rangle$ (Fig. 3.6b) and $|1, 0\rangle \rightarrow |0, 0\rangle$ (Fig. 3.6a), with equal weights. The transitions can be driven with equal strength in either direction using an equal (up to a relative phase) linear combination of vertically ($E \parallel B$) and horizontally ($E \perp B$) polarised light. The polarisation of spontaneously emitted light depends on the direction ($\phi, \theta$). The mutually orthogonal geometry for excitation and detection is shown here, where $B = z$ is the magnetic field direction, excitation happens along the $x$-axis and fluorescence is detected in the $y$-direction. The colour of the surface indicates the distance from the origin.
3.3.3 Modelling of time-dependence of the angular transition amplitude

Time-dependence due to the time evolution operator (Eq. 3.20) is modelled by iterative rotation of angular transition amplitude surfaces around the quantisation axis. Angular transition amplitude surfaces corresponding to transitions from coherent superposition states are rotated at a frequency $\omega_r = (E_1 - E_2)/(2\hbar)$, where $E_1$ and $E_2$ are the energies of the superposed states. This models the time evolution of the wavefunctions that determine the angular transition amplitude. Angular transition amplitude surfaces for transitions from non-superposition states are kept stationary.

The time-dependence of the total transition rate in any direction due to the decay of the excited state population is modelled by iteratively multiplying the angular transition amplitude surface by $\exp\left(-\frac{t}{\tau}\right)$ where $\tau$ is the excited state lifetime. This lifetime is taken to be the same for all substates of the excited state [28].

3.3.4 Modelling of detector signals by angular integration

The model can be used to simulate the angular transition intensity over time $I(\phi, \theta, t)$, which is directly proportional to a signal measured by a fluorescence detector that samples emission into a limited solid angle. Simulation of the transition intensity at a certain time is done by first summing over all angular transition amplitudes for the different transitions. The square of the sum of the amplitudes is then integrated over the solid angle $\sigma$ spanned by the detector to simulate the fluorescence signal

$$S(t) = \int_\sigma \left| \sum_{(a \rightarrow b)} A(\phi, \theta, t)_{a \rightarrow b} \right|^2 d\Omega = \int_\sigma I(\phi, \theta, t) d\Omega. \quad (3.30)$$

The presence of an analyser in the detection channel might be modelled by projection of the polarisation components of emission onto the transmission axis of the analyser. In the current implementation, the signal in the absence of such an analyser is modelled. The time-dependence of the fluorescence signal is obtained by repeating this integration for every time step in which time-evolution is modelled as described in the previous section. The model thus intends to fully capture the time-dependence of a fluorescence signal.
3.4 Model validation: simulation of the Hanle effect

To validate the implementation of time-dependence in the numerical model, the signal $S(t)$ for transitions from Zeeman substates is simulated and integrated over time. For this simulation, a simple two-level system is used (see Fig. 3.8), in which the excited state splits linearly into three levels under the application of a magnetic field. The results for different magnetic fields and corresponding Larmor frequencies are compared to Eq. 3.28.

![Figure 3.8. Schematic of the energy levels of the simulated system. The excited state ($j = 1$) splits up in a magnetic field which allows excitation to superposition states. The ground state ($j = 0$) is non-degenerate.](image)

3.4.1 Simulation parameters: polarisation & time-dependence

To maximise the sensitivity to the applied magnetic field, simulations were performed in which the polarisation of the excitation radiation was parameterised as $\varepsilon = 1000$ and $\beta = \pi / 2$. This simulates linearly polarised light with the electric field orthogonal to the magnetic field. This polarisation disallows transitions for which $\Delta m = 0$, and allows coherent transitions for which $\Delta m = \pm 1$. The frequency content of the excitation radiation was modelled such that the $|j = 1, m = \pm 1\rangle$ excited states were populated equally for all strengths of the magnetic field. Thus, the only transition allowed with these parameters is $\frac{1}{\sqrt{2}}(|1, -1\rangle + |1, +1\rangle) \rightarrow |0, 0\rangle$. The rotation frequency $\omega_r$ for the corresponding angular transition amplitude surface was
taken equal to the Larmor frequency:

$$\omega_r(B) = \omega_L = g \mu_B B,$$  \hspace{1cm} (3.31)

with $g = 1$. Fluorescence detection was simulated for a collection solid angle of $\sigma = 4\pi \cdot 10^{-4}$ sr at a position $(\gamma, \delta) = (\pi/2, \pi/2)$. The lifetime $\tau$ was set equal to 50 ns, which is of the same order as typical atomic or molecular excited state lifetimes [35]. The time step was $dt = 0.1$ ns, and signals were integrated from the time of excitation at $t = 0$ until a time $t = 10^3$ ns to yield the response $R$:

$$R(B) = \int S(t) dt = \int_{t=0}^{10^3} \int_{\sigma} I(\phi, \theta, t) d\Omega dt.$$ \hspace{1cm} (3.32)

### 3.4.2 Results & Discussion: Modelled magnetic field dependence of time-integrated fluorescence signals

Typical signals obtained for various values of the magnetic field can be seen in Fig. 3.9. In Fig. 3.10, the integrated signal $R(B)$ is plotted for various values of the magnetic field. As is evident from this figure, the simulated response as a function of the applied field follows the theoretically predicted Lorentzian (Eq. 3.28). This confirms that the model is able to qualitatively capture the Hanle effect through the modelled time-dependence of the angular transition amplitude.
Figure 3.9. Time-resolved fluorescence signals simulated using the numerical model described in Sec. 3.3 are shown for different magnitudes of the magnetic field. In the model, angular transition amplitude surfaces are rotated at $\omega_r = \omega_L$, inducing a modulation of the fluorescence signal at twice the Larmor frequency.
Figure 3.10. Simulated values (red dots) of the time-integrated fluorescence signal (the Response, Eq. 3.32) for different magnitudes of the magnetic field are plotted with the theoretically predicted Lorentzian (blue curve). The FWHM lies at $B = \pm 7 \cdot 10^{-4}$ T, which corresponds to the point where $2\omega_r/\tau = 1$ for the simulated system.
3.5 Simulation of time-resolved fluorescence signals for BaF

The numerical model described above will be used to model the time-resolved fluorescence signal from the radiative decay of the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ states of BaF as measured in an experiment [5]. Specifically, the contribution of quantum beats to a LIF signal given various experimental conditions and properties of the BaF molecule will be quantified. A quantitative understanding of the modulation of the LIF signal due to quantum beats allows the excited state lifetime to be determined from the experimental data with high precision.

3.5.1 Experimental method and conditions

3.5.1.1 Laser pulses and power spectral density

The method employed in the current experiment [5] incorporates time-resolved LIF detection. A continuous wave tunable titanium sapphire laser is modulated through an acousto-optic modulator (AOM) to yield pulsed light in the detection chamber which propagates orthogonal to the molecular beam (see Fig. 3.11). The pulses have an approximately rectangular intensity profile in time, with a duration of 40 ns, and a fall time (between 90 and 10% of the amplitude) of 11 ns. The frequency bandwidth of the laser pulses is Fourier-limited. The power spectral density of the laser pulses is not expected to have been constant over the full data collection time, due to small changes in the configuration of the laser and the optics.

3.5.1.2 Light collection

Part of the emitted fluorescence of the molecules is focused onto a photomultiplier tube (PMT) using lenses, so that light from a solid angle of $0.026 \cdot 4\pi$ is collected. The PMT is located above the interaction region where the molecular beam and laser pulses cross, so that it collects light in a direction orthogonal to both the propagation of the molecules and the excitation radiation. The time distribution of the number of photons detected by the PMT after each light pulse is recorded for a large number of pulses.

3.5.1.3 Polarisation

The polarisation of the light pulses was not controlled, and is expected to be elliptical due to birefringence in e.g. the optical fibres that transport the light. Additionally,
the polarisation of the laser pulses is not expected to have been constant over the full
data collection time, due to small changes in the configuration and properties of the
laser and the optics.

3.5.1.4 Magnetic field
The magnetic field was measured at two points exterior to the detection chamber at a
distance of around 30 cm from the interaction region using a Hall probe (see Fig. 2.7).
A linear interpolation of these measurements was done to approximate the field in
the interaction region. This yielded a magnetic field with a magnitude of $10^{-4}$ T, in
a direction (in the lab frame as shown in Fig. 2.7) $(x_L, y_L, z_L) = (0.33, 0.93, -0.13)$. This measurement does not provide an accurate value for the magnetic field in the
interaction region, but provides a good estimate of its order of magnitude. It is likely
that the measurement was influenced by the proximity of vacuum gauges attached to
the vacuum chamber, and the measurement therefore provides an upper bound on
the magnetic field in the interaction region.
3.5.2 Modelling of experimental conditions: determination of simulation parameters

The parameters to be used in the model for the simulation of the time-resolved fluorescence signal cannot all be determined based on experimental conditions, as many of the relevant variables are unknown. The spectral power density and polarisation of the radiation, and the magnitude and direction of the magnetic field, are crucial in quantifying the contribution of quantum beats to the fluorescence signal. These parameters are not known precisely, but are experimentally constrained, so that only a subset of the total parameter space relevant for consideration can be identified.

3.5.2.1 Excitation geometry

The excitation radiation propagates horizontally, orthogonal to the direction of detection. The angle $\eta$ between the propagation vector and the magnetic field, and the parameters $\varepsilon$ and $\beta$ determine the decomposition of the polarisation ellipse of the pulses into the spherical basis. This dictates the relative strength of $\Delta m = +1$, $\Delta m = -1$ and $\Delta m = 0$ transitions. The measurements of the magnetic field suggest that $\eta \approx 71^\circ$. As the exact polarisation of the excitation radiation is not known, the parameters $\varepsilon$ and $\beta$ can not be greatly constrained.

3.5.2.2 Allowed transitions

Because the polarisation of the excitation radiation is not known, all transitions for which $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$ must be considered. The frequency of the excitation radiation is tuned such that it is resonant with the $A^2\Pi_{1/2}(\nu = 0; J = 1/2) \leftarrow X^2\Sigma^+ (\nu = 0)$ (860 nm) or $A^2\Pi_{3/2}(\nu = 0; J = 3/2) \leftarrow X^2\Sigma^+ (\nu = 0)$ (815 nm) electronic transition. The excited and ground states are however split into different hyperfine, rotational, and Zeeman substates, which drastically increases the number of possible transitions.

