10. Triplet state

10.1. Optical saturation with a triplet

We have discussed the optical saturation of a two-level system: the fluorescence intensity is limited by the lifetime of the excited state. Other states, especially if they are long-lived, may also limit fluorescence. This is the case of the triplet state, whose lifetime can range from microseconds to seconds for aromatic compounds. Note that the triplet lifetime correlates with the triplet energy according to the energy gap law: the more energetic the triplet, the longer the lifetime. In general, no resonant level can be reached from the triplet state by absorption of a laser photon (triplet-triplet absorption can take place, but it won't be resonant, and triplet-triplet fluorescence often has very low quantum yield). Therefore, a molecule in the triplet state is virtually dark, i.e., non-fluorescent. This limitation of fluorescence by the triplet will be more severe for high triplet yield η_T (i.e., branching ratio from the excited singlet) and for long triplet lifetime τ_T. For a triplet yield much smaller than unity, the maximal number of photons per second a molecule can emit is about $(\eta_T \tau_T)^{-1}$, i.e. 1 million per second for a triplet yield of 10^{-3} and a lifetime of 1 ms. These conditions on the triplet parameters severely limit the number of compounds which can be useful in single-molecule spectroscopy and microscopy.

The triplet 'state' is in fact a manifold of three sublevels. Even in zero magnetic field, the degeneracy of the three sublevels is lifted, mainly by magnetic dipole-dipole interactions between the unpaired electrons and spin-orbit coupling. For a molecule with D_{2h} symmetry (which is the case of several aromatic hydrocarbons, for example pentacene or terrylene), the spin eigenstates can be labelled according to the molecular axes, the state $|X\rangle$ having its spin polarized in the (Y, Z) plane, perpendicular to axis X. Z is usually chosen as the axis normal to the molecular plane, X along the long axis, and Y along the medium axis. The energy splitting between state Z and the middle of X and Y, called D, is on the order of a few GHz, while the half of the X-Y splitting, called E, is significantly lower, usually less than a GHz (see scheme in Fig. 10.1). Because the matrix elements of the spin-orbit coupling depend on spin orientation with respect to the orbital, the three sublevels have in general different population rates from the excited singlet, and different relaxation rates towards the ground singlet. Usually, the Z-state is less coupled than the other two.

$$\mathcal{D} = \mathcal{E}_Z - \frac{1}{2}\left(\mathcal{E}_X + \mathcal{E}_Y\right)$$

$$E = \frac{1}{2}\left(\mathcal{E}_X - \mathcal{E}_Y\right)$$

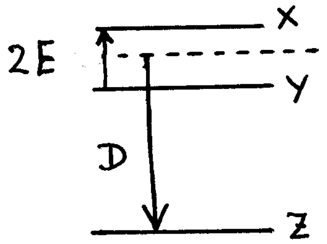

Figure 10.1 : Level scheme of the triplet sublevels split by the anisotropic dipolar interaction. The D and E parameters are the energy differences defined in the diagram.

The optical saturation in the case of intersystem crossing to and from a triplet has the same form as that of the two-level system, but the saturation intensity, and the maximal number of counts at saturation are both *reduced* relative to their values for a two-level system without triplet metastable state(s) by the factor :

$$\xi \;=\; 1+\frac{1}{2}\sum_i \frac{a_i}{b_i} \;=\; 1+\frac{1}{2\tau_f}\sum_i \eta_i \tau_i \;, \qquad [10.1]$$

where the sum runs over the triplet sublevels, and $a_i\,(b_i)$ are the population (depopulation) rates of each sublevel from (to) the excited (ground) singlet state, equivalently expressed with the respective triplet yields η_i and triplet lifetimes τ_i, and τ_f is the fluorescence lifetime.

10.2. Photon bunching

The shape of saturation curves is the same for two and three-level saturation. It is therefore impossible from a saturation analysis alone to conclude about the role of the triplet state. To find this, we need further information, which must be of a dynamical, or time-dependent nature. In other words, the saturation only provides us with a ratio of population and depopulation rates (see the expression of ξ), but we have to find at least one of the rates to determine both of them.

