

Two-electron systems

Laboratory exercise for FYSC11

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Goal

In this laboration we will make use of a modern spectroscopic technique to study the gross structure of a two electron system, to study transitions and structure in a small part of this system.

The lab includes registration of a spectrum, measurements of wavelengths and intensities of spectral lines from some multiplets in Ca I. We will also derive energies of the levels and compare them with simple theoretical energy and intensity relations.

A calcium atom has two electrons outside a closed shell, and is therefore one of the most simple many electron systems. Such a system is hence suitable for an introductory study of atomic structure.

The calcium spectral lines are emitted by a plasma created in a hollow cathode discharge and recorded with a Fourier transform spectrometer. The experimental equipment is described in the following sections.

The spectral lines that we will study are the transitions between the lower term $3d4s\ ^3D$ and upper terms $3d4p\ ^3D$ and 3F . The energy of the $3d4s$ levels are known. The energies of the $3d4p$ levels will be derived from the observations. The observed intensities will be compared with intensities calculated assuming LS coupling. The fine structure splitting will be compared with the Landé interval rule which is valid in LS coupling. The results can be used to discuss the validity of the LS approximation.

Before the laboration the following sections in should be studied in addition to this instruction:

- The Central Field Approximation, Foot 4.3-4.6, Demtröder 6.4.1-6.4.3
- LS Coupling, Foot 5-5.5, Demtröder 6.5
- Deviations form Pure LS Coupling, Foot 5-5.5, Demtröder 6.5
- Selection Rules and Multiplets in LS Coupling, Foot 5-5.5, Demtröder 6.5

Exercises to be solved before the laboration:

1. The width of a spectral line in the hollow cathode discharge is determined by the Doppler effect. Use equation 8.17 in Spectrophysics or 8.6 in Foot, to calculate the Doppler width (in nm and cm^{-1}) of a calcium spectral line at 600 nm if the temperature in the light source is 500 K. (Hint Demtröder p. 266)
2. How far should the moving mirror in an FTS instrument move in order to get an instrumental line profile smaller the the Doppler width in the previous question?

3. Give the total electron configuration of a calcium atom in the ground state.
4. The attached table includes the lowest experimentally determined levels in neutral calcium (Ca I). Draw an energy level diagram including the ground state and the levels in the $4snl$ configuration (observe that the $3d4s$ also belongs to this configuration). Draw the energy diagram in the same way as the energy level diagrams are drawn in Chap. 3 in Spectrophysics. Do not try to draw the individual levels in the triplets, draw the triplets as a box instead.
5. Mark the strongest spectral line in the diagram (the resonance line).
6. Are there any metastable levels in Ca I? If so, which? Motivate!
7. We shall experimentally determine the energy of two terms in the $3d4p$ configuration by measurements of the wavenumber of the transitions between these terms and the $3d4s$ configuration. Derive all possible states (L, S, J) in the configurations $3d4s$ and $3d4p$. Give the level designation in the LS notation, $^{2S+1}L_J$.

Theory and equipment

The most important method for investigating atomic structure is emission spectroscopy, i.e. the measurement of the energy distribution of the photons that are emitted from excited atoms. To do these measurements we need an excitation device (light source) and an instrument for energy analysis (spectrometer). In atomic spectroscopy many different methods are used optimized for different energy intervals and ionization conditions. The technique described here gives the highest precision over a very large energy interval when studying neutral and singly ionized atoms.

Excitation

See Spectrophysics 15.1, especially 15.1.4.

When investigating an atomic system, in principle one single transition, one spectral line, can be studied, e.g. using laser spectroscopy. This is possible, at least for neutral atoms, in the wavelength region where tunable lasers are available, and the method is used for studies of special problems. Already for simple systems, e.g. the one-electron system for alkali metals, you need to measure the energy for hundreds of transitions in order to determine the energy levels in the lower parts of the energy level system. That is why methods are used that allow for registration of as many transitions as possible at one time. For complex many-electron systems you may need to measure thousands of spectral lines in order to determine the main features

of the structure of the atom.

