Quantum theory of light-matter interaction: Fundamentals

Lecture 10
Selected topics in laser spectroscopy

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BEFEKTETÉS A JÖVŐBE

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Overview

- Laser technology has greatly expanded the potential of atomic and molecular spectroscopy, but the same techniques for describing the interaction of light with matter also apply to the traditional arc lamps and flash discharges, and the more recent synchrotron radiation sources.
- This Lecture develops theoretical techniques to describe absorption and emission spectra, using concepts introduced in the previous Lectures.

  The simplest cases are treated, some of these should be already familiar to the reader from laser physics or spectroscopy courses. Here we focus on the theoretical description of the interaction of quantized matter with light.

Reminder: index of refraction

The complex index of refraction for a medium containing harmonically bound charges:

$$
\begin{aligned}
n(\omega) &= \sqrt{1+\frac{N\alpha(\omega)}{\epsilon_0}} \approx 1+\frac{N\alpha(\omega)}{2\epsilon_0} \\
&= 1+\frac{Ne^2}{2m\epsilon_0}\left(\frac{\mathrm{i}\gamma\omega+(\omega_0^2-\omega^2)}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}\right) = n'+\mathrm{i}n''
\end{aligned}
$$

The expansion is valid when the density of atoms N is low.

The imaginary part of the index of refraction causes damping of a plane wave, i.e. absorption.

Absorption lines

The absorption of light through the medium shows a resonant behaviour near $\omega \approx \omega_0$ determined by

$$n''(\omega) = \frac{Ne^2}{2m\epsilon_0}\left(\frac{\gamma\omega}{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}\right) \approx \frac{\pi Ne^2}{4m\epsilon_0\omega_0}\left(\frac{\gamma/2\pi}{(\omega_0-\omega)^2+\gamma^2/4}\right)$$

This is called an absorptive lineshape. When the single electron is harmonically bound, its interaction with radiation is found in this response. For a real atom, the response of the electron is divided among the various transitions to other states. The fraction assigned to one single transition is characterized by the oscillator strength f_n. In ordinary linear spectroscopy, the laser is tuned through the resonance $\omega \approx \omega_0$, and the value of ω_0 is determined from the lineshape. Several closely spaced resonances can be resolved if their spacing is larger than their widths: $|\omega_0^{(1)} - \omega_0^{(2)}| < \gamma$.

Speed of light

The velocity of light in the medium shows a dispersive behaviour around the resonance

$$c_{\text{eff}} = \frac{c}{n'} \approx c \left[1 - \frac{Ne^2}{2m\epsilon_0} \left(\frac{(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2} \right) \right]$$

Note that at resonance it is the speed of light in vacuum. Below resonance $c_{\text{eff}} < c$ since the polarization is in phase with the driving field, thus by storing the incoming energy, the driving field retards the propagation of the radiation.

For a harmonically bound charge, the refractive index always stays absorptive and it is independent of the intensity of the laser radiation. This no longer holds for discrete-level atomic systems.

Reminder: two-level atoms

The steady-state solution for the density matrix elements of a two-level atom in dipole interaction with a nearly resonant plane wave, in RWA:

$$\varrho_{ee} = \frac{\Omega_r^2\gamma}{2\Gamma}\,\frac{1}{\Delta^2+\gamma^2+\Omega_r^2\gamma/\Gamma},$$
$$\varrho_{eg} = \frac{\mathrm{i}\Omega_r}{2}\,\frac{\varrho_{gg}-\varrho_{ee}}{\gamma+\mathrm{i}\Delta} = \frac{\mathrm{i}\Omega_r}{2}\,\frac{\gamma-\mathrm{i}\Delta}{\Delta^2+\gamma^2+\Omega_r^2\gamma/\Gamma}.$$

What are the meanings of the Greek letters above?

