Chapter 3

Decoherence

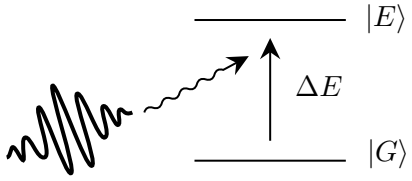
In this chapter, we will be discussing what happens when our two-state system interacts with the outside world. Obviously, our two-level system would not simply exist in a vacuum - it has to interact with the "outside" in order for us to manipulate it.

I the Bloch Equations

Before we go into details of decoherence, we should be able to describe the dynamics of the two-level system fully using a system of differential equations. We have seen from the previous section that the dynamics of spin-1/2 systems can often be described by the Hamiltonian,

$$\hat{H} = A \underbrace{\hat{\sigma}_z}_{\text{DC field (Larmor)}} + B(t) \underbrace{\hat{\sigma}_x}_{\text{AC field (Rabi)}},$$

where the DC term is time-independent while the AC term is time dependent. This is actually a very common potential we will encounter. For instance, consider a two level atom as follows.



The transition frequency between the two energy levels would therefore be,

$$\Delta E = \hbar\omega_0,$$

whereas the Hamiltonian can similarly be expressed as,

$$\hat{H}_{\text{atom-photon}} = \frac{\Delta E}{2}\hat{\sigma}_z - \underbrace{\vec{d}\cdot\vec{E}(\vec{r},t)}_{\text{interaction with photon}} \hat{\sigma}_x.$$

If $\vec{E}$ is sinusoidal, the Hamiltonian above can be expressed in matrix form,

$$\hat{H}_{\text{atom-photon}} = \begin{pmatrix} \frac{\Delta E}{2} & \hbar\Omega\exp(i\omega t) \\ \hbar\omega\exp(-i\omega t) & \frac{\Delta E}{2} \end{pmatrix}.$$

Here, we defined $\hbar\Omega = \vec{d}\cdot\vec{E}_0$, while the sinusoidally oscillating electric field would be in the form $\vec{E}(\vec{r},t) = \hat{E}_0\cos(\omega t)$. The density operator for the two level system would be,

$$\hat{\rho} = \begin{pmatrix} \rho_{ee} & \rho_{eg} \\ \rho_{ge} & \rho_{gg} \end{pmatrix}, \quad \rightarrow \quad \mathrm{Tr}(\hat{\rho}\hat{\sigma}_z) = \rho_{ee} - \rho_{gg} = n.$$

The term n is called the **population inversion**, or the population difference between the ground and the excited states. Similarly, the off-diagonal terms $\rho_{eg} = \rho^*_{ge}$ are proportional to the dipole transitions of the two states.

Using the Liouville-von Neumann equation,

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{H},\hat{\rho}],$$

we can express all the terms of the density matrix as a differential equation,

$$\begin{cases} \dot{\rho}_{ee} - \dot{\rho}_{gg} & = 2i\Omega\exp(-i\omega t)\rho_{ge} + \text{ c.c.} \\ \dot{\rho}_{ge} & = i\Omega\exp(i\omega t)(\rho_{ee} - \rho_{gg}) + i\omega_0\rho_{ge}. \end{cases}$$

Substituting in the definitions of n and d, we will yield the **optical Bloch equations**, as follows.

Theorem 3.1: the Optical Bloch Equations

$$\begin{cases} \dot{n} & = 2i\Omega\exp(-i\omega t)d + \text{c.c.} \\ \dot{d} & = i\Omega\exp(i\omega t)n + i\omega_0 d \end{cases}$$

With the initial conditions $n(0)$ and $d(0)$, we can solve exactly $n(t)$ and[1] $d(t)$. Physically, if $d = 0$, no photons will be emitted by the system (as in, no transitions); however, if d reaches its maximum value, there will be lots of atomic transitions occurring. In this case, we see that d^2 is proportional to the **intensity** of the light emitted, while its complex conjugate, $(d^2)^*$, can be interpreted as the absorption experienced by the system.

II Decoherence

Previously, we assume that the system does not interact with external factors. However, we can fortunately discuss phenomenological, "how" the system interacts with factors outside the system. In order to fully understand the phenomenon of decoherence, we need to define three different "T" parameters, as follows.

Theorem 3.2: Decoherence Time Parameters

1. **Relaxation decay** T_1 is the time constant of the decay rate of the population due to interaction of the system with a **thermal reservoir.**
2. **Pure dephasing** T_2^*, also known as the *phase lifetime*, is the time constant of the decay rate of the **total magnetisation** of the ensemble due to the inhomogeneity of phase created by **field inhomogeneity** that the system experiences.

[1] One technique we were familiar with was perturbation theory. While in perturbation theory we need the perturbation to be very week compared to the original Hamiltonian, we do not need $\vec{d}\cdot\vec{E}_0$ to be weak in this case.

3. **Dephasing** T_2 is the time constant of the **ideal** decay rate of the **total magnetisation** of the ensemble when the effects of field inhomogeneity are cancelled.

II.1 Phenomenological Relaxation Coefficients

The time T_1 is the time constant of the decay rate of the population when a **thermal bath** is present,

$$\boxed{\dot{n} = \dot{\rho}_{ee} - \dot{\rho}_{gg} = -\underbrace{\frac{1}{T_1}}_{\text{time constant of time-decay}} (n - n_0)},$$

where n_0 is the population inversion during thermal equilibrium. If we solve the differential equation above, we yield,

$$\boxed{n(t) = n_0 + \Delta n \exp\left(-\frac{t}{T_1}\right)}.$$

Analogously, T_2 is defined as the optical decoherence time, which can similarly be expressed as a differential equation,

$$\boxed{\dot{d} = d\left(i\omega_0 - \frac{1}{T_2}\right)}.$$

It is *because* of the interaction with the environment that we need to introduce the parameters T_1 and T_2, which causes the system to lose some of its population.

II.2 Decoherence Time T_1: Thermal Equilibrium

We will now be studying the physics of the T_1 relaxation time. We again assume that we are in a two-level quantum system with eigenenergies E_1, E_2, such that $\Delta E = E_2 - E_1$. If the quantum system is interacting with an external thermal bath, the quantum system would naturally behave like a canonical ensemble with the form,

$$\boxed{\frac{P(E_2)}{P(E_1)} = \exp\left(-\frac{\Delta E}{k_B T}\right)}.$$

Let's consider an ensemble of spin-1/2s undergoing a DC Zeeman splitting as an example. The initial state at thermal equilibrium would be,

$$\hat{\rho} = P_+ \left|+\mathbf{z}\right\rangle \left\langle+\mathbf{z}\right| + P_- \left|-\mathbf{z}\right\rangle \left\langle-\mathbf{z}\right|,$$

where $\Delta E = g\mu_B B_0$. According to the conservation of probability, we again mandate that the trace of the system must be equal to 1; $\mathrm{Tr}(\hat{\rho}) = 1$, implying that $P_\uparrow + P_\downarrow = 1$. Therefore, if the spin-1/2 system is interacting with an external thermal bath at temperate T, the proper density matrix accounting for the canonical ensemble would be,

$$\hat{\rho} = \frac{1}{1 + \exp\left(\dfrac{-g\mu_B B_0}{k_B T}\right)} \left[\exp\left(\frac{-g\mu_B B_0}{k_B T}\right) \left|+\mathbf{z}\right\rangle \left\langle+\mathbf{z}\right| + \left|-\mathbf{z}\right\rangle \left\langle-\mathbf{z}\right|\right].$$

In summary, we can associate the decoherence terms T_1 and T_2 with the density matrix of our two-level system as follows.

