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FROM GEOMETRIC PHASES TO INTRACELLULAR SENSING: NEW APPLICATIONS OF THE DIAMOND NITROGEN-VACANCY CENTRE

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Abstract

This thesis consists of two parts, each of which proposes a new application of the diamond nitrogen-vacancy (NV) centre. We first consider the NV centre as a device to detect geometric phases. We show that the Aharonov-Casher phase and Berry's phase may be produced in the NV centre's spin sublevels and observed using existing experimental techniques. We give the background theory to geometric phases, then show how these phases apply to the NV system. Finally, we outline a number of realistic experiments to detect these phases.

The second part considers the behaviour of an NV centre within a diamond nanocrystal which rotates, in a Brownian sense, in a fluid. Our aim is to understand the effect of rotational motion on the initialisation, evolution and readout of an NV centre, motivated by the idea of using colloidal nanodiamonds for biological imaging. We first develop a model to describe the quantum evolution of a rotationally diffusing nanocrystal. The model uses theory developed in NV magnetometry and also the geometric phase theory developed in the first part of this thesis. We then explore the consequences of this model for nanoscale sensing. We show that the tumbling NV system may be used as a sensitive magnetometer with nanoscale resolution and also as a probe of its own rotational motion.

DECLARATION

This is to certify that:

- (i) the thesis comprises only my original work towards the MPhil except where indicated in the Statement of Contributions,
- (ii) due acknowledgement has been made in the text to all other material used,
- (iii) the thesis is less than 50,000 words in length, exclusive of table, maps, bibliographies and appendices.

Dougal Maclaurin

STATEMENT OF CONTRIBUTIONS

This thesis, in Chapters 4 to 7, presents original research conducted since February 2009, except where indicated by reference to other authors. The ideas were developed with my two supervisors, Lloyd Hollenberg and Andrew Martin, and three other collaborators: Andrew Greentree, Liam Hall and Jared Cole. The analytical calculations and numerical simulations are my own.

PUBLICATIONS

The work presented in chapter 4 of this thesis led to the publication of the following article.

Dougal Maclaurin, Andrew D. Greentree, Jared H. Cole, Lloyd C.L. Hollenberg and Andrew M. Martin Single atom-scale diamond defect allows a large Aharonov-Casher phase, Physical Review A, **80** 040104(R) (2009).

In addition, a second manuscript is currently being finalised for submission, based on the work of chapters 6 and 7.

Dougal Maclaurin, Liam T. Hall, Andrew M. Martin and Lloyd C.L. Hollenberg Nanoscale magnetometry and motion imaging with quantum control of a rotationally diffusing nanodiamond (manuscript in preparation)

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INTRODUCTION

The diamond nitrogen-vacancy (NV) centre's electronic spin is a rare example of a solidstate quantum mechanical system that is clean, robust and accessible. Any unitary operation on the spin can be effected using microwave pulses, while non-unitary evolution under optical excitation permits complete spin polarisation and projective readout. Nestled in the uniform diamagnetic environment of the diamond crystal lattice, the NV centre's quantum coherence, a scarce resource in the noisy environment of room-temperature condensed matter systems, can be maintained for milliseconds.

This remarkable system has been the focus of many theoretical [1, 2, 3, 4, 5] and experimental [6, 7, 8, 9, 10, 11] investigations in recent years. It has been proposed as a qubit for quantum information processing [12] and as a highly sensitive sensor of nanoscale magnetic fields [9, 10, 3, 4, 11, 5]. It is this magnetometry context which is most relevant to the present work. To measure magnetic fields a Ramsey-type experiment is typically performed. In such an experiment, the spin is initialised into a coherent superposition of spin states which precess under the influence of magnetic fields by the Zeeman effect. The extent of precession, measured optically, allows very sensitive measurement of the field. Theoretical [5] and experimental [9, 11] studies have shown that magnetic fields can be detected this way with sensitivity as low as $\mu T Hz^{-1/2}$ and nanometre spatial resolution.

This thesis proposes and explores two new applications of the NV system. Firstly, in Chapters 3 and 4, we consider the NV centre as a tool to detect geometric phases, a fundamental prediction of quantum mechanics. The canonical example of a geometric phase is the Aharonov-Bohm (A-B) effect [13], in which a charged particle circulating a solenoid acquires a phase. Crucially, this phase depends only on the amount of magnetic flux enclosed by the particle's trajectory and not on the speed or other details of the particle's motion. The phase is thus termed 'topological' or 'geometric'.

In Chapter 3 we propose an experiment to produce and measure the Aharonov-Casher (A-C) effect using the NV system. The A-C effect is a direct analogue of the A-B effect [14] in which a magnetic dipole encircles a line of charge, acquiring a phase which depends only on the linear density of the enclosed charge. The A-C effect has been detected in a number of systems to date, including atom and neutron beams [15, 16, 17] and in mesoscopic rings [18].

We consider two geometries. Firstly, following the traditional approach, we envisage a diamond crystal mounted on a spinning disk with a charged axle. The phase is measured through a conventional Ramsey-type pulse sequence. We then consider a second, more experimentally feasible, geometry in which the disk spins between the charged plates of a capacitor. The A-C phase thus accrued will alternate as the disk rotates. The alternating phase accumulation is rectified by means of a spin echo pulse sequence which has the additional advantage of extending the coherence lifetime of the NV centre. We find that a phase on the order of 10 radians may be generated this way, larger than that produced in most other systems. Moreover, this would be the first demonstration of the A-C phase in a single quantum system mechanically forced along a macroscopic trajectory. This work was reported in Physical Review A in 2009 [19].

Another geometric phase is Berry's phase, the phase acquired by a system subjected to an adiabatically changing Hamiltonian [20]. In Chapter 4 we show that this phase, too, may be observed using the diamond NV centre by spinning a diamond crystal on its axis. As with the A-C phase we consider two geometries, one which produces a constant rate of phase accumulation and another in which the phase accumulated alternates and a spin echo pulse sequence must be used. We also explore the possibility of producing the phase using nuclear spins, which would dramatically increase coherence times.

After Chapter 4, we turn our attention from the fundamental physics of geometric phases to practical applications of the NV centre to nanoscale biological sensing. Researchers working with NV centres would like to put diamond nanocrystals inside biological cells as nanoscale sensors of magnetic fields. While nanodimaonds have been successfully used as fluorescent biomarkers [21, 22], intracellular nanodimaonds have not yet been used as magnetometers. Part of the difficulty is that previous work with NV magnetometry applies to crystals whose orientation is fixed, whereas a crystal within a cell will diffuse spatially and rotationally. In chapters 5 to 7 we confront this problem. We investigate quantum control and measurement of an NV system within a crystal experiencing classical Brownian rotation.

This research direction was inspired by the previous work with geometric phases, which considered the interplay between classical motion and quantum evolution. Indeed, we will find that Berry's phase is an important effect for a 'tumbling' nanocrystal, arising as a consequence of the rotation of the quantisation axis. Previously we considered Berry's phase merely as an interesting phenomenon in its own right. Here, however, Berry's phase is an unavoidable complication to quantum measurements on a rotating crystal and potentially a valuable source of information.

We build a model of the quantum evolution of a rotationally diffusing NV centre which takes into account Berry's phase and the anisotropic interaction of the NV centre with microwave control pulses and magnetic fields. We show that magnetometry is still possible with a crystal whose axis rotates diffusively, though the sensitivity of the magnetometer is worsened through shorter coherence times and reduced signal contrast. We also show that the fluorescence signal from magnetometry-type experiments can contain valuable information about the rate of the crystal's rotation. 1. INTRODUCTION

2

BACKGROUND TO THE NV CENTRE

2.1 The NV system

The NV centre is a naturally occurring defect in diamond. It consists of a substitutional nitrogen atom in place of a carbon atom next to a vacancy in the crystal lattice as shown in Figure 2.1(a). Corresponding to the tetrahedral crystal structure of diamond, the NV axis has four possible orientations within the crystal.



Figure 2.1: (a) Diagram of NV centre in the diamond lattice. (b) Energy levels and important transitions of the NV centre.

The electronic structure of the NV centre is not entirely understood. Various models have been constructed, involving wavefunctions of up to six electrons [1, 2]. For the purposes of this work, however, the electronic structure may be taken to be that shown in Figure 2.1(b). The important features are the spin triplet ground state, the 532 nm optical excitation, and the ¹A metastable state. Subtleties such as hyperfine states and the excited state structure become important in some sophisticated uses of the NV centre. We will discuss these later in the context of their use. The spin triplet ground state has a 2.88 GHz zero-field splitting between the m = 0($|0\rangle$) and $m = \pm 1$ ($|\pm 1\rangle$) states. The $|\pm 1\rangle$ states can be further split by a magnetic field **B**. The Hamiltonian of the ground state can be taken to be

$$H = \frac{1}{\hbar} DS_z^2 + \gamma \boldsymbol{B} \cdot \boldsymbol{S}, \qquad (2.1)$$

where $D = 2\pi \cdot 2.88$ GHz is the zero-field splitting constant, $\gamma \equiv g\mu_B/\hbar = 2\pi \cdot 28$ GHz/T is the gyromagnetic ratio of the NV centre, and the z-axis lies along the NV crystallographic axis. Common symbols are listed in the appendix. Coherent oscillations between spin states can be achieved with microwave pulses tuned to the appropriate transition as discussed in the next section.

One of the NV centre's great strengths is its coherence time, the time taken for the quantum state of an ensemble of systems to diverge. It is customary to follow the terminology of nuclear magnetic resonance (NMR) in describing coherence times with the symbols T_1 , T_2 and T_2^* .

The 'spin relaxation time' is labelled T_1 . It is the time taken for the spin to thermally equilibrate with its surroundings. In practical terms, this means the time it takes for an ensemble initialised in the $|0\rangle$ state to decohere into a thermal mixture of all three spin sublevels. The NV centre has a very high Debye temperature leading to long T_1 times on the order of ms at room temperature [23].

The 'inhomogeneous broadening' and 'homogeneous broadening' times are labelled T_2^* and T_2 respectively. These are also known as 'dephasing' times as they relate to the loss of phase information over time. If an ensemble of NV centres, each member subjected to a slightly different magnetic field, is initialised in some superposition of $|0\rangle$ and $|1\rangle$, the phase between sublevels will evolve at a slightly different rate for each member of the ensemble. The term 'broadening' is used because of the reciprocal relationship between dephasing times and linewidths. The width of a resonance peak is approximately the inverse of the dephasing time.

In the context of NMR the ensemble of systems is both spatial and temporal, consisting of multiple runs, each involving many spins spread over some region of space. The inhomogeneous/homogeneous distinction refers to the spatial homogeneity of the magnetic field responsible for dephasing. Inhomogeneous broadening may be reduced or eliminated using a spin echo pulse technique, which we discuss further below. In the context of the NV centre the terms are less appropriate as we commonly consider an ensemble of measurements taken over time on a single NV centre, and the spatial homogeneity or otherwise of magnetic fields is unimportant. Following the NV literature, however, we keep the NMR terminology, using them to distinguish between dephasing times with and without a refocusing π -pulse. In physical terms, T_2 refers to dephasing caused by fast-fluctuating fields (compared with the timescale of a single measurement) while T_2^* refers to dephasing from slowly fluctuating fields.

The reason for the NV centre's remarkably long dephasing times is the lack of magnetic moment in the ${}^{12}C$ atoms which make up the diamond crystal. The dephasing which does occur is due to the nuclear spin of isotopic impurities, such as ${}^{13}C$, which mostly determine T_2 , and the electronic spin of diamagnetic impurities such as nitrogen atoms, which contribute to T_2^* . Typical dephasing times are μ s for T_2^* [7] and up to ms for T_2 [10] in isotopically pure diamond.

The optical transitions in the NV centre are important for spin initialisation and readout, both of the which both exploit the ¹A metastable state. Illumination with 532 nm light excites the NV centre which emits photons as it decays. This fluorescence cycle preserves the spin state. During each cycle, there is also a chance of spontaneous decay from the excited triplet to the dark metastable singlet which decays to the $|0\rangle$ state only, with a lifetime of around 250 ns [24].

Excitation with 532 nm light thus effects optical pumping into $|0\rangle$. The same process also allows readout of the spin. Spontaneous decay to the metastable state occurs preferentially for the $|\pm 1\rangle$ states. Since the system produces no fluorescence during its time occupying the metastable state, the $|\pm 1\rangle$ states contribute fewer overall fluorescence counts than the $|0\rangle$ state. This method of readout does have the disadvantage that the $|\pm 1\rangle$ states are necessarily pumped into the $|0\rangle$ state, so that the spin information is destroyed upon measurement. One way to avoid this is to store the spin information in the long-lived nuclear spin, and repetitively read out the state in measurements of the electron

spin [8]. It should be noted that, in general, the spin state will be some superposition of $|0\rangle$ and $|\pm 1\rangle$, and the measurement constitutes a projective quantum measurement onto $|0\rangle$.

2.2 NV magnetometry with DC fields

Most of the present work is based on the idea of using the NV spin state to detect magnetic fields by measuring the Zeeman splitting of Equation (2.1). The approach is to initialise the spin into $|0\rangle$, then to perform some controlled operations on the spin using microwave pulses, such that a final measurement of the spin state will give information about the magnitude of the Zeeman splitting. The techniques are very similar to those developed for NMR, and we borrow heavily from NMR terminology.

For completeness, we briefly review the theory of Rabi oscillations for a general two level system. Consider a two-level system, with Hamiltonian

$$H = \frac{\hbar\omega_0}{2}\sigma_z + \frac{\hbar\Omega}{2}\cos(\omega t)\sigma_x.$$
 (2.2)

The first term is the energy separation between the two states, which in the NV context will be a combination of the zero-field splitting D and the Zeeman splitting from a magnetic field. The second term is due to an applied field, oscillating at ω , which couples the two states with coupling frequency Ω . In the NV context this will be a microwave frequency magnetic field. Provided $\Omega \ll \omega$, the rotating wave approximation may be used to give solutions to the Schrödinger equation which describe coherent spin oscillations of frequency $\Omega_R^2 = \omega^2 + (\Delta \omega)^2$ and amplitude Ω/Ω_R , where $\Delta \omega = \omega - \omega_0$ is the detuning. In the cases we will consider, the detuning will either be small enough (compared with Ω) to be neglected, or else sufficiently large that Rabi oscillations are suppressed.

We will frequently make use of the Bloch sphere representation of a two state system. A general state,

$$\psi = \begin{pmatrix} e^{i\Phi}\cos\frac{\theta}{2}\\ \sin\frac{\theta}{2} \end{pmatrix},\tag{2.3}$$

is represented on the lab frame Bloch sphere as a vector on the unit sphere with polar angle θ and azimuthal angle Φ . This vector precesses about the z-axis due to the energy separation ω_0 . A more useful representation of the state is the rotating frame Bloch sphere, in which the azimuthal angle of the Bloch vector is $\Phi + \omega t$. This vector precesses at the detuning frequency $\Delta \omega$. When we refer to the 'phase' between two states it is generally this angle which we mean, since we are typically interested in the phase relative to the phase of the microwave field.

On the rotating frame Bloch sphere, the Rabi oscillations just described (without detuning) correspond to rotations of the Bloch vector about the x-axis. By changing the phase of the microwave field, rotations can be made to occur about any axis in the x-y plane. Rabi oscillations of finite duration are described by the angle through which the Bloch vector is rotated. A ' π -pulse' thus refers to a pulse which produces an inversion of states and so forth.

We now return to the NV system. The magnetic field of (2.1) is composed of three parts: an applied static magnetic field B_0 along the z-direction, a 'signal' magnetic field $B_s(t)$ also along \hat{z} , and a microwave Rabi field $B_R(t)$ which can be turned on or off, and oscillates along the x-axis at some frequency ω . In general, these fields may have any orientation. However, provided the field strengths (multiplied by γ) are small compared with the zero-field energy splitting, we can neglect all but the z-components of the static or slowly varying fields, B_0 and B_s , and we can neglect the z-component of B_R , which oscillates at frequencies on the order of 2.88 GHz. This is known as the secular approximation, which is valid to first order in the ratio of the field strengths to the zero-field splitting. We can write the approximate Hamiltonian as

$$H \approx \frac{1}{\hbar} DS_z^2 + \gamma (B_0 S_z + B_s S_z + B_{Rx} S_x + B_{Ry} S_y), \qquad (2.4)$$

where $B_0 = \mathbf{B}_0 \cdot \hat{\mathbf{z}}$, $B_s = \mathbf{B}_s \cdot \hat{\mathbf{z}}$, $B_{Rx} = \mathbf{B}_R \cdot \hat{\mathbf{x}}$ and $B_{Ry} = \mathbf{B}_R \cdot \hat{\mathbf{y}}$. The object is to measure the strength of the signal field by appropriately controlling the Rabi field. Initialisation into $|0\rangle$ and projective measurement onto $|0\rangle$ are performed using 532 nm illumination and photon collection. These processes, described in the previous section, are not captured by the above Hamiltonian.

A simple method for measuring B_s is to use optically detected magnetic resonance (ODMR). The microwave field and a 532 nm laser are applied continuously and the rate of fluorescence is observed. If the microwave field is not in tune with either of the two transitions, then the laser will optically pump the system into the $|0\rangle$ state, resulting in a high level of fluorescence. If the microwave field is in tune, however, then the system will oscillate between $|0\rangle$ and (say) $|1\rangle$ and a lower level of fluorescence will be observed. By scanning the microwave frequency and plotting fluorescence rate against frequency, the size of B_s may be inferred from the position of the resonance troughs.

A more sophisticated and sensitive approach is a Ramsey-type experiment (see Figure 2.2(a)). Formally 'Ramsey's method of separated oscillatory fields', the principle of the experiment is as follows. The system is initialised into $|0\rangle$. A $\pi/2$ -pulse is applied, tuned to the $|0\rangle - |1\rangle$ transition based on the known strength of B_0 , obtaining a coherent superposition of $|0\rangle$ and $|1\rangle$ states which then evolves for some time τ under the influence of B_s . During this time, the system will acquire a relative phase, $\Phi = \gamma B_s \tau$, between $|0\rangle$ and $|1\rangle$. Finally, a second $\pi/2$ pulse is applied, which converts this phase information into a population difference. The final population will be $\frac{1}{2} - \frac{1}{2}\cos(\Phi)$, which is measured by illumination and fluorescence detection.

The final data point consists of an average fluorescence count over an ensemble of many runs. This is obtained for various evolution times to obtain a signal $S(\tau)$ given by

$$S(\tau) = \frac{1}{2} + \frac{1}{2}\cos(\gamma B_s \tau/\hbar)e^{-(\tau/T_2^*)^2},$$
(2.5)

which is shown in Figure 2.3(a). We quote S here (and do so throughout) in normalised units, such that S = 1 and S = 0 correspond to the average number of fluorescence counts for the $|0\rangle$ and $|1\rangle$ states respectively. The signal envelope decays over time T_2^* due to dephasing. The uncertainty ΔB in measuring B_s is then

$$\Delta B = \Delta S \frac{dB_s}{dS} = 2\Delta S \frac{1}{\gamma \tau} e^{-(\tau/T_2^*)^2}, \qquad (2.6)$$

where ΔS is the uncertainty in the signal. We have assumed that the oscillating part of



Figure 2.2: Pulse sequence and Bloch sphere illustrations for Ramsey and spin echo experiments.

the signal is midway between its maximum and minimum after evolution time τ , which gives maximal slope and, hence, optimal sensitivity. This can always be ensured by modifying the phase of the second microwave pulse relative to the first, which produces a corresponding change in the phase of the signal.



Figure 2.3: (a) Fluorescence signal as a function of evolution time for a Ramsey pulse sequence and a DC signal field. Solid curve: signal. Dashed curve: signal envelope due to dephasing. (b) Fluorescence signal as a function of evolution time for a spin echo pulse sequence and an AC signal field. Solid curve: Signal for a spin echo sequence and an AC field of unknown phase. Dashed curve: Gaussian curve for comparison.

Measurement of the spin state by fluorescence is an inherently probabilistic projective measurement. As just mentioned, the optimal sensitivity to magnetic fields occurs when there is nearly equal likelihood of measuring $|0\rangle$ or $|1\rangle$. The probability of measuring $|0\rangle$ exactly N_0 times out of N measurements then follows a binomial distribution, with mean $\langle N_0 \rangle = N/2$ and standard deviation $\Delta N_0 = \sqrt{N/2}$. If photon collection efficiency were perfect, then the signal would be just $S = N_0/N$, and the uncertainty in measuring magnetic fields would be:

$$\Delta B = \frac{1}{\sqrt{T\tau N_{NV}}} \frac{\sqrt{2}}{\gamma} e^{-(\tau/T_2^*)^2},$$
(2.7)

where T is the total averaging time and N_{NV} is the number of NV centres taking part in each run (so that $N = N_{NV}T/\tau$). Optimising Equation (2.7) with respect to τ gives $\tau = T_2^*.$

Since the uncertainty ΔB depends on the total averaging time T, it is common to quote the 'sensitivity' η of a measurement technique, defined as the product of the uncertainty and the square root of the averaging time:

$$\eta \equiv \Delta B \sqrt{T} = \frac{1}{C\sqrt{N_{NV}T_2^*}} \frac{\sqrt{2}}{\gamma}.$$
(2.8)

Here we have included a factor C, discussed in detail in Chapter 4, which takes into account experimental realities such as photon collection efficiency and the finite fluorescence of the $|1\rangle$ state [5]. In typical experiments, $C \approx 0.05$.

