LECTURE 11

In this lecture, we will focus on configurations where the angular frequency of the light is close to some transition frequency of the medium. In particular, we will start with a brief outline of how the non-resonant susceptibilities may be modified in such a way that weakly resonant interactions can be taken into account. Having formulated the susceptibilities at weakly resonant interaction, we will proceed with formulating a non-perturbative approach of calculation of the polarization density of the medium. For the two-level system, this results in the Bloch equations governing resonant interaction between light and matter.

The outline for this lecture is:

- Singularities of the non-resonant susceptibilities
- Alternatives to perturbation analysis of the polarization density
- Relaxation of the medium
- The two-level system and the Bloch equation
- The resulting polarization density of the medium at resonance

Singularities of non-resonant susceptibilities

In the theory described so far in this course, all interactions have for simplicity been considered as non-resonant. The explicit forms of the susceptibilities, in terms of the electric dipole moments and transition frequencies of the molecules, have been obtained in lecture six, of the forms

$$\chi^{(1)}_{\mu\alpha}(-\omega;\omega) \sim \frac{r^{\mu}_{ab}r^{\alpha}_{ba}}{\Omega_{ba}-\omega} + \{\text{similar terms}\}, \qquad \text{[B. \& C. (4.58)]}$$

$$\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma;\omega_1,\omega_2) \sim \frac{r^{\mu}_{ab}r^{\alpha}_{bc}r^{\beta}_{ca}}{(\Omega_{ba}-\omega_1-\omega_2)(\Omega_{ca}-\omega_2)} + \{\text{similar terms}\}, \qquad \text{[B. \& C. (4.63)]}$$

$$\chi^{(3)}_{\mu\alpha\beta\gamma}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) \sim \frac{r^{\mu}_{ab}r^{\alpha}_{bc}r^{\beta}_{cd}r^{\gamma}_{da}}{(\Omega_{ba}-\omega_1-\omega_2-\omega_3)(\Omega_{ca}-\omega_2-\omega_3)(\Omega_{da}-\omega_3)} + \{\text{similar terms}\}, \qquad \text{[B. \& C. (4.64)]}$$

$$\vdots$$

To recapitulate, these forms have all been derived under the assumption that the Hamiltonian (which is the general operator which describes the state of the system) consist only of a thermal equilibrium part and an interaction part (in the electric dipolar approximation), of the form

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{I}}(t).$$

This is a form which clearly does not contain any term related to relaxation effects of the medium, that is to say, it does not contain any term describing any energy flow into thermal heat. As long as we consider the interaction part of the Hamiltonian to be sufficiently strong compared to any relaxation effect of the medium, this is a valid approximation.

However, the problem with the non-resonant forms of the susceptibilities clearly comes into light when we consider an angular frequency of the light that is close to a transition frequency of the system, since for the first order susceptibility,

$$\chi^{(1)}_{\mu\alpha}(-\omega;\omega) \to \infty, \quad \text{when } \omega \to \Omega_{ba},$$

or for the second order susceptibility,

$$\chi^{(2)}_{\mu\alpha\beta}(-\omega;\omega_1,\omega_2) \to \infty, \quad \text{when } \omega_1+\omega_2 \to \Omega_{ba} \text{ or } \omega_2 \to \Omega_{ca}.$$

This clearly non-physical behaviour is a consequence of that the denominators of the rational expressions for the susceptibilities have singularities at the resonances, and the aim with this lecture is to show how these singularities can be removed.

Modification of the Hamiltonian for resonant interaction

Whenever we have to consider relaxation effects of the medium, as in the case of resonant interactions, the Hamiltonian should be modified to

$$\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{I}}(t) + \hat{H}_{\mathrm{R}}, \tag{1}$$

where, as previously, $\hat{H}_0$ is the Hamiltonian in the absence of external forces, $\hat{H}_{\mathrm{I}}(t) = -\hat{Q}_\alpha E_\alpha(\mathbf{r},t)$ is the interaction Hamiltonian (here taken in the Schrödinger picture, as described in lecture four), being linear in the applied electric field of the light, and where the new term $\hat{H}_{\mathrm{R}}$ describes the various relaxation processes that brings the system into the thermal equilibrium whenever external forces are absent. The state of the system (atom, molecule, or general ensemble) is then conveniently described by the density operator formalism, from which we can obtain macroscopically observable parameters of the medium, such as the electric polarization density (as frequently encountered in this course), the magnetization of the medium, current densities, etc.