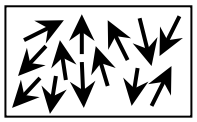
Theorem 3.3: Relaxation Coefficients and the Density Matrix

$$T_1 \leftrightarrow \text{diagonal elements}, \quad T_2 \leftrightarrow \text{off-diagonal elements}$$

which we will show in great detail in the next two sections.

II.3 Decoherence Time T_2^*: Spin Coherence

Spin coherence relates to the relaxation time T_2; consider a system that consists of an ensemble of spins that interacts with an external magnetic field, as seen in the figure below.



Even if we apply an external magnetic field $\vec{B} = B_0\hat{z}$, the total magnetic field experienced by every position would actually be,

$$\vec{B}_{\text{eff}}(\vec{r}) = \underbrace{B_0\hat{z}}_{\text{external}} + \text{field by solid.}$$

This effect is called **field inhomogeneity**, where every location of the solid experience a different magnetic field.

Recall that the Larmor frequency is in the form,

$$\Omega_0(\vec{r}) = \frac{g\mu_B}{\hbar}\vec{B}^{\text{eff}}(\vec{r}).$$

When the field is inhomogeneous, the Larmor frequency would also be inhomogeneous. The Larmor frequency can therefore be expressed as,

$$\boxed{\omega = \underbrace{\omega_0}_{\text{centre term}} + \underbrace{\Delta\omega(\vec{r})}_{\text{inhomogeneity term}}}.$$

This broadening of the Larmor frequency spectrum is an example of **inhomogeneity broadening**.

the Spin Echo Experiment

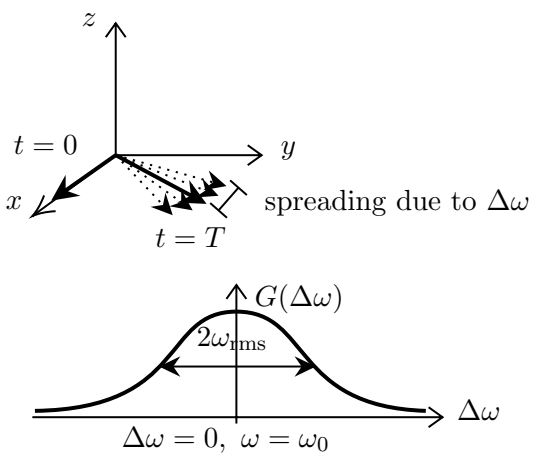
We now consider an ensemble of spins and apply a DC magnetic field in the direction $B_0\hat{z}$. If the initial Bloch vector is in the form $\hat{a}(t=0) = a_0\hat{x}$ with no field, the time evolution due to a DC magnetic field in the z-direction would be,

$$\hat{a}(\vec{r},t) = a_0 \underbrace{\hat{x}\cos(\omega_0 + \Delta\omega(\vec{r})t) + \hat{y}\sin(\omega_0 + \Delta\omega(\vec{r})t)}_{\text{free Larmor precession}}.$$

Pictorially, the Bloch vectors would look as follows:

To simplify matters, we can assume that the distribution of spreading obeys that of a Gaussian distribution,

$$\boxed{G(\Delta\omega) = \frac{1}{\sqrt{2\pi\Delta\omega_{\text{rms}}^2}}\exp\left(-\frac{1}{2}\left[\frac{\Delta\omega}{\Delta\omega_{\text{rms}}}\right]^2\right)},$$



which if we plot this expression, we will yield the distribution curve that looks as follows, where the distribution function above obviously has to obey a normalisation condition,

$$\int G(\Delta\omega')d\omega' = 1.$$

One important macroscopic quantity to the ensemble would be the magnetisation associated with this system. Experimentally, we see that the magnetisation obeys the form,

$$\vec{M}(t) \propto \int \underbrace{\vec{a}(\vec{r},t)}_{\text{spin moment of individual particles}} d\vec{r} = \int G(\Delta\omega)\vec{a}(\Delta\omega,t)d\Delta\omega.$$

The density matrix associated with a two-state system, again, can be expressed in the form,

$$\begin{pmatrix} \boxed{\rho_{11}} & \rho_{12} \\ \rho_{21} & \boxed{\rho_{22}} \end{pmatrix}.$$

The boxed term above indicates **population**, while the unboxed term above indicates the magnitude of coherence the system is in. In a spin system, coherence is represented by the off diagonal element in $\hat{\rho}$. For example, consider the $\hat{S_x}$ operator:

$$\hat{S_x} = \frac{\hbar}{2}\hat{\sigma}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Notice that $\hat{S_x}$ itself is a measurement of superposition between $|+\mathbf{z}\rangle$ and $|-\mathbf{z}\rangle$, as in,

$$\langle\hat{S_x}\rangle \propto \hat{a}_x.$$

Recall that the time evolution of a Bloch vector of a due to a $\vec{B}$ field in the z-direction interacting with spin-1/2 particles in the spin-x state[2] would be,

$$\hat{a}(\vec{r},t) = a_0\hat{x}\cos(\omega_0 + \Delta\omega(\vec{r})t) + \hat{y}\sin(\omega_0 + \Delta\omega(\vec{r})t)$$

The component of this Bloch vector in the x unit vector would be,

$$\hat{a}_x(t) = a_0\cos(\omega_0 + \Delta\omega)t$$

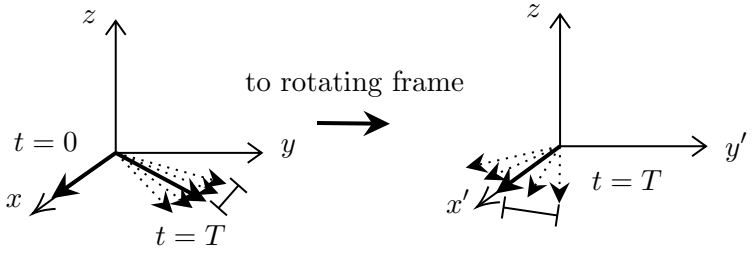
[2]This can be accomplished by applying a $\pi/2$ pulse to a spin ensemble initialised in the $|-\mathbf{z}\rangle$ state.