A convenient way to obtain this time-dependent information is to record a correlation function of the fluorescence intensity. As we have seen earlier in our discussion of photon bunching, excursions of a single molecule into its triplet dark state lead to strong fluctuations of its fluorescence intensity. For a single triplet sublevel, the analysis is identical to the one we presented for room temperature, and leads to a single exponential decay in the normalized correlation function:

$$g^{(2)}(\tau) = 1 + \frac{k_{13}}{k_{31}} e^{-(k_{13}+k_{31})\tau} \qquad [10.2]$$

where k_{31} is the decay rate of the triplet state to the ground singlet, and k_{13} is the effective population rate of the triplet state, which can be expressed as a function of the Rabi frequency, the relaxation times and the intersystem crossing rate k_{23} :

$$k_{13} = \frac{k_{23}}{2} \frac{\Omega^2 T_1 T_2}{1+\Omega^2 T_1 T_2}. \qquad [10.3]$$

In case two or three triplet sublevels must be considered, the solution of Bloch equations leads to two or three exponential components in the correlation function. Because relaxation to the ground state couples the different sublevels, the rates appearing in the exponentials take on more complicated forms than in the simple mono-exponential case above. In many cases, the parameters of the X and Y sublevels are too close to distinguish them in experimental data. Then an effective triplet state with two sublevels suffices to fit the correlation function with a bi-exponential decay. Figure 10.2 shows the intensity dependence of the contrasts and decay rates of the two exponential components in the correlation function of a single DBATT molecule in a hexadecane matrix.

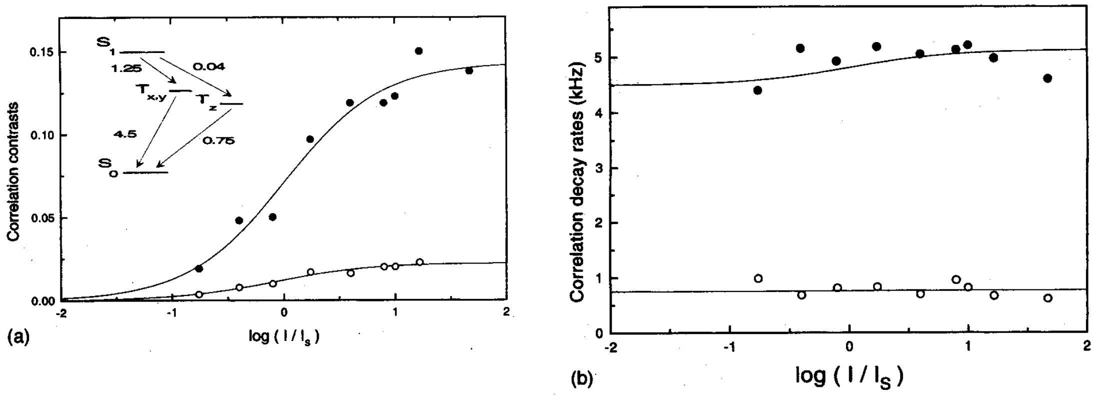

Figure 10.2 : Contrast (a) and rates (b) of the two exponential components in the correlation function of a single DBATT molecule. The population and depopulation rates of the triplet deduced from these plots are shown in the insert [A.-M. Boiron et al. J. Chem. Phys. 105 (1996) 3969].

An alternative way of obtaining dynamic information about the triplet state is to directly observe the on- and off-times in the fluorescence signal. This is particularly efficient in the case of weak intersystem crossing rates, if the dark intervals have sufficient duration. These direct observations were first made on a single terrylene molecule in a p-terphenyl crystal (see Fig. 10.3). Building histograms of on- and off-times, one directly obtains the above two rates k_{13} and k_{31}, and hence the triplet lifetime and the intersystem crossing rate. This direct method can only be applied to single molecules, because one can focus on a few rare events. The corresponding signal often disappears in time-averaged correlation measurements.