The Fourier limited bandwidth of the pulse of excitation radiation is $\sim 16$ MHz, which is too small for the coherent excitation of the different hyperfine levels of the $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ states [36, 37]. Thus, the excitation radiation was only resonant with a single hyperfine component of the excited state for a given pulse.

The magnetic field in the interaction region and the power spectral density of the excitation radiation does allow for the coherent excitation of Zeeman substates for which $\Delta m_F = \pm 2$, as the magnetic interaction energies in low magnetic fields are
\[ \Delta E_Z(2^2\Pi_{1/2}) = 0.30 \cdot 10^4 \cdot m_F \cdot B \quad \text{MHz} \cdot \text{T}^{-1}, \]  
(3.33)

\[ \Delta E_Z(2^2\Pi_{3/2}) = 1.1 \cdot 10^4 \cdot m_F \cdot B \quad \text{MHz} \cdot \text{T}^{-1}. \]  
(3.34)

The laser pulse might therefore excite the BaF molecule to a coherent superposition of e.g. the \(|F = 1, m_F = 1\rangle\) and \(|F = 1, m_F = -1\rangle\) substates of the \(A^2\Pi_{3/2}\) state, as their energy separation in the measured magnetic field is within the bandwidth of the laser pulses. Quantum beats are then expected to be observable due to the transition

\[
(I) : \quad \frac{1}{\sqrt{2}}(|1, 1\rangle + |1, -1\rangle) \rightarrow |0, 0\rangle,
\]

at a frequency of 2.2 MHz. The polarisation component of the light that excites the molecules to a non-superposition state contributes to the strength of transitions like e.g.

\[
(II) : \quad |1, 0\rangle \rightarrow |0, 0\rangle,
\]

which do not produce quantum beats, and when observed together with transitions like (I), decrease the contrast of the modulation of the fluorescence [39].

For a geometry in which the excitation radiation propagates perpendicularly to the magnetic field (\(\eta = 90^\circ\)), the transitions (I) and (II) are the only possible decays to the ground state for excitation to the \(F = 1\) hyperfine component of the \(A^2\Pi_{1/2}(J = 1/2)\) and \(A^2\Pi_{3/2}(J = 3/2)\) excited states.

### 3.5.2.3 Excitation times

The experimental pulse duration of 40 ns allows for a corresponding range of excitation times for different molecules. However, as the expected period of the Zeeman quantum beats is much greater than the pulse duration, the difference in excitation times will only lead to a small difference in the phase of quantum beats from molecules excited at different times. The fluorescence is therefore simulated for the case that all molecules are excited simultaneously at \(t = 0\).
3.5.2.4 Detection geometry parameters

As described in Sec. 3.5.1.4, the direction of the magnetic field was determined to be approximately vertical. Specifically, based on the measurements taken, the magnetic field makes an angle of around $\delta = 19^\circ$ with the viewing direction of the PMT. The uncertainty in this angle is however rather large, due to the crude nature of the measurement of the magnetic field. Correspondingly, the azimuthal angle of detection $\gamma$ is also uncertain.

The modelled detection solid angle $\sigma$ can be set equal to the experimentally determined solid angle of $0.026 \cdot 4\pi$ sr centred on the viewing direction of the PMT.

3.5.3 Survey of simulated signals for various polarisations and detection directions

To investigate the effect on the time-resolved fluorescence signal of different experimental parameters that are unknown, a survey of simulated signals using a range of simulation parameters corresponding to different experimental conditions was conducted.

For this survey, simulation of radiative decay from the $F = 1$ hyperfine component and its Zeeman substates of the $A^2\Pi_{3/2}(J = 3/2)$ excited state to the ground state ($X^2\Sigma^+(J = 1/2, F = 0)$) was chosen.

The polarisation as parameterised by $\epsilon$ and $\beta$, and the detector polar and azimuthal angles $\delta$ and $\gamma$ were varied. The angle between the propagation vector of the radiation and the magnetic field $\eta$ was kept constant at $\eta = 90^\circ$. Specifically, simulations were carried out for $\epsilon \subset [1, 10]$, $\beta \subset [0, \pi/2]$, and $(\delta, \gamma) \subset [0, \pi/2]$. The magnetic field was set equal to $10^{-4}$ T. The lifetime for spontaneous decay was set as $\tau = 50$ ns, which is close to the value reported in previous measurements of the excited state lifetime [35, 40]. Signals were simulated using a small detection solid angle of $\sigma = 4\pi \cdot 10^{-4}$ sr for rapid angular integration and to maximise the sensitivity to the detection direction.

3.5.3.1 Results & Discussion

Simulated time-resolved fluorescence signals for the decay of the $A^2\Pi_{3/2}(J = 3/2, F = 1)$ excited state to the ground state are plotted in Fig. 3.12 for $\gamma = 0$, and 3.13 for $\gamma = \pi/4$.

A harmonic modulation of the exponential decay with a frequency of 2.2 MHz
can be seen in the data, which is the expected frequency for Zeeman quantum beats produced by the simulated transition (see Sec. 3.2). In the figure, the signal is plotted over 400 ns, which is only 88% of a full beat period.

Signals for $\varepsilon = 10$ correspond to approximately linear polarisation. The different values of $\beta$ then correspond to the orientation of the electric field relative to the magnetic field. As can be seen in the plots, the modulation of the exponential decay due to quantum beats is very pronounced for light polarised perpendicular ($\beta = \pi/2$) to the magnetic field, and disappears for a polarisation parallel ($\beta = 0$) to the magnetic field. Specifically, the amplitude of the modulation of the time-resolved fluorescence signal is proportional to the strength of the polarisation component perpendicular to the magnetic field.

From the signals for elliptical polarisations ($\varepsilon = 2$), it can be concluded that the modulation of the signal due to quantum beats is suppressed for smaller polar detection angles $\delta$. Moreover, the modulation amplitude decreases for smaller angles between the detection direction and the magnetic field as $\sin^2(\delta)$.

It can be seen that a changing the azimuthal angle of fluorescence detection $\gamma$ by $\pi/4$ causes an equal shift in the phase of the harmonic modulation, which evidences that the azimuthal angle of fluorescence detection $\gamma$ determines the phase of the quantum beat signal.
Figure 3.12. Simulated time-resolved fluorescence signals for the decay of the $A^2\Pi_{3/2}$ state are shown on a linear (a) and (b) logarithmic scale, for a variety of excitation and detection parameters, using a lifetime of $\tau = 50$ ns. $\epsilon$ is the ratio of the semi-major axis of the ellipse to the semi-minor axis, $\beta$ is the angle between the magnetic field and the semi-major axis of the polarisation ellipse, and $\delta$ is the angle between the direction of fluorescence detection and the magnetic field. $\epsilon = 1$ corresponds to circular polarisation, and the corresponding fluorescence signal is therefore a pure exponential. The azimuthal angle of fluorescence detection is $\gamma = 0$ for all signals in this plot, and the detection solid angle is small: $\sigma = 4\pi \cdot 10^{-4}$ sr. Note that the blue curve ($\epsilon = 10, \delta = \pi/2, \beta = 0$) coincides with the pure exponential ($\epsilon = 1$), and the purple ($\epsilon = 2, \delta = \pi/8, \beta = \pi/2$) and orange ($\epsilon = 2, \delta = \pi/8, \beta = \pi/4$) curves very nearly do.
Figure 3.13. Simulated time-resolved fluorescence signals for the decay of the $A^2\Pi_{3/2}$ state are shown on a linear (a) and (b) logarithmic scale, for a variety of excitation and detection parameters, using a lifetime of $\tau = 50$ ns. $\epsilon$ is the ratio of the semi-major axis of the ellipse to the semi-minor axis, $\beta$ is the angle between the magnetic field and the semi-major axis of the polarisation ellipse, and $\delta$ is the angle between the direction of fluorescence detection and the magnetic field. $\epsilon = 1$ corresponds to circular polarisation, and the corresponding fluorescence signal is therefore a pure exponential. The azimuthal angle of fluorescence detection is $\gamma = \pi/4$ for all signals in this plot, and the detection solid angle is small: $\sigma = 4\pi \cdot 10^{-4}$ sr. Note that the blue curve ($\epsilon = 10, \delta = \pi/2, \beta = 0$) coincides with the pure exponential ($\epsilon = 1$), and the purple ($\epsilon = 2, \delta = \pi/8, \beta = \pi/2$) and orange ($\epsilon = 2, \delta = \pi/8, \beta = \pi/4$) curves very nearly do.
3.5.4 Simulated experimental signal: upper bound on quantum beat modulation

To provide an upper bound on the modulation of the exponential decay signal due to quantum beats, the time-resolved fluorescence signal was simulated using model parameters that mirror experimental conditions as closely as possible. Unknown experimental parameters were modelled using values that yield the largest modulation of the signal within experimental constraints.

For the current simulation, the case that a laser pulse excites the molecules to the Zeeman substates of the $A^2\Pi_{3/2}(J = 3/2, F = 1)$ excited state at $t = 0$ after which they are left to decay spontaneously to the $X^2\Sigma^+(J = 1/2, F = 0)$ state is modelled. The signal from the decay of the $A^2\Pi_{1/2}$ state is expected to be similar, but the frequency of the quantum beats will be lower due to the smaller Zeeman splitting (Eq. 3.33).

The largest contrast of the quantum beats is obtained for polarisation perpendicular to the magnetic field. Therefore, $\beta$ was set to $\pi/2$, and $\epsilon$ was set to an arbitrary value of 2 to describe an elliptical polarisation perpendicular to the magnetic field. The angle between the propagation direction of the excitation radiation and the magnetic field was set to $\eta = 71^\circ$, matching experimental conditions.

The detection geometry relative to the magnetic field was parameterised to match the experimental geometry. Signals were simulated for the large experimental collection solid angle of $\sigma = 0.0026 \cdot 4\pi$ sr centred around a direction $(\gamma, \delta) = (68^\circ, 19^\circ)$.