Emission of many spectral lines assume excitation to a large amount of energy levels. Many different processes are possible, but the most effective is excitation by electron collisions. Free electrons with enough kinetic energy, transfer this energy to the bound electrons in the collisions. At low energies only the least bound electron, the valence electron, will be excited. At higher energy one or more electrons will be knocked out, the atom is ionized. The ion can in turn be excited through new electron collisions.

An effective excitation through electron collision will take place in a partly ionized gas, a plasma, at low pressure, which is exposed to an electric field. A current will flow through the gas, where the charge carriers are mobile free electrons and slow positive ions. The atomic states that are excited through collision with the free electrons are deexcited through photon emission, the gas will glow. This phenomena is known as gas discharge in classic physics .

Hollow cathode discharge lamp

A special kind of discharge will occur if the cathode is formed as a tube with an inner diameter of 3-10 mm, see Fig. 1. When an electric field is

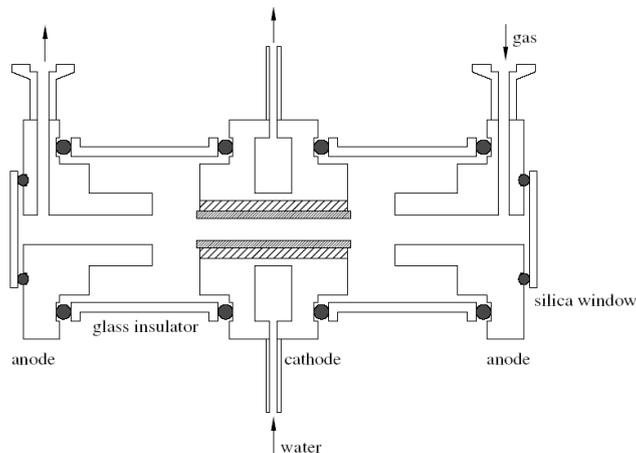


Figure 1: Hollow cathode discharge lamp.

connected between anode and cathode the discharge will start with the help of the few free electrons that are always there. Through electron collisions the gas will be further ionized, until equilibrium between ionization and recombination is achieved and a constant current is flowing. At the same time the excitation occur and the gas is glowing. In a certain pressure interval, 0.1 - 5 torr, the excitation and the emitting of the light will only occur in

the area inside the cathode, which then gets a very high luminance.

The gas in the discharge is called a carrier gas, and is always a noble gas. The positive gas ions that are formed are accelerated in the electric field and hit the inside of the cathode. At the collisions atoms from the walls of the cathode are set free and sent out in the plasma. This phenomena is called sputtering. The sputtered atoms will also be excited. In addition to the electron excitation in the plasma the metal atoms can also react with the noble gas ions and become ionized and excited. This is called charge transfer. The observed spectrum will consist of both spectral lines from the cathode material and the carrier gas. The hollow cathode can thus be used to produce spectra from both gases and solids.

The current through the discharge and the voltage drop between anode and cathode is determined from the building of space charges, which depend on the mobility of the ions, the pressure of the gas, the dimensions of the cathode etc. The complex balance determines the voltage drop and this together with the recombination in the plasma limits the ionization. This means that neutral and one time ionized atoms dominates the plasma. A very small contribution from doubly ionized atoms can under certain conditions be observed.

As all gas discharges the hollow cathode has a negative current-voltage-characteristic, and the current must thus be limited with a series resistance and/or a current limited power supply.

Spectrometers and interferometers

In a traditional spectrometer, the spectral decomposition of the radiation is accomplished through refraction in a prism or diffraction in a grating. Different wavelengths achieve different directions in space. The spectrum is registered either photographically or using a CCD-detector through direct imaging of a broad spectral interval, or with a slow rotation of a grating so the spectrum sweeps by a photoelectric detector which registers the radiation.