Since the sensitivity improves with the number of NV centres taking part, large crystals can be used to give better sensitivity. However, spatial resolution is one of the strengths of an NV magnetometer over atomic or SQUID magnetometers. It can thus be important to use only a small volume of NV centres and increase the density of NV centres instead. One problem is that as the number of NV centres per unit volume increases, the interaction between NV centres becomes a significant source of dephasing, reducing the coherence time and consequently impairing the sensitivity. The balance between these counter-prevailing influences is considered theoretically by Taylor *et al.* [5], arriving at an optimal concentration of NV centres of around 10^{16} cm⁻³.

This discussion has assumed that the Rabi fields used are sufficiently weak, relative to the applied DC field, to selectively excite only one of the $|\pm 1\rangle$ states, allowing us to treat the NV spin as an effectively two state system. This is indeed how most experiments are performed and it has the particular advantage of detuning those NV centres that lie along different crystallographic axes. It is possible, however, to perform exactly the same kind of experiment with no applied DC field. In this case, both $|\pm 1\rangle$ states are occupied simultaneously, and they acquire equal and opposite phases under the influence of some signal magnetic field [7].

2.3 Detecting AC fields of known phase

The procedure just described for measuring DC fields will not work for detecting AC fields which oscillate on a faster timescale than the evolution time. The phase will evolve back and forwards under an AC field, with little or no net precession. The solution is to use a 'spin echo' or 'Hahn echo' pulse sequence. This was originally developed in the context of NMR, as a way of extending the coherence time (or, equivalently, reducing linewidths).

The principle is similar to the Ramsey experiment except that a π -pulse is applied midway through the free evolution time. The consequence of such a sequence on coherence times can be seen in Figure 2.2(b). As the ensemble of systems evolves, each member is subjected to a slightly different magnetic field. The π -pulse 'refocuses' the divergent phase evolution of the ensemble under these fields. The phase acquired before the π -pulse is subtracted from the phase acquired after the π -pulse so that no net phase is contributed from any fields which are relatively constant over the timescale of the evolution (these are fields due to ¹³C nuclear spins in the case of NV). Instead, phase divergence can only be caused by fast-fluctuating fields (from nitrogen atom electronic spins in the case of NV), extending the coherence time from T_2^* to T_2 .

As well as extending coherence times, a spin echo pulse sequence allows AC magnetometry. If the length of time before and after the π -pulse is half the period of the AC field, and the initial $\pi/2$ pulse is timed to coincide with the AC field crossing zero, then the phase accumulation due to the AC field is a 'rectified' sinusoidal curve.

More complicated sequences are also possible. A sequence of many π -pulses interspersed with free evolution time allows evolution under an effectively rectified AC field for longer than a single period of the field's oscillation. Concatenated π -pulses will also reduce the bandwidth of the system, allowing different frequencies to be distinguished, as the range of frequencies to which the system will respond will be on the order of $1/\tau$ where τ is the total free evolution time. More complicated sequences include the CPMG sequence [25] and sequences proposed by Uhrig [26], which can extended coherence times (and enhance sensitivities) further.

2.4 Decoherence magnetometry: fluctuating fields and AC fields of unknown phase

In the scenarios discussed in the previous two sections, the same signal field is experienced by each member of the ensemble, which all develop the same phase as a result. The only non-deterministic fields considered so far are those fields due to other electron and nuclear spins in the crystal, whose effects are captured by the decoherence rate implied by T_2 or T_2^* .

Instead, let us now consider an AC signal field whose phase is unknown and imagine what happens under the spin echo pulses sequence just described. Each member of the ensemble of NV centres experiences an AC field of a different phase and consequently precesses through a different angle. The average phase (precession) evolved by the spins due to the AC field is then zero. The variance of the evolved phases, however, is non-zero. An increasing phase variance amounts to decoherence and by measuring the rate of this decoherence the strength of the AC field may be inferred. This concept, 'decoherence magnetometry', was proposed more generally by Cole and Hollenberg [3].

If the distribution of phases of an ensemble of NV centres is Gaussian, with zero mean and a variance of $(\Delta \Phi)^2$, then the final signal amplitude is given by:

$$S = \frac{1}{2} + \frac{1}{2} \int \frac{d\Phi}{\Delta\Phi\sqrt{2\pi}} \exp\left[\frac{-\Phi^2}{2(\Delta\Phi)^2}\right] \cos\Phi = \frac{1}{2} + \frac{1}{2}e^{-(\Delta\Phi)^2}.$$
 (2.9)

That is, the signal decays exponentially in the phase variance. In the case of AC field detection, the signal will thus decay approximately as

$$S = \frac{1}{2} \exp\left[-\left(\frac{\sqrt{2}\tau\gamma B_s}{\pi}\right)^2\right],\tag{2.10}$$

where the AC field has amplitude B_s and frequency ω and the evolution time is $\tau = 2\pi/\omega$. Figure 2.2(b) plots the actual signal, which differs from the approximation because the distribution of the evolved phases is not Gaussian. In particular, notice the beating which occurs. The same principle may be applied to the measurement of fields which fluctuate randomly, as explored by Hall *et al* [27]. This idea will be developed further in chapters 6 and 7, but the qualitative behaviour is the same as for the case just described.

2.5 Nanodiamond NV centres as biomarkers

In addition to its use in magnetometry and quantum information processing, the NV centre is finding increasing application as a fluorescent marker in cell biology. The attractiveness of the NV system in this context comes not from its spin characteristics but from its fluorescence properties and the behaviour of diamond as a material.

The fluorescence spectrum of the NV centre is well-separated from other biological sources of fluorescence [21], and the NV centre, unlike many conventional biomarkers, does not blink or photobleach [28]. Diamond is also highly biocompatible. Nanodiamonds are intrinsically noncytotoxic [28], are readily absorbed into cells [29] and can be produced with functionalised surfaces [30].

NV centres can also be located spatially with subwavelength resolution, using techniques such as stimulated emission depletion (STED) [31]. In STED a donut-shaped laser mode causes stimulated emission of all NV centres in the laser spot ('depleting' them) except for the small central region which may be much smaller than the wavelength of the light, allowing adjacent NV centres to be resolved, with resolution approaching nanometres.

It is this biological application of nanodiamonds which motivates the work of chapters 6 and 7. We seek to apply the spin control ideas discussed in this chapter to a colloidal nanodiamond diffusing freely in a fluid.

BACKGROUND TO GEOMETRIC PHASES

In 1959 Aharonov and Bohm published a paper [13] in which they demonstrated a surprising implication of quantum mechanics: they showed that electromagnetic potentials can affect the dynamics of a particle which moves in a field-free region of space. An electron travelling inside a charged cylinder acquires a phase due to the cylinder's voltage, though the electric field inside the cylinder is zero. Similarly, an electron travelling near a solenoid acquires a phase dependent on the vector potential encircling the solenoid, even though the magnetic field outside the solenoid vanishes.

These findings initially received surprise, even skepticism. They suggested either nonlocality in quantum mechanics or otherwise a physical basis for electromagnetic potentials, which had previously been treated as mathematical conveniences only. Experiments soon verified the predictions [32] and the Aharonov-Bohm (A-B) effect became a textbook example of the counter-intuitiveness of quantum mechanics.

Later, in 1984, M.V. Berry developed an elegant and powerful mathematical framework which established the A-B effect as just one instance of a far more general class of phenomena [20]. Berry considered the evolution of a system under a Hamiltonian which is adiabatically (slowly) changed over time. He showed that the state of such a system acquires a phase which is deeply geometrical in nature. The phase depends only on the system's path in parameter space, specifically the flux of some field enclosed by that path. The field in question is a gauge field, akin to those found in quantum field theories, which arises naturally in Berry's formalism. In the special case of the A-B effect, the gauge field is simply the electromagnetic vector potential.

Berry's work has since been applied to a diversity of phenomena, which can be broadly

grouped under the umbrella of 'geometric phases' or 'topological phases' [33, 34]. Specific instances of these geometric phases include the following: various analogues of the A-B effect such as the Aharonov-Casher [14], Casella [35] and the He-McKellar [36] phases; the rotation of the polarisation of light in twisted optical fibres, which was recognised by Pancharatnam well before Berry's paper [37]; the so-called 'molecular Aharonov-Bohm effect' which introduces a gauge field to nuclear degrees of freedom in the Born-Oppenheimer approximation to molecular dynamics [38]; and even the dynamics of classical systems such as low Reynolds number hydrodynamics [39].

Geometric phases have also proved a fruitful avenue of investigation for mathematical physicists due to their rich topological properties and their close connection with gauge theories of quantum fields. Examples include mathematically formulating geometric phases in terms of the holonomy of line bundles [40] and directly using Berry's phase to help explain fractional statistics in the quantum Hall effect [41] and the origin of Wess-Zumino terms in theories of quantum chromodynamics [42].

The diamond NV system presents itself as an excellent tool for studying geometric phases. The electron spin is the canonical quantum system and the NV centre offers a system in which a single spin which can be initialised, coherently controlled, and measured. It is also possible to mechanically move the diamond crystal, and the NV with it, about some cyclical macroscopic trajectory within the spin coherence lifetime.

In chapters 4 and 5 we will show how two types of geometric phases, the Aharonov-Casher phase and Berry's phase (in its simplest incarnation), may be produced and measured using a single NV centre. In chapter 6 we show how Berry's phase, aside from being an interesting phenomenon in its own right, plays an important role in the quantum evolution of an NV centre in a diamond nanocrystal diffusively rotating in a fluid. In the present chapter we first introduce the A-B effect by way of illustration, we then treat the Aharonov-Casher effect and finally the general case of Berry's phase.

3.1 The Aharonov-Bohm effect

We begin by reviewing the A-B effect as a striking and simple illustration of a geometric phase. Consider a charged particle which is confined to a simply connected region of vanishing magnetic field, but nonzero vector potential A(r). As a specific example, take an electron which moves near a solenoid as shown in Figure 3.1(a). Its Hamiltonian is

$$H = \frac{1}{2m} \left(\boldsymbol{p} - e\boldsymbol{A}(\boldsymbol{r}) \right)^2 + V(\boldsymbol{r}), \qquad (3.1)$$

where $V(\mathbf{r})$ is a potential responsible for the motion of the electron. Let $\psi_0(\mathbf{r}, t)$ be the electron wavefunction in the absence of the vector potential. In the presence of the vector potential, Schrödinger's equation is satisfied by

$$\psi(\mathbf{r},t) = e^{i\Phi(\mathbf{r})}\psi_0(\mathbf{r},t),\tag{3.2}$$

where $\Phi(\mathbf{r}) = \int_C \frac{e}{\hbar} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'$. The vector potential modifies the wavefunction only by a position-dependent phase Φ . The path of integration C that defines Φ may be any path in the region from some \mathbf{r}_0 to \mathbf{r} . Since the region is simply connected and $\nabla \times \mathbf{A} = \mathbf{B} = 0$ within the region, $\Phi(\mathbf{r})$ is single-valued. This single-valued phase cannot lead to any observable effects. This can be seen by noting that a gauge transformation of the form $\mathbf{A} \to \mathbf{A} + \nabla \chi$ can be made such that $\Phi(\mathbf{r})$ vanishes.



Figure 3.1: (a) The Aharonov-Bohm effect concerns a charged particle moving near a solenoid. At any instant, the particle is localised within some simply-connected region (dashed curves) of vanishing magnetic field but nonvanishing vector potential. (b) Interference experiment to detect the Aharonov-Bohm effect. There is a relative phase between the two beams when they interfere, which depends only on the amount of magnetic flux between the two trajectories.

The interesting behaviour arises when we allow the electron to move in a region which is not simply connected. Now the path of integration C must be taken as the path of the electron and Φ is no longer single-valued. For example, consider an electron on a closed trajectory which encircles a solenoid and returns to its starting point. Using Stokes' law, the phase accumulated is then given by

$$\Phi = \frac{e}{\hbar} \int_{S} \nabla \times \boldsymbol{A} \cdot d\boldsymbol{S} = \frac{e}{\hbar} \int_{S} \boldsymbol{B} \cdot d\boldsymbol{S}, \qquad (3.3)$$

where S is the surface enclosed by the electron's path C. The phase Φ is now gaugeindependent. If an electron is diffracted about a solenoid, as in Figure 3.1(b), interference fringes will occur, which depend on the strength of **B**. This was the approach taken in a successful experimental verification of the A-B effect in the year following Aharonov and Bohm's paper [32].

There are two interesting points to note. Firstly, the phase depends only on the topology of the electron's trajectory. The phase will be unaffected by changes in the electron's speed or topology-preserving deformations of the electron's path. Secondly, the electron experiences this phase even though it never occupies the region of magnetic field. There is something disturbingly nonlocal about the effect.

It is worth commenting on our assertion that the path of integration C must be the 'path of the electron'. Since an electron's wavefunction has some spatial extent, it would seem that the 'path of the electron' is not a well-defined object. Moreover, the wavefunction of (3.2) cannot satisfy Schrödinger's equation if it is not single-valued. The difficulty can be resolved by requiring that the electron is at all times confined to some simply connected region of vanishing magnetic field. The region of confinement can change in time but must only be deformed continuously. The formal constraint on the integration path C is that it must share the same topology as the trajectory of this region. Unlike the trajectory of the electron, the trajectory of its confining region is well-defined.

This point may seem pedantic, but there are some physical systems where this requirement is not met. Consider for example a mesoscopic ring penetrated by a line of magnetic flux. An electron's wavefunction may encircle the line of flux, instantaneously
occupying a non-simply connected region. Single-valuedness of the wavefunction demands that the phase accumulated around the ring must be a multiple of 2π . Even without the A-B effect, this leads to the quantisation of angular momentum. The geometric phase modifies the quantisation condition and can even produce spontaneous currents [18]. Requirements on electron confinement will be particularly important when we consider the Aharonov-Casher phase, where non-Abelian effects complicate the matter.

3.2 The Aharonov-Casher effect

Electricity and magnetism have a satisfying way of complementing one another. It should come as no surprise that there is an analogous effect to the Aharonov-Bohm phase, in which the roles of electric charges and magnetic dipoles are reversed. Whereas the Aharonov-Bohm phase occurs when an electric charge orbits what is effectively a line of magnetic dipoles, an equivalent phenomenon occurs when a magnetic dipole orbits a line of electric charges. This is known as the Aharonov-Casher (A-C) effect [14].

The analogy is imperfect, as magnetic dipoles are inherently more complicated than electric charges. In the case of magnetic dipoles arising from spin, their structure consists of two or more quantum states. The U(1) phase factor of the Aharonov-Bohm effect thus becomes an SU(2) operator in the Aharonov-Casher effect, with all the additional complications that entails.

We begin, however, by treating a classical dipole (belonging to a neutral quantum particle) with a fixed orientation, following Aharonov and Casher's original article [14]. Consider such a particle, with magnetic dipole moment μ , moving at velocity v in a region containing static charges but no (lab frame) magnetic fields. In the particle's reference frame, there is a magnetic field B, due to the apparent motion of the charges, which produces a force on the particle $F = \nabla(\mu \cdot B)$. We apply Maxwell's equations and note that (provided $v \ll c$) the lab-frame electric field E is related to the particle-frame



Figure 3.2: (a) The Aharonov-Casher effect: a magnetic dipole moving near a line of charge feels no force but acquires a phase. (i) The geometry considered by Aharonov and Casher. The dipole is oriented in the z-direction for both paths. (ii) The same effect occurs when the two paths are the same, but with opposite dipole directions. The two 'paths' can now be achieved using a superposition of spin states of a single particle. (iii) If the paths are not spatially separated, the electric field needn't be produced by a line of charge. Capacitor plates will work just as well. (b) Schematic of the first A-C experiment, using neutron interferometry, reproduced from [43]. (c) Schematic of an experiment using superposition of the spin states of an atomic beam, reproduced from [17].

magnetic field by $\boldsymbol{v} \times \boldsymbol{E} = c^2 \boldsymbol{B}$, giving

$$F = \frac{1}{c^2} \boldsymbol{v} \times [\boldsymbol{\mu} \nabla \cdot \boldsymbol{E} - (\boldsymbol{\mu} \cdot \boldsymbol{\nabla}) \boldsymbol{E}]$$

$$\approx \frac{1}{c^2} \boldsymbol{v} \times [\nabla \times (\boldsymbol{\mu} \times \boldsymbol{E})] + \frac{1}{c^2} (\boldsymbol{v} \cdot \nabla) (\boldsymbol{\mu} \times \boldsymbol{E}). \qquad (3.4)$$

The final term of Equation (3.4) is due to the changing momentum carried in the crossed electric and magnetic fields, which will be sufficiently small to neglect in the systems we consider.

The force of Equation (3.4) is a velocity-dependent force much like the Lorentz force and it is incorporated into the Hamiltonian in the same way,

$$H = \frac{1}{2m} \left(\boldsymbol{p} - \frac{1}{c^2} \boldsymbol{\mu} \times \boldsymbol{E} \right)^2 + V(\boldsymbol{r}).$$
(3.5)

Comparing Equations (3.5) and (3.1), the analogy between the A-B and A-C effects is clear. Instead of the vector potential A, we have an analogous vector field, $\mu \times E$. The curl of this vector field vanishes outside the region of charge density, provided the charge distribution is uniform along the direction of the dipole moment μ . As in the A-B case, the particle thus acquires a phase as it circles the line of charge which depends only on the topology of its path:

$$\Phi_{AC} = \frac{1}{\hbar c^2} \int_C \boldsymbol{\mu} \times \boldsymbol{E} \cdot d\boldsymbol{r}.$$
(3.6)

The system just described is isomorphic to the Aharonov-Bohm effect. The situation becomes much more interesting, however, when we elevate the dipole moment from a classical variable μ to a quantum mechanical operator μS . Consider a spin-half neutral particle, a neutron for example. The Aharonov-Casher phase is a first order relativistic phenomenon, and we therefore use the Dirac equation of relativistic quantum mechanics and take the (almost) nonrelativistic limit to find our Hamiltonian. The Dirac Lagrangian for a particle of dipole moment μ in an electric field is:

$$\mathcal{L} = \bar{\psi} \left[i \gamma^{\nu} \partial_{\nu} - m - \frac{1}{2} \mu F^{\nu \kappa} \sigma_{\nu \kappa} \right] \psi, \qquad (3.7)$$

where $\hbar = c = 1$. With the usual Dirac-Pauli choice of γ matrices, and setting $\psi = \begin{pmatrix} \phi_A \\ \phi_B \end{pmatrix}$, we obtain the Euler-Lagrange equations:

$$i\dot{\phi}_A = -i\boldsymbol{\sigma}\cdot(\boldsymbol{\nabla}-\mu\boldsymbol{E})\phi_B + m\phi_A$$
(3.8)

$$i\phi_B = -i\boldsymbol{\sigma} \cdot (\boldsymbol{\nabla} + \mu \boldsymbol{E})\phi_A - m\phi_B$$
 (3.9)

The nonrelativistic approximation applies when m is much larger than other energy scales. In this case ϕ_A is just the two-component spinor of Schrödinger's equation and the Hamiltonian for our particle is

$$H = \frac{1}{2m} \boldsymbol{\sigma} \cdot (\boldsymbol{p} - i\frac{\mu}{c^2} \boldsymbol{E}) \boldsymbol{\sigma} \cdot (\boldsymbol{p} + i\frac{\mu}{c^2} \boldsymbol{E})$$

$$= \frac{1}{2m} \left(\boldsymbol{p} - \frac{\mu}{c^2} \boldsymbol{\sigma} \times \boldsymbol{E} \right)^2 - \frac{\mu^2 E^2}{2mc^4}.$$
 (3.10)

This is close to what we would have obtained had we just replaced μ of Equation (3.5) with its quantum mechanical equivalent, except for the final term. This term is small, and was ignored in Aharonov and Casher's paper. We, too, will ignore it for now.