3.5.4.1 Results & Discussion

The simulated experimental signal is shown in Figs. 3.14a and 3.14b.

A harmonic modulation of the exponential decay signal with a frequency of 2.2 MHz can be seen in the data, which is the expected frequency for Zeeman quantum beats for the simulated transition. The contrast of the quantum beats is small due to the modelled experimental conditions used in the time-resolved fluorescence detection. As noted in Sec. 3.5.3, the small angle between the detection direction and the magnetic field causes a strong suppression of the modulation amplitude.

Additionally, the elliptically polarised excitation pulses used in the experiment excite both superposition and non-superposition excited states. These non-superposition states are stationary (except for the spontaneous decay), and observing
their decay decreases the contrast of the quantum beats.

Quantum beats in the measured signal are expected to have an even lower contrast than the simulated signals. This is due to the fact that the modelled signal simulates the fluorescence for a single hyperfine and rotational component of the $A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$ transition. As the excitation radiation was likely not resonant with a single hyperfine transition over the full data collection time, decay signals from different excited hyperfine states were summed over. As the $g_F$ factors for different hyperfine states can be significantly different, the signal may contain beats at different frequencies, thus washing out the modulation of the signal when it is averaged over all laser pulses [37, 41]. The beat contrast is expected to be mitigated through a similar mechanism for different excited rotational states.

Structure in the ground state (rotational or hyperfine), also decreases the contrast of quantum beats. As transitions to different ground states are fundamentally distinguishable, the angular transition amplitudes for these transitions do not interfere with each other, and therefore decrease the relative contribution of beats to the signal. Quantum beats due to degeneracy of the ground state are possible in coherent ensembles of atoms and molecules, but can only occur when the separations between the atoms or molecules are small compared to the optical wavelength [24], which is not the case in the experiment.

The laser pulse duration of 40 ns entails a range of excitation times, which would cause the phase of quantum beats in the signal to vary over a corresponding range of around $30^\circ$ ($8^\circ$ for the $^2\Pi_{1/2}$ state). This effect again diminishes the contrast of the modulation.
Figure 3.14. Simulated time-resolved fluorescence signals for the decay of the $A^2\Pi_{3/2}(\nu = 0; N = 0; F = 1)$ state are shown on a linear (a) and logarithmic (b) scale, for excitation and detection parameters that mirror experimental conditions, using a lifetime of $\tau = 50$ ns. $\epsilon$ is the ratio of the semi-major axis of the ellipse to the semi-minor axis, $\beta$ is the angle between the magnetic field and the semi-major axis of the polarisation ellipse. Signal were simulated for the collection solid angle used in the experiment of $\sigma = 0.0026 \cdot 4\pi$ sr centred around a direction $(\gamma, \delta) = (68^\circ, 19^\circ)$. $\epsilon = 1$ corresponds to circular polarisation, and the corresponding fluorescence signal is therefore a pure exponential.
3.6 Conclusions

3.6.1 Quantum beats in lifetime measurements using time-resolved LIF detection

The time-evolution of excited coherent superposition states manifests as a modulation of the transition probability to the ground state, which causes a corresponding modulation of a time-resolved fluorescence signal known as quantum beats. LIF spectroscopy experiments using pulsed excitation in which excited state lifetimes are measured by extracting the time constant from a time-resolved fluorescence signal are sensitive to these quantum beats. An exact determination of the radiative lifetime using this method therefore requires a quantitative understanding of the quantum beats so that the modulation of the exponential decay can be factored out.

3.6.2 Numerical model for time-resolved fluorescence signals

To quantify the contribution of quantum beats to an experimental time-resolved fluorescence signal, a numerical model was developed. This numerical model can be used to simulate fluorescence signals given experimental conditions and properties of the atom or molecule. The angle- and time-dependent intensity of fluorescence is captured through the rotation of angular transition amplitude surfaces. These surfaces represent the angular part of the dipole transition matrix elements, where the length of a vector from the origin to the surface is the transition amplitude for a direction that corresponds to the orientation of the vector. These surfaces are rotated to model the action of the time-evolution operator. The numerical model thus explicitly simulates the precession of the transition dipole moment.

3.6.3 Model validation: Simulation of the Hanle effect

To validate the implementation of time-dependence in the numerical model, the fluorescence signal $S(t)$ for transitions from Zeeman substates of a simple two-level system was simulated and integrated over time (see Fig. 3.10). The time-integrated simulated signals as a function of the applied field follow the theoretically predicted Lorentzian, which confirms that the model is able to qualitatively capture the Hanle effect.
3.6.4 Survey of simulated signals for various polarisations and detection directions

To investigate the effect of different experimental conditions on Zeeman quantum beats in a fluorescence signal, a survey was performed for a range of simulation parameters corresponding to a variety of excitation polarisations and detection geometries (see Figs. 3.12 and 3.13). It was found that the amplitude of the modulation of the time-resolved fluorescence signal is proportional to the strength of the polarisation component perpendicular to the magnetic field. Moreover, the modulation amplitude decreases for smaller angles between the detection direction and the magnetic field as $\sin^2(\delta)$. The azimuthal angle of fluorescence detection $\gamma$ determines the phase of the quantum beat signal.

3.6.5 Simulated time-resolved fluorescence signal of BaF: upper bound on quantum beat modulation

An upper bound on the amplitude of Zeeman quantum beats present in a measured time-resolved fluorescence signal for the $A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$ transition of BaF has been determined using the numerical model. The amplitude for quantum beats in the $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ transition is expected to be similar, but the frequency will be lower due to the smaller Zeeman splitting of the excited state (Eq. 3.33). In the experiment, the magnetic field and the polarisation of the excitation radiation were not controlled.

From the simulated signals (see Figs. 3.14a & 3.14b), it can be concluded that quantum beats in the experimental signal are strongly suppressed due to the small angle between the detection direction and the magnetic field. Additionally, the contrast of the quantum beats is mitigated by detection of the decay from non-superposition states, which the molecules are excited to by the elliptically polarised radiation pulses.

Moreover, the laser pulses in the experiment were likely resonant with different hyperfine and rotational transitions over the full data collection time, which yield quantum beats of different frequencies. The accumulated signal thus contains beats of different frequencies, which washes out the modulation of the exponential decay. In addition, degeneracies in the ground state allow multiple distinguishable transitions from a single excited state, which also decreases the contrast of the quantum beats.

All molecules were modelled to have been excited simultaneously, whereas the 40 ns excitation pulse in the experiment allows a range of excitation times and
corresponding phases of the quantum beats to be present in the signal.

In the simulations, the time-resolved fluorescence signal for the decay from a single hyperfine level and its Zeeman substates to a non-degenerate ground state after excitation of all molecules at a single time was modelled, which thus yields an upper bound on the modulation of the experimental signal due to quantum beats.
4 Summary

The supersonic BaF source of the NL-eEDM collaboration is used to test various elements of the full experimental strategy and to perform spectroscopy of the BaF molecule. A laser-induced fluorescence detection setup is currently coupled to the supersonic source. At the start of this project, the signal-to-noise ratio of the fluorescence detection was rather low (Fig. 2.1), and an effort was made to improve it through the suppression of stray light and the enhancement of fluorescence collection.

The former entailed the development and application of a measurement method to quantify the relative reflectance of NIR-absorbing surfaces. This method allowed various candidate surfaces for application in the LIF detection chamber to be compared quickly and quantitatively. Application of the chosen surface onto components inside the detection led to a reduction of stray light in the detection chamber by an order of magnitude, and facilitated (nearly) background-free spectroscopy of the BaF molecule (see e.g. Fig. 4.1).

Using the improved LIF detection setup, a lifetime measurement of the excited state of BaF using time-resolved fluorescence detection following pulsed excitation was performed. A measurement of this type is sensitive to quantum beats, and a determination of the lifetime therefore requires a quantitative understanding of the modulation induced by these beats so that their effect on the extracted lifetime might be eliminated in the analysis.

To this end, a quantitative model of time-resolved fluorescence was developed and implemented numerically. Using this model, the dependence of the frequency, amplitude, and phase of Zeeman quantum beats on experimental parameters was quantified. Time-resolved fluorescence signals for the excited state of BaF given the known detection geometry and properties of the excitation radiation were simulated to yield an upper bound on the modulation of the measured signal induced by Zeeman quantum beats (Fig. 3.14). It was concluded that this upper bound is within the
Figure 4.1. Laser-induced fluorescence spectroscopy of the different hyperfine subtransitions of the $A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$ transition which shows very little background signal. Seven Lorentzian functions with a FWHM of 7 MHz were fitted to the data, which is close to the natural linewidth. In the lifetime measurement of this excited state, the laser frequency was scanned over these hyperfine transitions which causes the total modulation due to quantum beats of different frequencies to be washed out in the accumulated signal.

The current statistical uncertainty of the lifetime measurement. The actual amplitude of quantum beats in the signal is expected to be lower, as fluorescence data from multiple hyperfine transitions (see Fig. 4.1) was accumulated in the signal as the laser frequency was scanned over them. These various transitions will produce beats at different frequency, whereby the modulation of the signal is washed out.
5 Appendix

5.1 Script for processing photographs

The Matlab script below converts the CCD photographs to intensity profiles as described in Sec. 2.2.2. Typical input and output of this script can be found in Figs. 5.1 and 5.2 respectively.

