

11. Quantum-classical treatment of the two-level system

In chapter 10, we considered the full quantum theory of molecule-radiation interaction, and in chapter 12 we will consider the full quantum-classical theory, which treats the electromagnetic field as a time-dependent perturbation. Usually, one-photon spectroscopic techniques are resonant, that is the photon energy corresponds very nearly to a molecular energy level difference. In that case, the system can be treated as a two-level system, leading to great simplifications and a convenient geometrical visualization. The resulting representation of quantum and classical models for system-field interactions is much simpler than in the full case, and we consider such two-level models in this section. Applications range from absorption spectroscopy to NMR (although there the electric dipole must be replaced by a magnetic dipole, see ch. 9).

11.1 The Bloch equations

At the end of section 3, we considered a two-level system interacting with a single oscillator, and saw that the oscillator can induce dephasing. In the limit of many oscillators, this dephasing can be very complete and is characterized by decay times T_1 and T_2 for the diagonal and off-diagonal elements, respectively. (Actually, every single matrix element has its own timescale in real life, but for a two-level system, the diagonal elements are connected by $\text{Tr}\{\rho\}=1$ and so have only one common lifetime T_1 , and likewise the hermitean property and phase randomization upon ensemble averaging discussed in section 3.2 results in only one timescale T_2 for the real and imaginary parts of the one independent off-diagonal matrix element.)

There are two kinds of oscillators that a two-level system can couple to: the radiation field, and other systems which induce dephasing. We saw a simple but exact analytical example in section 3.6, and the full quantum treatment for many-level systems in section 10. In this section we will treat the radiation classically, and the dephasing *ad hoc* by simply introducing lifetimes T_1 and T_2 into the equations. This treatment results in the Bloch equation, which provide a nice approximate solution in many cases.

The quantum-classical two-level system approximation consists of replacing eq. 10-17 by

$$H = H_0 - \mu \varepsilon_0 \cos \omega t. \quad 11-1$$

where $\{|0\rangle, |1\rangle\}$ are the eigenstates of the two-level systems, $H_0 = \hbar(|0\rangle \omega_0 \langle 0| + |1\rangle \omega_1 \langle 1|)$ is the Hamiltonian of the two-level system, μ is the dipole moment (now a number), and $\varepsilon_0 \cos \omega t$ is the classical field. An arbitrary state of the system can be expanded as

$$|\Psi\rangle = c_0(t)|0\rangle + c_1(t)|1\rangle. \quad 11-2$$

Inserting into the time-dependent Schrödinger equation

$$H|\Psi\rangle = i\hbar \frac{\partial}{\partial t} \Psi \quad 11-3$$

we obtain

$$(H_0 - \mu \varepsilon_0 \cos \omega t)\{c_0|0\rangle + c_1|1\rangle\} = i\hbar\{\dot{c}_0(t)|0\rangle + \dot{c}_1(t)|1\rangle\} \quad 11-4$$

and taking matrix elements

$$\begin{aligned} \dot{c}_0 &= i\{R \cos \omega t c_1 - \omega_0 c_0\} \\ \dot{c}_1 &= i\{R \cos \omega t c_0 - \omega_1 c_1\} \end{aligned}, \quad R = \frac{\mu_{01} \varepsilon_0}{\hbar}. \quad 11-5$$

As long as the system remains in a pure state, its reduced density matrix is given by

$$\begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix} = \begin{pmatrix} c_0 c_0^* & c_0 c_1^* \\ c_1 c_0^* & c_1 c_1^* \end{pmatrix} \quad 11-6$$

In order to arrive at a geometrical interpretation of the absorption and emission process, we define three new quantities s_i which are constructed to have the same symmetry as the Pauli matrices of chapters 3 and 5:

$$s_1(t) = c_0 c_1^* + c_0^* c_1 \quad 11-7a$$

$$s_2(t) = -i(c_0 c_1^* - c_0^* c_1) \quad 11-7b$$

$$s_3(t) = |c_1|^2 - |c_0|^2. \quad 11-7c$$

The first two of these correspond to σ_x and σ_y ; they are nonzero while the two-level system interacts with the field or decays from a coherent state after interacting with the field. They describe the off-diagonal matrix elements of the density matrix 11-6. The third is a measure of the population difference with the symmetry of σ_z . It equals -1 in the ground state of the TLS and +1 in the excited state. It describes the diagonal elements of the density matrix in eq. 11-6. Note that the density matrix can be uniquely reconstructed from eq. 11-7 because hermiticity and unit trace imply that there are only three independent parameters in eq. 11-6 (one diagonal element and one complex off-diagonal matrix element). The utility of the s_i is that the 3-vector \mathbf{s} is a unit vector whose magnitude is conserved upon interaction with the radiation field because the norm of $|\Psi\rangle$ is conserved. (Note that the magnitude may not be conserved if we allow for relaxation or dephasing because of averaging over many two-level system; this will be discussed further on.) The conservation of norm follows from

$$\begin{aligned} |s_1|^2 + |s_2|^2 + |s_3|^2 &= 2|c_0|^2|c_1|^2 + c_0^2 c_1^{*2} + c_0^{*2} c_1^2 + \\ &\quad 2|c_0|^2|c_1|^2 - c_0^2 c_1^{*2} - c_0^{*2} c_1^2 + \\ &\quad |c_0|^4 + |c_1|^4 - 2|c_0|^2|c_1|^2 \\ &= (|c_0|^2 + |c_1|^2)^2 = 1 \end{aligned} \quad 11-8$$

