Abstract

All the possible nitrogen-vacancy (NV) centre applications are related to electron spin readout. It had been previously established that electron spin affects the rate of the non-radiative transition of NV centre. Quantitative relation between non-radiative transition rate and a readout signal is, however, yet to be established. In this work we derive a general formula for electron paramagnetic resonance (EPR) contrast as function of non-radiative transition rate. The formula allows for EPR contrast calculation for any given model of internal NV centre transitions.

Introduction

Nitrogen-vacancy (NV) centre in diamond is susceptible to microwave radiation [1][2]. Application of microwave of resonance frequency induces electron spin flip transition in an NV centre [3]. This effect is commonly known as electron paramagnetic resonance (EPR). Electron spin states of NV centre affect its photoluminescence and photocurrent, therefore it is possible to detect EPR optically (ODMR) [4] and electrically (PDMR) [5]. The relative change in signal (either photoluminescence or photocurrent) because of the resonance is called contrast.

EPR is a result of energy level transitions in an NV centre, therefore it is possible to observe the response of quantum characteristics of the centre to external influence such as magnetic field [6], temperature [7], stress [8], laser power [9] etc. through EPR behaviour. The simplest example of this is Zeeman shift - EPR lines move in static magnetic field signifying change in energies of quantum levels. However, while the frequency of EPR has a very specific meaning, the size of an EPR peak lacks a clear representation on energy level diagram.

One of the ways to observe EPR is via photoluminescence of NV centre - when electromagnetic wave is on resonance with NV electron spin transition photoluminescence signal changes. In order to interpret this change it is necessary to represent photoluminescence signal as a function of NV quantum level parameters.

Rate equations. Common method.

The common way to calculate contrast is via rate balance equations [9]. Transition rate k is the frequency of the transition if the source state is always full and the destination state is always empty, it is the inverse of transition period $k = \frac{1}{\tau}$. For simplicity NV centre is assumed to be a four level system (fig.1) at first. The only time an NV centre produces a photon is when a radiative transition from excited state happens. k_r is the frequency of this transition if excited state is always full, i.e. $n_e = 1$, where n_e is the population of excited state. For a general case the frequency of this transition is $n_e k_r$. Therefore

$$I \sim n_e k_r \tag{1}$$

where I is NV photoluminescence.

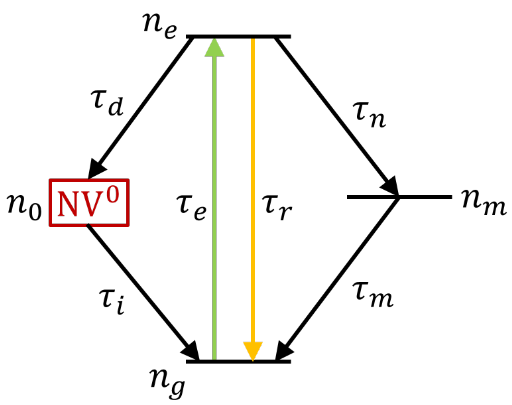

Figure 1: Energy diagram of an NV centre as a four-level system. The four energy levels are ground (n_g), excited (n_e), metastable (n_m) and NV^0 states (n_0). The six transitions are excitation (τ_e), radiative transition from excited state (τ_r), non-radiative transition from excited state (τ_n), transition from metastable state (τ_m), ionization (τ_i) and deionization (τ_d). To each energy level corresponds population n, to each transition corresponds period τ.

The same way charge carrier creation frequency can be calculated. Every time ionization or deionization happens a hole or an electron is created. Additionally, because total charge is conserved, the frequencies of ionization and deionization have to be equal.

$$\dot{Q} = n_e k_d + n_0 k_i = 2 n_e k_d \tag{2}$$

where $\dot{Q}$ is charge carrier creation frequency. Contrary to photoluminescence, however, photocurrent dependence on the number of charge carriers might not be linear.

Each transition creates population flux $n_{j_1} k_{j_2}$, where n_{j_1} is population of the state from which the transition happens. In a steady state all populations are constant, which means that the net population flux is zero. This allows to write a rate balance equation for each energy level in the system.

