B3 Quantum Notes: Two-level system and Rabi flopping

Dr D.M.Lucas, MT 2018

These notes give a summary of most of the "Quantum" part of this course, to complement Prof. Ewart's notes on Atomic Structure, and Prof. Hooker's notes on Molecular Structure and Laser Physics. They are not intended as a substitute for textbooks, as there are several excellent books, but should serve to remind you of what was covered in the lectures so that you can refer to the relevant sections of the recommended books for more details (see list of references at end).

1. Light-atom interaction

1.1 Introduction

We give in this section the standard semi-classical treatment of the light-atom interaction for a hypothetical two-level atom. The treatment is called "semi-classical" because the atom is treated quantum mechanically, but the light field is treated classically (a fully quantum treatment requires the techniques of quantum electrodynamics, well beyond the scope of this course). It is usually an excellent approximation to consider only two energy levels of an atom, since atomic transitions are very narrow in frequency space and we can consider a particular transition between two levels in isolation from other energy levels. We will consider two cases: (i) excitation by broadband, low-intensity radiation (the "weak field" limit), where we relate this to the simple rate equation treatment and Einstein B coefficient; (ii) excitation by monochromatic radiation (the "strong field" limit).

1.2 Time-dependent perturbation theory

We remind ourselves of the standard techniques of time-dependent perturbation theory as applied to a two-level system. (This should be familiar from second year QM, so this section serves mostly to establish the notation.) We will not concern ourselves yet with the specific form of the perturbation, except to specify that it depends only on time t. We consider a two-level atom whose energy levels are $E_1 = \hbar\omega_1$ and $E_2 = \hbar\omega_2$ (where $E_2 > E_1$), so that the transition (angular) frequency is $\omega_0 = \omega_2 - \omega_1$. Our starting point is the time-dependent Schrödinger equation for the *unperturbed* atom, with Hamiltonian $\hat{H}_0$:

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = \hat{H}_0\Psi \tag{1.1}$$

whose solutions are (with $n = 1, 2$ labelling the states):

$$\Psi_n(\mathbf{r}, t) = \mathrm{e}^{-\mathrm{i}\omega_n t}\ \psi_n(\mathbf{r}) \tag{1.2}$$

where

$$\hat{H}_0\psi_n = E_n\psi_n \tag{1.3}$$

is the time-independent Schrödinger equation for the unperturbed eigenstates ψ_n. We now include a time-dependent perturbation $\hat{V}(t)$, so that the Hamiltonian becomes $\hat{H} = \hat{H}_0 + \hat{V}(t)$. We write the wavefunction as a superposition of the solutions to the unperturbed system:

$$\Psi(\mathbf{r}, t) = c_1(t)\ \mathrm{e}^{-\mathrm{i}\omega_1 t}\ \psi_1(\mathbf{r}) + c_2(t)\ \mathrm{e}^{-\mathrm{i}\omega_2 t}\ \psi_2(\mathbf{r}) \tag{1.4}$$

where the expansion coefficients $c_n(t)$ are time-dependent and satisfy $|c_1|^2 + |c_2|^2 = 1$. On substituting this expression for Ψ into the new time-dependent Schrödinger equation,

$$\mathrm{i}\hbar\frac{\partial\Psi}{\partial t} = [\hat{H}_0 + \hat{V}(t)]\Psi \tag{1.5}$$

we obtain (after cancelling some terms):

$$\mathrm{i}\hbar[\dot{c}_1\mathrm{e}^{-\mathrm{i}\omega_1 t}\psi_1 + \dot{c}_2\mathrm{e}^{-\mathrm{i}\omega_2 t}\psi_2] = \hat{V}c_1\mathrm{e}^{-\mathrm{i}\omega_1 t}\psi_1 + \hat{V}c_2\mathrm{e}^{-\mathrm{i}\omega_2 t}\psi_2 \tag{1.6}$$

where $\dot{c}_1 = \dfrac{\mathrm{d}c_1}{\mathrm{d}t}$. Pre-multiplying by ψ_1^* and integrating over all space gives:

$$\mathrm{i}\hbar\dot{c}_1\mathrm{e}^{-\mathrm{i}\omega_1 t} = c_1\mathrm{e}^{-\mathrm{i}\omega_1 t}V_{11} + c_2\mathrm{e}^{-\mathrm{i}\omega_2 t}V_{12} \tag{1.7}$$

where the *matrix elements* V_{nm} are defined by

$$V_{nm} = \langle\psi_n|\hat{V}|\psi_m\rangle = \int \psi_n^*\hat{V}\psi_m \mathrm{d}^3\mathbf{r} \tag{1.8}$$