It is tempting, looking at (3.10), to suggest that the geometric phase for this system is simply

$$\hat{\Phi}_{AC}(\boldsymbol{x}) = -\frac{\mu}{\hbar c^2} \int_C \boldsymbol{\sigma} \times \boldsymbol{E}(\boldsymbol{x}') \cdot d\boldsymbol{x}'$$
(3.11)

which is now a SU(2) operator. We will make a symbolic distinction between $\hat{\Phi}_{AC}$, an operator which operates on a particle's spin, and Φ_{AC} , a scalar phase acquired by a particular spin state. The problem is that Equation (3.11) is not single-valued, even in a simply-connected region, and unless $\hat{\Phi}_{AC}$ commutes with itself for different \boldsymbol{x} , the Schrödinger equation is not satisfied. To ensure single-valuedness, the curl of the integrand must vanish within the simply connected region:

$$0 = \nabla \times (\boldsymbol{\sigma} \times \boldsymbol{E})$$

= $\boldsymbol{\sigma} \frac{\rho}{\epsilon_0} - (\boldsymbol{\sigma} \cdot \nabla) \boldsymbol{E}.$ (3.12)

which, since σ necessarily has components in all three direction, is only true for the special case of a uniform electric field. To ensure single-valuedness and commutativity, the Aharonov-Casher effect is usually treated in 2 + 1 dimensions, either explicitly [36], or effectively [44], by assuming that both the charge distribution and the wavefunction are independent of the z-coordinate. In the latter case, the path of integration C lies in the x-y plane and the vanishing of the z-component of momentum ensures that Schrödinger's equation is satisfied, exactly in the case of a spin-half particle, and up to terms of order $\mu^2 E^2/(mc^4)$ otherwise. In the next chapter we outline an original derivation which treats a particle of arbitrary spin in which the restriction to two dimensions, and hence the single-valuedness of (3.11), arises from physical confinement of the particle to the plane.

The full richness of the A-C effect is seen when the particle moves in three dimensions, in which case $\mu \times E$ acts as a non-Abelian SU(2) gauge field. One of the remarkable consequences of geometric phases is that such simple and familiar quantum mechanical systems can posses the kind of mathematical structures that are seen in quantum field theories of fundamental interactions. In the following chapter we discuss this behaviour in the context of the NV centre by considering out-of-plane motion of the crystal.

As a relativistic effect, the Aharonov-Casher phase tends to be harder to detect than the Aharonov-Bohm phase (notice the $1/c^2$ term in the gauge field). Nevertheless, the effect has been observed in a number of physical systems. The first experiment used neutron interferometry [43], producing an A-C phase of a few mrad. The experiment was truly in the spirit of Aharonov and Casher's proposal, involving a neutron, the simplest neutral particle with a magnetic moment, diffracting about a 'wedge' of charge (see Figure 3.2(b)).

Larger phases were possible in atomic systems [15, 16, 17], which used the magnetic moment of the electron spin, three orders of magnitude larger than that of the neutron. Rather than sending atoms along two separate paths, the atoms were prepared in a superposition of spin states. The different spin states acquired different phases, which could then be measured (see Figure 3.2(c)). These experiments have been criticised for not capturing the 'topological' character of the Aharonov-Casher effect, since no charge is enclosed by the path. The effect observed in such a geometry is sometimes termed the 'Casella effect' [35]. We will discuss this further in Chapter 3.

The Aharonov-Casher effect has also been observed in condensed matter systems, most notably in mesoscopic rings [18]. As mentioned, these are particularly interesting in that the electrons' wavefunctions extend throughout the ring. The Aharonov-Casher effect can then give rise to spin currents as a consequence of the physical requirement of single-valuedness of the wavefunction.

3.3 Berry's phase

Berry's paper [20] showed the universality of the geometric phase. To explain Berry's argument we start with the adiabatic theorem. We will give a derivation of the adiabatic theorem which makes Berry's phase particularly obvious. We will use this derivation in Chapter 4 when considering higher order terms in the adiabatic approximation.

The adiabatic theorem concerns the evolution of a quantum system under a slowly changing Hamiltonian. The theorem states that in the adiabatic limit, the limit of infinitesimally slow change of the Hamiltonian, a system initially in an eigenstate of the Hamiltonian will remain in an eigenstate of the instantaneous Hamiltonian. To demonstrate this, and to derive the conditions for approximate adiabaticity, we consider a system, subject to a time-varying Hamiltonian H(t), whose instantaneous eigenstates are $|n(t)\rangle$ with eigenvalues $\hbar\omega_n$. That is,

$$H(t)|n(t)\rangle = \hbar\omega_n|n(t)\rangle \quad \forall n, t.$$
 (3.13)

We are interested in the probability $p_{n\to m}$ that the system, initialised in some eigenstate $|n(0)\rangle$, ends up in a different eigenstate $|m(t)\rangle$ after time t. This probability is given by

$$p_{n \to m} = |\langle m(t) | U(t) | n(0) \rangle|^2,$$
 (3.14)

where U(t) is the time-evolution operator satisfying the usual Schrödinger equation, $i\hbar \dot{U} =$

HU. It is helpful to break the time evolution into a number of steps. We write

$$U(t) = D(t)B(t)E(t),$$
 (3.15)

where

$$D(t) = \Sigma_n |n(t)\rangle \langle n(0)|, \qquad (3.16)$$

$$E(t) = \Sigma_n e^{-i\omega_n t} |n(0)\rangle \langle n(0)|, \qquad (3.17)$$

and B(t) is some operator to be determined. Qualitatively, E(t) accounts for the usual (dynamical) phase evolution of a state with energy $\hbar\omega$, D(t) accounts for the change in the instantaneous eigenstate due to the changing Hamiltonian, and B(t) accounts everything else. The time evolution matrix elements can now be written as:

$$\langle m(t)|U(t)|n(0)\rangle = e^{-i\omega_m t} \langle m(0)|B(t)|n(0)\rangle.$$
(3.18)

Substituting (3.15) into the Schrödinger equation gives $\dot{B}(t) = \left[E^{\dagger}\dot{D}^{\dagger}DE\right]B$, whose solution can be expressed as a Dyson series,

$$B(t) \approx 1 + \int_0^t dt' [E^{\dagger} \dot{D}^{\dagger} DE](t') + \int_0^t dt' [E^{\dagger} \dot{D}^{\dagger} DE](t') \int_0^{t'} dt'' [E^{\dagger} \dot{D}^{\dagger} DE](t'') + \dots \quad (3.19)$$

In the perturbative limit, we take only the first order term. We obtain

$$\langle m(0)|B(t)|n(0)\rangle \approx \int_0^t e^{i(\omega_m - \omega_n)t'} \alpha_{m,n} dt'$$
 (3.20)

where
$$\alpha_{m,n}(t) = \left(\frac{d}{dt} \langle m(t)|\right) |n(t)\rangle.$$
 (3.21)

Provided $\alpha_{m,n}$ is slowly varying compared with $\omega_m - \omega_n$, we obtain the criterion for adiabaticity:

$$p_{n \to m} \approx \frac{\langle \alpha_{m,n} \rangle^2}{(\omega_m - \omega_n)^2} \ll 1,$$
 (3.22)

where $\langle \alpha_{m,n} \rangle$ is the mean of $\alpha_{m,n}$ over the time period. Loosely, the rate of change of the Hamiltonian (which defines $|n(t)\rangle$) must be slow compared with the transition frequency

between states. The adiabatic theorem holds in the limit as $p_{n \to m} \to 0$.

Berry's phase directly follows from equations (3.18) and (3.20) by taking n = m:

$$\langle n(t)|U(t)|n(0)\rangle = e^{-i\omega_n t} \langle n(0)|B(t)|n(0)\rangle = e^{-i\omega_n t} e^{i\Phi_B}$$
(3.23)

where
$$\Phi_B = \int_0^t \left(\frac{d}{dt} \langle n(t')| \right) |n(t')\rangle dt'.$$
 (3.24)

The exponent Φ_B is Berry's phase. Emphasising its geometric rather than time-dependent nature, it is usually expressed another way. If, rather than depending explicitly on time, the Hamiltonian depends on a set of time-varying parameters $\mathbf{R}(t)$ then Equation (3.24) can be rewritten as a path integral in parameter space:

$$\Phi_B = \operatorname{Im} \int_C \langle n(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} | n(\boldsymbol{R}) \rangle \cdot d\boldsymbol{R}.$$
(3.25)

Presented this way, Berry's phase seems to follow naturally from the adiabatic theorem. It is remarkable that it was not noticed until half a century after Born and Fock demonstrated the adiabatic theorem [45].

If the path C of the system in the space of the parameters \mathbf{R} is closed, and \mathbf{R} has three dimensions, then Equation (3.25) takes on the special form,

$$\Phi_B = \int_S \nabla \times \boldsymbol{A} \cdot d\boldsymbol{S}, \qquad (3.26)$$

where
$$\boldsymbol{A}(\boldsymbol{R}) = \operatorname{Im}\langle n(\boldsymbol{R}) | \nabla_{\boldsymbol{R}} | n(\boldsymbol{R}) \rangle,$$
 (3.27)

which is a surface integral over the curl of a vector field taken over the surface S enclosed by the system's path C in parameter space. We have suggestively labeled this vector field A. If R has more than three dimensions, then Equation (3.26) still holds if the cross product is replaced with its higher dimensional generalisation, the wedge product. In this case A is not a vector field but a two-form.

The vector field \boldsymbol{A} is in fact a gauge field. There is an arbitrariness in defining the phase relation between eigenstates of different parameters. A gauge transformation may be made of the form $|n\rangle \rightarrow \exp[i\chi(\boldsymbol{R})]|n\rangle$ which modifies \boldsymbol{A} as $\boldsymbol{A} \rightarrow \boldsymbol{A} + \nabla_{\boldsymbol{R}}\chi$. Since the curl of $\nabla_{\boldsymbol{R}}\chi$ vanishes, Berry's phase around a closed path is unchanged by the transformation.

The choice of gauge will be important in Chapter 4 when we consider Berry's phase for paths which are not closed.

Berry's analysis can be applied to the Aharonov-Bohm effect. The electron is confined around some coordinate \mathbf{R} (so that it does not overlap with the magnetic flux) by some potential $V(\mathbf{r} - \mathbf{R})$ where \mathbf{r} is the coordinate of the electron. In the absence of a vector potential, the electron has some wavefunction $\psi_0(\mathbf{r} - \mathbf{R})$, which is modified upon the introduction of the vector potential \mathbf{A} to give

$$\psi_R(\boldsymbol{r}) = \exp\left[i\int_{\boldsymbol{R}}^{\boldsymbol{r}} \frac{e}{\hbar}\boldsymbol{A}(\boldsymbol{r}') \cdot d\boldsymbol{r}'\right]\psi_0(\boldsymbol{r}-\boldsymbol{R})$$
(3.28)

The integral in Equation (3.28) poses no problems since the magnetic field vanishes in the region to which the particle is confined. The coordinate \mathbf{R} is the changing parameter which produces Berry's phase according to (3.25). The gauge potential of Berry's formalism whose surface integral gives Berry's phase is then, from equation (3.27),

$$\langle \psi_R | \nabla_R | \psi_R \rangle = \frac{-e}{\hbar} \boldsymbol{A}.$$
 (3.29)

which, astonishingly, is simply that archetypal gauge field, the electromagnetic vector potential. In a similar way, Berry's approach can explain the Aharonov-Casher phase.

Following Berry's paper, there have been several experimental verifications of Berry's phase. The first measured the polarisation of light after travelling through coiled optical fibres [46]. Berry's phase emerges as a consequence of the solid angle swept out by the photon's momentum and manifested as an easily observable change in polarization. Other notable verifications include a neutron interferometry experiment in which the direction of a magnetic field is varied along the neutron's path [47]; NMR experiments where it is the rotating-frame magnetic field which is varied adiabatically [48]; and a nuclear quadrupole resonance experiment in which the Hamiltonian's variation is produced by physically spinning the sample [49].

3. Background to Geometric Phases

Aharonov-Casher Phase Detection Using NV

In this chapter we outline a proposed experiment to produce the Aharonov-Casher effect using the diamond NV centre. Unlike previous measurements of the A-C effect this would be a measurement on a single quantum system whose motion is controlled mechanically. The experiment consists of moving a diamond crystal through an electric field and performing a Ramsey or spin echo experiment, of the form described in Chapter 2, to detect the resulting A-C phase. This work was reported in reference [19].

4.1 Aharonov-Casher effect in the NV centre

To treat the A-C effect for the NV centre we need to extend the analysis of the previous chapter to account for a particle which has spin one, exists in three dimensions with finite spatial extent, and has spin-dependent terms in its Hamiltonian besides $S \times E$.

First we derive the Hamiltonian for a spin one particle in an electric field. We showed in the previous chapter that for the special case of a spin-half particle the Hamiltonian is

$$H = \frac{1}{2m} \left(\boldsymbol{p} - \frac{\mu}{c^2} \boldsymbol{\sigma} \times \boldsymbol{E} \right)^2 - \frac{\mu^2 E^2}{2mc^4}.$$
(4.1)

It is tempting, though incorrect, to simply replace the magnetic dipole operator for a spinhalf particle, $\mu\sigma$, with its generalisation for a particle with arbitrary spin, $\mu S/\hbar$, where S is the spin operator. Equation (4.1) was derived by taking advantage of the special properties of the Pauli matrices which do not hold for a general spin operator.

The spin magnetic dipole operator of the NV centre, $\boldsymbol{\mu} = \gamma \boldsymbol{S}$, is due to the spin of as many as six electrons [1]. We can write the total electron spin as the sum of the spins

of the individual electrons,

$$\boldsymbol{S} = \Sigma_i \frac{\hbar}{2} \boldsymbol{\sigma}_i. \tag{4.2}$$

where σ_i acts on the *i*th electron of the NV centre. Expanding (4.1), which is correct when applied to each electron separately, gives

$$H = \frac{1}{2m}\boldsymbol{p}^2 - \frac{1}{m}\boldsymbol{p} \cdot \frac{\mu}{c^2}\boldsymbol{\sigma} \times \boldsymbol{E} + \frac{\mu^2 E^2}{2mc^4}.$$
(4.3)

The total Hamiltonian is the sum of (4.3) over each electron, which can now be written as

$$H = H_0 + \frac{1}{2m} \left(\boldsymbol{p} - \frac{\gamma}{c^2} \boldsymbol{S} \times \boldsymbol{E} \right)^2 + \frac{\gamma^2 \hbar^2 E^2}{2mc^4} - \frac{\gamma^2}{2mc^4} [\boldsymbol{S} \times \boldsymbol{E}]^2.$$
(4.4)

Where \boldsymbol{p} refers to the centre-of-mass momentum of the electrons and H_0 contains all the internal degrees of freedom. We have absorbed into H_0 terms of the form $\boldsymbol{p}_i \cdot \boldsymbol{\sigma}_i \times \boldsymbol{E}$, where \boldsymbol{p}_i are the momenta of the individual electrons relative to the centre-of-mass momentum. In the experiments we discuss, the relative motion of the electrons is at least five orders of magnitude smaller than the centre-of-mass motion and these terms can be safely neglected.

We have chosen this approach to emphasise the several-electron nature of the NV centre spin. The same result may be obtained by treating the NV centre ground state as a single particle of spin one, and using the Bargmann-Wigner formalism, a generalisation of the Dirac equation for a particle of arbitrary spin, as shown in [36]. For now, however, we ignore the final two terms in (4.4) as they are of second order in the small parameter $\gamma E/c^2$.

As discussed in the previous chapter, the SU(2) phase (3.11) arising from a Hamiltonian such as Equation (4.4) is only single valued under particular conditions. The usual approach is to restrict the particle to two dimensions. We will show how single-valuedness may be obtained if the NV centre is sufficiently localised, even if it moves in three dimensions.

Take a particle, highly localised to some position r, with Hamiltonian

$$H = \frac{1}{2m} \left(\boldsymbol{p} - \frac{\gamma}{c^2} \boldsymbol{S} \times \boldsymbol{E} \right)^2 + H_0, \qquad (4.5)$$

where H_0 includes the confining potential and may include spin-dependent terms. The confining potential is taken along some classical trajectory $\mathbf{r}(t)$ (due to the motion of the crystal containing the NV centre, for example) so that at any instant the particle is confined to a small region about $\mathbf{r}(t)$. Let $|\psi_0; t\rangle$ be a solution to the Schrödinger equation in the absence of the electric field \mathbf{E} . A solution to the Schrödinger equation in the presence of the electric field can then be written as

$$|\psi\rangle = FG|\psi_0\rangle,\tag{4.6}$$

where

$$F \equiv 1 + i \frac{\gamma}{\hbar c^2} \boldsymbol{S} \times \boldsymbol{E}(\boldsymbol{r}(t)) \cdot [\boldsymbol{x} - \boldsymbol{r}(t)], \qquad (4.7)$$

and the operator G is a function of r which satisfies

$$G(\mathbf{r}(t)) = 1 + i \int_0^t \dot{\hat{\Phi}}_{AC}(t') G(\mathbf{r}(t')) dt'$$
(4.8)

where
$$\dot{\hat{\Phi}}_{AC}(t) = \frac{\gamma}{\hbar c^2} [\boldsymbol{S} \times \boldsymbol{E}(\boldsymbol{r}(t)) \cdot \dot{\boldsymbol{r}}(t)].$$
 (4.9)

The effect of the $\mathbf{S} \times \mathbf{E}$ term of the Hamiltonian has now been broken into two steps. The operator F is a small modification which ensures that the Schrödinger equation is satisfied throughout the particle's small though finite spatial extent. It is a function of the quantum mechanical centre-of-mass position operator \mathbf{x} chosen for its convenient commutation relation, $[\mathbf{p}, F] = (\gamma \hbar^{-1} c^{-2}) \mathbf{S} \times \mathbf{E}$. We assume that the particle is sufficiently localised around \mathbf{r} that $F |\psi_0\rangle \approx |\psi_0\rangle$.

The operator G is the SU(2) A-C 'phase factor' analogous to $\exp[i\hat{\Phi}_{AC}]$ with $\hat{\Phi}_{AC}$ given by (3.11). Unlike (3.11), however, G depends on the well-defined trajectory $\mathbf{r}(t)$ and is single-valued. Expressing G as the solution to an integral, rather than as $\exp[i\hat{\Phi}_{AC}]$ also allows for the noncommutativity of $\dot{\Phi}_{AC}$ at different times.

In order for (4.6) to satisfy the Schrödinger equation, G must commute with H_0 , which contains the zero field splitting of the NV centre and interactions with external magnetic fields. This commutation relation will be satisfied if the magnetic field points along the N-V ('z') axis, $E_z = 0$, and $\mathbf{r}(t)$ is confined to the x-y plane. In this case, Equation (4.8) simply reduces to the familiar A-C phase factor,

$$G = \exp\left[i\frac{\gamma}{\hbar c^2}\int_C \boldsymbol{S} \times \boldsymbol{E}(\boldsymbol{r}(t)) \cdot d\boldsymbol{\dot{r}}\right] = \exp\left[i\hat{\Phi}_{AC}\right],\tag{4.10}$$

where the path of integration C is the trajectory $\mathbf{r}(t)$. Here, $\hat{\Phi}_{AC} \propto S_z$, and we have an effectively U(1) phase.

4.2 'Charged spindle' experimental geometry

An experiment such as the neutron diffraction experiment of Cimmino *et al* [43] in which a particle takes a superposition of two spatial trajectories is clearly not possible with a macroscopic object such as a diamond crystal. Instead, the A-C phase in diamond can be observed by placing the NV centre into a superposition of spin states, which act as the arms of the interferometer, each acquiring a different A-C phase as the crystal is taken along a (single) trajectory.

We first consider the geometry shown in Figure 4.1(a). A diamond crystal is taken on a circular path about a line of charge. This could be achieved by mounting a crystal on a charged 'spindle' which is spun very quickly. As the diamond moves, the spin state of an NV centre will be modified by the A-C effect according to Equation (4.10),

$$|\psi\rangle \to \exp\left[i\frac{\lambda\gamma}{\epsilon_0c^2}\theta S_z\right]|\psi\rangle = \exp\left[\frac{i}{\hbar}\Phi_{AC}S_z\right]|\psi\rangle$$
 (4.11)

where λ is the linear charge density of the line of charge, and θ is the angle through which the spindle is rotated. Note that we have defined $\hat{\Phi}_{AC} = \Phi_{AC}S_z/\hbar$, making the distinction between the spin operator $\hat{\Phi}_{AC}$ and the scalar phase Φ_{AC} . The $|\pm 1\rangle$ states acquire a phase of $\pm \Phi_{AC}$, while the $|0\rangle$ state remains unchanged. The idea is to detect the relative phase between spin states by a Ramsey-type experiment, as follows.

As discussed in the previous section, (4.10) only applies if G commutes with H_0 . In light of (2.1), we must therefore only use NV centres whose N-V axes point along the z-axis (the spindle's axis). The crystal must be oriented such that one of its crystallographic axes lies in the z-direction. A static magnetic field, homogeneous over the range of the



Figure 4.1: (a) 'Charged spindle' experimental geometry. The diamond crystal is mounted on the side of a charged spinning spindle with a static magnetic field \boldsymbol{B} in the direction of the spindle's axis. (b) Targets on the crystal's path for microwave pulses, laser illumination, and photon collection. (c) Pulse sequence for the 'charged spindle' proposed A-C effect experiment. Time axis is not to scale.

crystal's motion, is applied (again in the z-direction, for reasons of commutativity arising from $\boldsymbol{B} \cdot \boldsymbol{S}$ terms in the Hamiltonian) which detunes those NV centres whose N-V axes are not parallel to \hat{z} . The magnetic field also splits the otherwise degenerate $|\pm 1\rangle$ states, allowing selective occupation with Rabi pulses.