In an interferometer each wavelength gives rise to an interference pattern, and all wavelengths patterns overlap. An interferometer can still give each wavelength another characteristic, which can be used for spectral decomposition. The principles for this method, Fourier Transform Spectroscopy (FTS) will be described later.

First lets compare the grating spectrometer with the interferometer. A detailed analysis shows that the interferometer has a number of great advantages:

- The interferometer gives better possibilities to achieve a high resolution.
- The interferometer gives a 10-100 times larger wavelength accuracy

with a very simple calibration.

- At the same resolution, the light flow through an interferometer is 10-100 times larger than through a grating spectrometer, giving a superior signal-to-noise ratio.
- The spectrum is produced directly in digital form for further analysis in a computer.

The disadvantages of the interferometer are mainly the following:

- The useful spectral interval is limited by the availability of transparent materials with a high surface accuracy. The lower wavelength limit for the FTS is 130 nm.
- The method described later demands a light source giving a constant emission with very small fluctuations. This means that spectrum from highly ionized atoms are in practice impossible.

The Fourier Transform Spectrometer

See Spectrophysics 13.5, 13.6.

The fundamental part of a FTS is a Michelson interferometer, see Fig. 2. Lets assume that the entrance aperture is illuminated with monochromatic

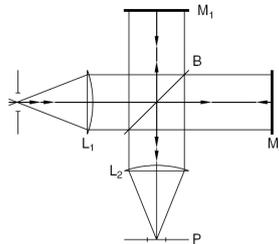


Figure 2: Michelson interferometer.

light with a wavelength λ , a wavenumber $\sigma = 1/\lambda$. The collimating lens L_1 gives parallel beams, and in the beamsplitter the light is divided so the amplitude of the electromagnetic field in each interferometer arm is the same. After reflection in the plane mirrors M_1 and M_2 and one more passage through the beamsplitter (where the amplitude is divided one more time) the two beams are recombined and registered by a detector at P. We call the amplitude of each beam a , and through vectorial addition we get the resulting amplitude, see Fig. 3. δ represents the phase difference, which depend on the difference x in optical path length between the two interferometer arms. The law of cosines gives:

$$A^2 = a^2 + a^2 + 2a^2 \cos \delta \quad (1)$$

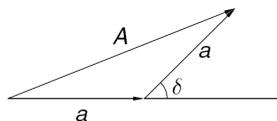


Figure 3: Addition of amplitudes.

Since the path difference one wavelength corresponds to a phase difference of 2π we can write $\delta/2\pi = x/\lambda$, i.e. $\delta = 2\pi\sigma x$, where x is the path difference. For the wavenumber σ the detector registers an intensity, I , which is a function of x and σ :

$$I_x = 2a^2(1 + \cos 2\pi\sigma x) = I_m(1 + \cos 2\pi\sigma x) \quad (2)$$

where I_m is the average intensity that hits the detector.

If we move one of the mirrors in the direction of the light beam at a constant velocity the detector will register a cosine signal, with a frequency that depends on the velocity and the wavenumber. If the mirror moves at a velocity of $v/2$ the path difference will change with the velocity v and thus $x = vt$, the signal varies as $\cos 2\pi\sigma vt = \cos 2\pi ft$. The frequency f of the signal is then σv . If we assume that v is 1 mm/s and $\lambda=1 \mu\text{m}$ ($\sigma=10\,000 \text{ cm}^{-1}$), $f=1 \text{ kHz}$.

Now we have what we wanted - the interferometer gives a signal with a frequency characteristic for the wavenumber of the radiation. We can say that the interferometer modulates the radiation with a for each wavenumber characteristic frequency. This frequency is easy to measure. If the entrance aperture of the interferometer is illuminated with radiation consisting of several different wavenumber component, the signal from the detector will become a sum of cosine functions with different frequencies. The spectrum can then be found through frequency analysis of the signal, then the signal is called an interferogram, see Fig. 4.

