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DIPLOMOVÁ PRÁCE

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Teorie agregátů fotosyntetických molekul: spektroskopie, struktura, přenosové jevy

Fyzikální Ústav Univerzity Karlovy

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Theory of aggregates of photosynthetic molecules: spectroscopy, structure, transport phenomena

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In Prague, August 9th 2013

Ján Lalinský

Název práce: Teorie agregátů fotosyntetických molekul: spektroskopie, struktura, přenosové jevy

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Abstrakt. Teorie absorpce světla v izotropním roztoku molekul byla formulována na základě elektromagnetické teorie částic s přihlédnutím k relativistické povaze jejich interakce a jejímu dopadu na spektrum cirkulárního dichroizmu. Byly provedeny výpočty absorpčních spekter jednoduchých systémů pro demonstraci vlastností matematického modelu. Také byly provedeny výpočty spekter modelů dimeru bakteriochlorofylů, které byly navrženy jako možná základní jednotka v lamelárním modelu vnitřní struktury chlorozomu. Experimentální spektra roztoku neagregovaného bakteriochlorofylu byla použita pro nastavení parametrů matematického modelu molekuly a pro tyto parametry byla spočtena spektra navržených modelů dimeru. Bylo zjištěno, že nové neelektrostatické členy v popisu vzájemné interakce částí molekuly jsou zanedbatelné pro výpočet obyčejného absorpčního spektra, ale mají silný vliv na spektrum cirkulárního dichroizmu. Protože prezentovaný model popisuje vazbu elektronů a jejich pohyb velice přibližným způsobem, není jej ještě možné použít pro přesvědčivou analýzu optických spekter komplikovaných systémů jako jsou molekuly a bakteriochlorofylu a jejich agregáty.

Klíčová slova: chlorozom, agregát molekul, bakteriochlorofyl, teoretická spektroskopie, cirkulární dichroizmus

Title: Theory of aggregates of photosynthetic molecules: spectroscopy, structure, transport phenomena

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Abstract. A theory of absorption of light in an isotropic solution of molecules was formulated on the basis of electromagnetic theory of particles with attention to relativistic nature of their interaction and its impact on the spectrum of circular dichroism. Calculations of the absorption spectra of simple systems were performed to demonstrate the properties of the mathematical model. Also calculations of the absorption spectra of the models of the bacteriochlorophyll dimer which were proposed as possible basic unit in the lamellar model of the interior of a chlorosome were performed. The experimental spectra of solution of non-aggregated bacteriochlorophyll were used to fit the parameters of the mathematical model of the molecule and for these parameters the spectra of the proposed models of a dimer were calculated. It has been found that the new non-electrostatic terms in the description of the mutual interaction of the parts of the molecule are negligible for calculations of ordinary absorption spectrum, but they have strong effect on the spectrum of circular dichroism. As the presented model describes the bonding of the electrons and their motion in a very approximate way, it is not yet possible to use it for compelling analysis of optical spectra of complicated systems such as the molecules of bacteriochlorophyll and their aggregates.

Key words: chlorosome, aggregate of molecules, bacteriochlorophyll, theoretical spectroscopy, circular dichroism

Contents

Theory of aggregates of photosynthetic molecules: spectroscopy, structure, transport phenomena

Chapter 1

Introduction

1.1 Chlorosome

The study of photosynthesis is an activity on the border of physics, chemistry and biology that studies the mechanisms which plants and microscopic organisms employ to feed directly on Sun's energy. Besides the study of photosynthesis in plants, one of the directions is the study of structure and working mechanism of photosynthetic apparatus of photosynthetic bacteria. Among many different kinds of such bacteria, the *green sulfur bacteria* receive special attention due to distinction in the organization of their photosynthetic apparatus.

In many kinds of photosynthetic bacteria, such as the purple photosynthetic bacteria (e.g. *Rhodobacter sphaeroides*) the harvest of light energy is carried out by a large collection of *bacteriochlorophyll* (BChl) molecules intermixed with protein molecules, called the *antenna complex*.

The antenna complex of the green sulfur bacteria such as *Chlorobium tepidum* is different; it is all contained within a small body called *chlorosome*, an ellipsoid organelle with dimensions of order 200 nm that contains hundreds of thousands of BChl molecules. Its interior is composed of the bacteriochlorophyll molecules, most usually the kind *c,d* and *e*, and there are almost no protein molecules inside.[1]

Inside the chlorosome, the molecules of bacteriochlorophyll are believed to undergo almost spontaneous aggregation with little or no help from the protein molecules and to form *aggregates* - more or less regular structures of densely packed molecules.[2]

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[1] Besides BChl molecules, there is also small amount of *carotenoids* and *quinones*.

[2] More introductory information on the chlorosome can be found in the paper G. T.

Based on the observations of chlorosomes by electron microscope and by other methods, various models of structure of these aggregates were proposed. According to the model proposed by Staehelin et al. (1980)[3] the BChl molecules are arranged cylindrically into long rods.