We thus obtain an equation for the rate of change of the coefficient c_1:

$$\dot{c}_1 = -\frac{\mathrm{i}}{\hbar}\left(c_1V_{11} + c_2V_{12}\mathrm{e}^{-\mathrm{i}\omega_0 t}\right) \tag{1.9}$$

where we have used $\omega_0 = \omega_2 - \omega_1$. Similarly (by pre-multiplying 1.6 by ψ_2^* instead) we get an equation for the rate of change of c_2:

$$\dot{c}_2 = -\frac{\mathrm{i}}{\hbar}\left(c_1V_{21}\mathrm{e}^{+\mathrm{i}\omega_0 t} + c_2V_{22}\right) \tag{1.10}$$

The matrix elements V_{nm} are functions of t but, given the perturbation $\hat{V}(t)$, we can in principle calculate them for any t because we know the eigenstates ψ_n of the unperturbed system. We can then solve this pair of coupled ordinary differential equations 1.9 and 1.10 to find $c_1(t)$ and $c_2(t)$ and hence the wavefunction $\Psi(t)$ at any time t.

1.3 Light-atom interaction

Let us now consider the specific form of the perturbation $\hat{V}(t)$ for a single-electron atom perturbed by electromagnetic radiation whose wavelength λ is much larger than the physical dimensions of the atom (this is an excellent approximation for optical transitions, where $\lambda \sim 500\,\mathrm{nm}$, and we recall the size scale of atoms is set by the Bohr radius $a_0 \approx 0.05\,\mathrm{nm}$). The electric field of the wave at the atom is then simply

$$\mathcal{E} = \mathcal{E}_0\cos\omega t \tag{1.11}$$

where $\mathcal{E}_0$ is the amplitude and ω is the angular frequency of the wave (not necessarily the same as the atomic transition frequency ω_0). The electron's potential energy in the electric field of the radiation is given by $(-\mathbf{p}.\mathcal{E})$ where $\mathbf{p} = -e\mathbf{r}$ is the atomic dipole moment. (We have ignored any interaction between the atomic magnetic moment and the B-field of the wave: convince yourself this is justified by considering the relative magnitudes of $-\mu.\mathbf{B}$ and $-\mathbf{p}.\mathcal{E}$ for a plane e.m. wave with $\mathcal{E} = cB$, taking $\mu \sim \mu_\mathrm{B}$ and $p \sim ea_0$.) If we take the e.m. wave to be linearly polarized along the x-axis, then the perturbation becomes

$$\hat{V}(t) = ex\mathcal{E}_0\cos\omega t \tag{1.12}$$

The diagonal matrix elements of the perturbation for our two-level atom are

$$V_{11} = \langle\psi_1|ex|\psi_1\rangle\mathcal{E}_0\cos\omega t \tag{1.13}$$

$$V_{22} = \langle\psi_2|ex|\psi_2\rangle\mathcal{E}_0\cos\omega t \tag{1.14}$$

and both of these *vanish* because atomic eigenstates have definite parity (either even or odd) and the expectation-value integrals contain the odd-parity operator x. The off-diagonal matrix elements are real quantities for bound states, so

$$V_{21} = V_{12}^* = V_{12} = \langle\psi_1|ex|\psi_2\rangle\mathcal{E}_0\cos\omega t \tag{1.15}$$

We define the *Rabi frequency* Ω by

$$\Omega = \frac{\mathcal{E}_0}{\hbar}\langle\psi_1|ex|\psi_2\rangle \tag{1.16}$$