Now we have the principle for the FTS method. We will discuss this in more detail, investigate what happens if the radiation does not consist of one or more monochromatic spectral lines but real lines with a certain broadening or of an arbitrary spectral distribution.

An arbitrary spectral distribution is denoted $B(\sigma)$, with a unit W/cm^{-1} . We let B exist all over the wavenumber interval zero to infinity. Instead of a sum of cosine functions we will now write the interferogram as an integral over the wavenumber interval:

$$I_x = \int_0^\infty B(\sigma)(1 + \cos 2\pi\sigma x)d\sigma = I + \int_0^\infty B(\sigma) \cos 2\pi\sigma x d\sigma \quad (3)$$

We will disregard the constant term, I which gives no information of wavenumber. Further the integral will not change value if we change the lower inte-

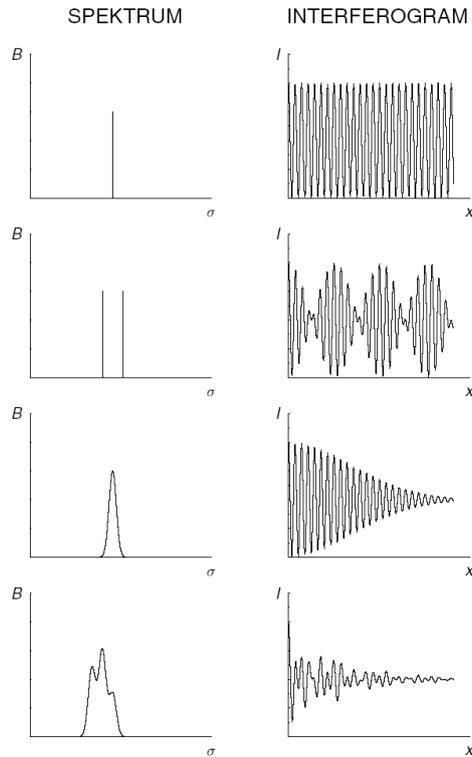


Figure 4: Spectrum and interferogram in four different cases (top to bottom): a monochromatic line, two monochromatic lines, a line with finite width (Gaussian profile), and a line with a more complex structure.

gration limit to $-\infty$ since $B(\sigma)=0$ for $\sigma < 0$ (negative wavenumbers have no physical meaning). This gives us:

$$I_x = \int_{-\infty}^{\infty} B(\sigma) \cos 2\pi\sigma x d\sigma \quad (4)$$

With knowledge of the theory of Fourier integrals we can now state that the interferogram $I(x)$ is the cosine transform of the spectrum $B(\sigma)$. And through Fourier theory we get the spectrum as the inverse transform:

$$B(\sigma) = \int_{-\infty}^{\infty} I(x) \cos 2\pi\sigma x dx \quad (5)$$

An overview of the connection between spectrum and interferogram is shown in Fig. 4.

In principle we can get a spectrum now, but in practice we have some problems. The mirror is moved a finite length instead of from $-\infty$ to ∞ . To be able to work with the interferogram in a computer, we need to digitize it,

i.e. register it in discrete points, corresponding to different values of x . This will give some complications. The finite moving result in that an infinitely thin spectral line will be shown as a distribution with a certain width. This is in direct correspondence with the fact that a grating spectrometer gives spectral lines with a certain width since the grating has a finite width. A simple calculation (see Spectrophysics 13.5.2) shows that the profile the instrument gives when the aperture is illuminated with monochromatic light has the shape:

$$S(\sigma) = \frac{\sin(2\pi(\sigma - \sigma_0)L)}{2\pi(\sigma - \sigma_0)L} \quad (6)$$

when the mirror is moved from $x = -L$ to $x = +L$. This instrument profile, shown in Fig. 5, has its first zero point at $\sigma = \pm 1/2L$. In analogy with the

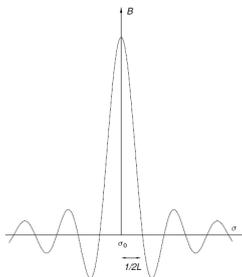


Figure 5: Instrument profile.