Eqs. for the dynamics of \mathbf{s} analogous to eq. 11-5 are obtained by inserting 11-7 into 11-5; for example,

$$\begin{aligned} s_3 &= c_1 c_1^* - c_0 c_0^* \Rightarrow \\ \dot{s}_3 &= \dot{c}_1 c_1^* + c_1 \dot{c}_1^* - \dot{c}_0 c_0^* - c_0 \dot{c}_0^* \\ &= i\{R \cos \omega t c_0 - \omega_1 c_1\} c_1^* - i\{R \cos \omega t c_0^* - \omega_1 c_1^*\} c_1 - \\ &\quad i\{R \cos \omega t c_1 - \omega_0 c_0\} c_0^* + i\{R \cos \omega t c_1^* - \omega_0 c_0^*\} c_0 \\ &= -2R \cos \omega t s_2(t) \end{aligned} \quad 11-9$$

The full set of equations of motion for the vector \mathbf{s} is (with $\omega_{10} = \omega_1 - \omega_0$)

$$\left. \begin{aligned} \dot{s}_1 &= -\omega_{10} s_2 \\ \dot{s}_2 &= \omega_{10} s_1 + 2R \cos \omega t s_3 \\ \dot{s}_3 &= -2R \cos \omega t s_2 \end{aligned} \right\} \text{or } \dot{\mathbf{s}} = \mathbf{\Omega} \times \mathbf{s}. \quad 11-10$$

The vector $\mathbf{\Omega}$ is given by

$$\mathbf{\Omega} = \begin{pmatrix} -2R \cos \omega \\ 0 \\ \omega_{10} \end{pmatrix}. \quad 11-12$$

The $z = \#3$ component of $\mathbf{\Omega}$ corresponds to the splitting of the two level system, while the $x = \#1$ component provides the driving force on the vector via the external field. In an NMR

experiment, ω_{10} would be proportional to the applied magnetic field; in an optical absorption experiment, ω_{10} would be constant splitting of the molecular energy levels; in both cases, R is the Rabi frequency provided by the excitation coil or excitation laser. A comparison of eq. 11-10 with the rotation transformation of chapter 5 shows that \mathbf{s} rotates along the 1,2,3 axes when the field $\epsilon_0 \cos \omega t$ is turned on.

The above form is still not very convenient because \mathbf{s} rapidly rotates with frequency ω_{10} about the $z = \#3$ axis. Near resonance, when $\omega \approx \omega_{10}$, this rotation can be eliminated by transforming \mathbf{s} to a coordinate system rotating at frequency ω about the z axis by using

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} \cos \omega t & +\sin \omega t & 0 \\ -\sin \omega t & \cos \omega t & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} s_1 \\ s_2 \\ s_3 \end{pmatrix}. \quad 11-13$$

Taking the time derivatives of this equation, for example

$$\begin{aligned} \dot{u} &= -\omega \sin \omega t s_1 + \cos \omega t \dot{s}_1 + \omega \cos \omega t s_2 + \sin \omega t \dot{s}_2 \\ &= -\omega \sin \omega t s_1 - \omega_{10} \cos \omega t s_2 + \omega \cos \omega t s_2 + \omega_{10} \sin \omega t s_1 + 2R \sin \omega t \cos \omega t s_3 \\ &= -(\omega_{10} - \omega)v + R \sin 2\omega t s_3 \\ &\approx -(\omega_{10} - \omega)v \end{aligned}$$

or

$$\begin{aligned} \dot{v} &= -\omega \cos \omega t s_1 - \sin \omega t \dot{s}_1 - \omega \sin \omega t s_2 + \cos \omega t \dot{s}_2 \\ &= -\omega \cos \omega t s_1 + \omega_{10} \sin \omega t s_2 - \omega \sin \omega t s_2 + \omega_{10} \cos \omega t s_1 + 2R \cos^2 \omega t s_3 \\ &= (\omega_{10} - \omega)u + R w + R w \cos 2\omega t \\ &\approx (\omega_{10} - \omega)u + R w \end{aligned} \quad 11-14$$

we obtain the full equations of motion

$$\begin{aligned} \dot{u} &= -(\omega_{10} - \omega)v \\ \dot{v} &= (\omega_{10} - \omega)u + R w, \quad R = \mu \epsilon_0 / \hbar. \\ \dot{w} &= -R v \end{aligned} \quad 11-15$$

These are known as the Bloch equations. They can be used to propagate a single two-level system in the absence of relaxation. Note that we cannot do the transformation of eq. 11-13 at frequency ω_{10} , or the trigonometric terms in eq. 11-14 would not simplify according to eq. 11-10; it has to be done at frequency ω . The Bloch equations make an approximation beyond equation 11-10, the "rotating wave approximation." It consists of throwing out all rapidly oscillating terms at frequency 2ω because they are highly off-resonant. The Bloch equations can therefore not be used to describe highly off resonant phenomena such as the Raman spectroscopy described in chapter 12. Note that the electric field $\epsilon_0 \cos \omega t$ is sometimes defined in terms of its rms amplitude instead of the maximum amplitude, for instance when the Ansatz $\epsilon = \epsilon_{\text{rms}} e^{-i\omega t} + \text{c.c.}$ is used. Then a factor of 2 needs to be added to the formula for R.