This model was (after quite a long time), questioned by Pšenčík et al. (2004)[4] who did electron microscopic and X-ray diffraction study of frozen chlorosome bodies from the bacteria of *Chlorobium tepidum* and concluded that for the chlorosome of this bacterium the rod model is unlikely. They suggested a new model which explains their observations better. In this model, called the *lamellar model*, the BChl molecules form stacked sheets that are parallel to the long axis of the chlorosome and undergo folding and undulations in the plane perpendicular to it.

The authors suggested two distinct possibilities of how the individual BChl molecules can be arranged to produce such lamellae - a *parallel* model proposed by Smith et al. (1983)[5] and an *anti-parallel* model of Brune et al. (1988).[6] We note that many more models were proposed for the aggregates of chlorosome bacteriochlorophylls, some of which are variations of these two. The basic unit of these structures consists of a pair of BChl molecules weakly bonded to each other, which we shall call *dimer*.

Oostergetel, H. v. Amerongen, E. J. Boekema, *The chlorosome: a prototype for efficient light harvesting in photosynthesis*, Photosynth. Res. (2010) 104:245-255, and the review N.-U. Frigaard, D. A Bryant, *Chlorosomes: Antenna Organelles in Photosynthetic Green Bacteria*, Microbiol. Monogr. 2006, Springer. See also the www page http://www.bio.ku.dk/nuf/research/chlorosome.htm .

[3] L. A. Staehelin, J. R. Golecki and G. Drews, *Supramolecular organization of chlorosome (Chlorobium vesicles) and of their membrane attachment site in Chlorobium Limicola*, Biochim. Biophys. Acta. 589:30–45., (1980).

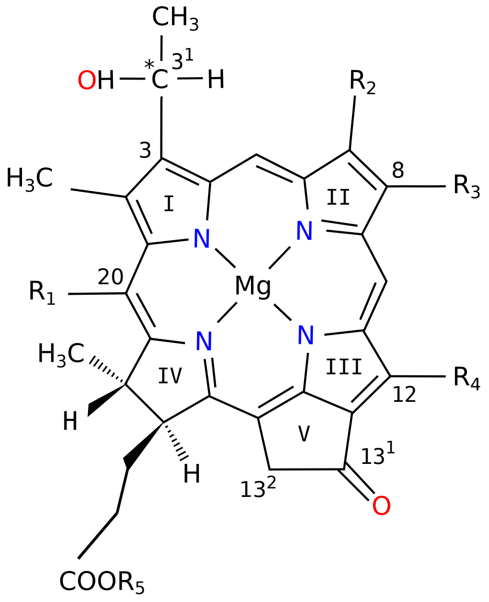
[4] J. Pšenčík et al., *Lamellar Organization of Pigments in Chlorosomes, the Light Harvesting Complexes of Green Photosynthetic Bacteria*, Biophysical Journal, Vol. 87, (2004), p. 1165-1172.

[5] K. M. Smith, L. A. Kehres and J. Fajer, *Aggregation of the bacteriochlorophylls c, d, and e. Models for the antenna chlorophylls of green and brown photosynthetic bacteria.*, J. Am. Chem. Soc. 105: 1387–1389 (1983)

[6] D. C. Brune, G. H. King and R. E. Blankenship, *Interactions between Bacteriochlorophyll c molecules in oligomers and in chlorosomes of green photosynthetic bacteria.* In: *Photosynthetic Light-Harvesting Systems* Scheer H and Schneider S (eds) Photosynthetic Light-Harvesting Systems, Walter de Gruyter, Berlin (1988), p. 141–151.

1.2 Bacteriochlorophyll c, d, e

In order to understand the geometry and binding of these dimers, we need to understand the structure of the chlorosome bacteriochlorophylls first. The general skeletal formula of these molecules, adopted from Blankenship et al. (1995)[7] is below.[8]



residue	BChl c	BChl d	BChl e
R_1	Me	H	Me
R_2	Me	Me	CHO
R_3	Et, nPr, iBu	Et, nPr,iBu, neoPent	Et, nPr, iBu, neoPent
R_4	Me, Et	Me, Et	Et
R_5	Stearyl, Farn., others	Farn. others	Farn., others

Table 1.1: Skeletal scheme of molecules bacteriochlorophyll *c, d, e* and possible residues substituted on the rim of the central chlorine ring I-II-III-IV. According to Blankenship et al. (1995).

The bacteriochlorophylls *c,d,e* differ from the other kinds of bacteriochlorophyll most notably in that they lack the methylcarboxyl group on the carbon C-13^2 and contain polar group OH substituted at the carbon

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[7] R. E. Blankenship, J. M. Olson, M. Miller, *Antenna Complexes from Green Photosynthetic Bacteria*, Advances in Photosynthesis, vol. 2, Kluwer, 1995, chap. 20.

[8] The picture file was adopted from https://pl.wikipedia.org/wiki/Bakteriochlorofile and modified with help of the program *Inkscape* available on http://www.inkscape.org.

atom C-3^1. The spontaneous aggregation of BChl *c,d,e* into dimers or larger aggregates with little or no help from proteins is explained by mutual bonding of this OH group of one molecule with the central Mg atom of another molecule. Chlorosomes may contain mixture of two or more kinds of the bacteriochlorophylls *c, d, e*, but the chlorosome of *Chlorobium tepidum* contains mainly the bacteriochlorophyll *c*. In the following text, we will focus on the kind *c* only. Detailed information on bacteriochlorophylls and chlorophylls can be found in the review by Scheer et al. (2006).[9]

1.3 Dimers

The two models of organization of bacteriochlorophyll in lamellae are depicted in the figures below. In both models, the stacking distance d of the chlorine rings of the dimer is believed to be in range $3.3 - 4.2$ Å, as suggested by Pšenčík et al. (2004).