This important quantity characterizes the size of the interaction through the amplitude $\mathcal{E}_0$ of the electric field of the radiation and the strength of the atomic response (the matrix element). We shall see physically what frequency Ω represents when we turn to the case of the "strong field" limit below. The coupled equations 1.9 and 1.10 for the time-evolution of the state coefficients now reduce to

$$\dot{c}_1 = -\mathrm{i}\Omega\cos\omega t\ \mathrm{e}^{-\mathrm{i}\omega_0 t}c_2 \tag{1.17}$$

$$\dot{c}_2 = -\mathrm{i}\Omega\cos\omega t\ \mathrm{e}^{+\mathrm{i}\omega_0 t}c_1 \tag{1.18}$$

1.4 Weak field limit

We first consider the solution of equations 1.17 and 1.18 in the so-called "weak field" limit, when the perturbation is sufficiently small that the transition probability from one state to the other remains low at all times, and seek to relate this to the simple rate-equation (Einstein coefficient) approach to transition rates that was given in the lecture on selection rules. Physically, this corresponds to excitation by broad-band radiation, containing a wide range of frequencies, such that the spectral intensity in the region of the narrow atomic frequency response is small. If the system is initially in state 1 then the weak field limit implies

$$c_2(t) \ll c_1(t) \quad \text{and} \quad c_1(t) \approx 1 \tag{1.19}$$

for all t. We then have, from 1.18,

$$\dot{c}_2 \approx -\mathrm{i}\Omega\cos\omega t\ \mathrm{e}^{+\mathrm{i}\omega_0 t} = -\tfrac{1}{2}\mathrm{i}\Omega\left(\mathrm{e}^{\mathrm{i}(\omega+\omega_0)t} + \mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}\right) \tag{1.20}$$

We integrate $\int_0^t \mathrm{d}t'$ to find $c_2(t)$:

$$c_2(t) = -\tfrac{1}{2}\Omega\left[\frac{\mathrm{e}^{\mathrm{i}(\omega+\omega_0)t'}}{(\omega+\omega_0)} - \frac{\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t'}}{(\omega-\omega_0)}\right]_0^t = +\tfrac{1}{2}\Omega\left[\frac{1-\mathrm{e}^{\mathrm{i}(\omega+\omega_0)t}}{(\omega+\omega_0)} - \frac{1-\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}}{(\omega-\omega_0)}\right] \tag{1.21}$$

where we have used the initial condition $c_2(0) = 0$. Typically we are interested in the response of the atom to radiation whose frequency ω is close to the transition frequency ω_0, so that

$$|\omega - \omega_0| \ll (\omega + \omega_0) \tag{1.22}$$

This means that we can safely neglect the first term in brackets in the equation above: this important simplification is called the *rotating wave approximation* (RWA). Within the RWA, we have:

$$c_2(t) = -\tfrac{1}{2}\Omega\left(\frac{1-\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t}}{(\omega-\omega_0)}\right) = -\tfrac{1}{2}\Omega\mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t/2}\left(\frac{\mathrm{e}^{\mathrm{i}(\omega-\omega_0)t/2} - \mathrm{e}^{-\mathrm{i}(\omega-\omega_0)t/2}}{(\omega-\omega_0)}\right) \tag{1.23}$$

We then find that the transition probability (that is, the probability of finding the atom in state 2 at time t) is

$$|c_2(t)|^2 = \left(\frac{\Omega}{2}\right)^2\left(\frac{\sin\frac{1}{2}(\omega-\omega_0)t}{\frac{1}{2}(\omega-\omega_0)}\right)^2 \tag{1.24}$$

We wish to relate this to the Einstein coefficient B_{12} for stimulated absorption that appears in the rate equations. We recall that the transition rate for stimulated absorption was (ρB_{12}) where $\rho(\omega)$ is the spectral energy density of the radiation. The volume energy density of radiation in a frequency interval $\mathrm{d}\omega$ is related to the electric field amplitude $\mathcal{E}_0$ by

$$\rho(\omega)\mathrm{d}\omega = \tfrac{1}{2}\epsilon_0\mathcal{E}_0^2 \tag{1.25}$$

where the factor of $\frac{1}{2}$ arises from $< \cos^2 \omega t >= \frac{1}{2}$. Using the definition of the Rabi frequency above we then have

$$\Omega^2 = \frac{\mathcal{E}_0^2 |\langle \psi_1 | ex | \psi_2 \rangle|^2}{\hbar^2} = \frac{2|\langle \psi_1 | ex | \psi_2 \rangle|^2}{\epsilon_0 \hbar^2} \rho(\omega) \mathrm{d}\omega \tag{1.26}$$