The spindle is first set spinning. As the crystal passes point A (Figure 4.1(b)) a 532 nm laser pulse is applied, optically pumping the NV centre into $|0\rangle$, followed by a $\pi/2$ Rabi pulse, tuned to the $|0\rangle$ - $|1\rangle$ transition, which produces the coherent superposition $|\psi\rangle = 1/\sqrt{2}(|0\rangle + |1\rangle)$. The spindle then rotates through some angle θ , during which time the $|1\rangle$ state acquires some A-C phase Φ_{AC} . A second $\pi/2$ pulse is then applied, converting the phase information into a population difference between $|0\rangle$ and $|1\rangle$, which is measured by fluorescence detection under 532 nm optical excitation.

This pulse sequence is shown in Figure 4.1(c). Note that each of the control and measurement steps - optical excitation, $\pi/2$ pulses and fluorescence measurements - are assumed to be sufficiently quick that the spindle does not rotate appreciably over their duration. Spindle rotation frequencies of kHz are envisaged, compared to pulses times which can be on the order of hundreds of nanoseconds.

The time over which the A-C phase can be acquired is limited by the inhomogeneous broadening coherence time T_2^* of the NV centre, which is usually on the order of a few μ s. Assuming a 2 kHz rotation frequency of the crystal, this would allow only a few mrad of crystal rotation. The A-C phase acquired during this time depends on the spindle's linear charge density but the geometry makes it awkward to apply large fields. Optimistically, assuming a 30 kV/cm electric field at the surface of a spindle of 1cm radius (corresponding to 1.7 μ C/m linear charge density) 10 mrad of spindle rotation would only give $\Phi_{AC} \approx 6$ mrad - detectable (double the phase detected in the first A-C experiment [43]) but not remarkable.

4.3 'Capacitor plates' experimental geometry

The geometry just proposed follows the spirit of Aharonov and Casher's paper, but it is experimentally unwieldy. We now explore a more elegant geometry, shown in Figure 4.2(a). This time the crystal is mounted on a spinning disk between two capacitor plates. An alternating A-C phase is then acquired as the disk spins,

$$\Phi_{AC} = \frac{\gamma E r}{c^2} [1 - \cos \theta], \qquad (4.12)$$

where E is the electric field between the plates, r is the disk's radius, and θ is the angle through which the disk rotates, with $\theta = 0$ corresponding to the crystal at point A shown in Figure 4.2(b).

As in the previous geometry, a Ramsey-type pulse sequence can be used to detect the A-C phase after the crystal has rotated through a few mrad. The great advantage of the present geometry, however, is that a spin echo pulse sequence may be used instead, since the A-C phase acquired is alternating. A spin echo pulse sequence will dramatically improve the NV centre's coherence time, allowing a much greater rotational angle and, hence, a much larger detected A-C phase.

The sequence of pulses, shown in Figure 4.2(c), is similar to that of the charged spindle geometry. The disk is set spinning. As the diamond passes point A in Figure 4.2(b), a pulse from the 532 nm laser followed by a $\pi/2$ pulse initialises the NV into a coherent superposition of $|0\rangle$ and $|1\rangle$. A π pulse is then applied whenever the crystal passes points B and D, which effectively rectifies the alternating accumulation of A-C phase. A final $\pi/2$ pulse, when the crystal is at C, followed by illumination and a fluorescence measurement, records the total accumulated A-C phase, expressed as a population difference between $|0\rangle$ and $|1\rangle$.

Under this geometry, the numbers look more favourable. The spin echo pulse sequence takes the coherence time from T_2^* out to T_2 , which can be as large as a few ms [10]. Electric fields of up to 30kV/mm could be produced by the capacitor plates (with the system is placed in a vacuum). Combined with a 2 kHz rotation frequency, this would give an A-C phase in the tens of radians.

It is worth pausing to consider the 'topologicalness' of the A-C phase. Geometric phases are traditionally considered in systems taken about a closed circuit. One theoretically important reason for this is that if the circuit is not closed, there can in principle



Figure 4.2: (a) Geometry for the proposed 'capacitor plates' A-C effect experiment. The crystal is mounted on a spinning disk between the charged plates of a capacitor. (b) Targets for the microwave pulses, laser pulses and photon collection. (c) Pulse sequence for the proposed experiment.

be a gauge transformation, of the form discussed in Chapter 3, which removes the phase. In the proposed experiments just described, the loop is not necessarily closed. The gauge transformation which would remove the phase is one which redefines the quantisation axis and phase relation for the spin eigenstates as a function of position. In our system, however, there is definitely a natural choice of gauge, in which the quantisation axis is always parallel to \hat{z} , defined by the crystal axis (or the external magnetic field), and the phase relation corresponds to the phase of the microwave field. This idea will be examined more closely in the next chapter.

Whether a phase such as that of our proposed experiment is truly an example of Aharonov and Casher's geometric phase, and indeed whether the A-C phase itself can be called 'geometric', has been a point of contention [50, 35]. Our method, a phase measured between a superposition of eigenstates, using a natural choice of gauge rather than a closed loop, is that same as that used by the atom beam A-C experimenters [16, 15, 17]. The term 'Casella phase' is sometimes preferred for such experiments (though never by the authors themselves). In any case these experiments certainly display the path-independence and nondispersiveness which are characteristic of topological phases.

4.4 Sensitivity and confounding factors

Both our proposed experiments would consist of many repetitions of the pulse sequence just described to get an average signal. The sensitivity of the measurement of the A-C phase is determined by the Poissonian statistics of spin projection, photon emission, and photon collection. The uncertainty $\Delta \Phi$ in the measurement of the A-C phase is related to the uncertainty ΔS of the normalised fluorescence signal S,

$$\Delta \Phi = \Delta S \left(\frac{dS}{d\Phi}\right)^{-1} = 2\Delta S. \tag{4.13}$$

The second equality arises because the normalised signal, a sinusoidal function of Φ_{AC} , has a maximum gradient of half. By appropriately retarding the phase of the final $\pi/2$ pulse by some amount Φ_{Rab} , it can be ensured that the sinusoid is at its steepest point at the time of measurement as shown in Figure 4.3(b).



Figure 4.3: (a) Imagined data points for the normalised signal as a function of electric field strength. The uncertainty ΔS is a function of the total collection time. (b) Theoretical normalised signal as a function of the A-C phase acquired. Sensitivity to Φ_{AC} is greatest when the slope of the sinusoid is maximum, as shown. Retarding the phase of the final $\pi/2$ pulse by Φ_{Rab} shifts the cosine curve as shown, moving the point of maximum slope to the position desired. (c) Probability tree diagram showing the combined effect of spin projection and photon collection noise. There is an even probability of projection into either $|0\rangle$ or $|1\rangle$. From there, Poissonian statistics dictate the number of photons which will be collected according to the parameters a_0 and a_1 as shown.

The normalised signal S is the number of photons collected over N_r runs, normalised so that $\langle S \rangle = 1/2$ when the populations of $|0\rangle$ and $|1\rangle$ are equal. If each measurement of $|0\rangle$ or $|1\rangle$ corresponded to the emission and detection of exactly one or zero photons respectively, then the variance of S would be $(\Delta S)^2 = 1/(2N_r)$. A more careful analysis, taking into account the statistics of (spontaneous) photon emission and imperfect detection, and the nonzero fluorescence of the $|1\rangle$ state, modifies the variance of the normalised signal by a factor C^2 , giving $(\Delta S)^2 = 1/(2C^2N_r)$.

The physical basis for the factor C ($C \approx 0.05$ for typical experiments and $C \approx 1$ in the ideal case) is described by Taylor *et al.* [5]. Let a_0 and a_1 be the average number of photons collected from a single measurement of the states $|0\rangle$ and $|1\rangle$ respectively, taking into account collection efficiency, collection time, and fluorescence rate, ~15 MHz. because of the ¹A metastable dark state, a_1 is less than a_0 , allowing discrimination between $|0\rangle$ and $|1\rangle$ states. The actual number of collected photons n corresponding to a particular measurement ($|0\rangle$ or $|1\rangle$) follows a Poissonian distribution, with variance equal to its average value. The total variance of n, allowing for equal likelihoods of a measurement of $|0\rangle$ or $|1\rangle$, is:

$$(\Delta n)^2 = \langle n^2 \rangle - \langle n \rangle^2 = \frac{1}{2} [(a_0^2 + a_0) + (a_1^2 + a_1)] - \frac{1}{4} (a_0 + a_1)^2, \qquad (4.14)$$

If n_i is the number of photons collected on the *i*th measurement, then the properly normalised signal is

$$S = \frac{\sum_{i}^{N_r} n_i}{N_r(a_0 - a_1)} - \frac{a_1}{a_0 - a_1},$$
(4.15)

and its standard deviation is

$$\Delta S = \frac{1}{C\sqrt{N_r}},\tag{4.16}$$

where C can now be expressed in terms of physical parameters,

$$\frac{1}{C} = \sqrt{1 + \frac{2(a_0 + a_1)}{a_0 - a_1}}.$$
(4.17)

We can now write the relative sensitivity in measuring Φ_{AC} as

$$\frac{\Delta\Phi}{\Phi}\sqrt{T} = \frac{1}{C\dot{\Phi}\sqrt{T_2}}, \quad \text{where} \quad \dot{\Phi} = \frac{\gamma}{c^2}rfE, \tag{4.18}$$

and f is the frequency of the disk's rotation. Based on the experimental parameters given in the previous section, this corresponds to a relative uncertainty in the measurement of Φ_{AC} of $0.5 \text{ Hz}^{-1/2}$, or a 1% uncertainty after three hours.

Our discussion has quietly assumed that only a single NV centre takes part in the experiment. This would make for an elegant experiment, demonstrating the A-C effect in a single quantum system. Single NV experiments are possible using a confocal photon detection arrangement and a photon antibunching measurement. Two nearby NV centres cannot be optically resolved if they are closer than wavelength of red light, but the fluorescence autocorrelation function from a fluorescent spot can be used to infer whether the spot contains exactly one NV centre. Since a single NV centre only generates a single photon per fluorescence cycle, the autocorrelation function dips to zero at zero delay.

Using an ensemble of NV centres, however, would allow higher sensitivity, modifying the error (4.18) by a factor of $1/\sqrt{N_{NV}}$ where N_{NV} is the number of NV centres taking part. A 1 mm³ crystal with 10¹⁴ NV centres per cm³ would give 1.5×10^{-6} Hz^{-1/2} relative sensitivity.

Since the proposed experiment involves large electric field it is worth considering the possible confounding effect of the Stark shift. In addition to the well known excited state Stark shift [51], Van Oort [52] has shown that the NV ground state experiences a Stark shift given by the Hamiltonian:

$$H_{\text{Stark}} = -\hbar E R_{2E} \left(e^{-3i\theta} |-1\rangle \langle 1| + e^{3i\theta} |1\rangle \langle -1| \right), \qquad (4.19)$$

where θ is the angle between the electric field and one of the crystal's three planes of symmetry containing the NV axis. The constant R_{2E} is around 20 Hz.cm/V, which, at first glance, is much larger than the rate of accumulation of the A-C phase, $\dot{\Phi}_{AC}/E \approx$ 2Hz.cm/kV. However, H_{Stark} from (4.19) contains off-diagonal terms only. Provided the energy associated with the stark shift is less than the splitting between $|\pm 1\rangle$ states provided by the static magnetic field, the change in energy levels will be second order in $H_{\text{Stark}}/(\hbar\gamma B)$. A 50 G field would then correspond to a Stark shift of around 250 kHz. Moreover, since the energy splitting is constant, its net effect will be eliminated by the π -pulse of the spin echo sequence. As well as measuring Φ_{AC} as a function of electric field, Φ_{AC} can also be measured as a function of f, the disk's spinning frequency. The measurement would be expected to be independent of f, giving a clean confirmation of the geometric nature of the A-C effect.

4.5 Non-Abelian behaviour

The A-C phase causes spin precession about an axis perpendicular to both the electric field E and the crystal's velocity \dot{r} . In the systems described above, the crystal's velocity and the electric field both lie in the x-y plane, so that the spin precesses about the z-axis, and spin precessions at different times commute. The integral equation, Equation (4.8) is then solved by an exponential function of S_z , (4.10). The interesting non-Abelian structure of the A-C phase arises when the axis of precession changes and the exponential solution is not permissible.

A simple way to achieve this experimentally is to tilt the capacitor plates through some angle θ_E about the y axis so that E no longer lies in the x-y plane, as in Figure 4.4(a). On its own, this is not enough to observe precession about different axes. Equation (4.8) was derived on the assumption that G commutes with H_0 , which contains S_z . Since the zero-field splitting of the crystal, 2.88 GHz, is much larger than the rate of A-C phase accumulation, (hundreds of Hz), precession about axes other than z will be suppressed to first order in $\dot{\Phi}/2.88$ GHz. The A-C phase acquired is then generated by S_z alone:

$$\dot{\hat{\Phi}}_{AC} = \frac{\gamma}{\hbar c^2} S_z [\hat{\boldsymbol{z}} \times \boldsymbol{E}(\boldsymbol{r}(t)) \cdot \dot{\boldsymbol{r}}(\boldsymbol{t})].$$
(4.20)

To observe rotations about all three axes, a 0.1 T static magnetic field can be applied, producing degenerate $|0\rangle$ and $|1\rangle$ states. The $|-1\rangle$ state is excluded from the experiment since it is separated from the $|0\rangle$ and $|1\rangle$ states by \sim 5GHz, which is much larger than any



Figure 4.4: (a) Tilting the capacitor plates allows the non-Abelian character of the A-C effect to be explored. (b) Numerical solution of (4.8) using (4.21) showing the non-Abelian A-C effect. Expected normalised signal is plotted as a function of the disk's rotation angle for different orientations, θ_E of the capacitor plates, given $2\pi r\gamma Ec^{-2} = 0.8$. Blue solid curve: $\theta_E = \pi/6$. Black dashed curve, $\theta_E = \pi/4$, Red dotted curve, $\theta_E = 2\pi/6$.

of the other energy scales operating on the NV spin. The NV centre can be treated then as a spin-half system, and the SU(2) A-C 'phase' produced as the crystal moves on its trajectory is given by G, defined by Equation (4.8) with

$$\dot{\hat{\Phi}}_{AC} = \frac{2\pi\gamma r f E}{\hbar c^2} \left[-S_x \sin\theta_E \sin\theta + S_y \sin\theta_E \cos\theta + S_z \cos\theta_E \sin\theta \right], \tag{4.21}$$

which does not commute with itself at different times. In this regime, Rabi pulses are not needed, as rotation between $|0\rangle$ and $|1\rangle$ can be achieved using the A-C effect alone. The population of $|0\rangle$ as a function of the disk's rotational angle θ , for initialisation into $|0\rangle$ at $\theta = 0$, can be calculated numerically as shown in Figure 4.4. It depends qualitatively on the ratio $\dot{\Phi}_{AC}/f \approx 2\pi r \gamma E c^{-2}$, the order of magnitude of A-C phase acquired after one rotation. Of course, in the regime of degenerate $|0\rangle$ and $|1\rangle$ states, spin relaxation decoherence will become a problem. Nevertheless, given a sufficiently pure crystal, the experiment would be a powerful and controlled way to explore a non-Abelian geometric phase.

5

BERRY'S PHASE EXPERIMENT

In this chapter we explore Berry's phase in the diamond NV system. The spin quantisation axis of the NV centre lies along the N-V axis. Berry's phase will arise when the crystal, and thus the quantisation axis, is rotated. We propose an experiment to detect this phase using a similar approach to that of the previous chapter. The analytical tools we develop in this chapter will be used in later chapters, when we consider a crystal which undergoes Brownian rotation.

5.1 Berry's phase in the NV centre

The NV centre has an anisotropic zero-field Hamiltonian (2.1) which depends on the orientation of the N-V axis, which we will call z'. We reserve z for the lab-frame coordinate system (see Figure 5.1(a) for reference, ignoring the 'spindle' and 'B_{Rabi}' for now). The eigenstates of this Hamiltonian are $|m_{z'} = 1\rangle$, $|m_{z'} = 0\rangle$ and $|m_{z'} = -1\rangle$, the eigenstates of spin projection along the z' axis. Consider an NV centre, initialised in one of these eigenstates, contained within a crystal whose orientation (and therefore z') changes over time. If the crystal rotation is sufficiently slow, then the NV centre will remain in that initial eigenstate (with respect to the instantaneous Hamiltonian) but will acquire a phase factor $\exp[i\Phi_B]$, where Φ_B is Berry's phase as described in Chapter 3.

First we establish a consistent system of notation. The the N-V axis is z', defined by the usual spherical coordinates, θ and ϕ with respect to the fixed z axis. The eigenstates of spin projection on the fixed z axis we label $|m\rangle_z$. The eigenstates of spin projection on the instantaneous z' axis we label $|m\rangle_{z'}$. These are the instantaneous eigenstates of the NV centre's zero-field splitting Hamiltonian and $|0\rangle_{z'}$ is the state which is produced by optical pumping and is measured by recording fluorescence. A general state $|\psi\rangle$ is represented in matrix notation with respect to the (lab frame) $|m\rangle_z$ basis as

$$|\psi\rangle = \begin{pmatrix} z\langle 1|\psi\rangle\\ z\langle 0|\psi\rangle\\ z\langle -1|\psi\rangle \end{pmatrix}_{z}, \qquad (5.1)$$

where we use the subscript z to emphasise the basis.



Figure 5.1: (a) Berry's phase proposed experimental geometry. The crystal is attached to a rotating spindle with the N-V axis z' of one of its NV centres at an angle θ to the spindle axis, z. Rabi pulses are produced by a microwave field linearly polarised with its magnetic field oscillating along the z axis. The magnitude of Berry's phase after a complete rotation of the spindle is given by the solid angle Ω subtended by the z' axis. (b) Alternative geometry, producing an alternating Berry phase which may be observed using a spin echo pulse sequence. The spindle is now at an angle θ_0 to the fixed z axis of the microwave field, and the N-V axis is perpendicular to the spindle axis. The actual path of the N-V (z') axis encloses a solid angle of 2π , which is not observable. The π -pulse of a spin echo experiment, however, rectifies the alternating Berry phase accumulation, producing a total phase of $4\theta_0$ after a full spindle rotation, the solid angle enclosed by the effective trajectory shown.

To evaluate (3.24) and obtain Berry's phase for the NV centre we must find the instantaneous eigenstates of the Hamiltonian in terms of the adiabatically varied parameters θ and ϕ . The zero-field splitting Hamiltonian can be written as

$$H = \frac{1}{\hbar} DS_{z'}^2 = D\hbar \begin{pmatrix} \cos^2\theta + \frac{1}{2}\sin^2\theta & \frac{1}{\sqrt{2}}e^{-i\phi}\cos\theta\sin\theta & \frac{1}{2}\sin^2\theta e^{-2i\phi} \\ \frac{1}{\sqrt{2}}e^{i\phi}\cos\theta\sin\theta & \sin^2\theta & \frac{1}{\sqrt{2}}e^{-i\phi}\cos\theta\sin\theta \\ \frac{1}{2}\sin^2\theta e^{2i\phi} & \frac{1}{\sqrt{2}}e^{i\phi}\cos\theta\sin\theta & \cos^2\theta + \frac{1}{2}\sin^2\theta \end{pmatrix}_z.$$
 (5.2)

One choice of instantaneous eigenstates is

$$|1\rangle_{z'} = \begin{pmatrix} \cos^2 \frac{\theta}{2} \\ \frac{1}{\sqrt{2}} e^{i\phi} \sin \theta \\ e^{2i\phi} \sin^2 \frac{\theta}{2} \end{pmatrix}_z \quad |0\rangle_{z'} = \begin{pmatrix} -\frac{1}{\sqrt{2}} e^{-i\phi} \sin \theta \\ \cos \theta \\ \frac{1}{\sqrt{2}} e^{i\phi} \sin \theta \end{pmatrix}_z \quad |-1\rangle_{z'} = \begin{pmatrix} e^{-2i\phi} \sin^2 \frac{\theta}{2} \\ -\frac{1}{\sqrt{2}} e^{-i\phi} \sin \theta \\ \cos^2 \frac{\theta}{2} \end{pmatrix}_z.$$
(5.3)

Berry's phase, given initialisation into $|m\rangle_{z'}$, after the crystal has been rotated along some trajectory C in the parameters θ and ϕ , is given by (3.24), yielding

$$\Phi_B = \int_C m(1 - \cos\theta) d\phi.$$
(5.4)

For a closed loop in parameter space, this is simply the solid angle enclosed by the trajectory of z', Figure 5.1(a). Equation (3.24) was derived in Chapter 3 using the adiabatic approximation which was shown to be valid under the condition

$$\frac{|z'\langle m|\frac{d}{dt}|n\rangle_{z'}|^2}{\omega_{mn}^2} \ll 1 \qquad \forall m \neq n.$$
(5.5)

This condition seems to be violated by the NV system since the $|\pm 1\rangle_{z'}$ states are degenerate. However, by examining (3.20) we see that the adiabatic approximation need not be invalid, since

$${}_{z'}\langle 1|\frac{\partial}{\partial\phi}|-1\rangle_{z'} = {}_{z'}\langle 1|\frac{\partial}{\partial\theta}|-1\rangle_{z'} = {}_{z'}\langle -1|\frac{\partial}{\partial\phi}|1\rangle_{z'} = {}_{z'}\langle -1|\frac{\partial}{\partial\theta}|1\rangle_{z'} = 0.$$
(5.6)

The criterion (5.5) for the NV centre is then simply

$$\frac{(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2)}{2D^2} \ll 1,\tag{5.7}$$

since, for (m, n) = (1, 0), (0, 1), (-1, 0) and (0, -1), we have

$$|_{z'}\langle m|\partial_{\phi}|n\rangle_{z'}| = \frac{\sin\theta}{\sqrt{2}} \quad \text{and} \quad |_{z'}\langle m|\partial_{\theta}|n\rangle_{z'}| = \frac{1}{\sqrt{2}}.$$
(5.8)

This implies that the adiabatic approximation is valid provided the angular velocity of the crystal is much less than the zero-field splitting frequency, $D = 2\pi \cdot 2.88$ GHz.