![Image of a typical CCD photograph](image-url)

**Figure 5.1.** A typical CCD photograph of the screen that light reflected from samples is projected onto, used as input for the image processing script (see 5.1).
<table>
<thead>
<tr>
<th>Intensity distribution</th>
<th>X-projection</th>
<th>Y-projection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodised Aluminium</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Intensity Distribution, X-projection, Y-projection](image)

**Figure 5.2.** The intensity profiles produced by the script using Fig. 5.1 as input.

```matlab
% Sander M. Vermeulen
% November 21, 2018
% photo2plots: Code to convert CCD photographs to intensity profiles

% load image
filename=('disk.bmp');
Img=imread(filename);
sampleshort=filename(1:end-4)
samplelong="Cleaning"
% convert to double precision greyscale
I=rgb2gray(Img);
I=double(I);
% average image
N = 25; %set block size
I = blkproc(I, [N N], 'mean2');

% subtract 'background'
backgr=imread('background.bmp');
backgr=rgb2gray(backgr);
backgr=blkproc(backgr, [N N], 'mean2');
I=I-backgr;
Pxbackgr=sum(backgr);
Pybackgr=sum(backgr,2);

% create projections
Px=sum(I);
Py=sum(I,2);
widthvector=linspace(0,18,length(Px));
heightvector=linspace(0,11,length(Py));

% get meta parameters
Itot=sum(sum(I))

% width
[Pxmax,xindexmax]=max(Px);
```
WidthAtMax = widthvector(xindexmax);
xindex1 = find(Px >= Pxmax/2, 1, 'first');
xindex2 = find(Px >= Pxmax/2, 1, 'last');
xFWHMindex = xindex2 - xindex1 + 1;
xFWHM = widthvector(xindex2) - widthvector(xindex1);
sigma_x = xFWHM / (2 * sqrt(2 * log(2)))
w_x = xFWHM / 2;

%height
[Pymax, yindexmax] = max(Py);
HeightAtMax = heightvector(yindexmax);
yindex1 = find(Py >= Pymax/2, 1, 'first');
yindex2 = find(Py >= Pymax/2, 1, 'last');
yFWHMindex = yindex2 - yindex1 + 1;
yFWHM = heightvector(yindex2) - heightvector(yindex1);
sigma_y = yFWHM / (2 * sqrt(2 * log(2)))
w_y = yFWHM / 2;

% Compute Gaussian integral (excl. numerical factors)
Jx = sigma_x * Pxmax;
Jy = sigma_y * Pymax;
Jtot = Jx * Jy;

% plot figures
[x, y] = size(I);
X = 1:x;
Y = 1:y;
[xx, yy] = meshgrid(Y, X);

set(0, 'defaultAxesFontSize', 20)

% set plot dimensions
ymin = 1;
ymax = length(Y);
xmax = length(X);
xmin = 1;
Lmax = 25;
PImax = 700;
Pimin = 0;

% show photo
% figure(1); imshow(Img)

% show 3D height map
figure(2); mesh(xx, yy, I, 'linewidht', 1.5);
figtype_surf = 'surf';
title(['Sample long', ': I_{tot} = ', num2str(Jtot/10^4, 2), ', w_{x,y} = ',
'(', num2str(w_x, 2), ', ', num2str(w_y, 2), ')']);
axis([ymin ymax xmin xmax 0 Lmax]);
%xlabel('width \~0.2 m')
%ylabel('height \~0.1 m')
lxlabel('intensity (arb. u.)')
set(gca,'xticklabel',[])
set(gca,'yticklabel',[])
caxis([Lmin Lmax]);
colorbar;

%Print the figure to PDF
h=figure(2);
set(h,'Units','Inches');
pos = get(h,'Position');
set(h,'PaperPositionMode','Auto','PaperUnits','Inches','PaperSize',[pos(3), pos(4)])
print(h,strcat(sampleshort,figtype_surf),'-dpng','-r0')
print(h,strcat(sampleshort,figtype_surf),'-dpdf','-r0')

%calculate Gaussians
Gx=Pxmax.*exp(-((widthvector-WidthAtMax)/(2*sigma_x)).^2);  
Gy=Pymax.*exp(-((heightvector-HeightAtMax)/(2*sigma_y)).^2);

%show projections and Gaussians
%Plot width projection
figure(3);plot(widthvector,Px,'linewidth',1.5);
figtype_Px='Px';
axis([min(widthvector) max(widthvector) 0 PPLmax]);
title([samplelong,: I_{max} = ',num2str(Pxmax,4),', w_x = ', num2str(w_x,2)]);
xlabel('width (cm)')
%set(gca,'xticklabel',[])
ylabel('intensity (arb. u.)')

%Print figure to PDF
h=figure(3);
set(h,'Units','Inches');
pos = get(h,'Position');
set(h,'PaperPositionMode','Auto','PaperUnits','Inches','PaperSize',[pos(3), pos(4)])
print(h,strcat(sampleshort,figtype_Px),'-dpng','-r0')
print(h,strcat(sampleshort,figtype_Px),'-dpdf','-r0')

%Plot height projection
figure(4);plot(heightvector,Py,'linewidth',1.5); %projection onto height
figtype_Py='Py';
axis([min(heightvector) max(heightvector) 0 PPLmax]);
title([samplelong,: I_{max} = ',num2str(Pymax,4),', w_y = ', num2str(w_y,2)]);
xlabel('height (cm)')
%set(gca,'xticklabel',[])}
ylabel('intensity (arb. u.)')

%Print figure to PDF
h=figure(4);
set(h,'Units','Inches');
pos = get(h,'Position');
set(h,'PaperPositionMode','Auto','PaperUnits','Inches','PaperSize',[pos(3), pos(4)]
print(h,strcat(sampleshort,figtype_Py),'-dpng','-r0')
print(h,strcat(sampleshort,figtype_Py),'-dpdf','-r0')
5.2 Painted components of the LIF setup

![Figures showing components of the LIF setup with paint applied](image)

**Figure 5.3.** Photos of the components with AZ Technology’s MLS-85-SB paint applied to them. (a) The anti-scatterer. (b) The mount that holds the lenses. (c) The copper discs that enclose the laser beam. (d) The beam dump.

5.3 Matlab code of the numerical model for time-resolved fluorescence signals

The numerical model in Sec. 3.3 is implemented as two Matlab scripts: ATA_3D and multiATA_3D. The first computes angular transition amplitudes and time-resolved fluorescence signals for a single transition, and the second computes signals for a
weighted sum of the $|1,1\rangle \rightarrow |00\rangle$ and $|1,0\rangle \rightarrow |00\rangle$ transitions corresponding to a certain polarisation and detection geometry.

5.3.1 Script: ATA_3D.m

```matlab
% Sander M Vermeulen
% 10-07-2019
% Numerical model for time-resolved fluorescence signals
%------------------------------------------------------
%------------------------------------------------------
% This script generates the angular transition amplitude for a transitions
% between angular momentum eigenstates in the form of a
% 3D closed surface. This surface is rotated according to the time
% evolution operator which is a function of the magnetic field.
% The signal is obtained by reading out the distance from the surface to
% the origin at a certain angular position (phi,theta) as it rotates.
% 
% Code was written and operated using Matlab R2018a

tic
% Set simulation parameters
RES=[20,400];% Set resolution of angular emission, which is the number of points
to calculate between 0 and 2pi.  
dt=1; %Timestep in ns
tmax=200;%Total time to simulate in ns

% Set time of excitation
% t_ex=0;

% Define constants (REQUIRED THAT L(DEGREE)>=M(ORDER))
Ja=1; %J of initial state
Ma=1; %M of initial state

Jb=0; %J of final state
Mb=0; %M of final state

DM=Mb-Ma; %Calculate Delta M
DJ=Jb-Ja; %Calculate Delta J

% Set magnetic field, lifetime, and gamma magnitudes
B=10*1.10311*10ˆ(-4);%0.6*10ˆ(-4); %Magnetic field in Tesla
tau=50;%10ˆ(-10); %lifetime in ns

gamma=2*pi*1.11*10ˆ4*10ˆ6*10ˆ(-9); %2*pi*1.11*10ˆ4*10ˆ6*10ˆ(-9); %rad*ns^-1*T^-1

% Set field directions
xvec=[1 0 0];
yvec=[0 1 0];
zvec=[0 0 1];
```

67/98
Bvec=[0 0 1];

if abs(DM)==1
    Evec=[0 1 0];
else
    Evec=[0 0 1];
end

alpha=atan2d(norm(cross(zvec,Evec)),dot(zvec,Evec)); %Calculate angle between E and z axis in degrees.

if Ja<Ma, error('The ORDER (Ma) must be less than or equal to the DEGREE(Ja).'); end
if Jb<Mb, error('The ORDER (Mb) must be less than or equal to the DEGREE(Jb).'); end

%------------------------------------------------------------------
% Calculate transition amplitude in 2D, in the y,z-plane
%------------------------------------------------------------------

% Set up a coordinate vector THETA
THETA=linspace(0,2*pi,RES(2)); % Elevation/latitude/angle from x,y-plane

% Check whether integer or half-integer spherical harmonics are needed
if floor(Ja)==Ja && floor(Jb)==Jb && floor(Ma)==Ma && floor(Mb)==Mb
    %Integer spherical harmonics
    Pmj_a=legendre(Ja,cos(THETA));
    Pmj_b=legendre(Jb,cos(THETA));
    if Ja˜=0
        Pmj_a=squeeze(Pmj_a(abs(Ma)+1,:,:));
    end
    if Jb˜=0
        Pmj_b=squeeze(Pmj_b(abs(Mb)+1,:,:));
    end

    a1=((2*Ja+1)/(4*pi));
    a2=factorial(Ja-Ma)/factorial(Ja+Ma);
    Ca=sqrt(a1*a2);
    Yjm_a=Ca*Pmj_a; %*exp(1i*M*PHI);
end

b1=((2*Jb+1)/(4*pi));

b2=factorial(Jb-Mb)/factorial(Jb+Mb);
Cb=sqrt(b1*b2);
Yjm_b=Cb*Pmj_b; % exp(1i*M*PHI);

elseif floor(Ja+Jb)==Ja+Jb && floor(Ma+Mb)==Ma+Mb
% Half-integer spherical harmonics (unnormalised)
Yjm=zeros(2,2,length(THETA));
Yjm_HI(1,1,:)=sqrt(sin(THETA));
Yjm_HI(2,1,:)=cos(THETA).*sqrt(sin(THETA));
Yjm_HI(2,2,:)=sin(THETA).^(3/2);
Yjm_a=transpose(squeeze(Yjm_HI(Ja+1/2,abs(Ma)+1/2,:)));
Yjm_b=transpose(squeeze(Yjm_HI(Jb+1/2,abs(Mb)+1/2,:)));
else
  error('Combination of J, M_j is not physical');
end