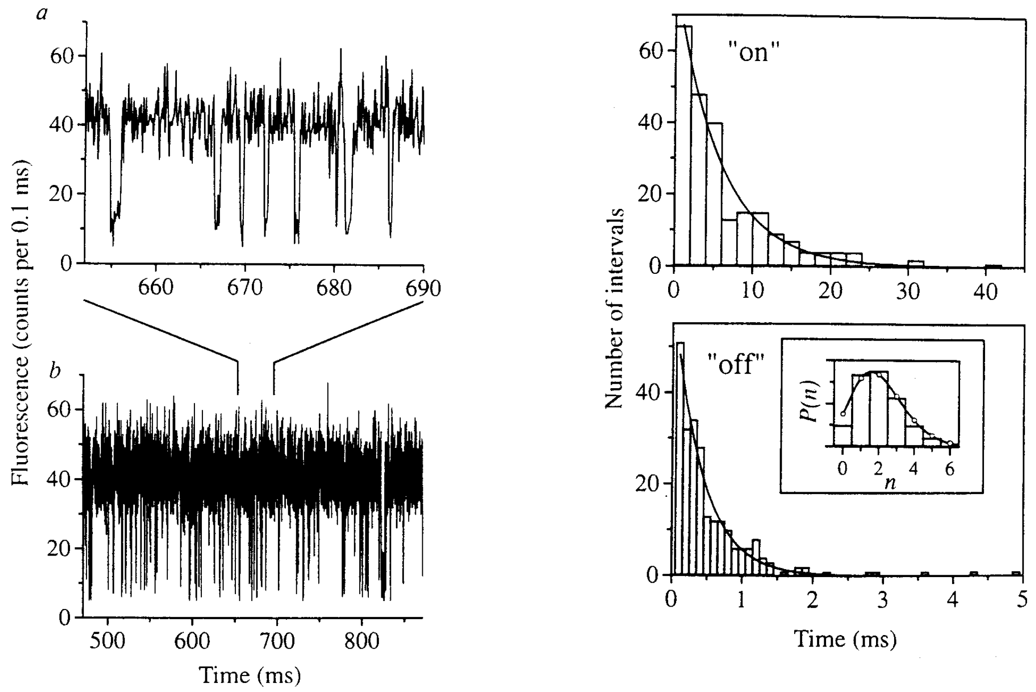

Figure 10.3 : On- and off-times in the fluorescence signal of a single terrylene molecule excited above saturation of the three-level system. The histograms of on- and off-times provide the population and decay rates of the triplet [Reproduced with authors' permission from Th. Basché, S. Kummer, Ch. Bräuchle, Nature 373 (1995) 132].

10.3. Optically detected magnetic resonance

Magnetic resonance is achieved when the spin state is changed under microwave irradiation. In usual experiments, the spin levels are split in a static magnetic field, but the triplet sublevels of molecules are already split in zero field by spin-orbit coupling and dipole-dipole magnetic interactions (zero-field splitting). Because of the different influence of each spin sublevel on optical saturation, the average fluorescence intensity will be changed if the occupation of the sublevels is modified. This opens the opportunity to observe magnetic resonance via variations of the fluorescence intensity.

Figure 10.4 presents the variations of the fluorescence intensity of a single pentacene molecule in a p-terphenyl crystal when a microwave is tuned in a range between 1.3 and 1.5 GHz. The two dips are due to microwave *Y-Z* and *X-Z* transitions. The fluorescence change upon the *X-Y* transition was too weak to be detected. The characteristic asymmetric shape of the dips is mainly due to hyperfine interactions with the spins on the 14 protons in the pentacene molecule. Hyperfine interactions contribute in second-order perturbation, and lead to further splitting of the *X* and *Y* sublevels. The sharp edges corresponds to zero total spin of the protons, which is the most likely configuration of the nuclear spins.

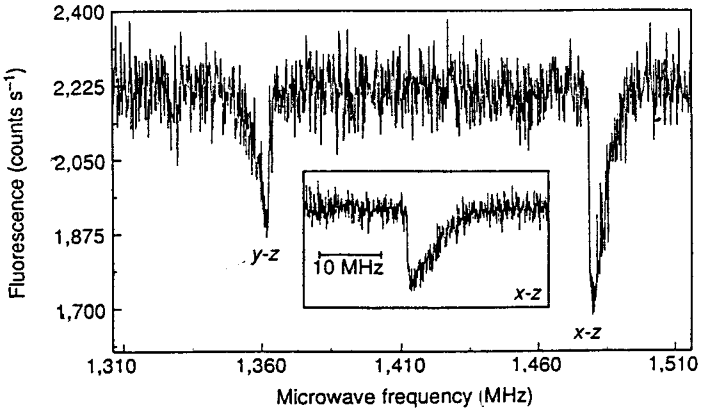

Figure 10.4 : Optically detected magnetic resonance of a single electronic spin. The fluorescence intensity of a single pentacene molecule excited at saturation shows dips when an applied microwave frequency coincides with transitions between triplet sublevels [J. Wrachtrup et al., Nature 363 (1993) 244 ; see also J. Köhler et al., ibid. 242] .