5.2 Choice of gauge

As discussed in Chapter 3, there is a gauge degree of freedom in defining the instantaneous eigenstates $|m\rangle_{z'}$. The geometric phase for a closed trajectory is independent of the choice of gauge. Here, and in later chapters, we will also be interested in Berry's phase for trajectories which are not closed and we must then be careful in choosing our gauge.

In the experiments we consider, Berry's phase is observed through interaction with a microwave magnetic field B_R and it is the phase difference between the NV centre and the microwave field, as seen by the NV centre, which is the observable quantity. Consider a linearly polarised microwave field tuned to the zero-field splitting transition, oscillating along the (fixed) z-axis, $B_R = B_R \cos(\omega t)\hat{z}$. The Hamiltonian for the interaction of this field with the NV centre is

$$H_{\rm int} = \gamma \boldsymbol{B}_R \cdot S = \gamma \hbar B_R \cos(\omega t) \begin{pmatrix} \cos \theta & \frac{\sin \theta}{\sqrt{2}} e^{i\phi} & 0\\ \frac{\sin \theta}{\sqrt{2}} e^{-i\phi} & 0 & \frac{\sin \theta}{\sqrt{2}} e^{i\phi}\\ 0 & \frac{\sin \theta}{\sqrt{2}} e^{-i\phi} & -\cos \theta \end{pmatrix}_{z'}$$

$$\approx \gamma \hbar B_R \cos(\omega t) \frac{\sin \theta}{\sqrt{2}} \begin{pmatrix} 0 & e^{i\phi} & 0\\ e^{-i\phi} & 0 & e^{i\phi}\\ 0 & e^{-i\phi} & 0 \end{pmatrix}_{z'}, \quad (5.9)$$

where the matrices are expressed with respect to the $|m\rangle_{z'}$ basis as defined by (5.3). The approximation of the second line neglects the term proportional to $S_{z'}$ and is valid provided the microwave field is weak, $\gamma B_R \ll \omega$.

The interaction Hamiltonian (5.9) depends on both the polar θ and azimuthal ϕ angles. The dependence on the polar angle is simply a matter of effective strength. Since the z' component of the microwave field can be ignored, the effective microwave field strength experienced by the NV centre is just $B_R \sin \theta$. The dependence on azimuthal angle is more interesting: it has the character of a phase. The effect of a microwave pulse on a state $|\psi\rangle$ when the N-V axis is at some azimuthal angle $\phi = \phi_0$ is the same as the effect when $\phi = 0$ and the eigenstates are modified by a phase factor $\exp(-im_{z'}\phi_0)$. Since the linearly polarised microwave field can be decomposed into two counter-rotating fields, it should be no surprise that the effective phase of the NV centre should be so closely linked to the the microwave field's angle relative to the NV axis.

We would like to eliminate this phase-like dependence of the interaction Hamiltonian on the NV orientation (5.9). We can do this through an appropriate choice of gauge. We are free to make a gauge transformation in the definition of eigenstates (5.3) of the form

$$|m\rangle_{z'} \to \exp[if_m(\theta,\phi)]|m\rangle_{z'},$$
(5.10)

which redefines the phase of the basis eigenstates as a function of θ and ϕ . Choosing $f_m = -m\phi$ eliminates the ϕ -dependence of the interaction Hamiltonian (5.9) as desired. Our new choice of basis eigenstates is:

$$|1\rangle_{z'} = \begin{pmatrix} e^{-i\phi}\cos^2\frac{\theta}{2} \\ \frac{1}{\sqrt{2}}\sin\theta \\ e^{i\phi}\sin^2\frac{\theta}{2} \end{pmatrix}_z \quad |0\rangle_{z'} = \begin{pmatrix} -\frac{1}{\sqrt{2}}e^{-i\phi}\sin\theta \\ \cos\theta \\ \frac{1}{\sqrt{2}}e^{i\phi}\sin\theta \end{pmatrix}_z \quad |-1\rangle_{z'} = \begin{pmatrix} e^{-i\phi}\sin^2\frac{\theta}{2} \\ -\frac{1}{\sqrt{2}}\sin\theta \\ e^{i\phi}\cos^2\frac{\theta}{2} \end{pmatrix}_z , \quad (5.11)$$

and Berry's phase becomes

$$\Phi_B = \int_C m \cos \theta d\phi. \tag{5.12}$$

This choice of gauge has absorbed the (azimuthal) angular dependence of (5.9) into Berry's phase. The final state produce by a microwave pulse now depends only on the explicit phase given by (5.12).

We should emphasise that the appropriate choice of gauge depends on the particular microwave field we consider. If we had considered a circularly polarised microwave field, or a microwave field polarised along an axis other than z, for example, we would have chosen a different gauge.

This issue of gauges arose when we discussed the A-C effect in the previous chapter. We are now in a position to explain it more thoroughly. Then, as now, we had a gauge degree of freedom in defining the phase of the eigenstates of the NV centre as a function of the disk's rotation angle. Since the angle of the NV axis did not change in that case, we were able to implicitly use the lab frame coordinate system for our basis states. We could have instead chosen to use, for example the crystal's frame as our coordinate system. This would have introduced a phase factor $\exp[im\theta]$ into our eigenstates, where θ is the disk's angle of rotation. Since the transformation would have also introduced a similar term into the interaction Hamiltonian, the change would naturally have had no physical implications. It is interesting to note that if the wire producing the microwave field were mounted on the spinning disk then the crystal frame basis would be the appropriate one to use and the extra phase it implies would actually be observed.

5.3 Proposed experiment

Because the diamond NV electron spin has such long coherence times it should be possible to observe Berry's phase by mechanically spinning a diamond crystal. The experiment we propose is very similar to the proposed A-C experiment of the previous chapter. A diamond crystal is mounted on a spinning spindle. Optical initialisation, coherent microwave control, and fluorescence detection are used to measure the phase evolved after a certain rotation angle. The experiment would be simpler than the A-C experiment in some ways, since strong electric fields are not required and the diamond's trajectory does not need to sweep out any area, permitting a very small spindle diameter.

The envisaged geometry is shown in Figure 5.1(a). The microwave field is linearly polarised with its magnetic field pointing along the spindle (z) axis so that we can use the basis eigenstates (5.11) of the previous section. The crystal itself is mounted such that the NV axis makes an angle θ to the spindle axis. We assume that some mechanism lifts the degeneracy of the $|\pm 1\rangle_{z'}$ states. This could be mechanical strain in the crystal, a static magnetic field along z (weak enough not to mix the NV eigenstates) or a magnetic field rotating with the spindle, produced, for example, by a permanent magnet mounted on the spindle.

A Ramsey-type experiment is performed. The spindle is first set spinning. As the azimuthal angle ϕ of the NV axis passes zero, a $\pi/2$ Rabi pulses is applied, tuned to the $|0\rangle_{z'} - |1\rangle_{z'}$ transition. As the spindle continues to rotate, a relative phase, Berry's phase,

evolves between the $|0\rangle_{z'}$ and $|1\rangle_{z'}$ states, given by (5.12)

$$\Phi_B = \phi \cos \theta. \tag{5.13}$$

After the spindle has rotated through some angle ϕ_0 , a second $\pi/2$ pulse is applied, converting the phase into a population difference, which is measured in the usual way by 532 nm illumination and a fluorescence recording.

A spindle rotation speed of f = 2 kHz and a 10 μ s T_2^* time would allow up to 20 mrad of Berry's phase to be produced. It would not, however, allow a complete rotation of the spindle before the NV spin dephases. Repeating the arguments of the previous chapter, the relative sensitivity, using a single NV centre, would be

$$\frac{\Delta \Phi_B}{\Phi_B} \sqrt{T} \approx \frac{1}{Cf\sqrt{T_2^*}}.$$
(5.14)

An experiment very similar to this was performed by Tycko [49] using 35 Cl nuclear quadrupole resonance in a spinning sample of NaClO₃. Unlike the A-C effect, Berry's phase does not depend on the spin's dipole moment, other than to ensure adiabaticity. The longer coherence time of nuclear spins makes nuclear resonance a more attractive platform than electron spin resonance. Nevertheless, unlike Tycko's experiment, ours would be an experiment performed on a single quantum system.

5.4 Alternative approaches - spin echo and nuclear spin

As with the proposed A-C experiment, a spin echo pulse sequence could extend the coherence lifetime of the NV electron spin and allow a larger geometric phase to be measured. A different geometry is necessary, shown in Figure 5.1(b), in which the spindle axis is placed at an angle θ_0 to the microwave field (z) axis, and the NV axis (z') is perpendicular to the spindle axis. Berry's phase produced by this geometry is alternating.

A spin echo control sequence, performed in the same way as that described in the previous chapter, with π pulses applied whenever the NV axis z' is perpendicular to z,

would rectify this alternating Berry's phase, producing a total phase of $\Phi_B = 4n\theta$ where n is the number of complete spindle rotations. By extending the coherence time from T_2^* to $T_2 \approx 2$ ms, a larger Berry's phase $\Phi_B \approx 4$ rad could be produced, with sensitivity

$$\frac{\Delta \Phi_B}{\Phi_B} \sqrt{T} \approx \frac{1}{Cf\sqrt{T_2}}.$$
(5.15)

Another way to observe Berry's phase using the NV centre could be to make use of an ancillary nuclear spin. Coherent control of nearby nuclear spins such as ¹³C or ¹⁴N has been demonstrated experimentally [12, 8, 53]. Hyperfine coupling between the electron and nuclear spin allows controlled-not (CNOT) operations to be performed, conditionally flipping one spin depending on the value of the other spin, which allows information to be exchanged between electron and nuclear spins.

Nuclear spin polarisation can achieved using a combination of CNOT operations and optical pumping. Optical illumination first polarises the electron spin, resulting in an incoherent mixture of nuclear spin states. These spin states are then mapped onto electron spin states using CNOT operations, π pulses tuned to the appropriate hyperfine transition. A second optical pumping cycle then creates a coherent nuclear spin state. Figure 5.2 shows this procedure for a spin-half nucleus such as ¹³C but the approach is easily extended to nuclei of other spins, such as the spin-one ¹⁴N.

Controlled rotations of the nuclear spin are achieved using radio-frequency (\approx MHz) fields. Readout of the nuclear spin is performed in a manner similar to polarisation. The nuclear spin states are mapped onto electron spin states which are projectively measured in the usual way. Since polarisation, coherent rotations, and readout of a nuclear spin can each be achieved, an experiment to detect Berry's phase in a nuclear spin could be carried out in an exactly analogous manner to that for the NV electronic spin.

The adiabatically varying Hamiltonian in a nuclear spin Berry phase experiment could come from a number of sources. It is known that the ¹⁴N spin of an NV centre has a 5 MHz zero-field nuclear quadrupole splitting along the NV axis, in complete analogy with the zero-field splitting of the NV electronic spin. The zero-field splitting of a ¹³C spin, however, will depend on its location. One approach would be to split the nuclear



Figure 5.2: Diagram showing how the hyperfine interaction between the NV electron spin and an ancillary nuclear spin can be used to polarise, coherently control, and measure the nuclear spin. Polarisation is achieved by mapping nuclear spin states onto electron spin states, essentially transferring the incoherence from the nuclear spin to the electron spin degree of freedom, which can be made coherent by optical pumping. Measurement is achieved similarly, by again mapping nuclear spin onto electron spin, and measuring the electron spin by fluorescence. Red dots indicate coherent states. Blue dots indicate incoherent mixtures.

spin states using a magnet mounted on the spindle which rotates with the crystal. The splitting of nuclear spin states will in any case be on the order of MHz, so adiabaticity (with kHz spindle rotation speed) is still maintained.

Due to their weaker interaction (by three orders of magnitude) with the environment, nuclear spins have longer coherence times than electronic spins, T_2^* on the order of ms [12] for ¹³C spin. A Berry phase experiment using nuclear spin would thus be both more sensitive and would allow a complete rotation of the spindle within the coherence time at the expense of a more complicated pulse sequence. The same approach, however, would not be an advantage in an A-C experiment, since the size of the A-C effect scales with the magnetic dipole moment.

6

ROTATIONALLY DIFFUSING NV -MODEL AND ASSUMPTIONS

From the fundamental quantum mechanics of geometric phases we now move to a more technological application of the diamond NV centre. In Chapter 2 we saw how the NV centre can be used as a highly sensitive magnetometer at the nanoscale. We also saw that nanodiamonds are being explored as fluorescent markers inside biological cells for their excellent fluorescence properties and biocompatibility. The question naturally arises: is it possible to perform magnetometry using a nanodiamond which is inside a living cell, imaging intracellular biological processes unavailable to macroscopic or probe-based magnetometers?

A significant challenge with such a proposal is that the orientation of a nanodiamond inside a cell would be constantly changing. As we have seen, the anisotropy of the NV zero-field Hamiltonian means that its interaction with magnetic fields, including microwave control fields, depends on its orientation. We have also seen how geometric phases arise from rotation itself, independent of any external fields. Previous work with NV magnetometry has avoided these issues by using crystals whose position and orientation is fixed.

In this chapter and the next we aim to meet this challenge. We develop a theory for quantum measurement, of the sort described in Chapter 2, on an NV centre whose orientation changes quickly in time (on the scale of μ s to seconds) governed by Brownian statistics. We predict the ensemble behaviour of the fluorescence signal and ask how much information it contains about the nanodiamond's rotational behaviour and the magnetic fields it experiences. The present chapter is concerned with developing a model for the motion and quantum evolution of such a nanodiamond. In Chapter 7 we explore the implications of this model.

6.1 Model of Brownian rotation of a nanodiamond

We model the rotational behaviour of a nanodiamond using classical hydrodynamics, taking the crystal to be a spherically symmetric body immersed in a homogeneous fluid of viscosity η . The crystal receives random 'kicks' of angular momentum from microscopic fluctuations in the fluid, which compete with the damping effects of the fluid's viscosity. Given sufficient damping, the crystal's rotational motion is described by rotational diffusion and characterised by a single diffusion constant k_D , the inverse of the mean time taken to rotate through one radian.

In this section we derive the equations which describe rotational diffusion, the conditions under which these equations are valid, and their relationship to macroscopic variables. We begin by reviewing the simple case of diffusion in one dimension, covered well in [54].

Consider a particle following a random walk in one dimension x whose position over time can be described by a Markov process. Its position $x + \Delta x$, at time $t + \Delta t$, depends probabilistically on its position x at time t according to some transition probability $w(x + \Delta x; t + \Delta t | x; t)$. On timescales longer than Δt and length scales longer than the typical size of the jumps, the evolution of the probability distribution function p(x; t) can be modelled by the Fokker-Planck equation,

$$\frac{dp}{dt} = -\frac{\partial}{\partial x} [D_1 p] + \frac{1}{2} \frac{\partial^2}{\partial x^2} [D_2 p], \qquad (6.1)$$

$$D_1 = \left\langle \frac{\Delta x}{\Delta t} \right\rangle = \frac{1}{\Delta t} \int d(\Delta x') \Delta x' w(x + \Delta x'; t + \Delta t | x; t), \tag{6.2}$$

$$D_2 = \left\langle \frac{(\Delta x)^2}{\Delta t} \right\rangle = \frac{1}{\Delta t} \int d(\Delta x') (\Delta x')^2 w(x + \Delta x'; t + \Delta t | x; t).$$
(6.3)

The coefficients D_1 and D_2 , which may be functions of the particle's position, respectively describe drift, the tendency (if any) for the particle to move in a particular direction, and diffusion, the broadening of the probability distribution function due to random movements left and right.

As a physically motivated model for this process, consider a particle of mass m moving in a one-dimensional fluid with a damping coefficient γ_d , subject to a fluctuating force F(t) with a vanishing ensemble average, $\langle F(t) \rangle = 0$. The force F(t) is due to microscopic
fluctuations and fluctuates on a sufficiently fast timescale that for convenience we may take it to be delta function correlated, $\langle F(t)F(t')\rangle = t_c F_0^2 \delta(t-t')$. The particle's position then follows a stochastic differential equation known as the Langevin Equation,

$$m\ddot{x} = -\gamma_d \dot{x} + F(t). \tag{6.4}$$

The particle's velocity, $v = \dot{x}$, can be solved directly as

$$v(t) = v(0)e^{-\gamma_d t/m} + \frac{1}{m}e^{-\gamma_d t/m} \int_0^t dt' e^{\gamma_d t/m} F(t').$$
 (6.5)

Using the ensemble properties of the fluctuating force F(t), we find that on timescales longer than m/γ_d , the ensemble average of the velocity disappears, $\langle v \rangle = 0$. The average squared velocity, however, reaches the steady-state value,

$$\langle v^2 \rangle = \frac{t_c F_0^2}{2m\gamma_d} = \frac{k_B T}{m}.$$
(6.6)

The second equality of (6.6) follows from the equipartition theorem if the particle is in thermal equilibrium at temperature T.

If the particle's position is sampled at time intervals Δt which are much larger than the velocity damping time m/γ_d then velocity information is lost between timesteps and the particle's trajectory is approximately Markovian. Since the particle's velocity relaxes quickly on this timescale, we can take $\dot{v} \approx 0$. Equation (6.4) then yields

$$\dot{x} = \frac{1}{\gamma_d} F(t) \tag{6.7}$$

Integrating (6.7) gives $\langle \Delta x / \Delta t \rangle = 0$ and $\langle (\Delta x)^2 / \Delta t \rangle = t_c F_0^2 / \gamma_d^2$, so the Fokker Planck equation is

$$\frac{dp(x,t)}{dt} = \frac{t_c F_0^2}{2\gamma_d^2} \frac{\partial^2 p(x,t)}{\partial x^2} = D \frac{\partial^2 p(x,t)}{\partial x^2}$$
(6.8)

where
$$D = \frac{k_B T}{\gamma_d}$$
, (6.9)

which is often called the Einstein-Smoluchowski equation. Notice that we now have a

diffusion equation expressed in terms of macroscopic parameters. The solution to (6.8) for a particle which starts at the origin, $p(x; 0) = \delta(x)$ is

$$p(x;t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left[\frac{-x^2}{4Dt}\right],\tag{6.10}$$

a Gaussian distribution whose width increases with \sqrt{t} , an important characteristic of diffusive behaviour.

These three descriptions of the one dimensional Brownian particle — the random walk, the Langevin equation and the Fokker-Planck equation — are all equivalent on timescales longer than m/γ_d . As we explore the consequences of rotational diffusion of a nanodiamond, we will use each of these frameworks. The random walk gives an intuitive picture, and a simple model for a Monte Carlo analysis. The Langevin equation allows us to determine the diffusion parameters in terms of measurable quantities and provides a more accurate model for simulation. The Fokker-Planck equation, which describes ensemble behaviour, is a convenient analytic tool. Variations of it will be used to describe the time-evolution of ensemble properties of the NV spin state.

Next we wish to apply these ideas to the stochastic evolution of the N-V axis in a nanocrystal diffusing in a fluid. We treat the evolution of the N-V axis as a random walk in order to obtain a Fokker-Planck (diffusion) equation for its motion. We use the Langevin equation to determine the physical parameters which characterise the motion and to find criteria for the validity of the Fokker-Planck equation.

The orientation of the N-V axis, which we call z' as before, is described with respect to the laboratory frame S (with axes (x, y, z)) by the usual two spherical coordinates, θ and ϕ , of the unit vector \hat{z}' . The axial symmetry of the NV Hamiltonian about z' means that the Cartesian coordinate system of the NV centre is only determined up to rotations about z'. We choose to define the instantaneous NV coordinate system S' so that \hat{x}' , \hat{z}' and \hat{z} are coplanar, as shown in Figure 6.1.