% Calculate dipole spherical harmonics
P1m=legendre(1,cos(THETA));
C11=sqrt(3/(8*pi));
C10=sqrt(3/(4*pi));
P11=squeeze(P1m(2,:,:));
P10=squeeze(P1m(1,:,:));
Y11=C11*P11;
Y10=C10*P10;
Y00=1;
Y1min1=(-1)*conj(Y11);
% Ysig=(Y10+4*exp(1i*pi/2)*Y11);
% Ypi=Y11;
% Ysigma=1+cos(THETA).^2;

% Plot photon spherical harmonics
figure(8)
polarplot(THETA,Y11.^2+Y10.^2,THETA,abs(Y11).^2,THETA,abs(Y10).^2,'b','LineWidth',1.5);

% Calculate transition
if abs(DM)==1 && abs(DJ)==1 % Check whether DeltaM less or equal 1, DeltaJ equal 1
  A=conj(Yjm_a).*Y11.*Yjm_b;
elseif DM==0 && abs(DJ)==1
  A=conj(Yjm_a).*Y10.*Yjm_b;
else
  error('|DeltaM| \ rangle 1 or |DeltaJ| \ neq 1, dipole transition is not physically possible');
end

% Normalise transition amplitude squared
I=normalize(abs(A).^2,'norm',1*RES(2));
A=sqrt(I);
\[
\text{I} = A^2 / (\text{sum}(A^2));
\]
\[
\text{A} = \sqrt{\text{I}};
\]

% Plot dipole transition amplitude in 2D

figure(1)
polarplot(THETA, abs(A)^2, 'k', 'LineWidth', 1.5);
title(['I(\theta): |', num2str(Ja), ', ', num2str(Ma), '\rangle', '\rightarrow |', num2str(Jb), ', ', num2str(Mb), '\rangle'])
set(gca, 'FontSize', 24)
Ax = gca; % current axes
% Ax.ThetaGrid = 'off';
% Ax.RGrid = 'off';
% rticks([])
% rticklabels({'0','1'})
thetaticks([0 45 90 135 180 225 270 315])
% Ax.RTickLabel = {'0','1'};
% Ax.ThetaTickLabel = {'0','90','180','270'};

%---------------------------------------------------------------------
%---------------------------------------------------------------------
% Calculate transition amplitude in 3D
%---------------------------------------------------------------------
%---------------------------------------------------------------------

% Rotate 2D emission pattern to align dipole axis with z-axis, to allow
correct surface of revolution to be made
[x,y] = pol2cart(THETA, A);
rotfig=figure;
emission2D=plot(x,y);
rotate(emission2D,[0 0 1],-alpha);
newx = emission2D.XData;
newy = emission2D.YData;
plot(newx,newy)
close(rotfig)
[THETA,A]=cart2pol(newx,newy);
figure(10)
polarplot(THETA,A)

% Form 3D emission pattern, by generating surface of revolution
PHI = linspace(0, pi, RES(1));
[THETA,PHI] = meshgrid(THETA, PHI);
A3D = A.*exp(1i*1*PHI);
A3Dsq=abs(A3D);
%A3Dsq = abs(A3D).^2; %Take absolute square of amplitude to obtain observable
intensity
[X3D,Y3D,Z3D]=sph2cart(PHI,THETA,A3Dsq); %Convert back to cart. coord. to obtain
rotable surface

% Plot 3D emission pattern
figure(2);
% set(gcf,'Position',[100 100 1650 1350])
set(gcf,'color','w')
set(gca,'color','w')
axes_max=1.5;
axes_min=-axes_max;
CM=cool(RES(1));
colormap(flipud(CM))
brightness(-0.5)
C=X3D.^2+Y3D.^2+Z3D.^2;
% axes('position',[0.1 0.05 0.8 0.8]);
ang_emission3D=surf(X3D,Y3D,Z3D,'FaceAlpha',1,'EdgeAlpha',0.1,'LineWidth',0.01,'EdgeColor','k'); %was 0.1
title(['I(\phi, \theta): |',num2str(Ja), ', ',num2str(Ma),']\rightarrow |',num2str(Jb), ', ',num2str(Mb),']')
set(gca,'FontSize',24)
view(135,30)
xlabel('x'); ylabel('y'); zlabel('z');
xlim([axes_min axes_max]); ylim([axes_min axes_max]); zlim([axes_min axes_max])

%Draw labeled origin centered axes
xl = xlim();
yl = ylim();
zl = zlim();
line(4*xl, [0,0], [0,0], 'LineWidth', 3, 'Color', 'r');
line([0,0], 4*yl, [0,0], 'LineWidth', 3, 'Color', 'b');
line([0,0], [0,0], 4*zl, 'LineWidth', 3, 'Color', 'g');
text(axes_max+0.2,0,0,'Laser','Color','r','FontSize',20)
text(0,axes_max+0.1,0,'FD','Color','b','FontSize',20)
text(0,0,axes_max+0.1,'B','Color','g','FontSize',20)

%Draw polarisation vector
if Evec==[0 0 1]
    line([1.2,1.2], [0,0], [-0.5,0.5], 'LineWidth', 3, 'Color', 'r', 'LineJoin','round' );
    line([1.2,1.2], [0,0.1], [-0.5,-0.4], 'LineWidth', 2, 'Color', 'r');
    line([1.2,1.2], [0,-0.1], [-0.5,-0.4], 'LineWidth', 2, 'Color', 'r');
    line([1.2,1.2], [0.1,0.1], [0.5,0.4], 'LineWidth', 2, 'Color', 'r');
    line([1.2,1.2], [0.1,-0.1], [0.5,0.4], 'LineWidth', 2, 'Color', 'r');
    text(1.2,0.6,0,'E','Color','r','FontSize',20)
else
    Evec=[0 0 1]
    line([1.2,1.2], [-0.5,0.5],[0,0], 'LineWidth', 3, 'Color', 'r');
    line([1.2,1.2], [-0.5,-0.4],[0,0.1], 'LineWidth', 2, 'Color', 'r');
    line([1.2,1.2], [-0.5,-0.4],[0,-0.1], 'LineWidth', 2, 'Color', 'r');
    line([1.2,1.2], [0.5,0.4],[0,0.1], 'LineWidth', 2, 'Color', 'r');
    line([1.2,1.2], [0.5,0.4],[0,-0.1], 'LineWidth', 2, 'Color', 'r');
text(1.2,0.6,0,'E','Color','r','FontSize',20)
end

axis off
caxis([0 1]);

colorbar('Ticks',[0,0.5,1])
% axis off

lightangle(135,45)  % create a light
lighting gouraud  % preferred method for lighting curved surfaces
material dull

%Rotate 3D emission pattern back to original orientation, with dipole axis
%aligned with Electric field vector-polarisation
rotate(ang_emission3D,[1 0 0],-alpha)
rotate(ang_emission3D,[0 0 1],90)

%Extract coordinates from 3D emission pattern in proper orientation
X3D=ang_emission3D.XData;
Y3D=ang_emission3D.YData;
Z3D=ang_emission3D.ZData;

figure(9)
surf(X3D,Y3D,Z3D,'EdgeAlpha',0.1);
xlabel('x'); ylabel('y'); zlabel('z');
xlim([axes_min axes_max]); ylim([axes_min axes_max]); zlim([axes_min axes_max]);

%Set depth ordering of plotted objects
ax=gca;
ax.SortMethod = 'depth';
avx.SortMethod=ChildOrder';

%Convert to spherical coordinates
clear PHI THETA A3Dsq
[PHI,THETA,A3Dsq]=cart2sph(X3D,Y3D,Z3D);

disp('Press any key to start simulation of transition amplitude over time.')
pause;

%---------------------------------------------------------------------------
%---------------------------------------------------------------------------
% Calculate transition amplitude over time in magnetic field
%---------------------------------------------------------------------------
%---------------------------------------------------------------------------

%Set up variables
t=(0:dt:tmax);
Atime=zeros(length(t),size(A3Dsq,1),size(A3Dsq,2));
A_PMT_3D=zeros(1,length(t));

%Set position of PMT=position in spherical coordinates to save amplitude
tover time. Theta position currently cannot be set, and is zero by default.
PMTpos=pi/2;
PMTpos_index=round((PMTpos)/(RES(1)/(pi)));
%Set up figure to plot 3D emission pattern over time
figure(3)
%Set up figure to plot PMT signal over time
figure(4)
set(gcf,'Position',[1300 10 900 750])
set(gcf,'color','w')
set(gca,'color','w')

%Set up array to store frames for movie
F(length(t)) = struct('cdata',[],'colormap',[]);

%Set up video recording, write frames directly to movie file
formatSpec = "d%d-d%d-d, RES=%0d, dt=%0d, tmax=%0d, B=%0d, gamma=%0d, tau=%0d.d.avi";
filename = sprintf(formatSpec,Ja,Ma,Jb,Mb,RES(1),dt,tmax,B,gamma,tau);
myVideo = VideoWriter(filename,'Motion JPEG AVI');
myVideo.Quality = 100;
open(myVideo);

formatSpec_signal = "SIGNAL d%d-d%d-d, RES=%0d, dt=%0d, tmax=%0d, B=%0d, gamma=%0d, tau=%0d.avi";
filename_signal = sprintf(formatSpec_signal,Ja,Ma,Jb,Mb,RES(1),dt,tmax,B,gamma,tau);
myVideo_signal = VideoWriter(filename_signal,'Motion JPEG AVI');
myVideo_signal.Quality = 100;
open(myVideo_signal);

for nn=1:length(t) %loop over time

%Reset variables to prevent bug in which arrays expand on every
%iteration
clearvars X3D Y3D Z3D

%Apply exponential decay to the wavefunction amplitude A
if nn>(t_ex/dt)
    Atime(nn,:,:)=(exp((-t(nn)+t_ex)/(1*tau))).*A3Dsq;
    A3Dsq_tnn=Atime(nn,:,:).*exp(1i*(1)*PHI);
    A3Dsq_tnn=squeeze(A3Dsq_tnn);
else
    Atime(nn,:,:)=0*A3Dsq;
    A3Dsq_tnn=Atime(nn,:,:).*exp(1i*(1)*PHI);
    A3Dsq_tnn=squeeze(A3Dsq_tnn);
end
%Convert back to cartesian coordinates
[X3D,Y3D,Z3D]=sph2cart(PHI,THETA,A3Dsq_tnn);