Under microwave illumination, the fluorescence correlation function is deeply changed. The long-lived component due to the *Z* sublevel is dramatically shortened, because the spins are brought back to the *X* or *Y* sublevels, where intersystem crossing relaxation towards the ground state is fast. The analysis of the correlation function provides evidence of magnetic resonance transitions, even in the cases where the fluorescence variation would be too small to detect. Brouwer et al. have observed the ODMR of a single terrylene molecule in p-terphenyl in this way (see Fig. 10.5), as well as the spin nutation.

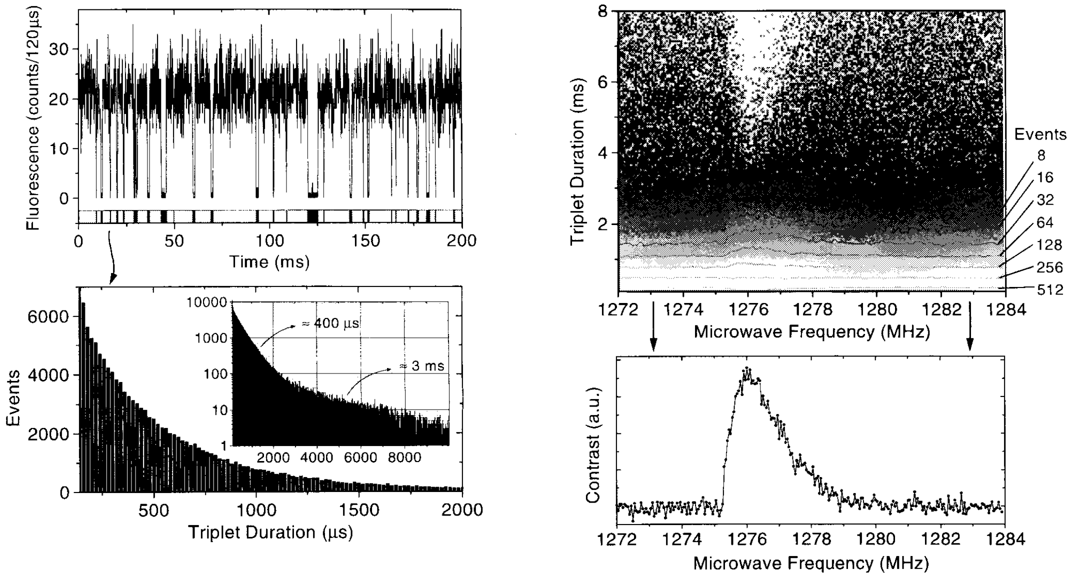

Figure 10.5 : Detection of magnetic resonance via the distribution of off-times (triplet duration). The method is much more sensitive than the average intensity, because it focuses on a few events, disregarding the noisy bright periods [Reprinted with permission from A. C. J. Brouwer et al. Phys. Rev. Lett. 80 (1998) 3944. Copyright 1998 Americal Physical Society].

10.4. Single nuclear spins

Figure 10.4 shows how the ODMR signal of a molecule is influenced by the spin state of the protons. Because the recording of the ODMR line lasts several minutes, the nuclear spins are sampling a large number of configurations, which fluctuate with a characteristic time of milliseconds. These dynamics of the nuclear spins lead to a spectral diffusion of the electron spin line. If the protons in the guest molecule and in the matrix are replaced by deuterons, which have a six times smaller magnetic moment, the second-order hyperfine interaction -and the ODMR linewidth- is reduced by a factor 36, giving rise to much narrower lines. A pentacene molecule contains 22 carbon atoms, and therefore has a probability of about 20% to contain a ^{13}C atom in natural abundance (1.1 %). The spin of the ^{13}C atom is also flipping as time goes, which leads to a spectral diffusion of the ODMR line between two positions, corresponding to two orientations of the nuclear spin with respect to the electron spin. This splitting has been observed on the ODMR spectra of single molecules. In these experiments, a single nuclear spin was detected, but its state was still undetermined.