Finally we add the relaxation terms, which arise because the system is dephased and relaxed by a bath as discussed in chapter 3. Adding exponential relaxation terms *ad hoc* (see section 11.3 for a summary of how to derive relaxation times), we have

$$\begin{aligned}
\dot{u} &= -(\omega_{10} - \omega)v & -\frac{u}{T_2} \\
\dot{v} &= (\omega_{10} - \omega)u + Rv & -\frac{v}{T_2} \\
\dot{w} &= & -Rv - \frac{(w - w_{eq})}{T_1}
\end{aligned}
\tag{11-16}$$

u and v represent the off-diagonal matrix elements of the two-level density matrix, which now can be impure; $w = s_3 = \rho_{11} - \rho_{00}$ (eq. 11-7) represents the population difference. w is allowed to decay exponentially to a thermal equilibrium value w_{eq} in time T_1 , while the off-diagonal elements decay to zero in time T_2 . As discussed above, for an ensemble-averaged two level system these are the only independent time scales if one assumes that the bath causes exponential decay. Because eq. 11-16 also applies to an incoherent or partially coherent density matrix (ensemble of two level systems), or to a two level system dephased by a bath (reduced density matrix, see chapter 3), the magnitude of the Bloch vector \mathbf{w} can be less than unity if the systems are not fully coherent. In terms of the density matrix in section 3.2, this happens because coherent off-diagonal matrix elements are added up randomly and cancel. Section 11.3 will sketch how the decay lifetimes are evaluated from the equation of motion of the reduced density matrix.

In vector form, the Bloch equation can be abbreviated as

$$\frac{d\mathbf{w}}{dt} = \boldsymbol{\Omega} \times \mathbf{w} - \frac{\mathbf{w} - \mathbf{w}_{eq}}{T_i} \quad \text{where } \boldsymbol{\Omega} = \begin{pmatrix} -R \\ 0 \\ \omega_{10} - \omega \end{pmatrix} \approx \begin{pmatrix} -R \\ 0 \\ 0 \end{pmatrix} \text{ at resonance.} \tag{11-17}$$

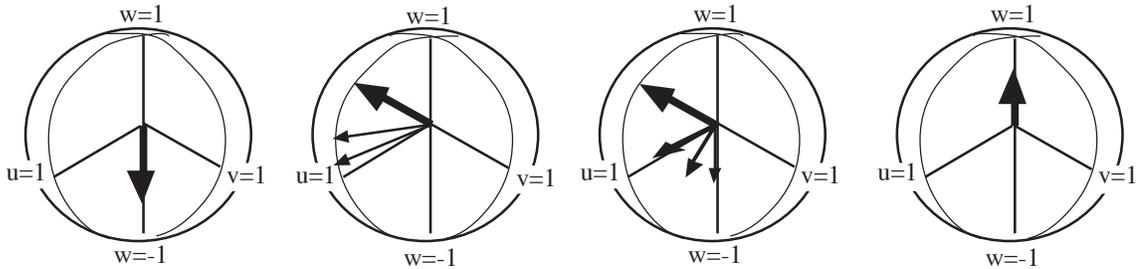


Fig. 11-1. Various cases for the Bloch vector discussed in 11.2. Left: Impure system at equilibrium, the Bloch vector $\mathbf{w} = (0,0,w_{eq})$ has no u and v components, and $w_{eq} > -1$. Middle left: the system has been excited by a $\pi/2$ pulse so $w=0$ exactly; if it is off-resonance and there is no relaxation, the \mathbf{w} vector will slowly rotate evolve in the u-v plane. Middle right: the system starts out in a coherent state in the u plane, and is relaxing back towards equilibrium, causing a shortening of the vector. Right: the system has been inverted by a π pulse; note that w_{invert} cannot exceed $|w_{eq}|$, so the π pulse does not create additional coherence.

11.2 Application examples of the Bloch equation

The utility of the vector picture is that it allows a geometrical interpretation of absorption and emission of radiation by a two-level system. In this section we briefly discuss some examples that illustrate the consequences of the Bloch equation. Fig. 11-1 illustrates the Bloch vector \mathbf{w} during various stages of evolution. \mathbf{w} moves **on** (or **within**, if we allow relaxation) the Bloch

unit sphere centered on the (u,v,w) axis-system because the Bloch equations are basically a rigid rotation, combined with damping, which may shorten the (u,v,w) vector.

1) Free propagation ($R = 0, T_{1,2} \rightarrow \infty$)

For an on-resonant system ($\omega_{10} - \omega = \Delta\omega = 0$ in eq. 11-16), $\dot{u} = \dot{v} = \dot{w} = 0$, and the Bloch vector undergoes no motion. Another important case occurs when the system has been excited (see 5) from $\mathbf{w} = (0,0,w_{eq})$ to the initial condition $\mathbf{w} = (0,v_{init}=w_{eq},0)$, and is then allowed to propagate freely. If $R \approx 0$ and the system is slightly off-resonance, eqs. 11-16 become

$$\dot{u} = -\Delta\omega v; \dot{v} = \Delta\omega u. \quad 11-18$$

The solution is $v = v_{init} \cos\Delta\omega t$ and $u = -v_{init} \sin\Delta\omega t$, so the vector rotates slowly in the u-v plane. Imagine that you had copies of similar systems in an environment where each had a slightly different ω_{10} . Such an environment is called an 'inhomogeneous' environment. In that case, different systems' Bloch vectors would rotate in the u-v plane at slightly different speeds. If one added them all up to obtain the average density matrix for the ensemble, the length of the Bloch vector would shrink. At a first glance, this shrinking looks like the 'homogeneous' dephasing and relaxation caused by $T_{1,2}$ in eq. 11-16, but in fact, inhomogeneous dephasing can be eliminated by pulse sequences (see 6).