%Plot the emission pattern at time t-nn
figure(3)
emission3D=surf(X3D,Y3D,Z3D,C,'EdgeAlpha',0.1 ,'FaceAlpha',1);
view(135,30)
colormap(flipud(CM))
xlim([axes_min axes_max]); ylim([axes_min axes_max]); zlim([axes_min axes_max]);
xlabel('x'); ylabel('y'); zlabel('z');
line(4*xl, [0,0], [0,0], 'LineWidth', 2.5, 'Color', 'r');
line([0,0], 4*yl, [0,0], 'LineWidth', 2.5, 'Color', 'b');
line([0,0], [0,0], 4*zl, 'LineWidth', 2.5, 'Color', 'g');
text(axes_max+0.2,0,0,'Laser','Color','r','FontSize',18)
text(0,axes_max+0.1,0,'FD','Color','b','FontSize',18)
text(0,0,axes_max+0.1,'B','Color','g','FontSize',18)

%Draw polarisation vector
if Evec==[0 0 1]
    line([1,1], [0,0], [-0.5,0.5], 'LineWidth', 3, 'Color', 'r');
    line([1,1], [0,0], [-0.5,-0.4], 'LineWidth', 3, 'Color', 'r');
    line([1,1], [0,-0.1], [-0.5,-0.4], 'LineWidth', 2, 'Color', 'r');
    line([1,1], [0.01], [0.5,0.4], 'LineWidth', 3, 'Color', 'r');
    line([1,1], [0,-0.1], [0.5,0.4], 'LineWidth', 2, 'Color', 'r');
    text(1,0.35,0,'E','Color','r','FontSize',18)
elseif Evec==[0 1 0]
    line([1,1], [-0.3,0.3],[0,0], 'LineWidth', 3, 'Color', 'r');
    line([1,1], [-0.3,-0.3],[0,0], 'LineWidth', 3, 'Color', 'r');
    line([1,1], [-0.3,-0.25],[0,0.05], 'LineWidth', 2, 'Color', 'r');
    line([1,1], [0.3,0.25],[0,0.05], 'LineWidth', 3, 'Color', 'r');
    line([1,1], [0.3,0.25],[0,-0.05], 'LineWidth', 2, 'Color', 'r');
    text(1.035,0,'E','Color','r','FontSize',18)
else
end

axis off
%lightangle(90,0) % create a light
%lighting gouraud % preferred method for lighting curved surfaces
%material dull

%Rotate the emission pattern according to precession in B-field
if nn>(t_ex/dt)
    DTHETA= B*gamma*t(nn); %Calculate precession angle at time t
    direction = Bvec;
    rotate(emission3D,direction,rad2deg(DTHETA))
else
end
% Extract data from rotated plot
newX3D = emission3D.XData;
newY3D = emission3D.YData;
newZ3D = emission3D.ZData;

[newPHI,newTHETA,newAsq]=cart2sph(newX3D,newY3D,newZ3D);
newPHI=mod(newPHI,2*pi); % Rescale PHI coordinates to be between 0 and 2pi

% Find 'PMT signal' - transition amplitude at certain azimuth in x,y-plane.
% Currently no support for B/=z, or PMT positions outside of the x,y plane.

if abs(DM)==1 % If DeltaM=1 then symmetry in Phi coordinate is lost,
 % Matlab rotate function then works such that rotations
 % around z(-B) only change Phi array. The amplitude at
 % fixed Phi (PMT position), can then be found by finding
 % the phi coordinate (=entry in newPHI array) closest to
 % the PMT position, and reading out the amplitude as the
 % entry in the newA array corresponding to that entry in
 % the newPHI array (same row,column).

    for ii=1:size(newPHI,1) % Loop over rows of newPHI array, to find index

        [Value, Index] = min(abs(abs(newPHI(ii,:))-PMTpos));

        if Value <= (pi)/(RES(1))
            PHIIndex=Index;
            Value;
            A_PMT_3D(nn)=newAsq(ii,PHIIndex);
        else

        end

    end

else % DeltaM=0, which means that symmetry in all coordinates is
 % more or less conserved under rotations around z(-B). However Matlab
 % rotate function changes the Phi array and only the Phi array
 % to manifest this rotation for some reason. Code below should
 % function for arbitrary Bvec and PMTpos but only works for Bvec=zvec
 % and PMTpos in x,y plane (THETA=0).

    for ii=1:size(newPHI,1) % Loop over rows of newPHI array, to find index


\[
\{\text{Value, Index}\} = \text{min}(\text{abs}(\text{abs}(\text{newPHI}(ii,:)) - \text{PMTpos}));
\]

\[
\text{if Value} \leq \frac{\pi}{\text{RES}(1)}
\]

\[
\text{PHIIndex} = \text{Index}; \quad \text{Value};
\]

\[
\text{else}
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
\text{for } jj=1:\text{size(newTHETA,2)} \% \text{Loop over rows of newTHETA array, to find index}
\]

\[
\{\text{Value, Index}\} = \text{min}(\text{abs}(\text{abs}(\text{newTHETA}(:,jj)) - \text{PMTpos}));
\]

\[
\text{if Value} \leq \frac{2\pi}{\text{RES}(2)}
\]

\[
\text{THETAIndex} = \text{Index}; \quad \text{Value};
\]

\[
\text{else}
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
\text{A\_PMT\_3D} = \text{newAsq} \text{(PHIIndex, THETAIndex)};
\]

\[
\text{end}
\]

\[
\text{figure(4)}
\]

\[
\text{plot}(t(1:nn), \text{A\_PMT\_3D}(1:nn), 'b', 'LineWidth', 1.5)
\]

\[
\text{xlabel('Time (ns)', 'FontSize', 24, 'color', 'k'); ylabel('Signal', 'FontSize', 24, 'color', 'k');}
\]

\[
\text{set(gcf, 'color', 'w')}
\]

\[
\text{set(gca, 'color', 'w')}
\]

\[
\text{set(gca, 'XColor', 'k')}
\]

\[
\text{set(gca, 'YColor', 'k')}
\]

\[
\text{Frame = getframe(figure(3)); writeVideo(myVideo, Frame);}
\]

\[
\text{Frame\_signal = getframe(figure(4)); writeVideo(myVideo\_signal, Frame\_signal);}
\]

\[
\text{time = t(nn)}
\]
5.3.2 Script: multi_ATA_3D.m

```matlab
% Sander M Vermeulen
% 10-07-2019
% Numerical model for time-resolved fluorescence signals
%------------------------------------------------------

% This script works the same as ATA_3D, but allows for the addition of ATAs
% for the 11->00 and 10->00 transitions according to the polarisation.
% In addition, this script accounts for the detection geometry relative to
% the magnetic field.
%
% Code was written and operated using Matlab R2018a

% Set simulation parameters
RES=[20,400]; % Set resolution of angular emission, which is the number of points
to calculate between 0 and 2pi. 1
dt=1; %Timestep in ns
tmax=200; %Total time to simulate in ns

% Set magnetic field, lifetime, and gamma magnitudes
B=10.*1.10311*10ˆ(-4); %Magnetic field in Tesla
tau=50*10ˆ10; %lifetime in ns
M_F=1; %1.33333; %average M_F
gamma=M_F*2*pi*1.11*10ˆ4*10ˆ6*10ˆ(-9); %rad*nsˆ-1*Tˆ-1

% Set field directions
xvec=[1 0 0];
yvec=[0 1 0];
zvec=[0 0 1];
Bvec=[0 0 1];

% Set PMT viewing angles
theta_0=0.3225; %Viewing cone opening angle
delta_0=0.3311; %Angle between B field and PMT viewing cone center axis
delta=pi/2; %delta_0-theta_0/2; %Coordinates on solid angle span
phi=0;

% Polarisation ellipse
```

end
figure(5)
plot(t,A_PMT_3D,'b','LineWidth',1.5)
close(myVideo);
close(myVideo_signal);
gamma*B;
sum(A_PMT_3D)*dt;
toc
% Set ratio of semi-major to semi-minor axis
eps=2;

% Set angle between semi-major axis and B field
beta=pi/2;

a=1;
b=1/eps;
% a=1; % requires a >= b
% b=0.1;
ratio=((a-b)/(a+b));
d11=(sin(delta))^2*ratio*(sin(beta))^2+1;
d00=2-d11;

% Y11 component
W(1)=d11; % Only works for W(1)>= w(2)
% Y00 component
W(2)=d00;
% Normalize weights
W=normalize(W,'norm');

%%%%%%%%%%%%%%%%%%%
% Calculate amplitudes of transitions
%%%%%%%%%%%%%%%%%%%

% Set up a coordinate vector THETA
THETA=linspace(0,2*pi,RES(2)); % Elevation/latitude/angle from x,y-plane

% Calculate dipole spherical harmonics
P1m=legendre(1,cos(THETA));
C11=sqrt(3/(8*pi));
C10=sqrt(3/(4*pi));
P11=squeeze(P1m(2,:,:));
P10=squeeze(P1m(1,:,:));
Y11=C11*P11;
Y10=C10*P10;
Y00=1;
Y1min1=(-1)*conj(Y11);

%%%%%%%%%%%%%%%%%%%
% TRANSITION 1 (No QB: 10 -> 00)
%%%%%%%%%%%%%%%%%%%

% Define constants (REQUIRED THAT L(DEGREE)>=M(ORDER))
J_1a=1; % J of initial state
M_1a=0; % M of initial state
J_1b=0; % J of final state
M_1b=0; % M of final state

% W(1)=1 ; % 1/sqrt(2);
DM1=M_{lb}-M_{la}; \quad \%\text{Calculate Delta M}
DJ1=J_{lb}-J_{la}; \quad \%\text{Calculate Delta J}