$$= a_0 \left(\cos\omega_0 t + \cos\Delta\omega t - \sin\omega_0 t - \sin\Delta\omega t\right).$$

Notice that $\Delta\omega$ obeys the Gaussian distribution, and the the Gaussian distribution is in fact an even distribution. Since the sine function has odd parity, the average value over all sines of $\Delta\omega$ would collapse into zero. Therefore, we see, if the spin incoherence $\Delta\omega$ is small enough, we can expand $\hat{a}_x(t)$ as,

$$\hat{a}_x(t) = a_0 \cos(\omega_0 t)\cos(\Delta\omega t) = a_0 \cos\omega_0 t \left[1 - \frac{1}{2}\Delta\omega t^2\right].$$

Now, we will convert this into the rotating frame by rotating about the *central* Larmor frequency[3]. Pictorically, this is the action,

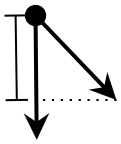


where from the picture, we know that the *spreading* due to the spin incoherence can be expressed by the term.

$$\Delta\omega_{\text{rms}} \approx \frac{1}{2}(\Delta\omega t)^2,$$

where this quantity physically means *how much* the projection is smaller due to the presence of spin incoherence, which obviously leads to a decrease of the magnetisation in the x' axis (rotating frame). In the rotating frame, we can compare the original Larmor precession with the decoherence due to field inhomogeneity as follows.

$$1 - \frac{1}{2}(\Delta\omega t)^2$$



We can therefore calculate the total magnetisation (in the x' frame) to be,

$$\vec{M}_{x'}(t) = \int G(\Delta\omega) M_{x'}(0) \left(1 - \frac{1}{2}(\Delta\omega t)^2\right) d\Delta\omega.$$

Since the spin decoherence is proportional to t^2, it is natural for us to ask, what is the time that $\vec{M}_{x'}(t)$ decays to zero? In other words, we are interested in the time T such that,

$$\lim_{t\to T} \int G(\Delta\omega)\frac{1}{2}(\Delta\omega t)^2 d\Delta\omega = 1,$$

which quantifies **decoherence**. Substituting the Gaussian distribution into $G(\Delta\omega)$, we yield,

$$\int G(\Delta\omega)\frac{1}{2}(\Delta\omega t)^2 d\Delta\omega = \frac{t^2}{2\sqrt{2\pi}\Delta\omega_{\text{rms}}} \int_{-\infty}^{\infty} d\Delta\omega (\Delta\omega))^2 \exp\left[-\frac{1}{2}\left(-\frac{\Delta\omega}{\Delta\omega_{\text{rms}}}\right)^2\right].$$

[3]The Larmor frequency due to a field $\vec{B} = B_0\hat{z}$ with no field inhomogeneity.

However, we know that the Gaussian integral evaluates to,

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2)dx = \sqrt{\frac{\pi}{\alpha}}.$$

Therefore, doing the substitution

$$x = \frac{\Delta\omega}{\sqrt{2}\Delta\omega_{\text{rms}}}, \quad dx = \frac{d\Delta\omega}{\sqrt{2}\Delta\omega_{\text{rms}}},$$

and using integration by parts, the above integral can be expressed as,

$$\frac{t^2}{2\sqrt{2\pi\Delta\omega_{\text{rms}}}} \int_{-\infty}^{\infty} d\Delta\omega(\Delta\omega))^2 \exp\left[-\frac{1}{2}\left(-\frac{\Delta\omega}{\Delta\omega_{\text{rms}}}\right)^2\right] = \frac{2t^2\Delta\omega_{\text{rms}}^2}{2\sqrt{\pi}} \underbrace{\int_{-\infty}^{\infty} x^2 \exp(-x^2)dx}_{\text{by parts},=\sqrt{\pi}/2} \to 1,$$

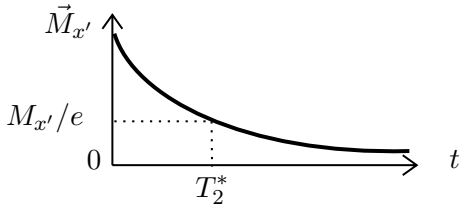
which then simplifies to,

$$\frac{t^2\Delta\omega_{\text{rms}}^2}{2} \to 1.$$

Therefore, the characteristic time it takes for the system to lose coherence would be,

$$\boxed{t = \frac{\sqrt{2}}{\Delta\omega_{\text{rms}}} \equiv T_2^*}.$$

We call this term T_2^*. Due to several inprecisions in the argument above, T_2^* is actually *not* the time it takes for the entire system to lose all of it's magnetisation. T_2^* is in fact the **time constant** in which the ensemble of spins loses $1/e$ of its magnetisation, as plotted in the figure below. After



a time T_2^*, the ensemble de-cohered by a factor of $1/e$ - this decay involving T_2^* is also called **free-induction decay**. We can also make an approximate argument that,

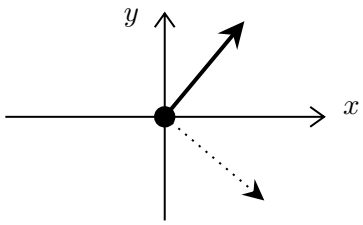
$$\boxed{\Delta\omega_{\text{rms}}T_2^* \sim \pi}.$$

II.4 the Rephasing Pulse: the Spin-Echo Experiment and Achieving T_2

Fromm the analysis of T_2^*, it seems like once the signal decohered, it never comes back. To make it come back, we need to introduce something called a **rephasing pulse,** or a π-pulse (from an AC field) that "refocuses" the ensemble of spin.

Now, let's consider a π-pulse (on resonance) around the $\hat{x}$ axis at time τ. The unitary operator associated with this π-pulse would be,

$$\hat{U}_{\pi,\hat{x}} = -i\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$



$$\boxed{\hat{S}_x \to \hat{S}_x,\ \hat{S}_y \to -\hat{S}_y}$$

Recall that, in the interaction picture, the π-pulse performs the folowing operation,

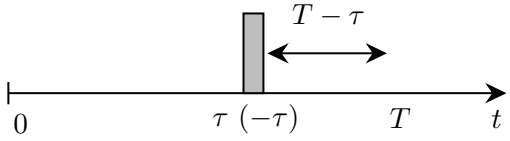
The Bloch vector just before the application of the pulse, say $t = \tau^-$, looks like,

$$\vec{a}(\vec{r}, t = \tau^-) = a_0 \left[\hat{x}\cos(\omega_0 + \Delta\omega(\vec{r}))\tau + \hat{y}\sin(\omega_0 + \Delta\omega(\vec{r}))\tau\right].$$

However, after the application of the pulse, the Bloch vector looks like,

$$\begin{aligned}\vec{a}(\vec{r}, t = \tau^+) &= a_0\Big[\hat{x}(\cos(\omega_0 + \Delta\omega(\vec{r}))\tau \underbrace{-}_{\pi-\text{pulse}} \hat{y}\sin(\omega_0 + \Delta\Omega(\vec{r}))\tau\Big] \\ &= a_0\Big[\hat{x}(\cos(\omega_0 + \Delta\omega(\vec{r}))(-\tau) + \hat{y}\sin(\omega_0 + \Delta\Omega(\vec{r}))(-\tau)\Big].\end{aligned}$$

We say that, at time τ^+, the spin vector is equivalent to the spin vector at $t = -\tau$.