2) Simple relaxation ($R = 0$)

At some finite temperature, the equilibrium value for the Bloch vector is $\mathbf{w}=(0,0,w_{eq})$, where w_{eq} is given by

$$w_{eq} = \rho_{11,eq} - \rho_{00,eq} = \frac{e^{-\hbar\omega_{10}/kT} - 1}{1 + e^{-\hbar\omega_{10}/kT}}$$

Now consider an initial condition ($0,0,w_0 > w_{eq}$), i.e. the system has been excited. If no field is applied so $R = \mu\mathcal{E}_0 / \hbar = 0$, inserting into eq. 11-16 and applying the boundary conditions yields

$$\dot{u} = \dot{v} = 0 \text{ always; } \dot{w} = \frac{-(w - w_{eq})}{T_1} \Rightarrow w = (w_0 - w_{eq})e^{-t/T_1} + w_{eq} \quad 11-19$$

The system relaxes back to equilibrium.

3) Steady state in applied field ($R=\text{const.}, t \rightarrow \infty$)

If a continuous field of given strength is applied to a TLS, eventually a steady state is reached where relaxation processes and excitation processes balance. Let the field $\mathcal{E}_0 \cos(\omega t)$ be applied continuously at resonance $\omega = \omega_0$. In steady state $\dot{u} = \dot{v} = \dot{w} = 0$, so

$$u = 0; v = \frac{\mu\mathcal{E}_0 T_2 w}{\hbar}; w = -\frac{\mu\mathcal{E}_0 T_1 v}{\hbar} + w_{eq}; \quad 11-20$$

combining the two equations for v and w,

$$w = w_{eq} \frac{1}{1 + \frac{\mu^2 \mathcal{E}_0^2 T_1 T_2}{\hbar^2}}. \quad 11-21$$

Thus, even with the strongest pump field, $w=0$ is the highest possible value that the population difference can achieve. A population inversion cannot be attained by any strength continuous field in a two level system. Saturation occurs when both terms in the denominator of eq. 11-21 are equal, or

$$I_{sat} = \frac{c}{4\pi} \mathcal{E}_0^2 = \frac{c}{4\pi} \frac{\hbar^2}{\mu^2 T_1 T_2} = \frac{\hbar^2 c}{4\pi \mu^2 T_1 T_2}. \quad 11-22$$

4) π -pulse

Consider a resonant pulse of duration $t_\pi = \pi\hbar / 2\mu\epsilon_0$ with large enough field so that relaxation is negligible during the pulse ($T_1, T_2 \gg t_\pi$). Let the system be in the state $\mathbf{w} = (0,0,-1)$ initially; this corresponds to a system completely in the ground state, or $T = 0$ K. In that case the Bloch equations become

$$\dot{u} = 0 \quad ; \quad \dot{v} = \frac{\mu\epsilon_0}{\hbar} w \quad ; \quad \dot{w} = -\frac{\mu\epsilon_0}{\hbar} v, \quad 11-23$$

with the general solution

$$w = -\cos\left(\frac{\mu\epsilon_0}{\hbar} t\right) \quad v = -\sin\left(\frac{\mu\epsilon_0}{\hbar} t\right). \quad 11-24$$

The \mathbf{w} vector, which initially points along the negative w axis if the system is at equilibrium, rotates in the v - w plane, and at $t_\pi = \pi\hbar / 2\mu\epsilon_0$ $w=1$ and $v=0$: the population has been completely inverted. The π pulse has rotated the vector \mathbf{w} by 180° . If the pulse is now switched off the population will relax according to example 1). Note that if $w = w_{eq} > -1$ initially, the same dynamics ensues, but with a shorter vector, corresponding to a less pure density matrix. π -pulses cannot magically improve purity. For example, in NMR experiments, w_{eq} is almost 0 because $\hbar\omega_{10} \ll kT$. After a π pulse, the population will be inverted to $-w_{eq}$, so only a very small population inversion can be achieved. Conventional NMR experiments are not very sensitive.

5) $\pi/2$ pulse and free induction decay

A on-resonant $\pi/2$ pulse of duration $t_{\pi/2} = t_\pi / 2$ leaves \mathbf{w} in the u - v plane. Inserting $t_{\pi/2}$ into eq. 11-24, one obtains $w=0$ and $v=-1$. Afterwards, it decays back to zero as

$$\dot{v} = -\frac{v}{T_2} \quad \dot{w} = \frac{-(w - w_{eq})}{T_1} \Rightarrow v = e^{-\frac{t}{T_2}} \quad w = (w - w_{eq})e^{-\frac{t}{T_1}} + w_{eq} \quad 11-25$$

In the space frame, this means s_1 and s_2 are precessing at frequency ω while decaying to zero. This leads to a decaying emission modulated at ω_{10} , which is the signal typically picked up in a simple NMR experiment.