The form (1) of the Hamiltonian is now to be analysed by means of the equation of motion of the density operator $\hat{\rho}$,

$$i\hbar\frac{d\hat{\rho}}{dt} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} = [\hat{H},\hat{\rho}], \tag{2}$$

and depending on the setup, this equation may be solved by means of perturbation analysis (for non-resonant and weakly resonant interactions), or by means of non-perturbative approaches, such as the Bloch equations (for strongly resonant interactions).

Phenomenological representation of relaxation processes

In many cases, the relaxation process of the medium towards thermal equilibrium can be described by

$$[\hat{H}_{\mathrm{R}},\hat{\rho}] = -i\hbar\hat{\Gamma}(\hat{\rho}-\hat{\rho}_0),$$

where $\hat{\rho}_0$ is the thermal equilibrium density operator of the system. The here phenomenologically introduced operator $\hat{\Gamma}$ describes the relaxation of the medium, and can can be considered as being independent of the interaction Hamiltonian. Here the operator $\hat{\Gamma}$ has the physical dimension of an angular frequency, and its matrix elements can be considered as giving the time constants of decay for various states of the system.

Perturbation analysis of weakly resonant interactions

Before entering the formalism of the Bloch equations for strongly resonant interactions, we will outline the weakly resonant interactions in a perturbative analysis for the susceptibilities, as previously developed in lectures three, four, and five.

By taking the perturbation series for the density operator as

$$\hat{\rho}(t) = \underbrace{\hat{\rho}_0}_{\sim[E(t)]^0} + \underbrace{\hat{\rho}_1(t)}_{\sim[E(t)]^1} + \underbrace{\hat{\rho}_2(t)}_{\sim[E(t)]^2} + \ldots + \underbrace{\hat{\rho}_n(t)}_{\sim[E(t)]^n} + \ldots,$$

as we previously did for the strictly non-resonant case, one obtains the system of equations

$$
\begin{aligned}
i\hbar\frac{d\hat{\rho}_0}{dt} &= [\hat{H}_0, \hat{\rho}_0],\\
i\hbar\frac{d\hat{\rho}_1(t)}{dt} &= [\hat{H}_0, \hat{\rho}_1(t)] + [\hat{H}_{\mathrm{I}}(t), \hat{\rho}_0] - i\hbar\hat{\Gamma}\hat{\rho}_1(t),\\
i\hbar\frac{d\hat{\rho}_2(t)}{dt} &= [\hat{H}_0, \hat{\rho}_2(t)] + [\hat{H}_{\mathrm{I}}(t), \hat{\rho}_1(t)] - i\hbar\hat{\Gamma}\hat{\rho}_2(t),\\
&\vdots\\
i\hbar\frac{d\hat{\rho}_n(t)}{dt} &= [\hat{H}_0, \hat{\rho}_n(t)] + [\hat{H}_{\mathrm{I}}(t), \hat{\rho}_{n-1}(t)] - i\hbar\hat{\Gamma}\hat{\rho}_n(t),\\
&\vdots
\end{aligned}
$$

As in the non-resonant case, one may here start with solving for the zeroth order term $\hat{\rho}_0$, with all other terms obtained by consecutively solving the equations of order $j = 1, 2, \ldots, n$, in that order.

Proceeding in exactly the same path as for the non-resonant case, solving for the density operator in the interaction picture and expressing the various terms of the electric polarization density in terms of the corresponding traces

$$P_\mu(\mathbf{r}, t) = \sum_{n=0}^{\infty} P_\mu^{(n)}(\mathbf{r}, t) = \frac{1}{V}\sum_{n=0}^{\infty} \mathrm{Tr}[\hat{\rho}_n(t)\hat{Q}_\mu],$$

one obtains the linear, first order susceptibility of the form

$$\chi^{(1)}_{\mu\alpha}(-\omega;\omega) = \frac{Ne^2}{\varepsilon_0\hbar}\sum_a \varrho_0(a)\sum_b \Big(\frac{r^\mu_{ab}r^\alpha_{ba}}{\Omega_{ba} - \omega - i\Gamma_{ba}} + \frac{r^\alpha_{ab}r^\mu_{ba}}{\Omega_{ba} + \omega - i\Gamma_{ba}}\Big).$$