\% Check whether integer or half-integer spherical harmonics are needed
if floor(J_{la})==J_{la} && floor(J_{lb})==J_{lb} && floor(M_{la})==M_{la} && floor(M_{lb})==M_{lb}
    \% Integer spherical harmonics
    Pmj_{la}=\text{legendre}(J_{la},\cos(\text{THETA}));
    Pmj_{lb}=\text{legendre}(J_{lb},\cos(\text{THETA}));
    if J_{la}~0
        Pmj_{la}=\text{squeeze}(Pmj_{la}(\text{abs}(M_{la})+1,:,:));
    end
    if J_{lb}~0
        Pmj_{lb}=\text{squeeze}(Pmj_{lb}(\text{abs}(M_{lb})+1,:,:));
    end
    a1=((2\times J_{la}+1)/(4\pi));
    a2=\text{factorial}(J_{la}-M_{la})/\text{factorial}(J_{la}+M_{la});
    Ca=\sqrt{a1\times a2};
    Yjm_{la}=Ca\times Pmj_{la};
else
    \% Half-integer spherical harmonics (unnormalised)
    Yjm=\text{zeros}(2,2,\text{length}(\text{THETA}));
    Yjm_HI(1,1,:)=\sqrt{\sin(\text{THETA})};
    Yjm_HI(2,1,:)=\cos(\text{THETA})\times\sqrt{\sin(\text{THETA})};
    Yjm_HI(2,2,:)=\sin(\text{THETA}).^3/2);
    Yjm_{la}=\text{transpose}(\text{squeeze}(Yjm_HI(J_{la}+1/2,\text{abs}(M_{la})+1/2,:)));
    Yjm_{lb}=\text{transpose}(\text{squeeze}(Yjm_HI(J_{lb}+1/2,\text{abs}(M_{lb})+1/2,:)));
end
\%Calculate transition
if abs(DM1)==1 && abs(DJ1)==1 \% Check whether DeltaM less or equal 1, DeltaJ equal 1
    A1=Yjm_{la}.*Y11.*Yjm_{lb};
elseif DM1==0 && abs(DJ1)==1
    A1=Yjm_{la}.*Y10.*Yjm_{lb};
else
    error('\text{|DeltaM| \rangle 1 or \text{|DeltaJ| \neq 1, dipole transition is not physically possible}');
end
\%Normalise transition amplitude 1 squared
I=\text{normalize}(\text{abs}(A1).^2,'\text{norm}',1\times\text{RES}(2));

A1=\sqrt{I};

%--------------------------------------------------------------------------
%TRANSITION 2 (QB: 11\rightarrow00)
%--------------------------------------------------------------------------
% Define constants (REQUIRED THAT L(\text{DEGREE})\geq M(\text{ORDER}))

J_{2a}=1; \quad & \text{\% J of initial state} \\
M_{2a}=1; \quad & \text{\% M of initial state} \\
J_{2b}=0; \quad & \text{\% J of final state} \\
M_{2b}=0; \quad & \text{\% M of final state}

DM2=M_{2b}-M_{2a}; \quad & \text{\%Calculate Delta M} \\
DJ2=J_{2b}-J_{2a}; \quad & \text{\%Calculate Delta J}

% Check whether integer or half-integer spherical harmonics are needed

\text{if} \quad \text{floor}(J_{2a})=J_{2a} \quad & \text{\% floor}(J_{2b})=J_{2b} \quad & \text{\% floor}(M_{2a})=M_{2a} \quad & \text{\% floor}(M_{2b})=M_{2b} \\
% Integer spherical harmonics
PMJ_{2a}=\text{legendre}(J_{2a},\cos(\text{THETA})); \\
PMJ_{2b}=\text{legendre}(J_{2b},\cos(\text{THETA})); \\
\text{if} \quad J_{2a}=0 \\
\quad PMJ_{2a}={\text{\%s}}queeze(PMJ_{2a}(\text{abs}(M_{2a})+1,:,:)); \\
\text{end}

\text{if} \quad J_{2b}=0 \\
\quad PMJ_{2b}={\text{\%s}}queeze(PMJ_{2b}(\text{abs}(M_{2b})+1,:,:)); \\
\text{end}

a1=((2\times J_{2a}+1)/(4\times\pi)); \\
a2=\text{factorial}(J_{2a}-M_{2a})/\text{factorial}(J_{2a}+M_{2a}); \\
Ca=\sqrt{a1\times a2}; \\
YJM_{2a}=Ca\times PMJ_{2a};

b1=((2\times J_{2b}+1)/(4\times\pi)); \\
b2=\text{factorial}(J_{2b}-M_{2b})/\text{factorial}(J_{2b}+M_{2b}); \\
Cb=\sqrt{b1\times b2}; \\
YJM_{2b}=Cb\times PMJ_{2b}; \\
\% exp(1i\times M\times PHII);

\text{elseif} \quad \text{floor}(J_{2a}+J_{2b})=J_{2a}+J_{2b} \quad & \text{\% floor}(M_{2a}+M_{2b})=M_{2a}+M_{2b} \\
% Half-integer spherical harmonics (unnormalised)
YJM=\text{zeros}(2,2,\text{length}(\text{THETA})); \\
YJM_HI(1,1,:)={\text{\%s}}quez(\sin(\text{THETA})); \\
YJM_HI(2,1,:)={\text{\%s}}quez(\sin(\text{THETA})\times\text{\%s}rnt(\sin(\text{THETA})))); \\
YJM_HI(2,2,:)={\text{\%s}}quez(\sin(\text{THETA})\times(3/2)); \\
YJM_{2a}=\text{transpose}(\text{squeeze}(YJM_HI(J_{2a}+1/2,\text{abs}(M_{2a})+1/2,:)))); \\
YJM_{2b}=\text{transpose}(\text{squeeze}(YJM_HI(J_{2b}+1/2,\text{abs}(M_{2b})+1/2,:))));
error('Combination of J, M_j is not physical');
end
%Calculate transition 2
if abs(DM2)==1 && abs(DJ2)==1 %Check whether DeltaM less or equal 1, DeltaJ equal 1
    A2=Yjm_2a.*Y11.*Yjm_2b;
elseif DM2==0 && abs(DJ2)==1
    A2=Yjm_2a.*Y10.*Yjm_2b;
else
    error('|DeltaM| \rangle 1 or |DeltaJ| \neq 1, dipole transition is not physically possible');
end
%Normalise transition amplitude 2 squared
I=normalize(abs(A2).^2,'norm',1*RES(2));
A2=sqrt(I);

%---------------------------------------------------------------------
%---------------------------------------------------------------------
% Take Weighted Sum of Amplitudes of Transitions
%---------------------------------------------------------------------
%---------------------------------------------------------------------

W(1)=1
W(2)=1/(sqrt(2))*W(1);
A=W(1)*A1+W(2)*A2;

%---------------------------------------------------------------------
%---------------------------------------------------------------------
%Plot dipole transition amplitude in 2D
%---------------------------------------------------------------------
%---------------------------------------------------------------------

figure(1)
polarplot(THETA,abs(A).^2,'k','LineWidth',1.5);
title([('I(\phi, \theta): |',num2str(J_1a), ', ',num2str(M_1a),') \rightarrow |',num2str(J_1b), ', ',num2str(M_1b),') + |',num2str(J_2a), ', ',num2str(M_2a),') \rightarrow |',num2str(J_2b), ', ',num2str(M_2b),')
set(gca,'FontSize',24)
Ax = gca; % current axes
% Ax.ThetaGrid = 'off';
% Ax.RGrid = 'off';
%rticks([])
%thetaticks([0 45 90 135 180 225 270 315])
% Ax.RTickLabel = {'0','1'};
% Ax.ThetaTickLabel = {'0','90','180','270'};
%---------------------------------------------------------------------
if W(1) >= W(2)
  if abs(DM1) == 0
    Evec = yvec;
  elseif abs(DM1) == 1
    Evec = zvec;
  else
    error('something wrong')
  end
elseif W(2) >= W(1)
  if abs(DM2) == 0
    Evec = yvec;
  elseif abs(DM2) == 1
    Evec = zvec;
  else
    error('something wrong')
  end
else
  error('something wrong')
end
alpha = atan2d(norm(cross(zvec,Evec)),dot(zvec,Evec)); % Calculate angle between E and z axis in degrees.

% Rotate 2D emission pattern to align dipole axis with z-axis, to allow correct surface of revolution to be made
[x,y] = pol2cart(THETA,A);
rotfig = figure;
emission2D = plot(x,y);
rotate(emission2D,[0 0 1],-alpha);
newx = emission2D.XData;
ewy = emission2D.YData;
plot(newx,newy)
close(rotfig)
[THETA,A] = cart2pol(newx,newy);
% figure(10)
% polarplot(THETA,A)

% Form 3D emission pattern, by generating surface of revolution
PHI = linspace(0, pi, RES(1));
[THETA,PHI] = meshgrid(THETA,PHI); A3D = A.*exp(1i*1*PHI); A3Dsq = abs(A3D).^2;
[X3D,Y3D,Z3D] = sph2cart(PHI,THETA,A3Dsq); % Convert back to cart. coord. to obtain rotatable surface