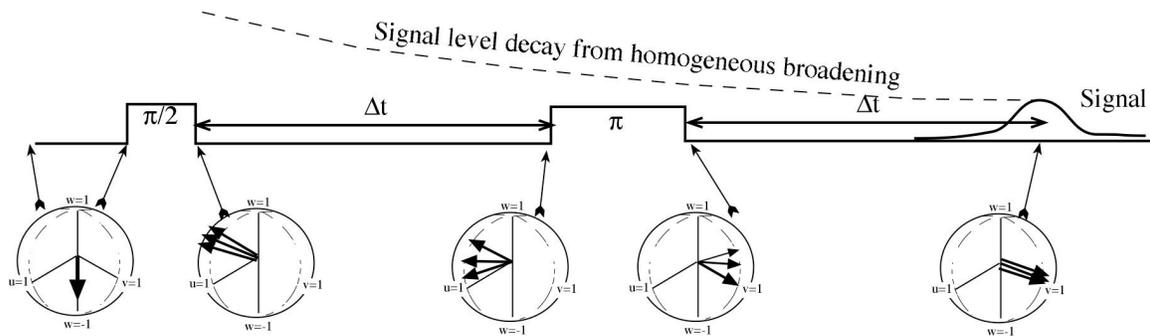


Fig 11-2. Photon echo experiment. The $\pi/2$ pulse excites three systems. They evolve freely during Δt in an inhomogeneous environment, causing collective coherence to be lost (shorter sum of arrows than if they were all 3 still lined up). At the same time, they individually dephase, causing individual coherence to be lost (shorter individual arrows and signal decay from homogeneous broadening). A π pulse rotates them by 180° , after which the three systems line up again. At this point of maximum phase coherence, their dipoles act like a giant dipole, and a signal $N|\mu|^2$ is emitted instead of a weaker signal $N|\mu|^2$. Population relaxation (T_1) is indicated by the dashed line. It corresponds to a shortening of each arrow, as individual molecules homogeneously relax towards equilibrium. As a result, the photon echo gets smaller as Δt is increased, even if the pulse sequence is perfect.

5) Photon echoes and inhomogeneous broadening

Now consider applying processes 4) and 3) in a sequence in the absence of dephasing or relaxation. The $\pi/2$ pulse will move the \mathbf{w} vector from its equilibrium position along the negative w -axis into the u - v plane. After a delay Δt_1 , during which \mathbf{w} slowly rotates in the u - v plane if ω is not exactly on resonance with ω_{10} , the π pulse will then flip the vector by 180 degrees, and it will propagate in time-reversal as a result. After another period $\Delta t_2 = \Delta t_1$, the vector \mathbf{w} will have slowly rotated back exactly 180° from where the $\pi/2$ pulse left it. (In the presence of relaxation, the vector \mathbf{w} will also spin downward to increase its negative $w = \#3$ -axis component; the time reversal applies only to the field-driven dynamics; it does not apply to the relaxation process, which continues during the second time period Δt_2 .)

This property allows one to eliminate a special kind of dephasing or line-broadening. So far, when we considered an ensemble of two-level systems by averaging their density matrices, it was assumed that all of these systems are identical copies of one another, except for random phases of the off-diagonal elements (ch. 3) which led to T_1/T_2 population decay and homogeneous dephasing. In reality, nominally identical copies of a system may in fact have properties that are distinguishable on the time scale of a measurement. Examples would be spins in a glass, which are in slightly different environments, or molecules flying at different speeds in a gas cell. The different transition frequencies of spins in the glass will lead to chemical shift broadening (among other mechanisms), and the different velocities of the molecules lead to Doppler broadening. These *inhomogeneous broadening* mechanisms are different from the *homogeneous broadening* mechanisms, which apply equally to all molecules during the measurement process. An example of a homogeneous process includes the pure fluorescence lifetime of a molecule discussed in chapter 10. Homogeneous broadening processes are often very well described by an exponential decay and the corresponding Lorentzian line shape; inhomogeneous processes can have very different lineshapes, from the complex lineshapes of spins in a solid matrix to the Gaussian shape of a Doppler-broadened line.

Because of the time-reversal property, photon echo experiments are insensitive to inhomogeneous broadening, as illustrated in fig. 11-2. Rather than averaging the \mathbf{w} for different two-level systems together, we consider them separately. The $\pi/2$ - Δt_1 - π - Δt_2 sequence first brings all TLS into the u - v plane. Because of inhomogeneous broadening, not all TLS are exactly in resonance, and they fan out on a time scale $T_2^* \sim \Delta\omega_{\text{inhomogeneous}}^{-1}$. The π pulse then reverses the evolution of all TLS (but not their homogeneous relaxation); after a time Δt_2 , all spins line up again 180° from where they started after the $\pi/2$ pulse (less some decay towards the $\#3$ -axis and shortening due to homogeneous decay of each individual spin). This in-phase addition leads to the emission of a pulse if the TLS have a dipole moment because the dipoles are once again coherent and

$$\left| \sum_i \bar{\mu}_i(\Delta t_1 + \Delta t_2) \right|^2 \approx N^2 |\bar{\mu}_i|^2 \gg \left| \sum_i \bar{\mu}_i(t \neq \Delta t_1 + \Delta t_2) \right|^2 \approx N |\bar{\mu}_i|^2 \quad 11-26$$

as discussed in section 3.2 for homogeneous broadening. As a result, any decay of the emission intensity at time $\Delta t_1 + \Delta t_2$ is not due to inhomogeneous broadening, but only to homogeneous broadening. If the inhomogeneous broadening is approximately described by an exponential lifetime, we can write

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{T_2^*} \quad 11-27$$

where T_2 is now the overall dephasing time of off-diagonal density matrix elements, T_2' is the homogeneous dephasing time which until now accounted for all of T_2 , and T_2^* is the inhomogeneous contribution to the dephasing time. Equation 11-27 should be taken with a large

grain of salt, however: most often the inhomogeneous process is not described by an exponential line shape, and adding up exponential decay rates as in eq. 11-27 is at best approximate. Finally, it should be noted that even homogeneous processes do not always have a Lorentzian line shape. For example, molecules fly through a laser beam in a finite time Δt , the maximum measurement time. This is a homogeneous process and applies to all molecules equally. Its temporal profile is not exponential however, but rather has a 'pillbox' shape. In the frequency domain this shape corresponds to a sinc-function profile with ripples in the wings of the line profile.