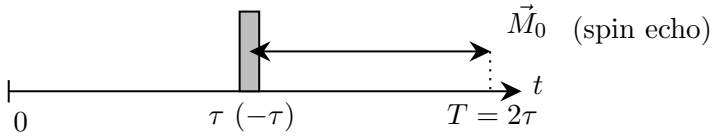
Now, we consider what is the magnetisation at time t, some time after the π-pulse. The Bloch vector would be,

$$\begin{aligned}\vec{a}(\vec{r}, t) \equiv\ &\text{free evolution for } T - \tau \text{ time} \\ = a_0 \Bigg(&\hat{x}\cos\Bigg[(\omega_0 + \Delta\omega(\vec{r}))\ \underbrace{(-\tau + [t - \tau])}_{\text{since after } \pi\text{-pulse, } \tau = -\tau.}\Bigg] + \hat{y}\sin\Bigg[(\omega_0 + \Delta\omega(\vec{r}))\ \underbrace{(-\tau + [t - \tau])}_{\text{since after } \pi\text{-pulse, } \tau = -\tau.}\Bigg]\Bigg)\end{aligned}$$

Now, when $t = 2\tau$, the Bloch vector becomes,

$$\vec{a}(\vec{r}, 2\tau) = a_0\hat{x} = \vec{a}(\vec{r}, 0),$$

which gets mapped to the original Bloch vector. This is called **spin-echoing**, as seen in the figure below. Notice that, *ideally*, after waiting for 2τ amount of time after applying a π-pulse at time τ



would "re-cohere" the system. Unfortunately, this is too good to be true; in the real world, we see,

$$\boxed{M(t = 2\tau) < M(t = 0)}.$$

This is due to the **intrinsic** decay of the spin vectors, $\vec{a}_x(t)$, as time goes by; this intrinsic decay is called the **spin-echo decay**, as follows.

Theorem 3.4: Spin-Echo Decay

The decay of the maximum possible magnetisation due to an ensemble of $\vec{a}_x(t)$ particles would be,

$$M(2\tau) \propto \exp\left(-\frac{2\tau}{T_2}\right),$$

where the time constant T_2 is the decay of spin echo, known as the **intrinsic coherence time**.

One important key point we should realise is the comparison of relative size between T_2 and T_2^*, as seen as follows,

Theorem 3.5: Comparison of Decoherence Time Constants

The effects of field inhomogeneity with T_2^* can be corrected using the spin-echo experiment, such that,

$$T_2 \geq T_2^*,$$

where the equality condition is matched when the spreading of the Larmor frequency due to field inhomogeneity is zero.

The current research we are undergoing is to maximise the T_2 and T_2^* time.

III Double Resonance

Up until now, we have solely been considering what happens when there are interactions between one electron and an external magnetic field. We ware now interested in considering what happens if we try to use *atoms* to build qubits.

III.1 Hamiltonian of Double Resonance

The Hamiltonian that we are now interested in analysing would be,

$$\hat{H} = \underbrace{\hat{H}_{EZ}}_{\text{electron Zeeman}} + \underbrace{\hat{H}_{\text{NZ}}}_{\text{nuclear Zeeman}} + \hat{H}_{\text{hyperfine}},$$

which, in symbolic form, would be,

$$\boxed{\hat{H} = g\mu_B \qquad \underbrace{-g_N\mu_N\vec{B}\cdot\hat{I}}_{\mu \text{ by nuclear spin has opposite sign}} \qquad + \mathcal{A}\hat{S}\cdot\hat{I}},$$

where μ_B is the Bohr magneton, μ_N is the nuclear magneton, $\hat{I}$ is the nuclear spin operator, and $\mathcal{A}$ is a constant that measures the magnitude of the hyperfine interaction. The **hyperfine interaction** is the interaction that occurs when the magnetic moment of an atomic electron interacts with the magnetic dipole field associated with the nuclear magnetic moment.

Example: Interaction of Electron with Spin-1/2 Nucleus

For example, let's consider what happens if we have a spin-1/2 electron with a spin-1/2 nucleus[4]. There will be four eigenstates in the combined Hilbert space (similar to the singlet-triplet system). If we do *not* have an external magnetic field, the total Hamiltonian would look like[5],

$$\hat{H}_{\vec{B}=0} = \mathcal{A}\hat{S}\cdot\hat{I} = \mathcal{A}\left(\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y + \hat{S}_z\hat{I}_z\right) = \mathcal{A}\Big(\hat{I}_z\hat{S}_z + \underbrace{\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+}_{\text{rewrite in terms of ladder}}\Big)$$

where we note that this Hamiltonian is very similar to the Hamiltonian experienced by the singlet-triplet system. Analogous to the singlet-triplet system, the energy splitting due to the hyperfine interaction would be,

$$E_1 = -\frac{3\hbar^2\mathcal{A}}{4}, \quad E_2 = \frac{\hbar^2\mathcal{A}}{4}, \quad \rightarrow \quad \boxed{\Delta E = \mathcal{A}\hbar^2}.$$

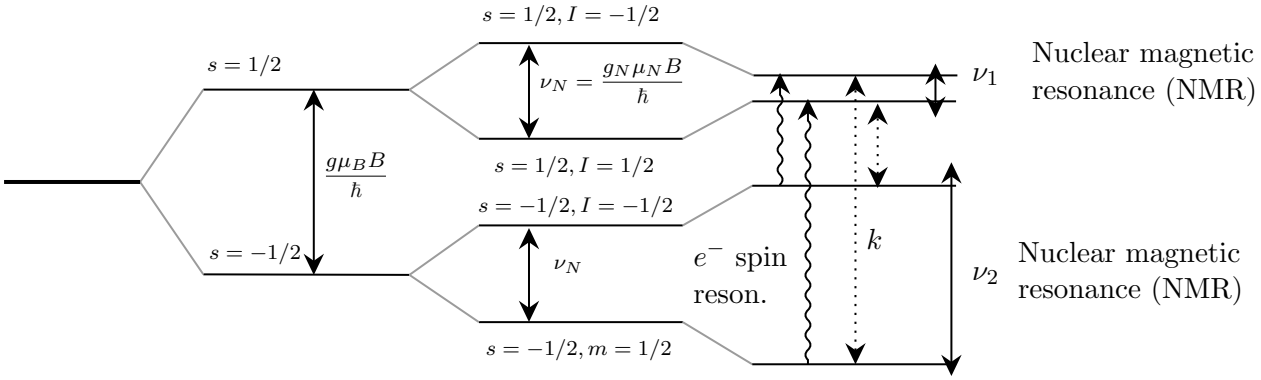
When $\vec{B} \neq 0$, the nuclear terms of both system will go to nonzero. Since the nucleus is so much more massive than the electron, we can safely assume that,

$$\mu_N \ll \mu_B.$$

Therefore, we can use time-independent perturbation theory to calculate the energy perturbations due to the Zeeman terms. The energy ordering of the Hamiltonian looks roughly like,

$$\hat{H}_{\text{Coulomb}} \gg \hat{H}_{\text{electron Zeeman}} \gg \hat{H}_{\text{nuclear Zeeman}} \gg \hat{H}_{\text{hyperfine}}.$$

Choosing a set of good quantum numbers and carrying out the perturbation, we yield the following diagram for energy splitting[6].