E.g. for the case of the four level system (fig.1) this leads to the following system of equations

$$\dot{n}_g = n_e k_r + n_m k_m - n_g k_e + n_0 k_i = 0 \tag{3}$$

$$\dot{n}_e = n_g k_e - n_e k_r - n_e k_r - n_e k_d = 0 \tag{4}$$

$$\dot{n}_0 = n_e k_d - n_0 k_i = 0 \tag{5}$$

$$n_e + n_0 + n_g + n_m = 1 \tag{6}$$

The solution of this system is

$$n_e = (\frac{k_r}{k_e} + \frac{k_n}{k_e} + \frac{k_d}{k_e} + \frac{k_n}{k_m} + \frac{k_d}{k_i} + 1)^{-1} \tag{7}$$

and since NV centre photoluminescence signal is proportional to excited state population further contrast calculation is trivial.

The main disadvantage of this calculation method is that it does not allow to obtain the general form of excited state population. Having the general form would simplify interpreting experimental results in terms of changes to existing transition rates and appearing of new ones.

Density of events. Proposed method.

The proposed way to calculate contrast is via density of events. In the absence of external perturbations excitation period τ_e is infinity, therefore laser illumination is used as a source of excitation. Consequently, τ_e depends on laser power - if it is not constant, populations n_g, n_e, n_m will be functions of time. On the other hand at constant illumination power NV centre reaches a steady state and all the populations can be assumed constant over time exceeding the longest τ. On a short time scale, however, NV centre still undergoes a lot of transitions (fig.2). It is these short term dynamics that define the long term average of level populations.

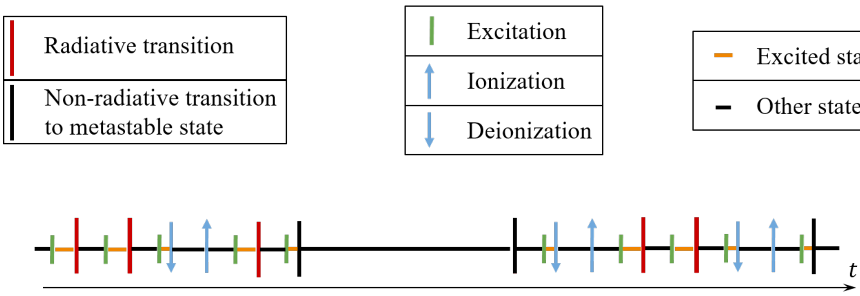

Figure 2: NV centre steady state dynamics. Any possible event (e.g. ionization, radiative transition) is considered instant and happening with period τ, counting, however, only the time spent on the level, from which the transition happens.

Population of excited state is the time NV centre spends in excited state compared to other states

$$n_e = \frac{T}{T + \sum N_j t_j} \tag{8}$$

where T is the time NV centre spends in excited state, j is the event type index (e.g. r for radiative transition, i for ionization, etc. Letters are used instead of numbers for simplicity.), N_j is the number of events of type j that happen during the time required for NV centre to spend time T in excited state, t_j is the time it takes to get back to excited state after a type-j event. Only the events that make the system leave excited state are included in the summation $\sum N_j t_j$.

On average an event j occurs every time when an NV centre has spent in total time τ_j in excited state since the last type-j event (fig.3). Number of events is therefore $N_j = \frac{T}{\tau_j}$, and excited state population is

$$n_e = (1 + \sum_j \frac{t_j}{\tau_j})^{-1} \tag{9}$$

This is the general form of (7) - it shows that a single transition from excited state to anywhere adds a $\frac{t_j}{\tau_j}$ term to denominator of photoluminescence, where τ_j is the period of the transition and t_j is the time it takes to return to excited state after this transition.