Photon echo experiments can tell us how much of a linewidth is due to phenomena that occur faster than or determined by the measurement process, and are therefore equally shared by all molecules, vs. how much of the linewidth is due to broadening because different molecules have different spectra on the time scale of the measurement. This information is not available by just scanning across the line shape of an ensemble of molecules: for example one cannot tell how much of the width is due to spontaneous fluorescence, and how much is due to matrix effects on an ensemble of molecules absorbed into a low-temperature rare gas matrix (assuming these are the only contributing effects in this example). A photon echo experiment will map out a decay along Δt_2 which corresponds to the fluorescence linewidth only. The rest of the width is due to the matrix which causes different molecules to fluoresce at slightly different wavelengths.

A final phenomenon due to inhomogeneous broadening worth noting: decreasing the time scale of an inhomogeneous process, which normally leads to even broader lines, can actually narrow lines if the process responsible for inhomogeneous broadening becomes faster than the inhomogeneous width T_2^{*-1} . For example, consider a spin 1/2 in two different environments with different chemical shifts in an NMR spectrum. For example, a molecule might have two isomers A and B, and a given spin might have different chemical shifts ω_A and ω_B . The splitting $\Delta\omega = \omega_A - \omega_B$ between the NMR peaks is effectively an inhomogeneous broadening, in contrast to the linewidth $\delta\omega \ll \Delta\omega$ of the individual NMR peaks. If the interconversion rate k of the reaction $A \rightleftharpoons B$ approaches $\Delta\omega$, the lines initially broaden, but finally coalesce into a single line of width

$\delta\omega$, centered at $(\omega_A + \omega_B)/2$, as $k \rightarrow \infty$: the inhomogeneous process is now so fast that the spin simply exists in an average environment on the time scale $\Delta\omega^{-1}$ of the experiment, and only the homogeneous broadening is observed. This narrowing is known as "motional narrowing." Two other examples from molecular spectroscopy: over a certain pressure range, the absorption linewidth actually decreases with increasing pressure; this occurs because the collision rate exceeds the absorption frequency at high pressure and is known as Dicke narrowing. At high vibrational energy, different vibrational states have different rotational constants, yet above a certain energy the rotational constants all tend to become the same because the vibrational mixing rate is exceeding the rotation rate: as a result, only a single rotational constant is observed for all the vibrational states.

11.3 Redfield equations for the two-level system

The derivation of lifetimes T_1 and T_2 from the reduced density matrix equation of motion in chapter 3 is rather lengthy (see Carrington, *Magnetic Resonance*, or Schatz & Ratner, *Introduction to Quantum Mechanics*). It also relies on a series of assumptions which are not necessarily always justified, as was the case with the Golden Rule. Nonetheless, a sketch of the derivation for a two-level system coupled to a bath of harmonic oscillators can be useful to guide those who wish to look at the full multi-page derivations.

We start with the exact perturbation equation for the density matrix from chapter 3,

$$\dot{\rho}_I^{\text{sys}}(t) = R(t)\rho_I^{\text{sys}}(t), \quad R = \dot{U}U^{-1}, \quad U = 1 + U^{(1)} + \frac{1}{2!}U^{(2)} + \dots \quad 11-28$$

If we neglect the fact that U and its time derivative do not necessarily commute (assumption 1), and we neglect the linear term which can only shift energy levels, not broaden them (assumption 2), we can write

$$R(t) \approx \frac{\partial \ln U}{\partial t} \approx \frac{1}{2}\dot{U}^{(2)} = -\int_0^t dt' \text{Tr}_b \{ \mathcal{L}_I(t) \mathcal{L}_I(t') \rho_{eq}^b \} \quad 11-29$$

The first approximate equality follows from the middle equation in 11-28, as can be seen by taking the derivative, and the second approximate equality follows by neglecting the $U^{(1)}$ term. The integral in the final equality comes from the second order double-integral in eq. 3-45 of chapter 3; only one integral is left because of the differentiation $\partial/\partial t$. Explicitly, the commutators act on ρ as follows (the $_$ indicate where ρ is to be inserted):

$$\begin{aligned} \dot{\rho}_I^{\text{sys}}(t) = & \int_0^t dt' \text{Tr}_b \{ V_I(t) V_I(t') \rho_{eq}^b - V_I(t) _ \rho_{eq}^b V_I(t') - \\ & V_I(t') \rho_{eq}^b _ V_I(t) + _ \rho_{eq}^b V_I(t') V_I(t') \} \rho_I^{\text{sys}} \end{aligned} \quad 11-30$$