We need to determine which of the transitions above are allowed. Using the **selection rules** of atomic transition, we know that the difference of angular momentum must be one quanta,

$$\Delta J = \left|j - j'\right| = 1.$$

[4]Of course, we can have nucleus that doesn't spin 1/2; the simplest case for this to happen is an electron orbiting a nucleus consisting of a proton and a neutron.

[5]Since $\hat{S}_i$ and $\hat{I}_j$ act in different degrees of freedom, we can safely assume that $[\hat{S}_i, \hat{I}_j] = 0$.

[6]The plot below seems to be in units of frequency

Thus, only the curly and solid transition rules in the figure above are allowed to happen alone[7].

The curly line indicates effects due to electron spin resonance (ESR), and the dark, straight line indicates effects due to nuclear magnetic resonance. The k term indicates the energy difference between the spn states $|s = 1/2, I = -1/2\rangle$ and $|s = 1/2, I = 1/2\rangle$. The resultant frequency due to NMR transitions, ν_1 and ν_2, re related to ν_N via the expression,

$$\boxed{\nu_1 = \nu_N - \frac{A}{2}, \quad \nu_2 = \nu_N + \frac{A}{2}}.$$

From the diagram above, we see that the nuclear spin resonances are in the range of radio waves[8], and in order for us to get to an energy level *less* than one quanta of radiowaave, we need to cool the system down to a few millikelvins, which is very hard.

III.2 Initialisation of Nuclear Spins: the Nuclear Overhauser Effect

As mentioned above, it is very difficult to cool down a system to a few millikelvins using traditional approaches. We thus need to derive an alternative approach for this to be achieved.

Hyperpolarisation

Before we discuss the physics of the initialisation techniques, we need to first introduce the formalism of hyperpolarisation. Let $n_{\uparrow\downarrow}$ be the population of electrons in the spin up/down state, while $I_{\uparrow\downarrow}$ be the electrons in the nuclear spin up/don states, respectively. The **hyperpolarisation** is defined as,

$$\boxed{P_N = \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow} \equiv \frac{I_\uparrow - I_\downarrow}{I}, \quad P_e = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} \equiv \frac{n_\uparrow - n_\downarrow}{n}}.$$

The population of spin in the up/down direction can therefore be expressed as,

$$\boxed{I_\uparrow = \frac{I}{2}(1 + P_N), \quad I_\downarrow = \frac{I}{2}(1 - P_N)}.$$

the Nuclear Overhauser Effect

The physics that allows us to initialise a population of nuclear spins using electron spins is driven by a "secret coupling" between the states,

$$|e_\uparrow I_\downarrow\rangle \xleftrightarrow{\text{cross relaxation}} |e_\downarrow I_\uparrow\rangle .$$

The **cross-relaxation** between these two states occur due to the presence of the ladder operators, $\hat{I}_+\hat{S}_-$ and $\hat{I}_-\hat{S}_+$, in the Hamiltonian, that collapses a spin eigenstate to a higher or lower spin eigenstate. With the **cross-relaxation** term present, our system can spontaneously relax from one state to another at an intrinsic of k, where k, as defined in the previous page, is the energy

[7] However, the dotted transitions can happen if both dotted transitions occur together. This is called the **nuclear Overhauser effect**, as we will see in the next section.

[8] in terms of megahertz

difference between the state $s = 1/2, I = -1/2$, and $s = -1/2, I = 1/2$. Thus, the differential equation dictating the population would be,

$$\frac{dI_\uparrow}{dt} = \underbrace{k(n_\uparrow I_\downarrow - n_\downarrow I_\uparrow)}_{\text{cross-relaxation}} - \Big(\underbrace{\frac{I_\uparrow - I_\uparrow^{T_0}}{T_1}}_{\text{thermal term}} \Big)$$

where $I_\uparrow^{T_0}$ is the population of nuclear spin up at thermal equilibrium, and T_1 is the T_1 relaxation decay rate *for the nucleus*, as defined previously. Similarly, the differential equation for $I_\downarrow$ would be,

$$\frac{dI_\downarrow}{dt} = -k(n_\uparrow I_\downarrow - n_\downarrow I_\uparrow) - \left(\frac{I_\downarrow - I_\downarrow^{T_0}}{T_1} \right).$$

Combining the two equations, we yield,

$$\begin{aligned}
\frac{d(I_\uparrow - I_\downarrow)}{dt} &= 2k\,(n_\uparrow I_\downarrow - n_\downarrow I_\uparrow) - \frac{(I_\uparrow - I_\downarrow) - (I_\uparrow^{T_0} - I_\downarrow^{T_0})}{T_1} \\
&= 2k\frac{I(n_\uparrow - n_\downarrow)}{2} - \frac{2kn(I_\uparrow - I_\downarrow)}{2} - \left[\frac{(I_\uparrow - I_\downarrow) - (I_\uparrow^{T_0} - I_\downarrow)}{T_1} \right]
\end{aligned}$$

which will therefore yield,

$$\boxed{\frac{dP_N}{dt} = knP_e - k_n P_N - \frac{P_n - P_N^{T_0}}{T_1}}.$$

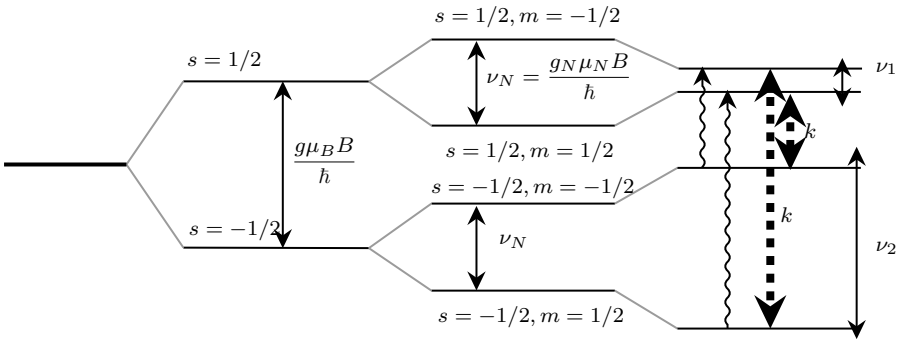
We can assume that T_1 is *extremely* long[9] In this case, since T_1 is long, the term where T_1 is the denominator naturally dies; however, the term kn from above then *becomes* the new T_1. In this case, we yield,

$$\frac{dP_N}{dt} = k_n(P_e - P_N).$$

When we wait for long enough such that the time derivative basically becomes zero, we see,

$$\frac{dP_N}{dt} = 0 = k_n(P_e - P_N), \quad \rightarrow \quad \boxed{P_e = P_N},$$

which means thaat the hyperpolarisation of the electron is actually *equivalent* to the hyperpolarisation to the nucleus, given that we wait a long enough time. In pictorial terms, we see the follows.