Substituting this in equation 1.24 and integrating over a range $\pm\Delta\omega$ around the atomic transition gives

$$|c_2(t)|^2 = \frac{|\langle \psi_1 | ex | \psi_2 \rangle|^2}{2\epsilon_0 \hbar^2} \int_{\omega_0 - \Delta\omega}^{\omega_0 + \Delta\omega} \rho(\omega) \left(\frac{\sin \frac{1}{2}(\omega - \omega_0)t}{\frac{1}{2}(\omega - \omega_0)} \right)^2 \mathrm{d}\omega \tag{1.27}$$

We assume that the response of the atom is narrow compared with the broad-band radiation, so that we can replace $\rho(\omega)$ by the constant value $\rho(\omega_0)$ and take it outside the integral; since most of the contribution to the integral comes from this narrow range, we can also take the integration limits to infinity, where we find the integral has the value $2\pi t$. Thus we obtain for the transition rate (i.e. the transition probability per unit time):

$$\frac{|c_2(t)|^2}{t} = \frac{\pi}{\epsilon_0 \hbar^2} |\langle \psi_1 | ex | \psi_2 \rangle|^2 \rho(\omega_0) \tag{1.28}$$

This was for the particular case of light linearly-polarized along the x-axis; more generally we have for unpolarized light a transition rate

$$R_{12} = \frac{\pi}{3\epsilon_0 \hbar^2} |\langle \psi_1 | e\mathbf{r} | \psi_2 \rangle|^2 \rho(\omega_0) \tag{1.29}$$

Equating this to the transition rate (ρB_{12}) in the rate equation treatment gives us finally an expression for the Einstein coefficient

$$B_{12} = \frac{\pi}{3\epsilon_0 \hbar^2} |\langle \psi_1 | e\mathbf{r} | \psi_2 \rangle|^2 \tag{1.30}$$

and through the relations $A_{21} = (\hbar\omega_0^3/\pi^2 c^3) B_{21}$ and $B_{21} = B_{12}$ we can also obtain an expression for the A coefficient (giving the spontaneous transition rate) in terms of atomic quantities,

$$A_{21} = \frac{\omega_0^3}{3\pi\epsilon_0 \hbar c^3} |\langle \psi_1 | e\mathbf{r} | \psi_2 \rangle|^2 \tag{1.31}$$

The remarkable result here is that, thanks to the Einstein treatment, we are able to calculate A_{21} from atomic properties (the wavefunctions), without having to know anything about quantum electrodynamics, even though spontaneous emission can only be explained by proper quantization of the radiation field.

1.5 Strong field limit

We now wish to relax the condition 1.19 and consider strong excitation by monochromatic radiation of frequency ω (for example, a laser). The coupled equations for the state coefficients 1.17 and 1.18 are

$$\dot{c}_1 = -\mathrm{i}\Omega \cos \omega t \ \mathrm{e}^{-\mathrm{i}\omega_0 t} c_2$$
$$\dot{c}_2 = -\mathrm{i}\Omega \cos \omega t \ \mathrm{e}^{+\mathrm{i}\omega_0 t} c_1$$

If we write $\cos \omega t = \frac{1}{2}(\mathrm{e}^{\mathrm{i}\omega t} + \mathrm{e}^{-\mathrm{i}\omega t})$ then the first of these becomes

$$\dot{c}_1 = -\tfrac{1}{2}\mathrm{i}\Omega \left(\mathrm{e}^{\mathrm{i}(\omega - \omega_0)t} + \mathrm{e}^{-\mathrm{i}(\omega + \omega_0)t} \right) c_2 \tag{1.32}$$