Calculating the polarization density $P = N\,\mathrm{Tr}[\hat{\varrho}\,\hat{d}]$ for a sample with density of two-level atoms N yields the complex polarizability

$$\alpha(\omega) = \frac{d^2}{\hbar}\,\frac{\mathrm{i}\gamma+\Delta}{\Delta^2+\gamma^2+\Omega_r^2\gamma/\Gamma}$$

and index of refraction with the oscillator strength $f_0 = 2d^2 m\omega_0/\hbar e^2$

$$n(\omega) = 1 + \frac{\pi N e^2}{4m\epsilon_0\omega_0}\,\frac{f_0}{\pi}\,\frac{\mathrm{i}\gamma+\Delta}{\Delta^2+\gamma^2+\Omega_r^2\gamma/\Gamma}$$

Homogeneous line broadening mechanisms

The effective width of a spectral line for two-level atoms is

$$\gamma_{\text{eff}} = \sqrt{\gamma^2 + \Omega_r^2 \gamma / \Gamma} \approx \frac{\Gamma}{2} + \gamma_{\text{ph}} + \frac{\Omega_r^2}{2\Gamma}$$

The $\gamma = \Gamma/2 + \gamma_{\text{ph}}$ contains all the transverse relaxation mechanisms.

- Pressure broadening: For low enough pressures in gases (usually below 100 Pa), collisional perturbations are proportional to the density of perturbing atoms, i.e. to the pressure:

  $$\gamma_{\text{ph}} \propto p$$

  with γ_{ph} having the order of magnitude of the inverse of the average free time between collisions.

Homogeneous line broadening mechanisms

The effective width of a spectral line for two-level atoms is

$$\gamma_{\text{eff}} = \sqrt{\gamma^2 + \Omega_r^2 \gamma / \Gamma} \approx \frac{\Gamma}{2} + \gamma_{\text{ph}} + \frac{\Omega_r^2}{2\Gamma}$$

- Power broadening: The term $\Omega_r^2/2\Gamma$ also makes the spectral line appear broader than in the harmonic case.
  Physically, this derives from a saturation of the two-level system in which the population of the upper level becomes an appreciable fraction of that of the lower level.
  In the limit $\Omega_r \to \infty$, $n(\omega) \to 1$ and the atom-field interaction effectively vanishes. In this limit, $\varrho_{ee} \to 1/2$ and the field induces as many upward transitions as downward transitions.

Relaxation processes that are active on each and every individual atom separately are called homogeneous broadening processes.

Inhomogeneous line broadening, Doppler broadening

A parameter shifting the individual atomic resonance frequencies by different amounts for the different individual atoms, leads to inhomogeneous broadening.

The most important inhomogeneous broadening is Doppler broadening, caused by the velocity distribution of atoms in a gas sample at temperature T:

$$P(v) = \frac{1}{\sqrt{2\pi u^2}} \exp\left(-\frac{v^2}{2u^2}\right)$$

with $u^2 = k_B T/M$.
A particular atom with velocity v in the direction of the optical beam with wave vector k then experiences the Doppler-shifted frequency $\omega - kv$ relative to a standing atom, and the effective detuning becomes $\Delta + kv$ for all the atoms with velocity v.

Inhomogeneous line broadening, Doppler broadening

The ground state population for this velocity group is

$$\varrho_{gg} = 1 - \frac{\Omega_r^2 \gamma}{2\Gamma} \frac{1}{(\Delta + kv)^2 + \gamma^2 + \Omega_r^2 \gamma / \Gamma}$$

If the field is strong enough to deplete the ground state population of atoms in this velocity group, then a Bennett hole (of width given by γ_{eff}) is seen in the velocity distribution of the atoms. When the laser frequency is tuned, the hole sweeps over the velocity distribution of the atoms. The atomic response is saturated at the velocity group of the hole, indicating that spectral hole burning has occurred.

Inhomogeneous line broadening, Doppler broadening

The observed spectrum is obtained by averaging the single atom response over the velocity distribution. From the imaginary part, the absorption response is

$$\alpha''(\omega) = \frac{d^2}{\hbar\sqrt{2\pi u^2}} \int_{-\infty}^{\infty} \frac{\gamma e^{-\frac{v^2}{2u^2}}}{(\Delta + kv)^2 + \gamma^2 + \Omega_r^2 \gamma/\Gamma} dv$$

In the limits $\Omega_r \to 0$ (no saturation), and $\gamma \ll ku$ (the Doppler limit), the Lorentzian line shape sweeps over the entire velocity profile, finding a resonant velocity group as long as $v \leq u$.

Thus, linear spectroscopy sees a Doppler broadened line of width ku. This is an inhomogeneous broadening.