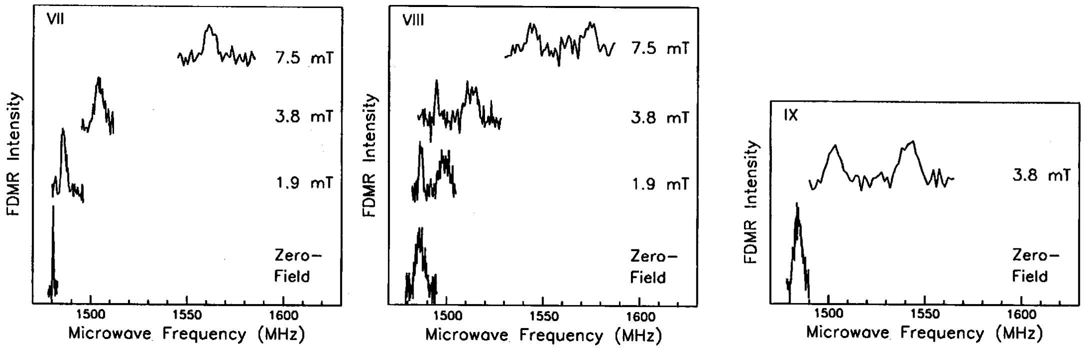

Figure 10.6 : ODMR spectra of fully deuterated single pentacene molecules containing only C12 atoms (left), or one C13 atom in two different positions (center, right). The splitting of the line under field is due to the two states of the nuclear spin [Reproduced with permission from J. Köhler et al., Science 268, 1995,1457. Copyright 1995 AAAS].

It was proved possible to go one step further, and to manipulate the nuclear spin with a resonant RF wave. In the same way the electronic transition is used to probe the electron-spin transition by ODMR, the electron spin transition can be monitored as the RF frequency is tuned in the range of nuclear spin transitions in an applied magnetic field, in a so-called ENDOR (electron-nuclear double resonance) experiment. It turns out that the ENDOR signal is too weak to detect with cw illumination by microwave and RF wave. However, if a pi/2 microwave pulse and RF pulses are applied, the ENDOR signal can be considerably enhanced, and be detected for a single molecule. Such spin manipulations are very promising for quantum computing and quantum network applications, since quantum states can be stored on much longer times by electronic spins (lifetimes ms) and nuclear spins (lifetimes of s) than by electronic states (lifetimes of ns).

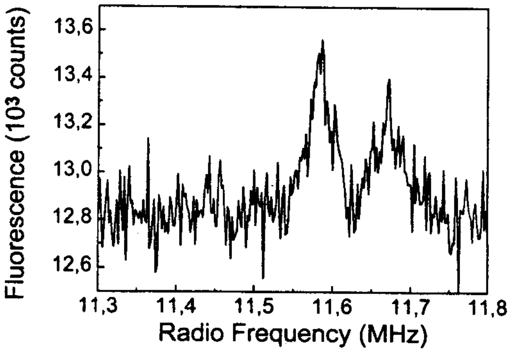

Figure 10.7 : ENDOR spectrum corresponding to the nuclear resonance of a single proton in a pentacene molecule containing two protons and twelve deuterons [Reprinted from J. Wrachtrup et al., Chem. Phys. Lett. 267, 1997, 179. Copyright 1997 with permission from Elsevier].

10.5. NV-center in diamond

Color centers in wide-gap insulators, particularly diamond, have molecule-like properties. The rigidity of the diamond lattice and the lightness of diamond give rise to very high phonon frequencies (Debye temperature about 2000 K) and to ZPL's still observable at room temperature, at least for some types of defects. The nitrogen-vacancy (NV) center consists of a nitrogen substituting a carbon atom, with a carbon vacancy in its first neighbor shell (see Fig. 10.8). It exists in two forms, neutral and negatively charged. Only the latter one will be discussed hereafter. That NV$^-$ form has spin unity (triplet states) in the ground state and the first optically allowed state, and singlet metastable states (see Fig. 10.9). Experiments on single NV$^-$ centers can be done at room and at low temperatures.

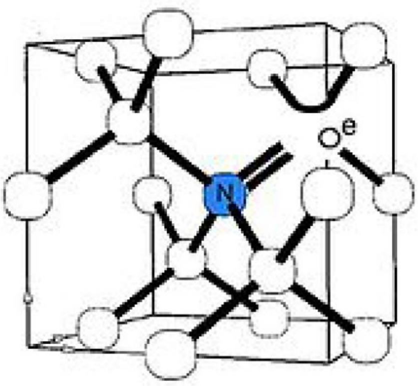

Figure 10.8 : Structure of the NV$^-$ center in diamond. The N inclusion (blue) has a lone electron pair directed towards a vacancy of C. The center accepts an additional electron, resulting in a triplet ground state (image taken from Wikipedia).