Next, we make assumption 3, that the two-level system is coupled to the bath of harmonic oscillators via a response linear in the bath coordinates $q_i = a_i^\dagger + a_i$. This assumption follows from Taylor expansion of the interaction Hamiltonian between system and bath, and implies that the model can be correct only for weak coupling (in the “linear response” limit). This is not much of an assumption once we have decided to truncate the perturbation series at $U^{(2)}$ (assumption 4) because the expansion can be valid at reasonably long times only if the coupling is weak. Our Hamiltonian thus becomes

$$\begin{aligned} H &= H_0 + V(t) \\ &= \omega_0 |0\rangle\langle 0| + \omega_1 |1\rangle\langle 1| + \sum_q \hbar \omega_q (n_q + 1/2) + \sum_q \lambda_q(t) |1\rangle\langle 0| a_q^\dagger + \lambda_q^*(t) |0\rangle\langle 1| a_q \end{aligned} \quad 11-31$$

in analogy to eq. 3-30. The coupling λ is allowed to depend on time so coupling of “solvent” modes to the two-level system can fluctuate. Inserting this coupling into eq. 11-30 leads to terms such as

$$\begin{aligned} (\dot{\rho}_I^{\text{sys}}(t))_{01} = & \langle 0 | \dot{\rho}_I^{\text{sys}}(t) | 1 \rangle = \langle 0 | \int_0^t dt' \text{Tr}_b \{ e^{iH_0 t'/\hbar} |0\rangle\langle 1| \lambda_q^*(t') a_q e^{-iH_0 t'/\hbar} \\ & \times |1\rangle\langle 0| e^{iH_0 t'/\hbar} \lambda_q(t') a_q^\dagger e^{-iH_0 t'/\hbar} \rho_{eq}^b \} \rho_I^{\text{sys}}(t) | 1 \rangle + \dots \end{aligned} \quad 11-32$$

The trace over the time-dependent factors is proportional a correlation function of the bath-system coupling, $C(t, t') = \text{Tr}_b \{ V_I(t) V_I(t') \}$. This correlation function is symmetric, so integration from 0 to t is simply half the integral from $-t$ to t . However, the correlation integral is not quite like the Fourier transform of the dipole moment correlation in chapter B: the integration has been cut off at t .

We now make the 5th assumption that $C(t, t') = C(t')$ does not depend on time (that is, the bath remains in quasi-equilibrium and does not itself relax; this means the bath must be large compared to the system). The 6th and final assumption is that the correlation function decays rapidly in time $t' < t_m$, a “molecular” time scale of the system-bath coupling; that means that modes of the bath coupled to the system are not correlated to one another directly or via the system. For example, a solvent where molecules move in and out of the solvation shell around a spin diffuses fast enough compared to the linewidth of the spin (typically 1 Hz for a proton in NMR) so this assumption is satisfied. It is *not* satisfied in a typical femtosecond coherence experiment, and one would not expect a simple exponential decay there.

This assumption allows us to extend the integration in eq. 11-32 from t to ∞ , turning eq. 11-32 and its analogs for multi-level systems into a Fourier transform relationship. We can rewrite 11-32 in general as

$$(\rho_I^{\text{sys}}(t))_{ii'} = \sum_{j,j'} R_{ii';jj'}(\rho_I^{\text{sys}}(t))_{jj'}, \quad R_{ii';jj'}(\Delta\omega) \sim \int_0^\infty dt' e^{i\Delta\omega_{ii';jj'} t'} C(t'). \quad 11-33$$

This set of first-order coupled linear differential equations is known as the Redfield equations. If the appropriate coefficients of R have real parts when evaluated at $\Delta\omega$ (i.e. if the frequencies are on resonance), for example if $-\text{Re}(R_{01;01}) = k_2 = 1/T_2$ or $-\text{Re}(R_{11;11}) = k_1 = 1/T_1$ for the two level system in eq. 11-32, then the reduced density matrix elements will decay exponentially.

11.4 Einstein coefficients

In chapter 10, we saw that emission and absorption coefficients of a molecule are not independent from one another. This can be derived from purely kinetic and thermodynamic considerations, without the detailed first-principles quantum mechanics of the last chapter. We do it here for the quantum-classical two-level system. Before we do this, we must first derive the properties of thermal radiation. Then we will consider a particularly simple type of master equation, first derived by Einstein; it is the simplest example of Redfield-type equations.

11.4.1 Thermal radiation

Consider a cavity at thermal equilibrium, a so-called 'black-body' cavity. The energy above the zero point of the radiation in such a cavity is given by the formula derived in ch. 2,

$$U(\{n_k\}) = \sum_k \hbar\omega_k n_k, \quad 11-33$$

The partition function corresponding to this Hamiltonian is given by

$$\begin{aligned} Q &= \sum_{\{n_k\}} e^{-\frac{U(\{n_k\})}{kT}} \\ &= \sum_{\{n_k\}} e^{-\sum_k \frac{\hbar\omega_k n_k}{kT}} \\ &= \prod_k \sum_n e^{-\frac{\hbar\omega_k n}{kT}}, \text{ and using } \sum x^k = \frac{1}{1-x} \\ &= \prod_k \left(1 - e^{-\frac{\hbar\omega_k}{kT}} \right)^{-1} \end{aligned} \quad 11-34$$

where $\{n_k\}$ indicates a summation over all combinations $\{n_1, n_2, \dots\}$ of photon states of the field. The simplification in the third line is possible because all possible values of n occur for each degree of freedom k in the exponential. Once the partition function is known, we can calculate the average energy

$$\begin{aligned}
\bar{U} &= \frac{1}{Q} \sum_{\{n_k\}} U(\{n_k\}) e^{-\frac{U(\{n_k\})}{kT}} \\
&= kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \\
&= \sum_k \frac{\hbar \omega_k}{e^{\frac{\hbar \omega_k}{kT}} - 1}
\end{aligned} \tag{11-35}$$