Inhomogeneous line broadening, Voigt profile

In the unsaturated regime, the atomic response function $\alpha''(\omega)$ is proportional to the imaginary part of the function

$$V(z) = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} \frac{\exp(-x^2/2\sigma^2)}{z - x} dx$$

at $z = -\Delta - \mathrm{i}\gamma$ and $\sigma = ku$. This is the Hilbert transform of the Gaussian, and its shape is called a Voigt profile. This has been widely used to interpret the data of linear spectroscopy.

Inhomogeneous line broadening, spatial hole burning

Another example of inhomogeneous broadening is the influence of the lattice environment on impurity spectroscopy in solids. The resonant light selectively excites atoms at those particular positions which make the atoms resonant. Thus only these spatial locations are saturated, and the phenomenon of spatial hole burning occurs. This has been investigated as a method for storing information, signal processing, and volume holography.

Nonlinear spectroscopy of two-level atoms: Concept

The previous slides show that a single laser cannot resolve beyond the Doppler width: inhomogeneous broadening masks the desired information by dominating the line shape. The availability of laser sources has made it possible to overcome this limitation, and to use the saturation properties of the medium to perform nonlinear spectroscopy.

If a strong laser is used to pump the transition, a weak probe signal can see the hole burnt into the spectral profile by the pump. This technique is called pump-probe spectroscopy.

This section discusses how Doppler broadening can be eliminated to achieve Doppler-free spectroscopy. Similar techniques may be used to overcome other types of inhomogeneous line broadening; a general name is then hole-burning spectroscopy.

Generalization for multimode fields

Consider now the case of several incoming electromagnetic fields of the form

$$E(z,t) = \sum_j \frac{1}{2} E_j(z) \exp(-\mathrm{i}\omega_j t - \mathrm{i}\varphi_j) + \text{c.c.}$$

The index j may range over several laser sources, the output of a multimode laser or the multitude of components of a flashlight or a thermal source.

Now we generalize the rate equations for this case, which needs some care regarding its derivation from the density matrix equations.

The steady state for ϱ_{eg} becomes:

$$\varrho_{eg} = \frac{\mathrm{i}}{2} \sum_j \frac{E_j\, d}{\hbar} \frac{\varrho_{gg} - \varrho_{ee}}{\gamma + \mathrm{i}\Delta_j} \exp(-\mathrm{i}\omega_j t - \mathrm{i}\phi_j) = \sum_j \varrho_{eg}^{(j)} \exp(-\mathrm{i}\omega_j t - \mathrm{i}\varphi_j)$$

i.e. the response of the atom now separates into individual contributions with detuning $\Delta_j = \omega_0 - \omega_j$, oscillating at the various ω_j.

Generalization for multimode fields

The time-dependent equation for the populations is

$$\dot{\varrho}_{ee} = -\dot{\varrho}_{gg} = -\Gamma \varrho_{ee} + \frac{\mathrm{i}}{2} \sum_j \frac{E_j\, d}{\hbar} \exp(-\mathrm{i}\omega_j t - \mathrm{i}\varphi_j) \varrho_{ge} - \text{c.c.}$$

which, inserting ϱ_{ge}, reads as

$$\dot{\varrho}_{ee} = -\Gamma \varrho_{ee} + \frac{d^2}{2\hbar^2} (\varrho_{gg} - \varrho_{ee}) \sum_{i,j} E_i E_j \exp(-\mathrm{i}(\omega_j - \omega_i)t - \mathrm{i}(\varphi_i - \varphi_j)) \frac{\gamma}{\Delta_j^2 + \gamma^2}$$

Since the contributions from the different frequency terms average to zero either by beating or by incoherent effects from the random phases, only the coherent sum survives to give

$$\dot{\varrho}_{ee} = -\Gamma \varrho_{ee} + (\varrho_{gg} - \varrho_{ee}) \frac{1}{2} \sum_j (\Omega_r^{(j)})^2 \frac{\gamma}{\Delta_j^2 + \gamma^2}$$

Generalization for multimode fields

This is a rate equation in the limit of many uncorrelated components of light, i.e. for a broadband light source. In this case the incoherence between the different components justifies the use of a rate approach, and no assumption like $|\dot{\varrho_{eg}}| \ll |\gamma + \mathrm{i}\Delta|\,|\varrho_{eg}|$ is needed. Thus, the limit $\gamma \to 0$ is also legitimate.