Rayleigh criteria at diffraction patterns, this is called the resolution limit $\delta\sigma$. The full width at half maximum, FWHM is $1.2/2L$. The resolution of a FTS instrument is thus determined from the maximum moving of the movable mirror.

The registration of the interferogram in discrete points, sampling, means that the Fourier integral instead will become a sum with a finite number of terms. This in turn means that the calculated spectrum will be repeated periodically in a way reminding of the spectral orders for a grating, see Fig. 6.

Both the finite moving and the sampling is treated mathematically easily with the convolution theorem, which says that the Fourier transform of a product of two functions is the convolution of the transforms of the two single functions. The finite moving is equivalent with a multiplication of an infinite interferogram with a rectangular function, whose transform is the $S(\sigma)$ -function above. The spectrum is thus convolved with this function. The measurements at discrete points, the sampling, is equivalent to a multiplication with a Dirac-comb, which transforms into another Dirac-comb, i.e. a periodic function which repeats the calculated spectrum.

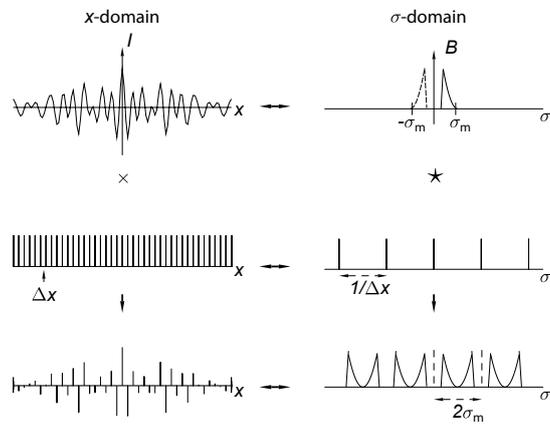


Figure 6: Repetition of the spectrum in different aliases due to the sampling.

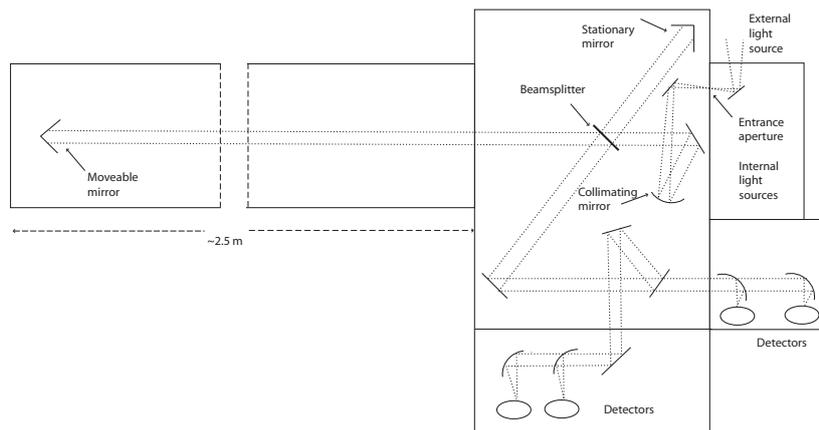


Figure 7: Schematic figure of the FTS.

Arrangement of Tables

The first table of energy levels presented here for neutral calcium is arranged in the usual way; the terms are listed in order of increasing energy without regard to configuration assignments. Because many long Rydberg series have been observed in Ca I, we present a second table for this spectrum in which the series are listed separately, followed by their series limits. This table reveals more clearly the character of the observed spectrum. The series are listed in order of increasing first series member. The series member with the largest value of n for each term type is followed by the limit or limits of that series in Ca II. The assignment of the limits is discussed by Brown et al. and graphically displayed in their figure 10.