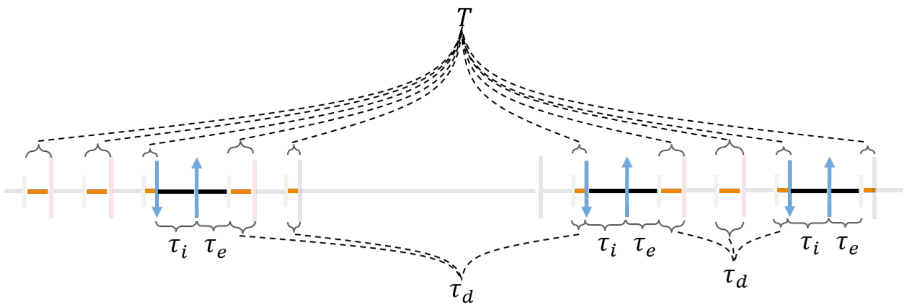

Figure 3: Some transition periods shown on the diagram of NV centre dynamics. τ_i is the time between deionization and ionization, τ_e is the time between ionization and excitation, τ_d is the time between two deionizations counting only excited state, time T is arbitrary.

This allows to write a general formula for contrast, which can be easily adapted to any model. On-resonant electromagnetic radiation (it is of microwave frequency, so it will be referred to as MW radiation) introduces the transition within the ground state, which changes the non-radiative transition period τ_n [10]. This changes photoluminescence and creates contrast.

$$C(P) = \frac{I(0) - I(P)}{I(0)} = \frac{\sum_j \left(\frac{t_j(P)}{\tau_j(P)} - \frac{t_j(0)}{\tau_j(0)} \right)}{1 + \sum_j \frac{t_j(P)}{\tau_j(P)}} = \frac{\frac{t_n}{\tau_n(P)} - \frac{t_n}{\tau_n(0)}}{1 + \frac{t_n}{\tau_n(P)} + \sum_{j \neq n} \frac{t_j}{\tau_j}} \tag{10}$$

where C is contrast and P is MW power.

E.g. for the case of the four level system (fig.1)

$$n_e = (1 + \frac{\tau_e}{\tau_r} + \frac{\tau_i + \tau_e}{\tau_d} + \frac{\tau_m + \tau_e}{\tau_n})^{-1} \tag{11}$$

$$C(P) = \frac{\frac{\tau_m + \tau_e}{\tau_n(P)} - \frac{\tau_m + \tau_e}{\tau_n(0)}}{1 + \frac{\tau_e}{\tau_r} + \frac{\tau_i + \tau_e}{\tau_d} + \frac{\tau_m + \tau_e}{\tau_n(P)}} \tag{12}$$

For a more complicated model (fig.4)

$$n_e = (1 + \frac{\tau_e}{\tau_r} + \frac{\tau_i + \tau_e + \tau_m}{\tau_d} + \frac{\tau_m + \tau_e + \tau_s}{\tau_n})^{-1} \tag{13}$$

$$C(P) = \frac{\frac{\tau_m + \tau_e + \tau_s}{\tau_n(P)} - \frac{\tau_m + \tau_e + \tau_s}{\tau_n(0)}}{1 + \frac{\tau_e}{\tau_r} + \frac{\tau_i + \tau_e + \tau_m}{\tau_d} + \frac{\tau_m + \tau_e + \tau_s}{\tau_n(P)}} \tag{14}$$

Summary

Density of events calculation method has allowed to obtain a general formula (10) for photoluminescence contrast. This makes the effect of any particular transition on the contrast more transparent - transitions that

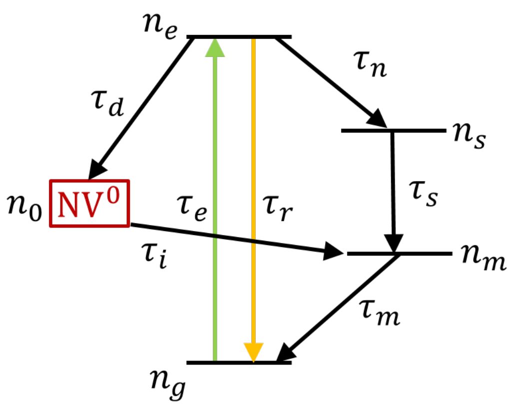

Figure 4: Energy diagram of an NV centre as a five-level system. Here the transition from NV^0 is assumed to be to the metastable state.

extend time t_n increase contrast, all other transitions decrease it. Additionally it allows to adapt the formula for excited state population to any model without recalculations. The density of events method is not specific, however, to EPR case and (9) can be used whenever an energy level population has to be estimated in a continuously excited system.

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