[9] So long that it may take several minutes, hours, days, or even months.

The Nuclear Overhauser Effect proposes that, despite the selection rule forbids the bolded, dotted transitions to occur, transitions connected by these dotted transitions are allowed **on the condition** that they occur simultaneously, or when cross-relaxation between the two states are present.

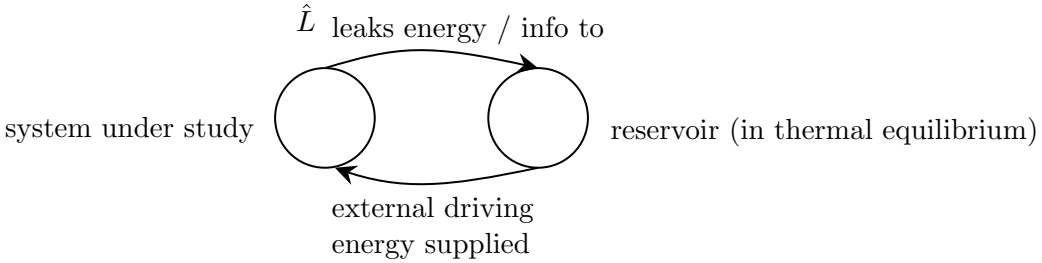
If we initialise our electron spins at the beginning, the equation above suggests that our nuclear spin will also be initialised. Electron splittings are typically in the microwave region, which corresponds to approximately 250 millikelvins. This is way easier to achieve than one millikelvin if we solely due with nuclear spin without consideration of the nuclear Overhauser effect.

IV Open Quantum Systems

So far, we have solely been dealing with systems that are **closed**, or systems that are not nesessarily able to exchange energy with the environment, meaning that we will let our system evolve by itself, and we we don't care how this system is exchanging energy with the environment. We sort of encountered open quantum through systems through the relaxation terms of the Bloch equations, which gives us a sense of how this energy actually can leave the system so that makes a system is not closed anymore.

IV.1 the Lindblad Equation

In reality, we can draw a schematic diagram of an open quantum system as follows. We assume



that the reservoir has no memory of the past that it does not give back energy to the system. Thus, our *goal* would be to find the density matrix of the open system at a later time $\hat{\rho}(t + \Delta t)$, given the current density matrix $\hat{\rho}(t)$, using the Liouville-von Neumann equation,

$$i\hbar \frac{d\hat{\rho}}{dt} = [\hat{H}, \hat{\rho}],$$

we can yield that the mathematical formalism of the Markovian assumption would be,

$$\hat{\rho}(t + \Delta t) = \hat{\rho}(t) + \frac{\hat{\rho}(t)}{dt}\Delta t.$$

We should therefore assume that $\hat{\rho}(t)$ is only dependent on its previous state, $\hat{\rho}(t - \Delta t)$, as in, it does not have memory of the past before $(t-\Delta t)$. This assumption is called a **Markovian process**, where the density matrix of a time $t + \Delta t$ will only depend on the density matrix at time t. The dynamics of an open quantum system can be expressed by the **Lindblad equation** as follows.

Theorem 3.6: the Lindblad Equation

$$\dot{\hat{\rho}}(t) = \mathcal{L}[\hat{\rho}] = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)] - \underbrace{\frac{K}{2}\{\hat{L}^\dagger \hat{L}, \hat{\rho}(t)\}}_{\text{dissipation}} + \underbrace{G\hat{L}\hat{\rho}(t)\hat{L}^\dagger}_{\text{generation}},$$

where K, G are constants, and $\hat{L}$ is the **Lindbladian operator**.

where the notation $\{\hat{A}, \hat{B}\}$ is called the **anti-commutator**, and can be expressed as,

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}.$$

Typically, the **Lindbladian operator**, or $\hat{L}$ as stated above, would be a projection operator. We can interpret the **dissipation term** as the energy that is moving from the system to the environment, while the **generation term** as the energy that is moving from the environment to the system[10].

Note that the dissipation term and generation term can often be attributed to different physical phenomenons. However, when the generation rates and dissipation rate equals to each other, then the "total size" of our ensemble of quantum states are preserved,

$$\boxed{\text{if } K = G, \quad \leftrightarrow \quad \text{Tr}\hat{\rho}(t) = 1},$$

which implies that an equal amount of energy is entering and leaving the system, simultaneously.

Example: Spontaneous Emission

[**NOTE:** This section is heavily based on *Quantum Computing: From Linear Algebra to Physical Realisations* by Nakahara et al.] Let us now consider a two-level Hamiltonian,

$$\hat{H} = -\frac{\omega_0}{2}\hat{\sigma}_z,$$

where ω_0 is the energy difference[11] between the ground state $|0\rangle$ and the excited state $|1\rangle$. Suppose that there is a Lindblad operator,

$$\hat{L} = |1\rangle\langle 0|$$

that correspond to the relaxation process $|1\rangle \to |0\rangle$ where the system becomes un-excited. The Lindblad equation therefore reads,

$$\begin{aligned}
\frac{\partial}{\partial t}\begin{pmatrix}\rho_{00} & \rho_{01}\\ \rho_{10} & \rho_{00}\end{pmatrix} &= -i[\hat{H}, \hat{\rho}] - \frac{K}{2}\left(\hat{L}^\dagger\hat{L}\hat{\rho} + \hat{\rho}\hat{L}^\dagger\hat{L}\right) + G\hat{L}\hat{\rho}(t)\hat{L}^\dagger \\
&= i\omega_0\begin{pmatrix}0 & \rho_{01}\\ -\rho_{10} & 0\end{pmatrix} - \frac{K}{2}\begin{pmatrix}0 & \rho_{01}\\ \rho_{10} & 0\end{pmatrix} + G\begin{pmatrix}\rho_{11} & 0\\ 0 & \rho_{11}\end{pmatrix} \\
&\xrightarrow[\text{if } K=G]{} i\omega_0\begin{pmatrix}0 & \rho_{01}\\ -\rho_{10} & 0\end{pmatrix} + K\begin{pmatrix}\rho_{11} & -\rho_{01}/2\\ -\rho_{10}/2 & -\rho_{11}\end{pmatrix}
\end{aligned}$$

[10] The commutator term is the "natural" behaviour of the system when there is no environment.
[11] Up to Planck's constant. This Hamiltonian is in the same form with Larmor precession.