We treat the evolution of the N-V orientation \hat{z}' as a random walk of small steps, of duration Δt , around the unit sphere, as shown in Figure 6.2. Consider a single step in which \hat{z}' moves from (θ_n, ϕ_n) at time t to $(\theta_{n+1}, \phi_{n+1})$ at time $t + \Delta t$. In the frame S'(t), this



Figure 6.1: Diagram illustrating the instantaneous coordinate system of the N-V axis. The unprimed coordinates are fixed in the laboratory frame, S. The instantaneous direction of the N-V axis is z', defined by θ and ϕ with respect to the lab frame S. The Cartesian coordinates x' and y' for the NV centre can be chosen so that x', z' and z are coplanar, as shown.

corresponds to a move from the z' axis to some orientation defined by (θ', ϕ') with respect to the S'(t) frame as shown in Figure 6.2, with some jump probability $w(\theta', \phi')$. Since the crystal is spherically symmetric (by assumption), $w(\theta', \phi')$ should be independent of the crystal's initial (lab-frame) orientation (θ, ϕ) and also of the azimuthal angle ϕ' with respect to S'(t). We also assume that the probability of large angular steps drops off quickly. The random walk is then completely described by the jump probability $w(\theta')$. That is, the probability of stepping through an angle between θ' and $\theta' + d\theta'$ at an azimuthal angle of between ϕ' and $\phi' + d\phi'$ over the time Δt is given by $w(\theta')d\theta'd\phi'/(2\pi)$.



Figure 6.2: Diagram showing a random walk of the NV axis about the unit sphere. The initial orientation is z'_1 . Each subsequent step can be described in terms of a polar angle θ' and an azimuthal angle ϕ' with respect to the NV coordinate system at the beginning of the step. This is shown for the first step, $z'_1 \to z'_2$.

To translate this into a diffusion equation with respect to the lab-frame coordinates (θ, ϕ) we perform a coordinate transformation to find the derivatives of θ and ϕ with respect to θ' . We transform from (θ', ϕ') to (x', y', z') then to (x, y, z) and finally to (θ, ϕ) . The primed and unprimed spherical coordinate systems are related to their Cartesian

counterparts in the usual way. The two Cartesian coordinate systems are related by:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos \phi' \cos \theta' & -\sin \phi' & \sin \theta' \cos \phi' \\ \sin \phi' \cos \theta' & \cos \phi' & \sin \theta' \sin \phi' \\ -\sin \theta' & 0 & \cos \theta' \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}.$$
 (6.11)

To produce a Fokker-Planck equation for (θ, ϕ) we need the ensemble expectation values of $\langle \Delta \theta \rangle$, $\langle \Delta \phi \rangle$, $\langle (\Delta \theta)^2 \rangle$, $\langle \Delta \theta \Delta \phi \rangle$ and $\langle (\Delta \phi)^2 \rangle$ for a single step. We find these by taking the derivatives of θ and ϕ with respect to θ' , and integrating over θ' and ϕ' weighted by the step size probability $w(\theta')$. We obtain the following:

$$\left\langle \Delta\phi\right\rangle = \left\langle \theta'\frac{d\phi}{d\theta'} + \frac{1}{2}\theta'^2\frac{d^2\phi}{d\theta'^2}\right\rangle = \int \frac{d\theta'd\phi'}{2\pi}w(\theta')\left[\theta'\frac{d\phi}{d\theta'} + \frac{1}{2}\theta'^2\frac{d^2\phi}{d\theta'^2}\right] = 0 \quad (6.12)$$

$$\left\langle \Delta \theta \right\rangle = \left\langle \theta' \frac{d\theta}{d\theta'} + \frac{1}{2} \theta'^2 \frac{d^2\theta}{d\theta'^2} \right\rangle = \frac{1}{4 \tan \theta} \left\langle \theta'^2 \right\rangle \tag{6.13}$$

$$\langle \Delta \phi^2 \rangle = \left\langle \theta^{\prime 2} \left(\frac{d\phi}{d\theta^{\prime}} \right)^2 \right\rangle = \frac{1}{2\sin^2 \theta} \langle \theta^{\prime 2} \rangle \tag{6.14}$$

$$\langle \Delta \theta^2 \rangle = \left\langle \theta^{\prime 2} \left(\frac{d\theta}{d\theta^{\prime}} \right)^2 \right\rangle = \frac{1}{2} \langle \theta^{\prime 2} \rangle$$
 (6.15)

$$\langle \Delta \theta \Delta \phi \rangle = \left\langle \theta'^2 \frac{d\theta}{d\theta'} \frac{d\phi}{d\theta'} \right\rangle = 0$$
 (6.16)

where

$$\langle \theta'^2 \rangle = \int d\theta' \theta'^2 w(\theta'),$$
 (6.17)

and we have retained terms up to $\langle \theta'^2 \rangle$. To avoid repetition we have only shown the explicit integral expression in the first of these equations. Our Fokker-Planck equation for the evolution of the probability distribution $p(\theta, \phi)$ of the orientation of the nanodiamond's N-V axis can now be written down:

$$\frac{1}{k_D} \frac{dp(\theta, \phi)}{dt} = -\frac{\partial}{\partial \theta} \left[\frac{1}{\tan \theta} p(\theta, \phi) \right] + \frac{\partial^2}{\partial \theta^2} p(\theta, \phi) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} p(\theta, \phi) = -\frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\frac{p(\theta, \phi)}{\sin \theta} \right) \right] + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} p(\theta, \phi).$$
(6.18)

The boundary conditions are vanishing for θ (with $0 < \theta < \pi$) and periodic in ϕ (with $0 < \phi < 2\pi$). The motion is now characterised by a single diffusion constant k_D which we

have defined as $k_D = \langle \theta'^2 \rangle / 4$.

To express k_D in terms of measurable parameters, we can use a Langevin equation for the nanocrystal's angular velocity,

$$I\dot{\boldsymbol{\omega}} = -\gamma_d \boldsymbol{\omega} + \boldsymbol{\tau}(t), \tag{6.19}$$

where I is the crystal's moment of inertia, $\boldsymbol{\omega} = (\omega_x, \omega_y, \omega_z)$ is the angular velocity of the nanocrystal, γ_d is a drag coefficient, and $\boldsymbol{\tau}(t)$ is a fluctuating torque, with $\langle \boldsymbol{\tau} \rangle = 0$ and $\langle \tau_i(t)\tau_j(t') \rangle = t_c \tau_0^2 \delta_{ij} \delta(t-t')$. The drag term γ_d is given by Stokes' law [55] for the drag on a rotating sphere of radius r in a fluid of viscosity η ,

$$\gamma_d = 8\pi\eta r^3. \tag{6.20}$$

In a manner completely analogous to the case of linear Brownian motion, we find that the steady-state ensemble average of the squared angular velocity is

$$\langle \boldsymbol{\omega} \cdot \boldsymbol{\omega} \rangle = \frac{3}{2} \frac{t_c \tau_0^2}{I \gamma_d} = 3 \frac{k_B T}{I}.$$
(6.21)

As before, the second equality follows from the equipartition theorem if the nanocrystal is in thermal equilibrium at temperature T.

Unlike the case of linear Brownian motion (6.8) the angles θ and ϕ cannot be obtained by a straightforward integration of ω . We can, however, make the analogy between spherical and linear Brownian motion by considering only a small part of the unit sphere, which may be approximated locally by its tangential plane. Considering only rotational motion of the crystal in the region where $\theta \approx \pi/2$ and $\phi \approx 0$, we have $\dot{\theta} \approx \omega_y$ and $\dot{\phi} \approx \omega_z$ and the integration can be done exactly as before, giving the approximate diffusion equation

$$\frac{dp(\theta,\phi)}{dt} \approx \frac{1}{2} \frac{t_c \tau_0^2}{\gamma_d^2} \left[\frac{\partial^2}{\partial \theta^2} p(\theta,\phi) + \frac{\partial^2}{\partial \phi^2} p(\theta,\phi) \right].$$
(6.22)

Comparing with (6.18), we find by inspection that

$$k_D = \frac{k_B T}{\gamma_d} = \frac{k_B T}{8\pi\eta r^3}.$$
(6.23)

The crystal's rotation occurs on a timescale of $1/k_D$, which is plotted as a function of crystal radius in Figure 6.3, for room temperature water.

The Fokker-Planck equation we have obtained (6.8) is valid on timescales longer than the velocity damping time t_d given by

$$t_d = I/\gamma_d = \rho r^2/(15\eta).$$
 (6.24)

This derivation has assumed that the angle through which the diamond rotates during this time is small. We can now state this condition in terms of the diffusion constant. We require that $k_D I/\gamma_d = \frac{k_B T \rho}{120 \pi \eta^2} \frac{1}{r} \ll 1$, where ρ is the density of diamond and r is the crystal's radius. This dimensionless parameter is indeed very small. For a 10nm diamond in room temperature water it is on the order of 10^{-6} .

We now have a mathematical description of the Brownian rotation of a nanodiamond. The actual environment of a cell will inevitably produce rotational behaviour more complicated than the model of spherically symmetric diffusion we have just described. The cell's cytoskeletal structure may impede the crystal's motion in ways not captured by a linear damping term, and may interact chemically with the crystal's surface. Our results aim to give a first approximation to the behaviour of an intracellular colloidal nanodiamond. Future experiments will help to inform a more accurate model.

6.2 Influence of rotation on NV quantum evolution

Having produced a model for the rotation of the nanodiamond, we now consider the ways in which this rotation will affect quantum measurement of the sort described in Chapter 2. It is the anisotropy of the NV's zero-field Hamiltonian which makes its rotational behaviour important. Under weak external fields, the NV Hamiltonian defines the spin quantisation axis and the fields merely perturb the energy levels in a manner dependent on their orientation with respect to the NV axis. The rotation of the NV Hamiltonian also affects the NV quantum evolution, through Berry's phase as described in the previous chapter.



Figure 6.3: Illustration of the different rotational timescales as a function of crystal radius in room temperature (T = 300K) water ($\eta = 10^{-3}$ Pa.s). Red: rotational diffusion timescale $1/k_D$ (6.23). Blue: population mixing timescale t_m (7.31). Purple: Angular velocity damping timescale t_d (6.24). Also shown are the approximate timescale associated with the NV spin state: Homogeneous broadening (T_2), inhomogeneous broadening (T_2^*) and zero-field splitting (1/D).

The NV Hamiltonian is once again given by

$$H = \frac{1}{\hbar} DS_{z'}^2 + \gamma \boldsymbol{B} \cdot \boldsymbol{S}.$$
(6.25)

As before, we take \hat{z}' to be the instantaneous direction of the NV axis, described by θ and ϕ with respect to the fixed z axis. If the magnetic field **B** is very large compared with the 2.88 GHz splitting, then it is the direction of this field which determines the quantisation axis. In this case, the orientation of the crystal has little effect on quantum measurement. Applying a large (much greater than 0.1 T) static magnetic field would thus be one way to perform magnetometry using a freely diffusing crystal without needing to account for the crystal's changing orientation.

Instead, we will consider weak external fields, much weaker than 0.1 T. We need to allow for both the microwave frequency control fields oscillating on the order of GHz, which we will call B_R , and the much more slowly varying fields, which we call B_s , including the signal field we wish to measure and any applied static field. Under the secular approximation, it is only the z' component of B_s and the x' and y' components of B_R which are important:

$$H \approx \frac{1}{\hbar} DS_{z'}^2 + \gamma (\hat{\boldsymbol{z}}' \cdot \boldsymbol{B}_s) S_{z'} + \gamma (\hat{\boldsymbol{x}}' \cdot \boldsymbol{B}_R) S_{x'} + \gamma (\hat{\boldsymbol{y}}' \cdot \boldsymbol{B}_R) S_{y'}.$$
 (6.26)

This approximation is valid to first order in the ratio of the field strengths to the zero-field splitting.

As before, we take the microwave field to be linearly polarised with the magnetic field oscillating along the fixed z axis. The effective strength of the microwave field is then $B_R \sin \theta$. We will assume that the microwave field is sufficiently strong that control pulses happen on a timescale much faster than $1/k_D$, so that we can take the orientation of the crystal to be effectively fixed for the duration of the pulse. A pulse which would cause a $\pi/2$ rotation for an optimally oriented crystal, will thus produce a $(\pi/2)\sin\theta$ rotation for a crystal of arbitrary orientation.

Between microwave pulses the crystal rotates as described in the previous section, under the influence of B_s and the zero-field Hamiltonian. Berry's phase, as described in Chapter 5, applies if the change in Hamiltonian due to the rotation is adiabatic. This will be the case if the crystal's typical angular velocity, given by (6.21), is much less than 2.88GHz. The evolution of the NV spin state will then consist of a change in phase between spin sublevels. There will be a geometric phase Φ_B given by (5.12) and a dynamical phase Φ_D due to \boldsymbol{B}_s ,

$$\Phi_m = \Phi_B + \Phi_D = m \int_C \cos\theta d\phi + m\gamma \int (\hat{\boldsymbol{z}}'(t) \cdot \boldsymbol{B}_s(t)) dt.$$
(6.27)

If the evolution is not adiabatic then the argument which lead to Berry's phase breaks down. Population mixing effects will then arise which we discuss in the next chapter.

Finally, there is the anisotropy of photon emission and absorption to consider. The optical transitions which allow polarisation and readout are dipole transitions, which preferentially emit and absorb photons in the $\pm \hat{z}'$ directions, with the usual dumbbell-shaped profiles. This means that optical pumping will take longer for some orientations than for others. Provided the NV centre is illuminated long enough to polarise even a nonoptimally oriented crystal, this anisotropy will not affect polarisation. Under a confocal arrangement, photon emission will be detected for nearly a full 2π sr of solid angle. The plane of symmetry of the dipole emission profile then means that orientation will not affect the fraction of photons collected. Since the change in photon flux which allows $|0\rangle$ to be discriminated from $|\pm 1\rangle$ is governed by the lifetime of the ¹A metastable state rather than by the effective power of the illuminating laser, the crystal's orientation should therefore not affect readout.

A single measurement consists of optical initialisation, microwave control pulses separated by periods of free evolution, and optical readout. We now have a model to describe the effect of the crystal's orientation on each of these steps, as summarised in Figure 6.4.

6.3 The ensemble-averaged signal

In practice, and even in theory, a single measurement contains very little information. The quantity which is measured by an experiment is a time-averaged signal from a large



Figure 6.4: Diagram showing an example orientation of the NV centre at each stage of a single measurement run. (a) Initialisation by optical pumping and microwave control is achieved while the NV axis has a particular orientation. We assume that this step is sufficiently fast that the NV orientation does not change appreciably for its duration. The angle through which the NV spin is rotated due to the microwave pulse is a function of its orientation. (b) Free evolution for time τ under the influence of the 'signal' magnetic field. During this time, the NV orientation diffuses along some rotational trajectory as shown. A phase evolves between the NV spin sublevels, which is the sum of Berry's phase from the rotational trajectory, and a dynamical phase due to B_s as given by (6.27). (c) Readout, like initialisation, occurs on a sufficiently fast timescale that the NV orientation remains approximately fixed. Again, the angle of spin rotation due to the microwave field depends on this instantaneous orientation.

ensemble of individual measurement runs. Decoherence is the classic ensemble effect. Environmental perturbations cause subtly different quantum evolution in each member of the ensemble, leading to a loss of information in an ensemble-averaged signal after a certain evolution time. In the case of the rotationally diffusing nanodiamond, the ensemble's members differ more dramatically. Each member has its own starting orientation and rotational trajectory.

Of course, the ensemble's members do not exist in some abstract 'ensemble space'. In practice, a series of sequential measurements is made which may involve several NV centres in a single crystal. If the time over which measurements are made is sufficiently small compared with the rotational diffusion time $1/k_D$ then the ensemble's members might have similar orientations. The situation would be comparable to the case of a static crystal.

In this work we take the opposite limit. We make the simplifying assumption that sufficiently many measurements are made that the final signal is an average over the full theoretical ensemble: all initial orientations and rotational trajectories are accounted for. As with the assumption of spherically symmetric diffusive rotation, experiments will show the directions in which our assumption must be corrected.

Consider a continuously applied microwave field, of amplitude B_R , tuned to the $|0\rangle_{z'}$ - $|1\rangle_{z'}$ transition. This will cause Rabi oscillations with a frequency which depends on the angle θ between the NV axis z', and z, the oscillation direction of the microwave magnetic field. Initialised into $|0\rangle_{z'}$, the population of $|0\rangle_{z'}$ for a single NV as a function of time is then $P_0 = \frac{1}{2} + \frac{1}{2} \cos(\Omega_R t \sin \theta)$, where $\Omega_R = \gamma B_R$ is the Rabi frequency when $\theta = \pi/2$. As usual, we have assumed that $\Omega_R \gg 1/k_D$. The ensemble-averaged signal is a superposition over all the possible different Rabi frequencies,

$$S(t) = \int_0^\pi d\theta \frac{1}{2} \sin \theta \left[\frac{1}{2} + \frac{1}{2} \cos(\Omega_R t \sin \theta) \right], \qquad (6.28)$$

which is plotted in Figure 6.5 along with the equivalent curve for a static crystal, with $\theta = \pi/2$, for comparison. The signal reaches its first minimum at $t\Omega_R \approx 1.16\pi$ and which point $S \approx 0.140$.



Figure 6.5: Red: Rabi signal averaged over the full ensemble of possible orientations, given by (6.28). Blue: Rabi signal for optimal orientation, $\theta = \pi/2$ for comparison.

Obtaining such a Rabi oscillation signal is the usual way to determine the pulse length required for a $\pi/2$ pulse. The required time is simply read off from the curve. In our system, we have a certain amount of freedom in deciding how long a $\pi/2$ pulse should be. We could take it to be $t_{\pi/2} = \pi/(2\Omega_R)$, which would produce a $\pi/2$ rotation for an optimally aligned ($\theta = \pi/2$) NV centre, and a smaller rotation otherwise. Alternatively, we could use $t_{\pi/2} = 1.16\pi/(2\Omega_R)$ which, based on Figure (6.5), would optimise the initial amplitude of a Ramsey-type experiment. One of the strengths of Ramsey-type experiments is their robustness to the $\pi/2$ pulse time chosen. We do not, therefore, expect this decision to be an important one (as simulations will show). For now we keep our discussion general, introducing a parameter, a, to describe the pulse time. When we refer to a ' $\pi/2$ ' pulse (keeping the quotation marks) we mean a pulse of length $t_{\pi/2} = a\pi/(2\Omega_R)$, where $a \approx 1$, which produces a spin rotation of $\Theta = a(\pi/2) \sin \theta$. (In this chapter and the next, we use the capital Θ to refer to an angle of spin rotation, to avoid confusion with the spatial angle θ .)

Now consider a Ramsey-type pulse sequence. The NV centre, starting with z' at some polar angle θ_1 to the z-axis, is first optically pumped into $|0\rangle_{z'}$. A ' $\pi/2$ ' pulse is then applied, tuned to the $|0\rangle_{z'} - |1\rangle_{z'}$ transition, producing a spin rotation of $\Theta_1 = a(\pi/2) \sin \theta_1$. The system is allowed to evolve for time τ , during which time the crystal rotates through some trajectory C and the $|1\rangle_{z'}$ state develops a phase Φ given by (6.27). A final ' $\pi/2$ ' pulse is applied. This final pulse may be in phase with the initial pulse, or out of phase by π . It produces a rotation of $\pm \Theta_2 = \pm a(\pi/2) \sin \theta_2$ where θ_2 is the final angle between z' and z and the '+' and '-' refer to the pulse being in and out of phase with the original pulse respectively. The final population P_0 of the $|0\rangle_{z'}$ state can then be written down explicitly as

$$P_{0} = \frac{1}{2} + \frac{1}{2}\cos\Theta_{1}\cos\Theta_{2} \pm \frac{1}{2}\sin\Theta_{1}\sin\Theta_{2}\cos\Phi.$$
 (6.29)

The final (normalised) signal is the ensemble average of this value,

$$S(t) = \langle P_0 \rangle, \tag{6.30}$$

where the ensemble average is taken over all possible starting orientations and rotational

trajectories.

In the presence of a small amount of detuning $\Delta \omega$, the phase Φ has a component $\Delta \omega t$ which is linear in time. The $\cos \Phi$ term of (6.29) then leads the signal to oscillate between two extremes, the upper and lower bounds of the 'signal envelope'. We are interested in the behaviour (typically decay) of this signal envelope, rather than the oscillations themselves. For the sake of our discussions we assume zero detuning. Instead, the upper and lower bounds of the 'signal envelope' are produced by the two curves implied by the ' \pm ' term of Equation (6.29), provided the mean phase vanishes, $\langle \Phi \rangle = 0$ (which will always be the case given the symmetry of our system). Physically, the two curves correspond to the phase (0 or π respectively) of the final $\pi/2$ pulse.

We have implicitly assumed that the $|\pm 1\rangle_{z'}$ states are nondegenerate, so that a Rabi pulse can produce, for example, a superposition of $|0\rangle_{z'}$ and $|1\rangle_{z'}$ with no occupation of $|-1\rangle_{z'}$. In experiments, the degeneracy is commonly lifted by an applied static magnetic field. Such an approach is clearly not appropriate for a rotationally diffusing nanodiamond. As the NV centre rotates, it would fall in and out of tune with the microwave field, the effective magnetic field strength depending on the orientation of the NV axis (6.26). Instead, we assume that there is some strain in the crystal which lifts the degeneracy independently of its orientation.