Similarly, the second order susceptibility for weakly resonant interaction is obtained as

$$
\begin{aligned}
&\chi^{(2)}_{\mu\alpha\beta}(-\omega_\sigma;\omega_1,\omega_2)\\
&\quad= \frac{Ne^3}{\varepsilon_0\hbar^2}\frac{1}{2!}\mathbf{S}\sum_a \varrho_0(a)\sum_b\sum_c \Big\{\frac{r^\mu_{ab}r^\alpha_{bc}r^\beta_{ca}}{(\Omega_{ac} + \omega_2 - i\Gamma_{ac})(\Omega_{ab} + \omega_\sigma - i\Gamma_{ab})}\\
&\qquad - \frac{r^\alpha_{ab}r^\mu_{bc}r^\beta_{ca}}{(\Omega_{ac} + \omega_2 - i\Gamma_{ac})(\Omega_{bc} + \omega_\sigma - i\Gamma_{bc})} - \frac{r^\beta_{ab}r^\mu_{bc}r^\alpha_{ca}}{(\Omega_{ba} + \omega_2 - i\Gamma_{ba})(\Omega_{bc} + \omega_\sigma - i\Gamma_{bc})}\\
&\qquad + \frac{r^\beta_{ab}r^\alpha_{bc}r^\mu_{ca}}{(\Omega_{ba} + \omega_2 - i\Gamma_{ba})(\Omega_{ca} + \omega_\sigma - i\Gamma_{ca})}\Big\}.
\end{aligned}
$$

In these expressions for the susceptibilities, the singularities at resonance are removed, and the spectral properties of the absolute values of the susceptibilities are described by regular Lorenzian line shapes.

The values of the matrix elements Γ_{mn} are in many cases difficult to derive from a theoretical basis; however, they are often straightforward to obtain by regular curve-fitting and regression analysis of experimental data.

As seen from the expressions for the susceptibilities above, we still have a boosting of them close to resonance (resonant enhancement). However, the values of the susceptibilities reach a plateau at exact resonance, with maximum values determined by the magnitudes of the involved matrix elements Γ_{mn} of the relaxation operator.

Validity of perturbation analysis of the polarization density

Strictly speaking, the perturbative approach is only to be considered as for an infinite series expansion. For a limited number of terms, the perturbative approach is only an approximative method, which though for many cases is sufficient.

The perturbation series, in the form that we have encountered it in this course, defines a power series in the applied electric field of the light, and as long as the lower order terms are dominant in the expansion, we may safely neglect the higher order ones. Whenever we encounter strong fields, however, we may run into trouble with the series expansion, in particular if we are in a resonant optical regime, with a boosting effect of the polarization density of the medium. (This boosting effect can be seen as the equivalent to the close-to-resonance behaviour of the mechanical spring model under influence of externally driving forces.)

As an illustration to this source of failure of the model in the presence of strong electrical fields, we may consider another, more simple example of series expansions, namely the Taylor expansion of the function $\sin(x)$ around $x \approx 0$, as shown in Fig. 1.

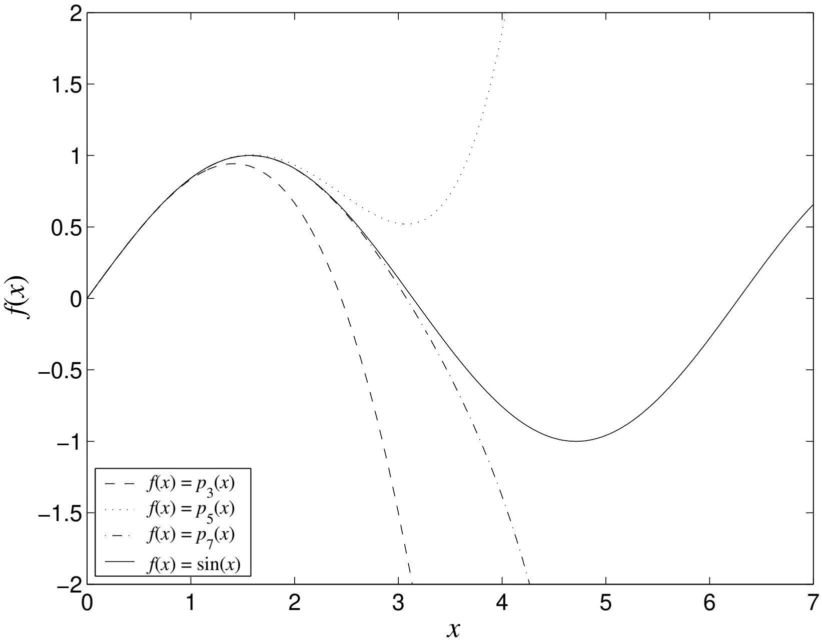

Figure 1. Approximations to $f(x) = \sin(x)$ by means of power series expansions of various degrees.