We can see that making the rotating wave approximation $|\omega - \omega_0| \ll (\omega + \omega_0)$ will again mean that we can neglect the rapidly-oscillating term $\mathrm{e}^{-\mathrm{i}(\omega+\omega_0)t}$ when we come to integrate the equations. Within the RWA, we thus have

$$\dot{c}_1 = -\tfrac{1}{2}\mathrm{i}\Omega \mathrm{e}^{+\mathrm{i}t\delta} c_2 \tag{1.33}$$
$$\dot{c}_2 = -\tfrac{1}{2}\mathrm{i}\Omega \mathrm{e}^{-\mathrm{i}t\delta} c_1 \tag{1.34}$$

where we have written $\delta = \omega - \omega_0$ for the "detuning" of the radiation from the atomic transition frequency ω_0.

1.5.1 Resonant excitation

For the case $\omega = \omega_0$, i.e. $\delta = 0$, the solution is particularly simple. We have

$$\ddot{c}_2 = -\tfrac{1}{4}\Omega^2 c_2 \tag{1.35}$$

so the state coefficient c_2 just undergoes simple harmonic motion! For the initial condition $c_2(0) = 0$ (i.e. the atom starts in state 1), the solution (up to an overall phase factor) is:

$$c_1(t) = \mathrm{i}\cos\tfrac{1}{2}\Omega t \tag{1.36}$$

$$c_2(t) = \sin\tfrac{1}{2}\Omega t \tag{1.37}$$

which give for the state *probabilities*:

$$|c_1(t)|^2 = \cos^2\tfrac{1}{2}\Omega t \tag{1.38}$$

$$|c_2(t)|^2 = \sin^2\tfrac{1}{2}\Omega t \tag{1.39}$$

So the system oscillates from state 1 to state 2 and back again with a period $2\pi/\Omega$: at last we see the physical significance of the Rabi frequency. This behaviour, called *Rabi oscillation* (or *Rabi flopping*) is completely different to the prediction of the rate equation picture, where all that can happen in the limit of strong excitation is that the populations of the two states reach a steady-state value of $\frac{1}{2}$. It is a coherent quantum effect, arising from the equations for $\dot{c}_1$ and $\dot{c}_2$.

If the resonant radiation is switched on at time $t = 0$ and off at time $t = \pi/\Omega$ then an atom initially in state 1 will be transferred to state 2 and vice versa; such a pulse of radiation is called a "π-pulse". Similarly a pulse of duration such that $\Omega t = \pi/2$ is called a "$\frac{\pi}{2}$-pulse"; some examples for the starting state 1:

$$\begin{array}{ll} \pi\text{-pulse:} & |1\rangle \longrightarrow |2\rangle \\ \frac{\pi}{2}\text{-pulse:} & |1\rangle \longrightarrow \frac{1}{\sqrt{2}}(\mathrm{i}|1\rangle + |2\rangle) \\ 2\pi\text{-pulse:} & |1\rangle \longrightarrow -\mathrm{i}|1\rangle \end{array}$$

(You might have wondered how these superposition states you have discussed for so long in quantum mechanics can actually be *created*: now you know a good method!) Note that a "2π-pulse" is not equivalent to the mathematical identity operation, because the state *amplitudes* c_n have period $4\pi/\Omega$ whereas the *probabilities* $|c_n|^2$ have period $2\pi/\Omega$. This leads to different conventions in different references as to what is meant by a "π-pulse"; you have been warned...

1.5.2 Off-resonant excitation

For the case $\delta \neq 0$ the solution of 1.33 and 1.34 is not quite so trivial, but sufficiently straightforward that we leave it as an exercise for the reader. The result, for the probability of finding the system in state 2 at time t given the initial condition $c_2(0) = 0$, is:

$$|c_2(t)|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2}\sin^2\left(\frac{t}{2}\sqrt{\Omega^2 + \delta^2}\right) \tag{1.40}$$

Thus for off-resonant excitation the system is never found in state 2 with unity probability, unlike the resonant case, and the population oscillates with a more rapid angular frequency given by $\sqrt{\Omega^2 + \delta^2}$.