It is, however, possible to perform the kinds of experiments we are proposing when the $|\pm 1\rangle_{z'}$ manifold is fully degenerate, or at least relatively degenerate compared to the frequency of the Rabi oscillations. After initialisation into $|0\rangle_{z'}$, a Rabi pulse can produce a coherent superposition of all three states. The $|\pm 1\rangle$ states evolve equal and opposite phases $\pm \Phi$ due to magnetic fields and Berry's phase (Berry's phase, like a magnetic field, amounts to an operation of $\exp[i\Phi_B S_{z'}]$). A final Rabi pulse converts this phase information into a population difference. While the approach is qualitatively the same as the two-state approach we have discussed, the specific equations are slightly different. For example, a $\pi/2$ rotation of the spin, followed by a phase evolution of $\pm \Phi$, followed by a second $\pi/2$ rotation will result in a final population of $P_0 = [\frac{1}{2} + \frac{1}{2} \cos \theta]^2$, the square of what we would expect for a two-state system. Such an approach is occasionally used in experiments [7]. 6. Rotationally Diffusing NV - Model and Assumptions

ROTATIONALLY DIFFUSING NV -RESULTS AND IMPLICATIONS

We now apply the results of the previous chapter to discover how the expected signal S(t)(6.30) changes as a function of the crystal's rotation rate and the character and strength of local magnetic fields. With sensing applications in mind, we are particularly interested in finding a way to extract information about these parameters from the signal.

We first consider the simplest case of diffusive rotation with no external fields (other than the brief control fields) to find the expected signal due to Berry's phase alone. Probing deeper, we then develop corrections to the adiabatic approximation which show population mixing effects if the angular velocity damping time t_d is small compared with the timescale of the 2.88 GHz zero-field splitting frequency. We next explore the expected signal when the nanodiamond is subject to magnetic fields. We consider slowly varying or DC fields, fluctuating (FC) fields, and sinusoidal (AC) fields, aiming to predict the magnetic field sensitivity of the rotationally diffusing nanodiamond magnetometer.

7.1 Berry's phase

With no external magnetic fields, the phase between sublevels acquired during free evolution (6.27) is just Berry's phase. The population of $|0\rangle_{z'}$ after a single measurement run (6.29) is a function of the initial and final polar angles of the NV axis, θ_1 and θ_2 , and Berry's phase Φ_B acquired during free evolution. Given a particular initial orientation θ_1 we can write the probability density of a particular final orientation θ_2 and Berry's phase Φ_B after time t as $p(\theta_2, \Phi_B; t | \theta_1)$. The ensemble-averaged signal (6.30) can then be expressed as the integral of the final ground state population over all possible θ_1 , θ_2 and Φ_B , weighted by the probability distribution function and the probability of the NV starting with orientation θ_1 :

$$S(t) = \int d\theta_1 d\theta_2 d\Phi_B \frac{1}{2} \sin \theta_1 p(\theta_2, \Phi_B; t|\theta_1) P_0(\theta_1, \theta_2, \Phi_B), \qquad (7.1)$$

where the final ground state population $P_0(\theta_1, \theta_2, \Phi_B)$ is given by (6.29). It remains, then, to find $p(\theta_2, \Phi_B; t | \theta_1)$.

The evolution of Φ_B depends on the evolution of the azimuthal angle ϕ of the z' axis, according to $\dot{\Phi}_B = \dot{\phi} \cos \theta$. Berry's phase Φ_B , like ϕ , therefore evolves as a Markov process on timescales longer than the crystal's angular velocity damping time. We can use the Fokker-Planck equation to find the time evolution of $p(\theta_2, \Phi_B; t|\theta_1)$. Using (6.12) and (6.14) we find that

$$\langle \Delta \Phi_B \rangle = \cos \theta \langle \Delta \phi \rangle = 0 \quad \text{and} \quad \langle (\Delta \Phi_B)^2 \rangle = \cos^2 \theta \langle (\Delta \phi)^2 \rangle = 2k_D \Delta t \cot^2 \theta,$$
(7.2)

and recalling (6.18), we can write down the Fokker-Planck equation:

$$\frac{1}{k_D} \frac{d}{dt} p(\theta_2, \Phi_B; t | \theta_1) = - \frac{\partial}{\partial \theta_2} \left[\sin \theta_2 \frac{\partial}{\partial \theta_2} \left(\frac{p(\theta_2, \Phi_B; t | \theta_1)}{\sin \theta_2} \right) \right] + \cot^2 \theta_2 \frac{\partial^2}{\partial \Phi_B^2} p(\theta_2, \Phi_B; t | \theta_1).$$
(7.3)

The boundary conditions are periodic in Φ_B (with $-\pi < \Phi_B < \pi$) and vanishing in θ (with $0 < \theta < \pi$). Since the ensemble is initially in phase ($\Phi_B = 0$ at t = 0) the initial condition is:

$$p(\theta_2, \Phi_B; t = 0|\theta_1) = \delta(\Phi_B)\delta(\theta_2 - \theta_1).$$
(7.4)

To find S(t) we simply solve (7.3) given the initial condition and boundary conditions, and use the solution in (7.1). By inspection, S(t) can be expressed in terms of a dimensionless time parameter $k_D t$ with no other free parameters.

The Fokker-Planck equation (7.3) can be solved numerically. Since we are not interested in the solution itself, but rather the solution integrated over the θ_1 , θ_2 and Φ_B , according to (7.1), we can make some simplifying steps to ease the burden of numerical computation. We define the following functions of θ_2 and t:

$$g_1(\theta_2, t) \equiv \frac{1}{2\sin\theta_2} \int_0^{\pi} d\theta_1 \int_0^{2\pi} d\Phi_B \cos\Theta_1 \sin\theta_1 p(\theta_2, \Phi_B; t|\theta_1)$$
(7.5)

$$g_2(\theta_2, t) \equiv \frac{1}{2\sin\theta_2} \int_0^{\pi} d\theta_1 \int_0^{2\pi} d\Phi_B \sin\Theta_1 \sin\theta_1 \cos\Phi_B p(\theta_2, \Phi_B; t|\theta_1), \quad (7.6)$$

so that the signal S(t) given by (7.1) is given by an integration over a single variable, θ_2 :

$$S(t) = \int_0^{\pi} d\theta_2 \sin \theta_2 \left[\frac{1}{2} g_1 \cos \Theta_2 \pm \frac{1}{2} g_2 \sin \Theta_2 \right].$$
 (7.7)

We are using the notation introduced in the previous chapter: $\Theta_i = a(\pi/2) \sin \theta_i$. By taking the time derivatives of (7.6) and (7.5) and using the Fokker-Planck equation (7.3), we get the following partial differential equations for g_1 and g_2 .

$$\frac{1}{k_D}\dot{g}_1 = \frac{1}{\sin\theta_2}\frac{\partial}{\partial\theta_2}\left(\sin\theta_2\frac{\partial}{\partial\theta_2}g_1\right),\tag{7.8}$$

$$\frac{1}{k_D}\dot{g}_2 = \frac{1}{\sin\theta_2}\frac{\partial}{\partial\theta_2}\left(\sin\theta_2\frac{\partial}{\partial\theta_2}g_1\right) - \cot^2\theta_2g_2,\tag{7.9}$$

where we have integrated twice by parts and used the periodic boundary conditions on $p(\theta_2, \Phi_B; t | \theta_1)$ to obtain the identity

$$\int_{0}^{2\pi} d\Phi_B \cos \Phi_B \frac{\partial^2}{\partial \Phi_B^2} p(\theta_2, \Phi_B; t | \theta_1) = -\int_{0}^{2\pi} d\Phi_B \cos \Phi_B p(\theta_2, \Phi_B; t | \theta_1).$$
(7.10)

The functions g_1 and g_2 have reflecting boundary conditions at $\theta_2 = 0, \pi$ and initial conditions:

$$g_1(\theta_2; t=0) = \frac{1}{2} \cos \Theta_2,$$
 (7.11)

$$g_2(\theta_2; t=0) = \frac{1}{2}\sin\Theta_2.$$
 (7.12)

We have solved g_1 and g_2 numerically and plotted the resulting S(t) in Figure 7.1(a). Note the only parameters in this solution are k_D and a. The rotational diffusion constant, k_D simply defines the timescale. The solution is relatively insensitive to the ' $\pi/2$ ' pulse duration, a. The solution is shown for a = 1 as well as a = 1.16, which optimises the initial amplitude. The solution for both choices shows approximately exponential decay on the timescale of $\tau_D \approx 1/k_D$.



Figure 7.1: Expected fluorescence signals due to rotation alone. (a) Signal envelope for a Ramsey-type pulse sequence with the phase acquired during free evolution due to Berry's phase under the adiabatic approximation. Blue: signal envelope with $a \approx 1.16$. Red: signal enveloped with a = 1. (b) Expected fluorescence signal as a function of free evolution time after optical pumping with no microwave control, in the regime where the adiabatic approximation breaks down. Population mixing reduces the signal to 1/3 of its maximum on a timescale t_m . Dotted curves are based on the theoretical exponential decay as given by (7.31). Solid curves are based on a Monte Carlo simulation of the Langevin Equation (6.19) to produce a time-dependent Hamiltonian, followed by numerical solution of Schrödinger's equation. Blue: $t_d D = 0.1$. Red: $t_d D = 1$. Green: $t_d D = 2$.

Measuring the timescale of the signal decay could give one way to measure the rotational diffusion constant k_D . The measurement sensitivity is

$$\sqrt{T}\Delta k_D = \sqrt{T}\Delta S \left(\frac{dS}{dk_D}\right)^{-1} \approx \frac{1}{C\sqrt{\tau_D}\sqrt{N_{NV}}}$$
(7.13)

where τ_D is the effective coherence time for a single measurement, due to Berry's phase and the fluctuating magnetic fields from the crystal itself. This will be on the order of $1/\tau_D \approx 1/T_2^* + k_D$. One important implication of the signal decay due to Berry's phase is that it gives an upper bound $1/k_D$ on the effective coherence time. This limits the time over which phase information persists, affecting, for example, magnetic field sensitivity, which we discuss below.

Berry's phase has traditionally been studied as a phenomenon of intrinsic interest. We have suggested here a practical application of Berry's phase, as a useful source of information about nanodiamond's rate of rotational diffusion.

7.2 Non-adiabatic evolution

Up to this point we have been working within the adiabatic approximation. The criterion for the validity of this approximation (5.7) was derived in Chapter 5. In the context of the NV centre, the criterion becomes

$$\alpha_{1,0}^2 = \frac{1}{2} (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \ll D^2.$$
(7.14)

The angular velocity of the nanodiamond is a consequence of thermal motion. Using the equipartition theorem, the adiabatic criterion for the rotationally diffusing nanodiamond is then:

$$D \gg \frac{k_B T}{I} = \frac{15}{8\pi} \frac{k_B T}{\rho r^3}.$$
 (7.15)

At room temperature, the adiabatic criterion will then be satisfied if the crystal radius is much greater than 1.2nm.

The derivation also made the second assumption, often overlooked, that $\alpha_{m,n}$ is not merely small compared with D, but also varies slowly on the timescale of 1/D. The timescale on which $\alpha_{m,n}$ changes is the angular velocity damping time t_d (6.24). Figure 6.3, which plots t_d against crystal radius for room-temperature water, shows that t_d is smaller than 1/D when the crystal radius is smaller than around 20nm.

To find the non-adiabatic corrections to the time evolution due to the rotating Hamiltonian we return to the derivation of Berry's phase given in Chapter 3. There we found that the matrix elements of the time evolution operator U with respect to the instantaneous eigenstates $|n(t)\rangle$ of a time-dependent Hamiltonian could be expressed in terms of the matrix elements of the operator B, with respect to the initial eigenstates (3.18). The operator B was defined according to (3.15) and was expressed as a Dyson series (3.19).

Consider now an NV centre which starts with its axis z' at an orientation given by (θ, ϕ) and rotates with constant angular velocity through a small angle θ' over time t_0 , in the azimuthal direction ϕ' in its instantaneous coordinate system S'. Refer to Figure 6.1 and Figure 6.2 for an illustration of these angles. Using the instantaneous eigenstates of the NV centre given by (5.11), the matrix elements of $U(t_0)$, to first order in the Dyson series (3.19) are

$$\langle \pm 1 | U(t_0) | \mp 1 \rangle = 0, \qquad (7.16)$$

$$\langle m|U(t_0)|m\rangle = e^{-i\omega_m t_0} [1 + im\Delta\phi\cos\theta], \qquad (7.17)$$

$$\langle \pm 1 | U(t_0) | 0 \rangle = \langle 0 | U(t_0) | \mp 1 \rangle = \frac{\pm \theta'}{\sqrt{2}Dt_0} e^{\mp i\phi'} \left[1 - e^{-iDt_0} \right]$$
 (7.18)

For economy of notation we have dropped the subscript z' on the eigenstate kets. For the rest of this thesis, a state written as $|m\rangle$ refers to spin projection m along the NV (z') axis. The diagonal terms (7.17) give Berry's phase. The off-diagonal terms imply mixing of the spin populations. In our derivation of Berry's phase we ignored these terms according to the adiabatic approximation.

These matrix elements as they stand imply a non-unitary time evolution operator. To restore unitarity we must take the diagonal terms to one higher order in the Dyson series (3.19):

$$\langle \pm 1 | U(t_0) | \pm 1 \rangle = e^{-i\omega_m t_0} \left[1 + \pm i\Delta\phi\cos\theta + \frac{{\theta'}^2}{2D^2 t_0^2} (e^{iDt_0} - 1 - it_0D) \right]$$
(7.19)

$$\langle 0|U(t_0)|0\rangle = e^{-i\omega_m t_0} \left[1 + \frac{\theta'^2}{D^2 t_0^2} (e^{-iDt_0} - 1 + it_0 D) \right].$$
(7.20)

Consider now an arbitrary initial state of the NV at the beginning of the step, t = 0:

$$|\psi\rangle = e^{i\Phi_1}\sqrt{p_1}|1\rangle + e^{i\Phi_0}\sqrt{p_0}|0\rangle + e^{i\Phi_{-1}}\sqrt{p_{-1}}|-1\rangle.$$
(7.21)

Operating on $|\psi\rangle$ with $U(t_0)$ then gives the populations P'_i of the spin sublevels at time

 $t = t_0$, once the step is complete:

$$P_{1}' = P_{1} - kt_{0}P_{1} + t_{0}kP_{0} + 2\sqrt{P_{1}P_{0}}\sqrt{kt_{0}}\cos(\Phi_{0} - \Phi_{1} + \phi'),$$

$$P_{0}' = P_{0} - 2kt_{0}P_{0} + t_{0}kP_{1} + kt_{0}P_{-1} - 2\sqrt{P_{1}P_{0}}\sqrt{kt_{0}}\cos(\Phi_{0} - \Phi_{1} + \phi')$$

$$-2\sqrt{P_{1}P_{0}}\sqrt{kt_{0}}\cos(\Phi_{0} - \Phi_{1} + \phi'),$$

$$P_{-1}' = P_{-1} - kt_{0}P_{1} + kt_{0}P_{0} + 2\sqrt{P_{1}P_{0}}\sqrt{kt_{0}}\cos(\Phi_{0} - \Phi_{-1} - \phi'),$$
(7.22)

where

$$k = \frac{\theta^{\prime 2}}{D^2 t_0^3} [1 - \cos(t_0 D)]. \tag{7.23}$$

We model the rotational diffusion of the nanodiamond as a 'random walk' of steps such as these. The durations of the steps t_0 and the angular change θ' of each step may both vary. The rate of angle change during each step, $\frac{\theta'}{t_0}$, is uncorrelated with t_0 and the azimuthal angle ϕ' of each step is uncorrelated from one step to the next. This second condition means that the terms of (7.22) that are sinusoidal in ϕ' vanish when we take the ensemble average of populations. On timescales much longer than t_0 , we can make the continuum approximation to obtain the following equations for the time evolution of the populations' ensemble averages:

$$\frac{d}{dt}\langle P_1 \rangle = -\langle k \rangle \langle P_1 \rangle + \langle k \rangle \langle P_1 \rangle, \qquad (7.24)$$

$$\frac{d}{dt}\langle P_0\rangle = \langle k\rangle\langle P_1\rangle + \langle k\rangle\langle P_{-1}\rangle - 2\langle k\rangle\langle P_1\rangle, \qquad (7.25)$$

$$\frac{d}{dt}\langle P_{-1}\rangle = -\langle k\rangle\langle P_{-1}\rangle + \langle k\rangle\langle P_{1}\rangle.$$
(7.26)

To find the ensemble average of k we need to know how t_0 is distributed. If we multiply the Langevin equation (6.19) by $\omega(0)$ and take the ensemble average we find that the correlation function of the angular velocity decays exponentially over time,

$$\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0) \rangle = \langle \boldsymbol{\omega}(0) \cdot \boldsymbol{\omega}(0) \rangle e^{-t/t_d}, \qquad (7.27)$$

where we have defined the damping time, $t_d = I/\gamma_d$. In order to retain this correlation function in our discrete 'random walk' approximation, the duration of a given step, t_0 , must be exponentially distributed. At any given instant, the fraction of the ensemble that is experiencing a step of duration t_0 is then given by the probability density:

$$p(t_0) = \frac{t_0}{t_d^2} e^{-t_0/t_d},$$
(7.28)

We do not need to know the exact distribution of angular velocities, merely that $\langle \theta'^2/t_0^2 \rangle = \frac{2}{3} \langle \boldsymbol{\omega} \cdot \boldsymbol{\omega} \rangle = \frac{2k_D}{t_d}$. The ensemble average population mixing rate is then given by a straightforward integral of (7.23) over t_0 , weighted by (7.28):

$$\langle k \rangle = \frac{1}{D^2} \left\langle \frac{\theta'^2}{t_0^2} \right\rangle \left\langle \frac{1}{t_0} (1 - \cos t_0 D) \right\rangle$$
(7.29)

$$= 2k_D \frac{1}{1 + t_d^2 D^2} \tag{7.30}$$

We now have an expression for the population mixing rate in terms of physical parameters: the zero-field splitting frequency D, the rotational diffusion rate k_D and the angular velocity damping time t_d .

We have made some assumptions in achieving this result. Most significantly, we have modelled the diffusive rotation of the nanodiamond as a series of discrete steps, using physical arguments to infer the appropriate statistical behaviour of the steps' sizes and durations. To check the validity of these approximations we have produced a numerical Monte Carlo simulation. The simulation models the Langevin equation (6.19), using a torque which fluctuates on finite but very small timescale, to produce a set of rotational trajectories. For each trajectory the Schrödinger equation is solved numerically. The results, for an NV centre which starts in $|0\rangle$, are plotted in Figure 7.1. They show excellent agreement with our analytical expression:

$$S(t) = \frac{1}{3} + \frac{2}{3}e^{-t/t_m},$$
(7.31)

where we will call $t_m = \frac{1}{3\langle k \rangle}$ the population mixing time.

The implication of this non-adiabatic behaviour is more than merely a correction to the behaviour expected from Berry's phase. Measuring the population mixing rate (effectively measuring T_1) provides another way to gauge the rotational diffusion rate. The usual timescales of population mixing for the NV centre (' T_1 ') are relatively long, on the order of ms or more [23], giving a low background population mixing rate to measure against. Moreover, the measurement can be achieved without microwave fields. It is enough to simply initialise the NV into $|0\rangle$ and observe the decay of the fluorescence rate as a function of free evolution time.

7.3 Sensing static and fluctuating fields

Berry's phase and its non-adiabatic corrections have given us a theoretical description of the quantum evolution of the rotationally diffusing NV centre in the absence of magnetic fields. We now address the original motivation for considering the rotationally diffusing NV centre: to examine the effect of magnetic fields on the rotating NV's fluorescence signal and explore the feasibility of using the system to sense nanoscale magnetic fields.

We first consider static (DC) and fluctuating (FC) magnetic fields. In the next section we address sinusoidal (AC) fields. Magnetic fields enter our model by advancing the phase of the NV centre's spin sublevels, as described in the previous chapter, equation (6.27). Under the secular approximation it is only the field component parallel to z' (the NV axis) which affects the phase. Since the orientation of z' changes randomly with time, a static field effectively behaves as a field which fluctuates on the timescale of rotational diffusion, $1/k_D$. We therefore briefly outline the theory of sensing fluctuating magnetic fields using an NV with a fixed orientation, which is covered well by Hall *et al.* [27].