In analogy to the susceptibility formalism, we may consider x to have the role of the electric field (the variable which we make the power expansion in terms of), and $\sin(x)$ to have the role of the polarization density or the density operator (simply the function we wish to analyze). For low numerical values of x, up to about $x \approx 1$, the $\sin(x)$ function is well described by keeping only the first two terms of the expansion, corresponding to a power expansion up to and including order three,

$$\sin(x) \approx p_3(x) = x - \frac{x^3}{3!}.$$

For higher values of x, say up to about $x \approx 2$, the expansion is still following the exact function to a good approximation if we include also the third term, corresponding to a power expansion up to and including order five,

$$\sin(x) \approx p_5(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!}.$$

This necessity of including higher and higher order terms goes on as we increase the value of x, and we can from the graph also see that the breakdown at a certain level of approximation causes severe difference between the approximate and exact curves. In particular, if one wish to calculate the value of the function $\sin(x)$ for small x, it might be a good idea to apply the series expansion.

For greater values of x, say $x \approx 10$, the series expansion approach is, however, a bad idea, and an efficient evaluation of $\sin(x)$ requires another approach.

As a matter of fact, the same arguments hold for the more complex case of the series expansion of the density operator[1], for which we for high intensities (high electrical field strengths) must include higher order terms as well.

However, we have seen that even in the non-resonant case, we may encounter great algebraic complexity even in low order nonlinear terms, and since the problem of formulating a proper polarization density is expanding more or less exponentially with the order of the nonlinearity, the usefulness of the susceptibility formalism eventually breaks down. The solution to this problem is to identify the relevant transitions of the ensemble, and to solve the equation of motion (2) exactly instead (or at least within other levels of approximation which do not rely on the perturbative foundation of the susceptibility formalism).

The two-level system

In many cases, the interaction between light and matter can be reduced to that of a two-level system, consisting of only two energy eigenstates $|a\rangle$ and $|b\rangle$. The equation of motion of the density operator is generally given by Eq. (2) as

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

with

$$\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{I}}(t) + \hat{H}_{\mathrm{R}}.$$

For the two-level system, the equation of motion can be expressed in terms of the matrix elements of the density operator as

$$i\hbar \frac{d\rho_{aa}}{dt} = [\hat{H}_0, \hat{\rho}]_{aa} + [\hat{H}_{\mathrm{I}}(t), \hat{\rho}]_{aa} + [\hat{H}_{\mathrm{R}}, \hat{\rho}]_{aa}, \tag{3a}$$

$$i\hbar \frac{d\rho_{ab}}{dt} = [\hat{H}_0, \hat{\rho}]_{ab} + [\hat{H}_{\mathrm{I}}(t), \hat{\rho}]_{ab} + [\hat{H}_{\mathrm{R}}, \hat{\rho}]_{ab}, \tag{3b}$$

$$i\hbar \frac{d\rho_{bb}}{dt} = [\hat{H}_0, \hat{\rho}]_{bb} + [\hat{H}_{\mathrm{I}}(t), \hat{\rho}]_{bb} + [\hat{H}_{\mathrm{R}}, \hat{\rho}]_{bb}, \tag{3c}$$

where the fourth equation for ρ_{ba} was omitted, since the solution for this element immediately follows from

$$\rho_{ba} = \rho^*_{ab}.$$

Terms involving the thermal equilibrium Hamiltonian

The system of Eqs. (3) is the starting point for derivation of the so-called Bloch equations. Starting with the thermal-equilibrium part of the commutators in the right-hand sides of Eqs. (3), we have for the diagonal elements

$$\begin{aligned}
[\hat{H}_0, \hat{\rho}]_{aa} &= \langle a|\hat{H}_0\hat{\rho}|a\rangle - \langle a|\hat{\rho}\hat{H}_0|a\rangle \\
&= \sum_k \underbrace{\langle a|\hat{H}_0|k\rangle}_{=\mathbb{E}_a\delta_{ak}} \langle k|\hat{\rho}|a\rangle - \sum_j \langle a|\hat{\rho}|j\rangle \underbrace{\langle j|\hat{H}_0|a\rangle}_{=\mathbb{E}_j\delta_{ja}} \\
&= \mathbb{E}_a\rho_{aa} - \rho_{aa}\mathbb{E}_a \\
&= 0 \\
&= [\hat{H}_0, \hat{\rho}]_{bb},
\end{aligned}$$