1.6 Bloch sphere*

A useful way of visualizing the state of a two-level system, and the effect of operations like π-pulses, is the *Bloch sphere*. The state of the system is represented by a vector of unit length, the *Bloch vector*, whose tail is at the origin and whose tip lies on the surface of the unit sphere. The relative amplitudes and complex phases of the two states $|1\rangle$ and $|2\rangle$ in a general superposition state are represented by the polar angle θ and azimuthal angle ϕ. Once again there are different conventions; we choose

$$c_1|1\rangle + c_2|2\rangle = \sin(\tfrac{\theta}{2})|1\rangle + \mathrm{e}^{\mathrm{i}\phi}\cos(\tfrac{\theta}{2})|2\rangle \tag{1.41}$$

Note that the normalization condition $|c_1|^2 + |c_2|^2$ is automatically satisfied. Thus state $|1\rangle$ lies at the "south pole" $(x, y, z) = (0, 0, -1)$ of the Bloch sphere, state $|2\rangle$ lies at the "north pole" $(0, 0, +1)$ and points around the "equator" represent superposition states of the form $\frac{1}{\sqrt{2}}(|1\rangle + \mathrm{e}^{\mathrm{i}\phi}|2\rangle)$. Rabi oscillations now correspond to rotation of the Bloch vector at an angular frequency Ω; the axis of rotation depends upon the detuning δ of the driving field (see for example pictures in Foot, §7.3).

The observant reader will have asked himself what has happened to the time-dependent phase factors $\mathrm{e}^{-\mathrm{i}\omega_1 t}$ and $\mathrm{e}^{-\mathrm{i}\omega_2 t}$ which were present in our original superposition state 1.4 (the *really* observant reader will have already asked herself this question where the example $\pi/2$-pulse was given above). The answer is that we have absorbed these in the states, so that $|1\rangle = \mathrm{e}^{-\mathrm{i}\omega_1 t}|\psi_1\rangle$ and similarly for $|2\rangle$. Since a global phase on the whole wavefunction is irrelevant, this is equivalent to a phase factor $\mathrm{e}^{-\mathrm{i}\omega_0 t}$ multiplying $|\psi_2\rangle$. Thus we can imagine two alternative pictures: the "lab frame" in which the Bloch vector representing a superposition state such as

$$\tfrac{1}{\sqrt{2}}(|\psi_1\rangle + \mathrm{e}^{-\mathrm{i}\omega_0 t}|\psi_2\rangle) \tag{1.42}$$

lies in the xy-plane and rotates around the z-axis with angular frequency $\omega_0 = \omega_2 - \omega_1$, or we can jump into a "rotating frame" which rotates with angular frequency ω_0 and consider this to be the same superposition state as

$$\tfrac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \tag{1.43}$$

which lies stationary in the xy-plane. Often one works in the rotating frame because it eliminates the need to keep track of the relative phase factor $\mathrm{e}^{-\mathrm{i}\omega_0 t}$ between the two states.

1.7 Damping: rate equations revisited

Throughout our treatment of the atom-light interaction we have neglected any damping processes, such as spontaneous decay from the upper level to the lower level. A treatment including the effects of damping is beyond the scope of this course, but of course it is enormously important in real situations. Its effect, as might seem reasonable intuitively, is to "damp" the Rabi oscillations (an imperfect analogy is the motion of a damped harmonic oscillator), but in such a way that we retrieve the behaviour predicted by the simple rate equation approach (at least in the limit of long time or strong damping). This explains why a rate equation treatment is still useful in the context of laser physics, despite the fact that the radiation field is intense and monochromatic. (The interested reader is referred to the discussion in Fox §9.5.)

Further reading

Atom-light interaction, Bloch sphere: Foot chapter 7, Fox chapter 9.
Pure and mixed states: Fox §9.2.
Foot: "Atomic Physics", C.J.Foot, Oxford Master Series, 2005.
Fox: "Quantum Optics", M.Fox, Oxford Master Series, 2006.

*This topic is no longer on the syllabus, but if you've got this far you'll want to know about it.