The ground and excited triplet states of the NV$^-$ center are split by its anisotropic structure (it has no spherical symmetry, but a third-order symmetry axis C_{3v}). Optical transitions from the ground triplet sublevels lead to singlet states by intersystem crossing. Optical pumping tends to favor population of the $m=0$ sublevel of the ground state (see Fig.10.9), causing spin polarization in the ground state upon illumination. As in molecules, this effect leads to ODMR signals, which are much easier to observe than with molecules because of the infinite lifetime of the electronic ground state of the NV$^-$ center. In particular, ODMR can be observed at room temperature. Because of the weak spin-lattice relaxation in diamond, ODMR and even hyperfine interactions of the electronic spin with nuclear spins of ^{14}N and residual ^{13}C or are visible at room temperature and have been used for nuclear spin manipulations. The density of nuclear spins in diamond is rather low (^{13}C abundance around 1.1 %) but is sufficient to yield spectral diffusion and dephasing. Because of the varying configurations of ^{13}C isotopes in the neighborhood of each center, characteristic transients are observed when exciting each individual center with pulses. The spin state of the NV center being sensitive to magnetic field and temperature, a single NV^- center can be used as a very accurate but small magnetometer and even thermometer. Many groups are active in this field, in particular the group of R. Hanson at TU Delft.

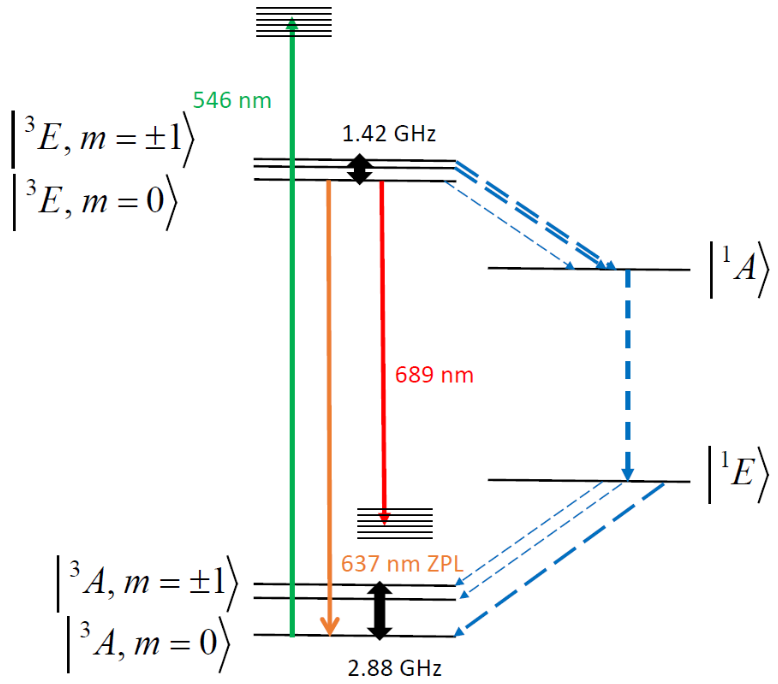

Figure 10.9 : Level diagram of the NV^- center in diamond. Optically allowed transitions start from the triplet ground state to the triplet excited state. They are usually excited through their broad phonon wing with green light (546 nm) and emit red light (689 nm) on the phonon wing. The zero-phonon line (637 nm) has a Debye-Waller factor of about 4%. The triplet levels are split in zero field by magnetic dipole-dipole interactions. Non-radiative relaxation occurs through singlet states and pump preferentially the m=0 sublevel of the ground state, giving rise to efficient spin alignment under laser illumination. The m=±1 states would be degenerate in perfect crystal C_{3v} symmetry, but their degeneracy is usually lifted by residual electric fields.

Exercise 10.1: *Consider the magnetic dipole-dipole interaction between two spins in a 3D parallelepipedic box with axis lengths a, b, c. Write the matrix elements of this perturbation between the three spin states corresponding to total spin 1. Diagonalize this matrix and show that, in each eigenstate, the spin is perpendicular to one of the axes of the box.*

Exercise 10.2: *Derive the saturation factor* ξ *in equation (10.1). Hint: Write Bloch's equations including the populations of the 3 triplet sublevels. Write the third Bloch equation as the evolution of the population of the excited singlet state, and note that the constant source term is reduced by storage of population in the triplet states. Solve these equations in steady state, first eliminating coherence to write a kinetic system for the populations of the five states involved.*

Exercise 10.3: *Write the optical Bloch equations for an optical two-level system of two singlet states, and add rate equations for population and decay of the populations of two triplet sublevels. Show that the second-order correlation function of this system when excited at resonance is bi-exponential. Hint: Use the condition that, after detection of one photon, all excited state populations are zero, including those of the triplet sublevels (see Boiron et al., J. Chem. Phys. 1996).*