[1] We may recall that the series expansion of the density operator is *the* very origin of the expansion of the polarization density of the medium in terms of the electric field, and hence also the very foundation for the whole susceptibility formalism as described in this course.

and for the off-diagonal elements

$$\begin{aligned}
[\hat{H}_0, \hat{\rho}]_{ab} &= \langle a|\hat{H}_0\hat{\rho}|b\rangle - \langle a|\hat{\rho}\hat{H}_0|b\rangle \\
&= \sum_k \underbrace{\langle a|\hat{H}_0|k\rangle}_{=\mathbb{E}_a\delta_{ak}}\langle k|\hat{\rho}|b\rangle - \sum_j \langle a|\hat{\rho}|j\rangle \underbrace{\langle j|\hat{H}_0|b\rangle}_{=\mathbb{E}_j\delta_{jb}} \\
&= \mathbb{E}_a\rho_{ab} - \rho_{ab}\mathbb{E}_b \\
&= -(\mathbb{E}_b - \mathbb{E}_a)\rho_{ab} \\
&= -\hbar\Omega_{ba}\rho_{ab}
\end{aligned}$$

Terms involving the interaction Hamiltonian

For the commutators in the right-hand sides of Eqs. (3) involving the interaction Hamiltonian, we similarly have for the diagonal elements

$$\begin{aligned}
[\hat{H}_{\rm I}(t), \hat{\rho}]_{aa} &= \langle a|(-e\hat{r}_\alpha E_\alpha(\mathbf{r},t))\hat{\rho}|a\rangle - \langle a|\hat{\rho}(-e\hat{r}_\alpha E_\alpha(\mathbf{r},t))|a\rangle \\
&= -eE_\alpha(\mathbf{r},t)\bigg\{\sum_k \langle a|\hat{r}_\alpha|k\rangle\langle k|\hat{\rho}|a\rangle - \sum_j \langle a|\hat{\rho}|j\rangle\langle j|\hat{r}_\alpha|a\rangle\bigg\} \\
&= -eE_\alpha(\mathbf{r},t)\bigg\{r^\alpha_{aa}\rho_{aa} + r^\alpha_{ab}\rho_{ba} - \rho_{aa}r^\alpha_{aa} - \rho_{ab}r^\alpha_{ba}\bigg\} \\
&= -e(r^\alpha_{ab}\rho_{ba} - r^\alpha_{ba}\rho_{ab})E_\alpha(\mathbf{r},t) \\
&= -[\hat{H}_{\rm I}(t), \hat{\rho}]_{bb},
\end{aligned}$$

and for the off-diagonal elements

$$\begin{aligned}
[\hat{H}_{\rm I}(t), \hat{\rho}]_{ab} &= \langle a|(-e\hat{r}_\alpha E_\alpha(\mathbf{r},t))\hat{\rho}|b\rangle - \langle a|\hat{\rho}(-e\hat{r}_\alpha E_\alpha(\mathbf{r},t))|b\rangle \\
&= -eE_\alpha(\mathbf{r},t)\bigg\{\sum_k \langle a|\hat{r}_\alpha|k\rangle\langle k|\hat{\rho}|b\rangle - \sum_j \langle a|\hat{\rho}|j\rangle\langle j|\hat{r}_\alpha|b\rangle\bigg\} \\
&= -eE_\alpha(\mathbf{r},t)\bigg\{r^\alpha_{aa}\rho_{ab} + r^\alpha_{ab}\rho_{bb} - \rho_{aa}r^\alpha_{ab} - \rho_{ab}r^\alpha_{bb}\bigg\} \\
&= -er^\alpha_{ab}E_\alpha(\mathbf{r},t)(\rho_{bb} - \rho_{aa}) - e(r^\alpha_{aa} - r^\alpha_{bb})E_\alpha(\mathbf{r},t)\rho_{ab} \\
&= \{\text{Optical Stark shift} : \delta\mathbb{E}_k \equiv -er^\alpha_{kk}E_\alpha(\mathbf{r},t), \quad k = a, b\} \\
&= -er^\alpha_{ab}E_\alpha(\mathbf{r},t)(\rho_{bb} - \rho_{aa}) + (\delta\mathbb{E}_a - \delta\mathbb{E}_b)\rho_{ab}.
\end{aligned}$$