By 'fluctuating field' we refer to a time-dependent field B(t) with vanishing mean, $\langle B \rangle = 0$, characterised by a typical field strength, $B_{FC} = \sqrt{\langle B(t)^2 \rangle}$, and fluctuation timescale t_c , such that the correlation $\langle B(t) \cdot B(0) \rangle$ decays on the timescale of t_c . In a Ramsey-type experiment, the final $\pi/2$ pulse turns the NV's acquired phase Φ into a population $P_0 = \frac{1}{2} \pm \frac{1}{2} \cos(\Phi)$ of the $|0\rangle$ state, with the ' \pm ' depending on the phase of the final pulse. In the case of a static magnetic field the ensemble's members all acquire identical phases due to the magnetic field. The quantity to be measured is then the mean of the acquired phases $\langle \Phi \rangle$. The signal $\langle P_0 \rangle$ is most sensitive to changes in the mean when $\Phi = \pi/2$, where $\langle P_0 \rangle$ is linear in $\langle \Phi \rangle$. In the case of fluctuating fields the reverse is true. The mean phase is zero, and it is the variance of the phase $\langle \Phi^2 \rangle$ which is observed. The signal is most sensitive to the phase's variance at the turning points of the sinusoid, when $\langle \Phi \rangle = 0$. For small phase variance, the signal is:

$$S = \langle P_0 \rangle = \frac{1}{2} \pm \frac{1}{2} \langle \cos(\Phi) \rangle$$
(7.32)

$$\approx \frac{1}{2} \pm \frac{1}{2} \left(1 - \frac{1}{2} \langle \Phi^2 \rangle \right). \tag{7.33}$$

To compute the signal for larger phases, we need to know the actual distribution of phases. For the special case of a Gaussian distribution, we have:

$$S = \langle P_0 \rangle = \frac{1}{2} \pm \frac{1}{2} \int \frac{d\Phi}{\sqrt{2\pi \langle \Phi^2 \rangle}} \cos(\Phi) e^{\frac{-\Phi^2}{2\langle \Phi^2 \rangle}} = e^{-\langle \Phi^2 \rangle}.$$
 (7.34)

The signal decays exponentially in the phase variance. Although the distribution of phases will not in general be Gaussian, the shape of S(t) will usually still be similar to (7.34), but may include 'beating' on the timescale of the signal decay, as we saw in Chapter 2 in the case of the measurement of AC fields of indeterminate phase.

The behaviour of the phase variance with time depends qualitatively on whether the fluctuation timescale t_c is fast or slow compared with the precession timescale, γB_{FC} . If the fluctuations are slow then the field is effectively static on the timescale of the signal decay. In this case, the phase of each of the ensemble's members increases linearly with time, and the phase variance increases quadratically in time, $\langle \Phi^2 \rangle \sim t^2 \gamma^2 B_{FC}^2$. The decay of the signal over time then follows a Gaussian envelope:

$$S \sim e^{-t^2 \gamma^2 B_{FC}^2}.\tag{7.35}$$

At the other extreme, when the fluctuations are fast, the phase variance increases linearly in time, and the decay is exponential:

$$S \sim e^{-t\gamma^2 B_{FC}^2 t_c}.$$
 (7.36)

The decoherence rate due to fast-fluctuating fields becomes smaller as the fluctua-

tion rate increases since the fields at different times tend to balance out. This effect is well-known in the context of NMR. Motional narrowing, for example, arises because the fields experienced by a molecule fluctuate as the molecule randomly rotates or translates, reducing decoherence effects and narrowing resonance linewidths [56]. Similarly, so-called 'magic angle spinning' [57] is a technique in which a sample is spun about an axis which is at an angle of $\cos^{-1}(1/\sqrt{3})$ to the applied magnetic field. The angle is chosen so that dipole fields average to zero over the course of rotation, dramatically reducing linewidths. These effects would be visible in the rotationally diffusing NV centre, except that dephasing due to Berry's phase means that the signal does not persist much beyond the timescale of a single rotation.

Since diffusion and random walks have been a theme of this work, it is worth pointing out that the evolution of the phase under a fluctuating magnetic field is exactly analogous to Brownian motion. The phase follows what is essentially a Langevin equation, $\dot{\Phi} = \gamma B(t)$, which is completely analogous to (6.4). On shorter timescales than the correlation time t_c of B(t), the phase progression is linear. On longer timescales, the phase progression is diffusive, giving the characteristic linear increase of the variance $\langle \Phi^2 \rangle$ with time.

We now return to the rotationally diffusing NV centre, considering first a static magnetic field. If the timescale of rotation, $1/k_D$, is much longer than $1/(\gamma B)$, then the field as seen by the NV is essentially static on the timescale of the signal's decay. The signal envelope is then given by:

$$S(t) = \int_0^{2\pi} \frac{d\phi}{2\pi} \int_0^{\pi} \frac{\sin\theta d\theta}{2} \left(\frac{1}{2}\cos^2\Theta \pm \sin^2\Theta\cos\left[\gamma(B_z\cos\theta + B_{xy}\sin\theta\cos\phi)\right]\right)$$
(7.37)

where the static magnetic field B has components B_z and B_{xy} in the z direction and in the x-y plane respectively. This function, plotted in Figure 7.2(a), shows the expected Gaussian decay behaviour, modified by decaying beats. Notice that the signal depends on the direction of the magnetic field. The magnetic field has the most effect when it is perpendicular to the microwave magnetic field, maximally affecting those NV centres which experience the greatest spin rotation.

As with our analysis of Berry's phase, we can produce a Fokker-Planck equation to de-



Figure 7.2: Figures illustrating the expected fluorescence signal from a Ramsey-type pulse sequence with a DC field applied during the system's free evolution. Blue curves: DC field is in the z-direction. Red curves: DC field is in the x-y plane. (a) Signal envelope in the limit that the time scale associated with the DC field is strong compared with the rotational diffusion rate (7.37). (b) Simulation of the expected signal when the time scale associated with the DC field is comparable to the rotational diffusion rate. Solid: no field. Dashed: $\gamma B/k_D = 3$. Dash-dot: $\gamma B/k_D = 10$. (c) Decoherence rate (relative to k_D) as a function of DC field strength (also relative to k_D). The decoherence rate is defined here as $1/\tau_D$ where τ_D is the time taken for the signal envelope to reach 1/e of its initial value.

scribe the evolution of the probability density of the orientation and phase. Unlike Berry's phase, the phase evolution due to a magnetic field depends explicitly on the azimuthal angle ϕ as well as the polar angle θ of z'. The Fokker-Planck equation is then:

$$\frac{1}{k_D} \frac{d}{dt} p(\theta_1, \phi, \Phi, t | \theta_0) = \frac{-\partial}{\partial \theta_1} \left[\sin \theta_1 \frac{\partial}{\partial \theta_1} \left(\frac{p}{\sin \theta_1} \right) \right] + \frac{1}{\sin^2 \theta_1} \left(\frac{\partial}{\partial \phi} + \cos \frac{\partial}{\partial \Phi} \right)^2 p \\
- \left(\frac{\gamma B_z}{k_D} \cos \theta_1 + \frac{\gamma B_x}{k_D} \sin \theta_1 \cos \phi \right) \frac{\partial}{\partial \Phi} p.$$
(7.38)

The signal S(t), as given by Equation (7.1), for this equation's solution is shown in Figure 7.2(b).

As anticipated, the decoherence envelope shows initially Gaussian decay. The exponential shape which we would expect on timescales longer than the effective fluctuation timescale, $1/k_D$ is suppressed, since Berry's phase prevents the signal from persisting beyond $1/k_D$. Again, the signal depends on the direction of the static magnetic field relative to the microwave control magnetic field.

The decay rate, defined here as the inverse of the time taken for the signal to reach 1/e of its initial value, is shown in Figure 7.2(c) as a function of the magnetic field strength B_{DC} . The decay rate is insensitive to B_{DC} for $\gamma B_{DC} < k_D$ since in this regime the decay is dominated by Berry's phase. Maximum sensitivity to magnetic fields occurs when $\gamma B_{DC} \approx k_D$, achieving a balance between too much decoherence that the sensitivity is worsened, and too little decoherence that the effect of the DC field is swamped by Berry's phase. The sensitivity at this optimal field strength is:

$$\Delta B \sqrt{T} \approx \frac{1}{\gamma} \frac{1}{C \sqrt{N_{NV} \tau_D}},\tag{7.39}$$

where the decoherence time τ_D is the total decoherence time, given approximately by $1/\tau_D \approx 1/T_2^* + k_D$. The objective in magnetometry is usually to detect very small fields. However, an applied static magnetic field could be used to bring the total field into region of optimal sensitivity. The NV magnetometer in this case would be most sensitive to fields in the direction of the applied field. This opens the possibility of using the system as a vector magnetometer. By applying fields in different directions, each component of the field could be measured.

This analysis of static magnetic fields applies directly to fields which fluctuate on longer timescales than the crystal's rotation. The details will depend on the specific distribution of the fluctuating fields. The signal will be similar to the signals plotted in Figure 7.2(a) and (b), integrated over the probability density of the different instantaneous field strengths.

Fluctuating fields which fluctuate on timescales much shorter than the rotational diffusion time affect the crystal's quantum evolution in a way which is very similar to Berry's phase. Consider a fluctuating field with correlation time $t_c \ll 1/k_D$ and mean squared field strength $\langle \mathbf{B}^2 \rangle = B_{FC}^2 \ll 1/(\gamma^2 t_c^2)$ which is isotropic, having no preferred direction. The Fokker-Planck equation is simply:

$$\frac{1}{k_D} \frac{d}{dt} p(\theta_2, \Phi; t | \theta_1) = -\frac{\partial}{\partial \theta_2} \left[\sin \theta_2 \frac{\partial}{\partial \theta_2} \left(\frac{p(\theta_2, \Phi; t | \theta_1)}{\sin \theta_2} \right) \right] \\
+ \left(\cot^2 \theta_2 + \frac{1}{6} \gamma^2 \frac{B_{FC}^2 t_c}{k_D} \right) \frac{\partial^2}{\partial \Phi^2} p(\theta_2, \Phi; t | \theta_1).$$
(7.40)

which is nearly identical to that for Berry's phase alone (7.3). The phase diffusion rate is simply modified by a constant. The results for a few values of $B_{FC}^2 t_c$ are plotted in Figure 7.3 along with the total decoherence rate as a function of the field strength. Notice that unlike the case of DC fields, fluctuating fields produce an exponential decay envelope, with a nonvanishing gradient even for small evolution times τ . The implication of this can be seen in Figure 7.3(b), which shows that the decoherence rate is linear in $B_{FC}^2 t_c$, unlike the equivalent plot for DC fields, Figure 7.2(c).

7.4 AC fields and spin echo control sequences

One proposed use of an NV-based magnetometer is to detect nuclear magnetic resonance (NMR). Conventional NMR imaging uses a pickup coil to detect the oscillating magnetic field produced by precessing spins. The spatial resolution, however, is limited not by the magnetic field gradients which can be applied, but by the number of spins which can be detected. With its excellent sensitivity, an NV-based magnetometer could detect



Figure 7.3: (a) Signal envelopes when the 'signal field' is fluctuating isotropically on a timescale larger than both $1/k_D$ and the timescale associated with the mean-squared field strength. The signal is based on the solution to (7.40) and it depends on the parameter $B_{FC}^2 t_c$ where B_{FC}^2 is the mean-squared field strength and t_c is the correlation time of the fluctuating field. Blue: zero-field. Red: $\gamma^2 B_{FC}^2 t_c = 6k_D$ Green: $\gamma^2 B_{FC}^2 t_c = 30k_D$. (b) Decoherence rate, again defined as the inverse of the time taken for the signal to reach 1/e of its initial value, as a function of fluctuating field strength relative to the rotational diffusion rate.

the precession of a very small number of nuclei permitting NMR imaging with spatial resolution on the scale of nanometres [5]. We therefore briefly consider the measurement of the sinusoidal (AC) fields which would be produced by precessing nuclei.

Detection of AC fields using a spin-based magnetometer is typically achieved using a spin echo pulse sequence. A π -pulse applied midway through the free evolution period rectifies the alternating phase produced by the sinusoidal field. The π -pulse also eliminates the effect of static fields. In the rotationally diffusing NV system, however, the effective DC field is a function of the crystal's orientation, which in general will have changed over the course of the free evolution time. The π -pulse will be unable to perfectly eliminate the effect of a DC field, especially given that very strong DC fields are often applied in NMR experiments.

This does not make a spin echo pulse sequence unfeasible, but it means that the timescale of free evolution must be much shorter than the rotational diffusion time. During a free evolution time of τ , the crystal will have typically rotated through an angle of $\Delta\theta \approx \sqrt{\tau k_D}$. The difference in effective DC field before and after a $\pi/2$ pulse will then be on the order of $\Delta B \approx B_{DC} \Delta \theta$. We can therefore estimate the timescale for decoherence due to a DC field under a spin echo pulse sequence as:

$$\tau_{n\pi}^3 \approx \frac{(n+1)^2}{4k_D} \left(\frac{1}{\gamma B_{DC}}\right)^2,\tag{7.41}$$

where we have allowed for n concatenated π -pulses during the free evolution time τ .

We take the limit in which very little rotation occurs on the timescale of free evolution. The problem is then a matter of simply averaging over the possible crystal orientations and initial phases of the AC field, rather than solving a Fokker-Planck equation. Consider a spin echo pulse sequence during which the crystal is oriented at some θ and the freeevolution time τ matches the AC field's period. The final population of $|0\rangle$ is given by

$$P_0(\theta, \Phi_{\text{field}}) = \frac{1}{2} + \frac{1}{2}\cos^2\Theta_1\cos\Theta_2 \pm \frac{1}{4}\sin^2\Theta_1(1 - \cos\Theta_2)\cos(2\Phi_{AC})$$
(7.42)

where $\Theta_1 = a(\pi/2) \sin \theta$ and $\Theta_2 = a\pi \sin \theta$ are the angles through which the spin is rotated during the $\pi/2$ pulses and π -pulse respectively. For an AC field oscillating along the z axis, the phase acquired by the NV centre before the π pulse is $\Phi_{AC} = (\tau/2)\gamma B_{AC} \cos\theta \cos\Phi_{\text{field}}$, where Φ_{field} is the phase of the AC field at the start of the period, and the phase acquired after the π pulse is $-\Phi_{AC}$. On the assumption that the DC field is much stronger than the AC field, we have already integrated over the possible phases produced by the DC field, which are the same before and after the π -pulse.

To find the ensemble-averaged signal, we integrate over all phases of the AC field, Φ_{field} , and all orientations, θ , weighted by $\frac{1}{2}\sin\theta$ as usual,

$$S = \int_0^\pi \frac{\sin\theta d\theta}{2} \int_0^{2\pi} \frac{d\Phi_{\text{field}}}{2\pi} P_0(\theta, \Phi_{\text{field}}).$$
(7.43)

The solution is plotted as a function of B_{AC} in Figure 7.4. Decoherence occurs on a timescale of $1/(\gamma B_{AC})$, which permits AC field detection with optimal sensitivity given by (7.39), with τ_D given approximately by $1/\tau_D \approx 1/T_2 + 1/\tau_{n\pi} + k_D$. As with measurement of DC fields, this sensitivity occurs when the rate of decoherence due to the AC field matches the decoherence rate from other sources. If the AC field is too weak, only the first (Gaussian-shaped) part of its decoherence curve is observed, and the signal is insensitive to changes in AC field. If the field is too strong, then the decoherence rate limits the sensitivity by limiting the available free evolution time. As before, a field could be applied to bring the total AC field into the region of optimal sensitivity. This, however, would require some knowledge about the phase of the AC field to be detected.



Figure 7.4: The expected signal envelope, as a function of the field strength, B_{AC} relative to the free evolution time τ , due to an AC field in the limit where the timescale associated with the field strength is much larger than the rotational diffusion timescale (7.43). The period of the AC field is taken to be the same as τ .

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CONCLUSIONS

This thesis has been a proposal and theoretical investigation of two new applications of the diamond nitrogen vacancy centre. We have shown that the NV centre can be used to produce two types of geometric phases and we have explored the consequences of spin control techniques on NV centres within a diamond nanocrystal which is rotationally diffusing.

In chapters 4 and 5 we showed that the NV centre can be used to detect the Aharonov-Casher effect and Berry' phase respectively. We showed how these effects may arise in the NV centre's spin sublevels and proposed experiments to measure them.

In chapters 6 and 7 we considered a nanodiamond which is free to diffuse rotationally. We first developed a model to capture the nanodiamond's rotational diffusion and the effect of this diffusion on an NV centre's quantum evolution and its interaction with magnetic fields. In chapter 7 we derived the expected fluorescence signal for such a system under different control sequences and local magnetic fields.

We found that Berry's phase, as explored in Chapter 5, plays an important role in the rotating NV centre's quantum evolution and that its effect on the fluorescence signal may give a method to measure the rotational diffusion rate. We also considered non-adiabatic corrections to Berry's phase which will produce mixing of spin populations, another measurable effect which contains information about the crystal's rotational behaviour. Both of these predicted effects can be tested using a nanodiamond suspended in a fluid.

Motivated by recent interest in the NV centre as a sensitive magnetometer, we explored the effect of magnetic fields on the fluorescence signal of the rotationally diffusing NV centre. We considered static, fluctuating and sinusoidal fields and showed that the

8. Conclusions

fluorescence signal can still be used to measure the strength of these fields even though the crystal is rotating and its orientation is unknown. The main differences we found between the rotating crystal and the conventional static crystal were the reduced coherence time due to rotation and the difference in interpretation of the fluorescence signal. In the static case the frequency of the signal's oscillations reveals the mean phase of the NV centre. In the rotating case the signal decay rate reveals the variance of phase of the NV centre.

Our results have direct experimental implications. The experiments we proposed in chapters 4 and 5 can be performed using proven experimental techniques. They offer a new tool to investigate the deep physics of topological phases. The results of Chapters 6 and 7 on the rotationally diffusing nanodiamond are directly verifiable and they have implications for the ongoing efforts to develop the NV centre as a tool for biological imaging. Combining nanodiamond NV as a biomarker with nanodiamond NV as a magnetometer could allow a radically new way of imaging biological processes at the nanoscale.

Although based on existing experimental principles, this thesis has been purely theoretical. The models we have used and developed are highly simplified. A nanodiamond inside a cell, for example, will not behave as a spherically symmetric body subject to a delta function correlated torque and a linear drag coefficient. Experiments will prove which of our assumptions need to be modified and will suggest future directions of theoretical investigation.

The diamond NV centre is the main focus of an increasing number of research groups around the world. We hope that the results of this thesis will contribute to the next generation of experiments on this interesting and highly promising system.
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A

The gyromagnetic ratio of the NV centre's ground state electronic spin, γ $\gamma = g\mu_B/\hbar.$ The rotational drag coefficient, given by (6.20). γ_d θ, ϕ polar and azimuthal angles respectively with respect to some spherical coordinate system. Angle through which a ' $\pi/2$ ' pulse rotates the spin, $\Theta = a \frac{\pi}{2} \sin \theta$ where Θ θ is the angle between the NV axis and the microwave magnetic field. Bohr magneton. μ_B Density of diamond, $\rho \approx 3,300 \text{kg/m}^2$. ρ Pauli matrices. σ Free evolution time. auTotal decoherence time. au_D A quantum phase, introducing a $e^{i\Phi}$ factor to a system's state. We will Φ always use the capital Greek letter Φ to refer to a phase, and the lower case ϕ to refer to an azimuthal angle. Parameter describing the length of a $\pi/2$ pulse, $a \approx 1$. a \boldsymbol{B} Magnetic field. We use B to refer to the magnitude of magnetic field B. CDepending on the context, either an experimental parameter describing imperfect collection efficiency and nonzero fluorescence of the $m = \pm 1$ states (C = 1 in the ideal case) or a path of integration. DZero-field splitting frequency $(2\pi . 2.88 \text{ GHz})$. Gyromagnetic ratio (≈ 2 for NV). għ Reduced Planck's constant.

LIST OF COMMON SYMBOLS

Ι	The nanocrystal's moment of inertia.
m angle	Eigenstates of spin projection m . In chapters 5 and 6, an important
	distinction is made between $ m\rangle_z,$ the eigenstates of spin projection along
	the lab-frame z axis, and $ m\rangle_z',$ the eigenstates of spin projection along
	the instantaneous NV (z') axis. The latter is implied if the subscript is
	absent.
N_{NV}	Number of NV centres which take part in an experiment.
P_m	Population of the spin state m . $P_m = \langle m \psi \rangle ^2$.
r	Radius of nanocrystal.
$oldsymbol{S}$	Spin operator, $\boldsymbol{S} = (S_x, S_y, S_z)$
S	Normalised fluorescence signal. There should be no confusion with the
	symbol for a spin operator, which will always be \boldsymbol{S} or S_z . We never use
	S to represent a particle's spin.
t_c	Correlation time for a fluctuating field.
t_d	Angular velocity damping time, $t_d = I/\gamma$.
t_m	Population mixing time under non-adiabatic evolution (7.31).
T	Either temperature or total averaging time, depending on the context.
T_1	Spin relaxation time.
T_2	Homogeneous broadening time.
T_2^*	Inhomogeneous broadening time.
x, y, z	Cartesian coordinates in the lab-frame.
x',y',z'	Cartesian coordinates in the frame of the nanocrystal. z' is the direction
	of the NV axis.
$\langle \rangle$	Ensemble average.