References

- Armstrong, J. A., Esherick, P., and Wynne, J. J. (1977), Phys. Rev. A **15**, 180.
 Armstrong, J. A., Esherick, P., and Wynne, J. J. (1979), J. Opt. Soc. Am. **69**, 211
 Back, E. (1925), Zeits. f. Phys. **33**, 579.

- Bohr, N. This discovery was noted by Wentzel, G. (1923), Phys. Zeits. **24**, 106.
 Borgström, S. A., and Rubbmark, J. R. (1977), J. Phys. B **10**, 3607.
 Brown, C. M., Tilford, S. G., and Ginter, M. L. (1973), J. Opt. Soc. Am. **63**, 1454.
 Camus, P. (1974), J. Phys. B **7**, 1154, and unpublished data.
 Friedrich, H., and Treffitz, E. (1969), J. Quant. Spectrosc. Radiat. Transfer **9**, 333.
 Garton, W. R. S., and Codling, K. (1965), Proc. Phys. Soc. **86**, 1067.
 Grafenberger, H. (1937), Ann. d. Phys. [5] **30**, 267.
 Humphreys, C. J. (1951), J. Res. Nat. Bur. Stand. **47**, 262.
 Mansfield, M. W. D., and Newsom, G. H. (1977), Proc. R. Soc. London A **357**, 77.
 McIlrath, T. J. (1974), J. Phys. B **7**, 393.
 Moores, D. L. (1966), Proc. Phys. Soc. **88**, 843.
 Newsom, G. H. (1966), Proc. Phys. Soc. **87**, 975.
 Palenius, H. P., and Risberg, G. (1977), J. Phys. B **10**, L435.
 Risberg, G. (1968), Ark. Fys. **37**, 231.
 Roth, C. (1969), J. Res. Nat. Bur. Stand. **73A**, 497.
 Russell, H. N. (1927), Astrophys. J. **66**, 184.
 Russell, H. N., and Saunders, F. A. (1925), Astrophys. J. **61**, 38.
 Russell, H. N., and Shenstone, A. G. (1932), Phys. Rev. **39**, 415.
 Saunders, F. A. (1920), Astrophys. J. **52**, 256.
 Seaton, M. J. (1966), Proc. Phys. Soc. **88**, 815.
 Wagman, N. E. (1937), Univ. Pittsburgh Bull. **34**, 325.

Ca I: Ordered by term values

Configuration	Term	J	Level (cm ⁻¹)	Configuration	Term	J	Level (cm ⁻¹)
4s ²	¹ S	0	0.000				
4s4p	³ P°	0	15 157.901	4p ²	³ P	0	38 417.543
		1	15 210.063			1	38 464.808
		2	15 315.943			2	38 551.558
3d 4s	³ D	1	20 335.360				
		2	20 349.260				
		3	20 371.000				
3d 4s	¹ D	2	21 849.634				
4s4p	¹ P°	1	23 652.304	4s6s	³ S	1	40 474.241
4s5s	³ S	1	31 539.495	4s6s	¹ S	0	40 690.435
4s5s	¹ S	0	33 317.264	4p ²	¹ D	2	40 719.847
				4s6p	¹ P°	1	41 673.008
4s5p	³ P°	0	36 547.688	4p ²	¹ S	0	41 786.276
		1	36 554.749	4s4f	³ F°	2	42 170.214
		2	36 575.119			3	42 170.558
		4	42 171.026				
4s5p	¹ P°	1	36 731.615	4s4f	¹ F°	3	42 343.587
4s4d	¹ D	2	37 298.287	4s6p	³ P°	0	42 514.845
4s4d	³ D	1	37 748.197			1	42 518.708
		2	37 751.867			2	42 526.591
		3	37 757.449				