Terms involving relaxation processes

For the commutators describing relaxation processes, the diagonal elements are given as

$$\begin{aligned}
[\hat{H}_{\rm R}, \hat{\rho}]_{aa} &= -i\hbar(\rho_{aa} - \rho_0(a))/T_a, \\
[\hat{H}_{\rm R}, \hat{\rho}]_{bb} &= -i\hbar(\rho_{bb} - \rho_0(b))/T_b,
\end{aligned}$$

where T_a and T_b are the decay rates towards the thermal equilibrium at respective level, and where $\rho_0(a)$ and $\rho_0(b)$ are the thermal equilibrium values of ρ_{aa} and ρ_{bb}, respectively (i. e. the thermal equilibrium population densities of the respective level). The off-diagonal elements are similarly given as

$$\begin{aligned}
[\hat{H}_{\rm R}, \hat{\rho}]_{ab} &= -i\hbar\rho_{ab}/T_2, \\
[\hat{H}_{\rm R}, \hat{\rho}]_{ba} &= -i\hbar\rho_{ba}/T_2.
\end{aligned}$$

A common approximation is to consider the two states $|a\rangle$ and $|b\rangle$ to be sufficiently similar in order to approximate their lifetimes as equal, i. e. $T_a \approx T_b \approx T_1$, where T_1 for historical reasons is denoted as the *longitudinal relaxation time*. For the same historical reason, the relaxation time T_2 is denoted as the *transverse relaxation time*.[2]

As the above matrix elements of the commutators involving the various terms of the Hamiltonian are inserted into the right-hand sides of Eqs. (3), one obtains the following system of equations for the matrix elements of the density operator,

$$i\hbar\frac{d\rho_{aa}}{dt} = -e(r^{\alpha}_{ab}\rho_{ba} - r^{\alpha}_{ba}\rho_{ab})E_{\alpha}(\mathbf{r},t) - i\hbar(\rho_{aa} - \rho_0(a))/T_a, \tag{4a}$$
$$i\hbar\frac{d\rho_{ab}}{dt} = -\hbar\Omega_{ba}\rho_{ab} - er^{\alpha}_{ab}E_{\alpha}(\mathbf{r},t)(\rho_{bb} - \rho_{aa}) + (\delta\mathbb{E}_a - \delta\mathbb{E}_b)\rho_{ab} - i\hbar\rho_{ab}/T_2, \tag{4b}$$
$$i\hbar\frac{d\rho_{bb}}{dt} = e(r^{\alpha}_{ab}\rho_{ba} - r^{\alpha}_{ba}\rho_{ab})E_{\alpha}(\mathbf{r},t) - i\hbar(\rho_{bb} - \rho_0(b))/T_b. \tag{4c}$$

(The system of equations (4) corresponds to Butcher and Cotter's Eqs. (6.35).) So far, the applied electric field of the light is allowed to be of arbitrary form. However, in order to simplify the following analysis, we will assume the light to be linearly polarized and quasimonochromatic, of the form

$$E_{\alpha}(\mathbf{r},t) = \mathrm{Re}[E^{\alpha}_{\omega}(t)\exp(-i\omega t)].$$

We will in addition assume the slowly varying temporal envelope $E^{\alpha}_{\omega}(t)$ to be real-valued, and we will also neglect the optical Stark shifts $\delta\mathbb{E}_a$ and $\delta\mathbb{E}_b$. In the absence of strong static magnetic fields, we may also assume the matrix elements er^{α}_{ab} to be real-valued. When these assumptions and approximations are applied to the equations of motion (4), one obtains

$$\frac{d\rho_{aa}}{dt} = i(\rho_{ba} - \rho_{ab})\beta(t)\cos(\omega t) - (\rho_{aa} - \rho_0(a))/T_a, \tag{5a}$$
$$\frac{d\rho_{ab}}{dt} = i\Omega_{ba}\rho_{ab} + i\beta(t)\cos(\omega t)(\rho_{bb} - \rho_{aa}) - \rho_{ab}/T_2, \tag{5b}$$
$$\frac{d\rho_{bb}}{dt} = -i(\rho_{ba} - \rho_{ab})\beta(t)\cos(\omega t) - (\rho_{bb} - \rho_0(b))/T_b, \tag{5c}$$

where the *Rabi frequency* $\beta(t)$, defined in terms of the spatial envelope of the electrical field and the transition dipole moment as

$$\beta(t) = er^{\alpha}_{ab}E^{\alpha}_{\omega}(t)/\hbar = e\mathbf{r}_{ab}\cdot\mathbf{E}_{\omega}(t)/\hbar,$$

was introduced.