Because the gap between successive frequencies ω is small even in a very small cavity, we can turn the summation into an integral. (In an infinitely large cavity, the integral would be exact). This means that instead of summing over state number, we must integrate over it. The number of states in an interval dk and solid angle $d\Omega$ was given in equation 10-20 as

$$dN = 2 \frac{V k^2 dk d\Omega}{\pi^3}. \tag{11-36}$$

Note that eq. 11-36 includes an additional factor of 2 for the two polarizations, which were summed explicitly in eq. 10-24 of that chapter. We can include it here directly because the thermal radiation field is isotropic. Integrating over the solid angle octant of positive k_i yields

$$dN = \frac{V k^2 dk}{\pi^2} = \frac{V \omega^2 d\omega}{\pi^2 c^3}. \tag{11-37}$$

Replacing the summation by the integration now yields

$$\bar{U} = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} \tag{11-38}$$

The energy density per unit frequency $\frac{1}{V} \frac{\partial \bar{U}}{\partial \omega}$ of thermal radiation is thus given by

$$u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\frac{\hbar \omega}{kT}} - 1}. \tag{11-39}$$

This is the famous Planck law for black-body radiation, which ushered in the era of quantum mechanics.

11.4.2 Einstein A and B coefficients

Consider a simple kinetic model involving a two-level system in a black body cavity at thermal equilibrium:

$$\begin{aligned}
\frac{d\rho_{00}}{dt} &= -B_{01}u(\omega)\rho_{00} + B_{10}u(\omega)\rho_{11} + A_{10}\rho_{11} \\
\frac{d\rho_{11}}{dt} &= B_{01}u(\omega)\rho_{00} - B_{10}u(\omega)\rho_{11} - A_{10}\rho_{11}
\end{aligned} \tag{11-40}$$

Here ρ_{ii} are the system populations and $\rho(\omega, T)$ is the radiation density. B_{01} is the transition rate per unit radiation density from 0 to 1, and B_{10} is the rate for the reverse process. In addition, the upper state can undergo spontaneous emission, which has a rate $A = \tau_{sp}^{-1}$. At thermal equilibrium, the following must be satisfied in addition:

$$\frac{\rho_{11}}{\rho_{00}} = \frac{g_1}{g_0} e^{-\frac{\hbar\omega}{kT}}, \quad \dot{\rho}_{00} = 0, \quad \dot{\rho}_{11} = 0. \quad 11-41$$

In this expression the g_i are the degeneracies of the two states, in this case both 1 (but we will keep them for the more general case). We can now set eq. 11-40 to zero, bring B_{01} to the left side, and insert eq. 11-41:

$$B_{01} = \frac{\rho_{11}}{\rho_{00}} \left(B_{10} + \frac{A_{10}}{\rho(\omega)} \right) = \frac{g_1}{g_0} e^{-\frac{\hbar\omega}{kT}} \left(B_{10} + \frac{A_{10}}{\rho(\omega)} \right) \quad 11-42$$

Finally, we solve eq. 11-42 for $\rho(\omega, T)$ and compare to eq. 11-39 to yield

$$\rho(\omega) = \frac{A_{10}}{B_{10}} \frac{1}{\frac{g_0 B_{01}}{g_1 B_{10}} e^{-\frac{\hbar\omega}{kT}} - 1} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1} \quad 11-43$$

Comparison of the two sides of this equation immediately yields

$$B_{10} = \frac{g_1}{g_0} B_{01} \quad \text{and} \quad A_{10} = \frac{\hbar\omega^3}{\pi^2 c^3} B_{10}. \quad 11-44$$

This is Einstein's famous result that shows that the spontaneous emission rate A_{10} is not independent of the absorption rate, and that the absorption rate is the same as the stimulated emission rate. An analogous result comparing spontaneous emission and absorption by a polarized laser was derived in section 10 exactly. In eq. 11-40, as in eq. 11-15, the homogeneous relaxation process due to A_{10} was of course put in *ad hoc*, not derived. Nonetheless, if one assumes that such a relaxation process exists, one can relate it to the absorption process without the use of second quantization (except for eq. 11-33, of course!). Such theorems relating dissipative processes (here absorption) to fluctuations (here spontaneous emission) are common in statistical mechanics, and are referred to collectively as fluctuation-dissipation theorems. Another example would be the matrix fluctuation-dissipation theorem relating energy level fluctuations to vibrational relaxation rates.

The above derivation may give the impression that one needs black body radiation to obtain $B_{10}=B_{01}$. Instead, if we calculate the time derivative of $w = \rho_{11} - \rho_{00}$, we obtain

$$\frac{dw}{dt} = 2B_{01}u(\omega)\rho_{00} - 2B_{10}u(\omega)\rho_{11} - 2A_{10}\rho_{11}. \quad 11-45$$

From the continuous wave Bloch equations on resonance ($\omega_{10} - \omega = 0$), we know that the first two terms, in absence of relaxation, should relax w to 0 (i.e. the laser pumps the system until the ground and excited state populations are equal). This can only happen in eq. 11-46 if $B_{10}=B_{01}=B$, yielding

$$\begin{aligned} \frac{dw}{dt} &= -2Bu(\omega)(\rho_{11} - \rho_{00}) - 2A_{10}\rho_{11} \\ &= -2Bu(\omega)w - 2A_{10}\rho_{11} \end{aligned} \quad 11-46$$

The first term will make w relax towards 0 (maximum continuous wave excitation, half the population is in the excited state), while the last term will make it relax towards -1 (because it relaxes ρ_{11} to 0, and $w = \rho_{11} - \rho_{00} = 2\rho_{11} - 1$).