Two-Level Doppler-Free Spectroscopy

In order to overcome Doppler broadening, suppose a strong laser (E_1 at ω_1) is used to pump the transition, and a weak probe signal (E_2 at ω_2) is used to see the hole burnt into the spectral profile by the pump. We use our previous results for the rate equations for multimode fields: $\varrho_{eg}^{(2)}$ carries the information about the linear response at frequency ω_2.
Let the pump and the probe propagate in opposite directions: their detunings are $\Delta_1 + kv$ and $\Delta_2 - kv$. Since the frequencies are close to each other, the two k-vectors are nearly equal in magnitude.
The linear response now becomes

$$\varrho_{eg}^{(2)} = \frac{\mathrm{i}}{2}\frac{E_2\, d}{\hbar}\,\frac{\varrho_{gg} - \varrho_{ee}}{\gamma + \mathrm{i}(\Delta_2 - kv)}$$

Two-Level Doppler-Free Spectroscopy

For the population difference, we consider only the strong pump:

$$\varrho_{eg}^{(2)} = \frac{1}{2}\frac{E_2\, d}{\hbar}\,\frac{\mathrm{i}\gamma + (\Delta_2 - kv)}{\gamma^2 + (\Delta_2 - kv)^2}\left[1 - \frac{(\Omega_r^{(1)})^2\gamma}{\Gamma}\frac{1}{\gamma^2 + (\Delta_1 + kv)^2 + (\Omega_r^{(1)})^2\gamma/\Gamma}\right]$$

This is the linear response of atoms moving with velocity v. To obtain the polarization of the whole sample, we must average over the velocity distribution. The first term in the [1 + ...] gives the linear response in the form of a Voigt profile. The second term contains the nonlinear response. This shows the details of the homogeneous features under the Doppler line shape. For simplicity, we assume the Doppler limit, neglect the variation of the Gaussian over the atomic line shape, and also neglect the power broadening due to the pump.

Two-Level Doppler-Free Spectroscopy

The result:

$$\begin{aligned}\alpha''(\omega) &= -\frac{d^2}{\hbar}\frac{(\Omega_r^{(1)})^2\gamma^2}{\sqrt{2\pi}\Gamma u}\int_{-\infty}^{\infty}\frac{dv}{[\gamma^2+(\Delta_2-kv)^2]\,[\gamma^2+(\Delta_1+kv)^2]}\\ &= -\frac{d^2}{\hbar}\frac{\sqrt{2\pi}(\Omega_r^{(1)})^2}{4\Gamma ku}\frac{\gamma}{(\omega-\omega_0)^2+\gamma^2}\end{aligned}$$

This denotes the energy absorbed from the probe, as induced nonlinearly by the intensity of the pump.
The resonance is still at ω_0, but with a *homogeneous atomic line shape*!
In the Doppler limit, the Doppler broadening is only seen in the prefactor.

Summary and further reading

- Modern laser spectroscopy is much more than sending a laser beam through the sample into the spectrograph. To understand and master how matter interacts with light, you need quantum mechanics at least for the atoms.
- References:

P. Meystre and M. Sargent: *Elements of Quantum Optics*, Spinger (Berlin, Heidelberg) (2007)

Gordon W. F. Drake (ed.): *Handbook of Atomic, Molecular, and Optical Physics*, Spinger (Berlin, Heidelberg) (2006)

B. E. A. Saleh and M. C. Teich: *Fundamentals of Photonics*, 2nd. ed., Wiley, 2007.

Questions

1. Explain what linear spectroscopy is, based on the complex index of refraction.
2. Which atomic resonances can be resolved?
3. What is pressure broadening?
4. What is power broadening?
5. What is a homogeneous broadening process?

Questions

6. What is an inhomogeneous broadening process?
7. Why is the velocity distribution Gaussian for a gas sample of atoms?
8. What is a Voigt profile and what is it good for?
9. Explain the key concepts that lead to a rate equation description of two-level atoms interacting with multimode light.
10. What are the roles of the pump and the probe in the Doppler-free spectroscopy?