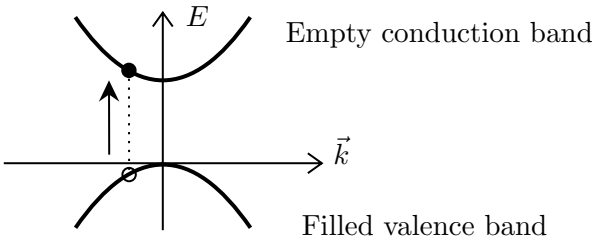
where, in the last step, we assumed that the dissipation and generation occurs at the same rate. The above equation is solved with the initial condition $\rho(0)$ as,

$$\hat{\rho}(t) = \begin{pmatrix} \rho_{00}(0) + \rho_{11}(0)(1 - e^{-Kt}) & \rho_{01}(0)e^{(i\omega_0 - K/2)t} \\ \rho_{10}(0)e^{(-i\omega_0 - K/2)t} & \rho_{11}(0)e^{-Kt} \end{pmatrix}.$$

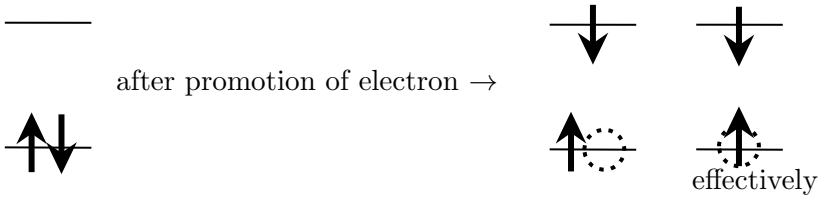
The population ρ_{11} in the excited state $|1\rangle$ decays with the characteristic time $T_1 = 1/K$, while the off-diagonal components ρ_{01} and ρ_{10} decay with time constants $T_2 = 2/\Gamma$.

IV.2 Exciton Generation and Recombination

An **exciton** is a bound state between an electron and a hole pair. When an electron has been moved up from a valence (lower) to a conduction band (higher) in a solid, the absence of the an electron in the valence band is called a **hole**, as seen in the figure below.



In a solid at where there *should* be an electron, the *non*-presence of an electron would induce the particles in the solid that surround the "non-presence" of the electron to act differently than had there be an electron. Thus, it is appropriate to treat a hole as a particle. We can also argue that the hole will have spin via the following pictorial description.



Effectively, the electron-hole pair has a net spin of zero, as in, it is possible for the system to take the following states,

$$|h_\uparrow, e_\downarrow\rangle\,, \quad \text{and,} \quad |h_\downarrow, e_\uparrow\rangle\,.$$

There are two interesting phenomenons relating to excitons. The **generation** process is which electrons gain energy and move from the valence band to the conduction band, thus creating an excitons. On the contrary, the **recombination** process is a process where an electron and a hole recombine into one state, thus destroying the exciton. The generation and recombination of excitons when the exciton is in the singlet state $|S\rangle$ for the electron-hole system,

$$|S\rangle = \frac{|\uparrow_h, \downarrow_e\rangle - |\downarrow_h, \uparrow_e\rangle}{\sqrt{2}}.$$

Excitons can be created or destroyed in the singlet state - the recombination process emits a photon only if the exciton is in the singlet state. Similar to the two electron Hilbert space in the singlet-triplet basis, the exciton can occupy the states,

$$|S\rangle\,, |T_0\rangle\,, |T_+\rangle\,, |T_-\rangle\,.$$

Since the $|T_+\rangle$ and $|T_-\rangle$ are energetically degenerate with the $|T_0\rangle$ state, they are irrelevant and we can simply truncate our density matrix to be in the basis $\mathcal{B} = \{|S\rangle, |T_0\rangle\}$,

$$\hat{\rho} = \begin{pmatrix} \rho_{SS} & \rho_{ST_0} \\ \rho_{T_0S} & \rho_{T_0T_0} \end{pmatrix}.$$

Exciton Pair Generation

For a moment, let's ignore recombination and consider solely the **generation process**. In this case, the Lindblad equation only has the generation term and the Liouville-von Neumann term due to the Hamiltonian,

$$\frac{d\hat{\rho}}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] + K\hat{L}\hat{\rho}\hat{L}^\dagger.$$

In this case, we assume that the Lindblad operator is equal to the projection operator $\hat{P}_S$ that finds the projection of any quantum state in the $\mathcal{B}$ basis onto the singular states. The Lindblad operator would look like,

$$\hat{L} = \hat{P}_S \equiv |S\rangle \langle S|.$$

We choose $\hat{P}_S$ to be our Lindblad operator since we can only inject energy or generating an exciton by *creating* a population in the singular states.

We further assume that since, in this case, we are most interested in studying the dynamics caused by the generation term, we assume that there are no dynamics generated by the Hamiltonian (thus the Liouville terms)[12].

We again assume that our initial state is in $|\uparrow_e\downarrow_h\rangle$, or if our electron is spinning up while our hole is spinning down. The initial density operator, converted into the singlet-triplet basis, would therefore be,

$$\hat{\rho} = |\uparrow_e\downarrow_h\rangle \langle\uparrow_e\downarrow_h| = \frac{1}{2}(|S\rangle + |T_0\rangle)(\langle S| + \langle T_0| = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix},$$

again in the $\mathcal{B} = \{|S\rangle, |T_0\rangle\}$ basis. We can now try to solve thie differential equation,

$$\frac{d\hat{\rho}}{dt} = \begin{pmatrix} \dot{\rho}_{SS} & \dot{\rho}_{ST_0} \\ \dot{\rho}_{T_0S} & \dot{\rho}_{T_0T_0} \end{pmatrix} = K \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_{|S\rangle\langle S|} \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}}_{(|S\rangle\langle S|)^\dagger},$$

which the differential equation modelled above would be expressed as,

$$\frac{d\rho_{SS}}{dt} = K\rho_{SS}, \qquad \frac{d\rho_{T_0T_0}}{dt} = 0, \qquad \frac{d\rho_{ST_0}}{dt} = \frac{d\rho_{T_0S}}{dt} = 0,$$

which gives us the new density matrix,

$$\hat{\rho}(t) = \frac{1}{2}\begin{pmatrix} \exp(Kt) & 1 \\ 1 & 1 \end{pmatrix}.$$

Notice that $\mathrm{Tr}(\hat{\rho}(t)) \neq 1$. Moreover, notice that when t approaches infinity, $\hat{\rho}(t)$ blows up. Even though this seems off, this is actually okay. From a physics point of view, this is not really surprising, since the **generation term** basically means we are adding energy into the system from the the reservoir[13]. Therefore, since the system becomes more energetic with time and there's no

[12] We simply assume that the Hamiltonian commutes with the density matrix.