The rotating-wave approximation

In the middle equation of the system (5), we have a time-derivative of ρ_{ab} in the left-hand side, while we in the right-hand side have a term $i\Omega_{ba}\rho_{ab}$. Seen as the homogeneous part of a linear differential equation, this suggests that we may further simplify the equations of motion by taking a new variable ρ^{Ω}_{ab} according to the variable substitution

$$\rho_{ab} = \rho^{\Omega}_{ab}\exp[i(\Omega_{ba} - \Delta)t], \tag{6}$$

where $\Delta \equiv \Omega_{ba} - \omega$ is the detuning of the angular frequency of the light from the transition frequency $\Omega_{ba} \equiv (\mathbb{E}_b - \mathbb{E}_a)/\hbar$.

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[2] For a deeper discusssion and explanation of the various mechanisms involved in relaxation, see for example Charles P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1978), available at KTHB. This reference is not mentioned in Butcher and Cotters book, but it is a very good text on relaxation phenomena and how to incorporate them into a density-functional description of interaction between light and matter.

By inserting Eq. (6) into Eqs. (5), keeping in mind that $\rho_{ba} = \rho^*_{ab}$, one obtains the system

$$\frac{d\rho_{aa}}{dt} = i(\rho^{\Omega}_{ba} \exp[-i(\Omega_{ba} - \Delta)t] - \rho^{\Omega}_{ab} \exp[i(\Omega_{ba} - \Delta)t])\beta(t)\cos(\omega t) - (\rho_{aa} - \rho_0(a))/T_a, \quad \text{(6a)}$$

$$\frac{d\rho^{\Omega}_{ab}}{dt} = i\Delta\rho^{\Omega}_{ab} + i\beta(t)\cos(\omega t)\exp[-i(\Omega_{ba} - \Delta)t](\rho_{bb} - \rho_{aa}) - \rho^{\Omega}_{ab}/T_2, \quad \text{(6b)}$$

$$\frac{d\rho_{bb}}{dt} = -i(\rho^{\Omega}_{ba} \exp[-i(\Omega_{ba} - \Delta)t] - \rho^{\Omega}_{ab} \exp[i(\Omega_{ba} - \Delta)t])\beta(t)\cos(\omega t) - (\rho_{bb} - \rho_0(b))/T_b, \quad \text{(6c)}$$

The idea with the rotating-wave approximation is now to separate out rapidly oscillating terms of angular frequencies $\omega + \Omega_{ba}$ and $-(\omega + \Omega_{ba})$, and neglect these terms, compared with more slowly varying terms. The motivation for this approximation is that whenever high-frequency components appear in the equations of motions, the high-frequency terms will when integrated contain large denominators, and will hence be minor in comparison with terms with a slow variation. In some sense we can also see this as a temporal averaging procedure, where rapidly oscillating terms average to zero rapidly compared to slowly varying (or constant) components.

For example, in Eq. (6b), the product of the $\cos(\omega t)$ and the exponential function is approximated as

$$\begin{aligned}\cos(\omega t)\exp[-i(\Omega_{ba} - \Delta)t] &= \frac{1}{2}[\exp(i\omega t) + \exp(-i\omega t)]\exp[-i\underbrace{(\Omega_{ba} - \Delta)}_{=\omega}t] \\ &= \frac{1}{2}[1 + \exp(-i2\omega t)] \to \frac{1}{2},\end{aligned}$$

while in Eqs. (6a) and (6c), the same argument gives

$$\begin{aligned}\exp[i(\Omega_{ba} - \Delta)t]\cos(\omega t) &= \frac{1}{2}[\exp(i\omega t) + \exp(-i\omega t)]\exp[-i\underbrace{(\Omega_{ba} - \Delta)}_{=\omega}t] \\ &= \frac{1}{2}[\exp(i2\omega t) + 1] \to \frac{1}{2}.\end{aligned}$$

By applying this *rotating-wave approximation*, the equations of motion (6) hence take the form

$$\frac{d\rho_{aa}}{dt} = \frac{i}{2}(\rho^{\Omega}_{ba} - \rho^{\Omega}_{ab})\beta(t) - (\rho_{aa} - \rho_0(a))/T_a, \quad \text{(7a)}$$

$$\frac{d\rho^{\Omega}_{ab}}{dt} = i\Delta\rho^{\Omega}_{ab} + \frac{i}{2}\beta(t)(\rho_{bb} - \rho_{aa}) - \rho^{\Omega}_{ab}/T_2, \quad \text{(7b)}$$

$$\frac{d\rho_{bb}}{dt} = -\frac{i}{2}(\rho^{\Omega}_{ba} - \rho^{\Omega}_{ab})\beta(t) - (\rho_{bb} - \rho_0(b))/T_b. \quad \text{(7c)}$$

In this final form, before entering the Bloch vector description of the interaction, these equations correspond to Butcher and Cotter's Eqs. (6.41).