% Plot 3D emission pattern
figure(2);
set(gcf,'Position',[100 100 1200 950])
set(gcf,'color','w')
set(gca,'color','w')
axes_max=1.5;
axes_min=-axes_max;
CM=cool(RES(1));
%colormap(CM)
colormap(flipud(CM))
%brighten(-0.5)
C=X3D.*2+Y3D.*2+Z3D.*2;
%figure(5); surf(C)
% axes('position',[0.1 0.05 0.8 0.8]);
ang_emission3D=surf(X3D,Y3D,Z3D,C,'FaceAlpha',1,'EdgeAlpha',0.1,'LineWidth',0.001,
 'EdgeColor','k');
% title(['I(\phi, \theta): |',num2str(J_1a), ', ',num2str(M_1a),'angle','
 |',num2str(J_1b), ', ',num2str(M_1b),'angle','+','|',num2str(J_2a),...
 |',num2str(J_2b),', ',num2str(M_2a),'angle','\rightarrow |',num2str(J_2b), ', ',num2str(M_2b),'angle'])
set(gca,'FontSize',24)
view(135,20)
xlabel('x'); ylabel('y'); zlabel('z');
xlim([axes_min axes_max]); ylim([axes_min axes_max]); zlim([axes_min axes_max])
xl = xlim();
yl = ylim();
zl = zlim();
line(4*xl, [0,0], [0,0], 'LineWidth', 3, 'Color', 'r');
line([0,0], 4*yl, [0,0], 'LineWidth', 3, 'Color', 'b');
line([0,0], [0,0], 4*zl, 'LineWidth', 3, 'Color', 'g');
text(xaxes_max+0.2,0.0,0.3,'Laser','Color','r','FontSize',20)
text(0,0,axes_max+0.1,'FD','Color','b','FontSize',20)
text(0,0,axes_max+0.1,'B','Color','g','FontSize',20)
%Draw polarisation vector
line([1.2,1.2], [-0.25,0.25], [-0.25,0.25], 'LineWidth', 3, 'Color', 'r');
line([1.2,1.2], [-0.25,0.25], [-0.25,0.25], 'LineWidth', 2, 'Color', 'r');
line([1.2,1.2], [-0.25,0.25], [-0.25,0.25], 'LineWidth', 2, 'Color', 'r');
line([1.2,1.2], [0.25,0.25], [0.25,0.25], 'LineWidth', 2, 'Color', 'r');
line([1.2,1.2], [0.25,0.25], [0.25,0.25], 'LineWidth', 2, 'Color', 'r');
text(1.2,0.3,0.3,'E','Color','r','FontSize',20)
%line([-1,1], [0,0], [0.5,0.5], 'LineWidth', 2, 'Color', 'k');
axis off
caxis([0 1]);
%colorbar('Ticks',[0,0.5,1],'Color','k')
% axis off
% lightangle(180,0) % create a light
% lighting gouraud % preferred method for lighting curved surfaces
% material dull
%Set depth ordering of plotted objects
ax=gca;
ax.SortMethod = 'depth';
% Rotate 3D emission pattern back to original orientation, with dipole axis aligned with Electric field vector-polarisation
rotate(ang_emission3D,[1 0 0],-alpha)

% If Evec(2)==1
rotate(ang_emission3D,zvec,90)
elseif Evec(3)==1
rotate(ang_emission3D,yvec,90)
end

% Rotate pattern to initial phase
rotate(ang_emission3D,[0 0 1],rad2deg(-phi));

% Extract coordinates from 3D emission pattern in proper orientation
X3D=ang_emission3D.XData;
Y3D=ang_emission3D.YData;
Z3D=ang_emission3D.ZData;

% Convert to spherical coordinates
[PHI,THETA,A3D]=cart2sph(X3D,Y3D,Z3D);

disp('Press any key to start simulation of transition amplitude over time.')
pause;

% Set up variables
t=(0:dt:tmax);
Atime=zeros(length(t),size(A3D,1),size(A3D,2));
A_PMT_3D=zeros(1,length(t));

% Set position of PMT=position in spherical coordinates to save amplitude over time. Theta position currently cannot be set, and is zero by default.
PMTpos=pi/2;
PMTpos_index=round((PMTpos)*RES(1)/(pi));

% Set up figure to plot 3D emission pattern over time
% Set up video recording, write frames directly to movie file
formatSpec = ";\%d\%d-\%d\%d + \%d\%d-\%d\%d, RES=\%d.0d, dt=\%d.0d, tmax=\%d.0d, B=\%d.0d, gamma
-\%d.0d, tau=\%d.0d.avi\";
filename = sprintf(formatSpec,J_1a,M_1a,J_1b,M_1b,J_2a,M_2a,J_2b,M_2b,RES(1),dt,
tmax,B,gamma,tau);
myVideo = VideoWriter(filename,'Motion JPEG AVI');
myVideo.Quality = 100;
open(myVideo);

formatSpec_signal = "SIGNAL \%d\%d-\%d\%d + \%d\%d-\%d\%d, RES=\%d.0d, dt=\%d.0d, tmax=\%d.0d, B
-\%d.0d, gamma=\%d.0d, tau=\%d.0d.avi\";
filename_signal = sprintf(formatSpec_signal,J_1a,M_1a,J_1b,M_1b,J_2a,M_2a,J_2b,
M_2b,RES(1),dt,tmax,B,gamma,tau);
myVideo_signal = VideoWriter(filename_signal,'Motion JPEG AVI');
myVideo_signal.Quality = 100;
open(myVideo_signal);

for nn=1:length(t) % loop over time
    % Reset variables to prevent bug in which arrays expand on every
    % iteration
    clearvars X3D Y3D Z3D

    % Apply exponential decay to the wavefunction amplitude A
    Atime(nn,:) = exp(-t(nn)/(1*tau)).*A3D;
    A3D_tnn = Atime(nn,:).*exp(1i*(1)*PHI);
    A3D_tnn = squeeze(A3D_tnn);

    % Convert back to cartesian coordinates
    [X3D,Y3D,Z3D] = sph2cart(PHI,THETA,A3D_tnn);
    % C = ones(size(X3D));
    % C = X3D.'*2+Y3D.'*2+Z3D.'*2;

    % Plot the emission pattern at time t=nn
    figure(3)
colormap(flipud(CM))
emission3D=surf(X3D,Y3D,Z3D,C,'EdgeAlpha',0.1);
view(145,20)
xlim([axes_min axes_max]); ylim([axes_min axes_max]); zlim([axes_min axes_max])
xlabel('x'); ylabel('y'); zlabel('z');
line(4*xl, [0,0], [0,0], 'LineWidth', 2.5, 'Color', 'r');
line([0,0], 4*yl, [0,0], 'LineWidth', 2.5, 'Color', 'b');
line([0,0], [0,0], 4*zl, 'LineWidth', 2.5, 'Color', 'g');
text(axes_max+0.2,0,0.1,'Laser','Color','r','FontSize',18)
text(0,axes_max+0.1,0,'FD','Color','b','FontSize',18)
text(0,0,axes_max+0.1,'B','Color','g','FontSize',18)

%Draw polarisation vector
line([1,1], [-0.25,0.25], [-0.25,0.25], 'LineWidth', 3, 'Color', 'r');
line([1,1], [-0.25,-0.15], [-0.25,-0.25], 'LineWidth', 2, 'Color', 'r');
line([1,1], [0.25,0.15], [0.25,0.25], 'LineWidth', 3, 'Color', 'r');
line([1,1], [0.25,0.25], [0.25,0.15], 'LineWidth', 2, 'Color', 'r');
text(1,0.3,0.3,'E','Color','r','FontSize',20)

axis off
%lightangle(90,0)  % create a light
%lighting gouraud  % preferred method for lighting curved surfaces
%material dull

%Rotate the emission pattern according to precession in B-field
DTHETA=B*gamma*t(nn); %Calculate precession angle at time t
direction = Bvec;
rotate(emission3D,direction,rad2deg(DTHETA))

%Extract data from rotated plot
newX3D = emission3D.XData;
newY3D = emission3D.YData;
newZ3D = emission3D.ZData;
[newPHI,newTHETA,newA]=cart2sph(newX3D,newY3D,newZ3D);
newPHI=mod(newPHI,2*pi); %Rescale PHI coordinates to be between 0 and 2pi
% newTHETA=mod(newTHETA,2*pi);
figure(5)
figure(6)
figure(7)
figure(8)
figure(9)
figure(10)
figure(11)
figure(12)
figure(13)
figure(14)
figure(15)
figure(16)
figure(17)
figure(18)
figure(19)
figure(20)

%Find 'PMT signal'=transition amplitude at certain azimuth in x,y-plane.
%Currently no support for B=/=z, or PMT positions outside of the x,y
%plane.
if abs(DM)==1 %If DeltaM=1 then symmetry in Phi coordinate is lost, %Matlab rotate function then works such that rotations %around z(-B) only change Phi array. The amplitude at %fixed Phi (PMT position), can then be found by finding %the Phi coordinate (=entry in newPHI array) closest to %the PMT position, and reading out the amplitude as the %entry in the newA array corresponding to that entry in %the newPHI array (same row,column).

for ii=1:size(newPHI,1) %Loop over rows of newPHI array, to find index

    [Value, Index] = min(abs(abs(newPHI(ii,:))-PMTpos));
    if Value <= (pi)/(RES(1))
        PHIIndex=Index;
        Value;
        A_PMT_3D(nn)=newA(ii,PHIIndex);
    else
        end
    end

else %DeltaM=0, which means that symmetry in all coordinates is %more or less conserved under rotations around z(-B). However Matlab %rotate function changes the Phi array and only the Phi array %to manifest this rotation for some reason. Code below should %function for arbitrary Bvec and PMTpos but only works for Bvec=zvec %and PMTpos in x,y plane (THETA=0).

for ii=1:size(newPHI,1) %Loop over rows of newPHI array, to find index

    [Value, Index] = min(abs(abs(newPHI(ii,:))-PMTpos));
    if Value <= (pi)/(RES(1))
        PHIIndex=Index;
        Value;
    else
        end
    end

for jj=1:size(newTHETA,2) %Loop over rows of newTHETA array, to find index
[Value, Index] = min(abs(abs(newTHETA(:,jj))-PMTpos));

if Value <= (2*pi)/(RES(2))
    THETAIndex=Index;
    Value;
else
    end

end

A_PMT_3D(nn)=newA(PIIIIndex,THETAIndex);

end

figure(4)
plot(t(1:nn),A_PMT_3D(1:nn),'b','LineWidth',1.5)
xlabel('Time (ns)','FontSize',24,'color','w'); ylabel('Signal','FontSize',24,'color','w');
set(gcf,'color','w')
set(gca,'color','w')
set(gca, 'XColor', 'k')
set(gca, 'YColor', 'k')

time=t(nn)
F(nn)=getframe(figure(3));
Frame=getframe(figure(3));
writeVideo(myVideo, Frame);
Frame_signal=getframe(figure(4));
writeVideo(myVideo_signal, Frame_signal);
end

close(myVideo);
close(myVideo_signal);
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7 Bibliography