[13] Basically a one way flow of energy into the system

dissipation that balance and out the generation, then it is natural that our density operator blows up.

To remedy this, we can always renormalise according to the trace,

$$\hat{\rho}(t) = \frac{1}{2\mathrm{Tr}(\hat{\rho}(t))} \begin{pmatrix} \exp(Kt) & 1 \\ 1 & 1 \end{pmatrix}.$$

Exciton Recombination Process

Similarly, we can discuss the **recombination process**, or when an electron and a hole recombine to destroy an exciton. Repeating the similar logic, we ignore the Liouville and generation term of the Lindblad equation to yield,

$$\frac{d\hat{\rho}}{dt} = -\frac{K}{2}\{\hat{L}^\dagger \hat{L}, \hat{\rho}\}.$$

Substituting the fact that,

$$\hat{L} = \hat{P}_S = |S\rangle \langle S| = |S\rangle \left(\langle S| \, |S\rangle\right) \langle S| = \hat{P}_S^2,$$

which the Lindblad equation then becomes,

$$\frac{d\hat{\rho}}{dt} = -\frac{K}{2}\left(\hat{P}_S\hat{\rho} + \hat{\rho}\hat{P}_S\right),$$

which, substituting in the matrix form will yield, in the $\mathcal{B}$ basis,

$$\frac{d\hat{\rho}}{dt} = -\frac{K}{2}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} + \frac{-K}{2}\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = -\frac{K}{2}\begin{pmatrix} \rho_{11} & \frac{\rho_{12}}{2} \\ \frac{\rho_{21}}{2} & 0 \end{pmatrix}$$

Solving the differential equation above, we will yield the density matrix to be,

$$\hat{\rho}(t) = \frac{1}{2}\begin{pmatrix} \exp(-Kt) & \exp(-Kt/2) \\ \exp(-Kt/2) & 1 \end{pmatrix}, \quad \lim_{t\to\infty}\hat{\rho}(t) = \frac{1}{2}\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

General Case: Generation and Recombination

If we now consider a process that involves both generation and recombination, the Lindblad equation would look like,

$$\frac{d\hat{\rho}}{dt} = -\frac{K_1}{2}\{\hat{P}_S, \hat{\rho}\} + K_2\hat{P}_S\hat{\rho}\hat{P}_S,$$

which, again by matching matrix elements, we yield,

$$\hat{\rho}(t) = \frac{1}{2}\begin{pmatrix} \exp\left(-(K_1 - K_2)t\right) & \exp(-K_1 t/2) \\ \exp(-K_1 t/2) & 1 \end{pmatrix}.$$

We see that the density matrix would not be trace-invariant with time. However, when the generation rates and dissipation rate are equal, as in, $K_1 = K_2$,, then our quantum states is preserved,

$$\boxed{K_1 = K_2 \quad \leftrightarrow \quad \mathrm{Tr}\hat{\rho}(t) = 1},$$

which implies that, in this case, an equal amount of excitons are being created and destroyed simultaneously.

IV.3 Connections to Spin Systems

In reality, the example of exciton generation is mathematically equivalent to a wide range of examples in real world to experiments. For example, let us consider a two-level spin-system in the $|\pm\mathbf{z}\rangle$ basis. There could be a physical processes that takes the system or energy out of the system by having the spins up stays decaying to nearby, other spins; the density matrix would still be in the form,

$$\hat{\rho}(t) = \frac{1}{2}\begin{pmatrix} \exp\left(-(K_1 - K_2)t\right) & \exp(-K_1 t/2) \\ \exp(-K_1 t/2) & 1 \end{pmatrix}$$
$$= \frac{\exp\left(-(K_1 - K_2)t\right)}{2}|+\mathbf{z}\rangle\langle+\mathbf{z}| + \frac{1}{2}|-\mathbf{z}\rangle\langle-\mathbf{z}| + \frac{\exp(-K_1 t/2)}{2}|+\mathbf{z}\rangle\langle-\mathbf{z}| + \frac{\exp(K_1 t/2)}{2}|-\mathbf{z}\rangle\langle+\mathbf{z}|$$

Recall again that the density matrix associated with a two-state system can be expressed in the form,

$$\hat{\rho} = \begin{pmatrix} \boxed{\rho_{11}} & \rho_{12} \\ \rho_{21} & \boxed{\rho_{22}} \end{pmatrix},$$

where the boxed diagonal term above indicates **population**, while the unboxed term above indicates the magnitude of **coherence** the system is in. Notice that we can further decompose the density matrix above as,

$$\hat{\rho} = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} = A\hat{\sigma}_z + (B\hat{\sigma}_x + C\hat{\sigma}_y),$$

where A corresponds to the diagonal elements while B corresponds to the off-diagonal elements. Naturally, we see that the difference $\hat{\rho}_{11} - \hat{\rho}_{22}$ corresponds to the population difference between the $|+\mathbf{z}\rangle$ and $|-\mathbf{z}\rangle$ eigenstates, or the states in the z-direction of the Bloch vector, and the off-diagonal elements correspond to the decay in the xy direction.

Comments

There are a few comments that we can make regarding the density matrix we saw above.

1. **Relation with spin decoherence time.** Matching the decay rate with the optical Bloch equations, we discover that, $K \propto 1/T_1, K \propto 1/2T_1 = 1/T_2$. The decay rates of the diagonal term is T_1 while the decay rates of off diagonal term is T_2. Recall that we have defined, for a density matrix,

   $$n \equiv \hat{\rho}_{11} - \hat{\rho}_{22}, \quad d \equiv \hat{\rho}_{12} - \hat{\rho}_{21},$$

   the parameters T_1 and T_2 are defined as, The time T_1 is the time constant of the decay rate of the population when a thermal bath is present,

   $$\dot{n} = \dot{\rho}_{ee} - \dot{\rho}_{gg} = -\underbrace{\frac{1}{T_1}}_{\text{time constant of time-decay}} (n - n_0),$$

   where n_0 is the population inversion during thermal equilibrium, and

   $$\dot{d} = d\left(i\omega_0 - \frac{1}{T_2}\right).$$

   This is consistent with the T_1 and T_2 that we have defined in the Bloch equations.

2. **Magnitude of spin decoherence times.** T_1 and T_2 are correlated through the following equation.

Theorem 3.7: T_1 and T_2 Decoherence Tines

If there are no excess dephasing processes that decays the off-diagonal terms[a] ($T_2^* \to \infty$), nor are there additional generation terms, the T_1 and T_2 times are related by the equation,

$$T_2 = 2T_1.$$

[a] Meaning that $K = G$ in the Lindblad equation.

The decay of the population from $|S\rangle$ causes decoherence between the $|S\rangle$ and $|T_0\rangle$ states. In practice, because there could be other excess dephasing process that decays the off-diagonal terms, we see,

$$T_2 \leq 2T_1.$$

In fact, in general, two-level systems will obey the identity,

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$