The Bloch equations

Assuming the two states $|a\rangle$ and $|b\rangle$ to be sufficiently similar in order to approximate $T_a \approx T_b \approx T_1$, where T_1 is the longitudinal relaxation time, and by taking new variables (u, v, w) according to

$$\begin{aligned}u &= \rho^{\Omega}_{ba} + \rho^{\Omega}_{ab}, \\ v &= i(\rho^{\Omega}_{ba} - \rho^{\Omega}_{ab}), \\ w &= \rho_{bb} - \rho_{aa},\end{aligned}$$

the equations of motion (7) are cast in the *Bloch equations*

$$\frac{du}{dt} = -\Delta v - u/T_2, \quad \text{(8a)}$$

$$\frac{dv}{dt} = \Delta u + \beta(t)w - v/T_2, \quad \text{(8b)}$$

$$\frac{dw}{dt} = -\beta(t)v - (w - w_0)/T_1. \quad \text{(8c)}$$

In these equations, the introduced variable w describes the population inversion of the two-level system, while u and v are related to the dispersive and absorptive components of the polarization density of the medium. In the Bloch equations above, $w_0 = \rho_0(b) - \rho_0(a)$ is the thermal equilibrium inversion of the system with no optical field applied.

The resulting electric polarization density of the medium

The so far developed theory of the density matrix under resonant interaction can now be applied to the calculation of the electric polarization density of the medium, consisting of N identical molecules per unit volume, as

$$\begin{aligned}
P_\mu(\mathbf{r}, t) &= N\langle e\hat{r}_\mu\rangle \\
&= N\,\mathrm{Tr}[\hat{\rho}e\hat{r}_\mu] \\
&= N\sum_{k=a,b}\langle k|\hat{\rho}e\hat{r}_\mu|k\rangle \\
&= N\sum_{k=a,b}\sum_{j=a,b}\langle k|\hat{\rho}|j\rangle\langle j|e\hat{r}_\mu|k\rangle \\
&= N\sum_{k=a,b}\{\langle k|\hat{\rho}|a\rangle\langle a|e\hat{r}_\mu|k\rangle + \langle k|\hat{\rho}|b\rangle\langle b|e\hat{r}_\mu|k\rangle\} \\
&= N\{\langle a|\hat{\rho}|a\rangle\langle a|e\hat{r}_\mu|a\rangle + \langle b|\hat{\rho}|a\rangle\langle a|e\hat{r}_\mu|b\rangle + \langle a|\hat{\rho}|b\rangle\langle b|e\hat{r}_\mu|a\rangle + \langle b|\hat{\rho}|b\rangle\langle b|e\hat{r}_\mu|b\rangle\} \\
&= N(\rho_{ba}er^\mu_{ab} + \rho_{ab}er^\mu_{ba}) \\
&= \{\text{Make use of } \rho_{ab} = (u + iv)\exp(i\omega t) = \rho^*_{ba}\} \\
&= N[(u - iv)\exp(-i\omega t)er^\mu_{ab} + (u + iv)\exp(i\omega t)er^\mu_{ba}].
\end{aligned}$$

The temporal envelope P^μ_ω of the polarization density, throughout this course as well as in Butcher and Cotter's book, is taken as

$$P^\mu(\mathbf{r}, t) = \mathrm{Re}[P^\mu_\omega \exp(-i\omega t)],$$

and by identifying this expression with the right-hand side of the result above, we hence finally have obtained the polarization density in terms of the Bloch parameters (u, v, w) as

$$P^\mu_\omega(\mathbf{r}, t) = Ner^\mu_{ab}(u - iv).$$

This expression for the temporal envelope of the polarization density is exactly in the same mode of description as the one as previously used in the susceptibility theory, as in the wave equations developed in lecture eight. The only difference is that now we instead consider the polarization density as given by a non-perturbative analysis. Taken together with the Maxwell's equations (or the proper wave equation for the envelopes of the fields), the Bloch equations are known as the *Maxwell–Bloch equations*.