In the parallel dimer, the second molecule is put below the first and translated in direction from OH to Mg so that the OH group of the 2nd molecule ends up below the Mg atom of the first molecule and they can form weak bond.

In the anti-parallel dimer, the second molecule is again put below the first, but then it is rotated in the plane of the ring around the Mg atom by 180° and translated in direction from Mg to OH, so that the Mg atom of the 2nd molecule ends up below the OH group of the 1st molecule and vice versa and they can form two weak bonds.

However, it is believed that only one arrangement is prevalent in chlorosome, so the next question is: assuming that these are the only basic possibilities, which one is closer to the actual structure of the aggregates in the chlorosome?

When such question about three-dimensional arrangement of atoms in large molecule (e.g. for a protein) arises, the usual course of action is to grow a crystal composed of many units of the studied molecule, perform an X-ray diffraction experiment and from the analysis of the diffractogram infer the structure of the unit cell, which is supposed to be similar to the natural structure of the molecule *in vivo*.

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[9] H. Scheer (auth.), B. Grimm, R. J. Porra, W. Rüdiger, H. Scheer (eds.), *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*, Advances in Photosynthesis and Respiration 25, Springer Netherlands, 2006.

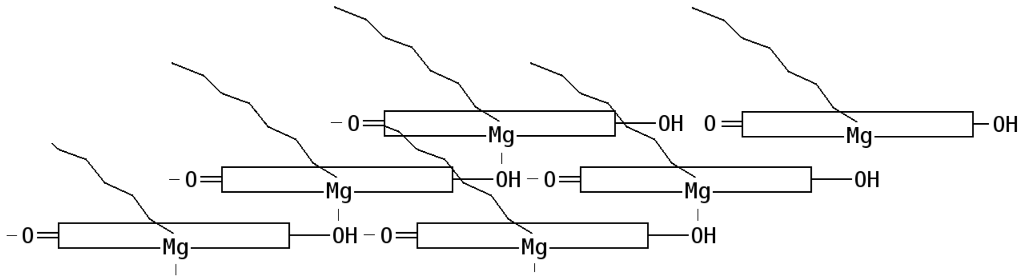

Figure 1.1: Parallel arrangement of bacteriochlorophylls. The molecules are viewed from the plane of the chlorine ring. According to Pšenčík et al. (2004).

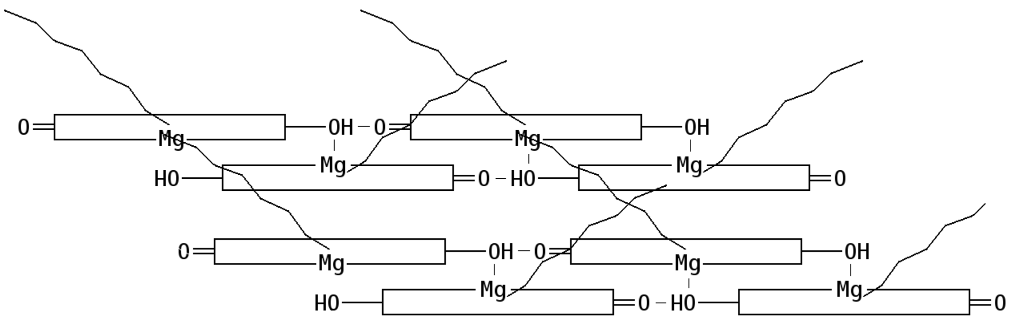

Figure 1.2: Antiparallel arrangement of bacteriochlorophylls. The molecules are viewed from the plane of the chlorine ring. According to Pšenčík et al. (2004).

However, in the case of bacteriochlorophyll aggregates, the manufacture of a crystal of sufficient size seems to be quite difficult task which has not been accomplished yet. For this reason, other methods have been adopted by scientists to study the structure of the chlorosome, both on the scale of the closest molecular neighbours and also on the scale of the assumed lamellae or rods made of large number of molecules.

1.4 Goal of the work

One of the methods that provides some information on the mutual position and orientation of the molecules is absorption spectroscopy. The measured spectrum and the relation between it and the structure can be used to infer which possible arrangement of the molecules is the most probable.

In this work we attempt to use the measured spectra of bacteriochlorophylls and their aggregates to infer which spatial arrangement of the molecules is most likely. We had at our disposal ordinary absorption spectra and circular dichroism spectra (differences of absorption of left-handed and right-handed light) of separate molecules, dimers and even larger aggregates of bacteriochlorophyll c molecules.

The methodology of our work should be as follows. First we formulate the theory explaining the absorption spectrum in terms of a microscopic model of the bacteriochlorophyll molecule. Then we try to find optimal parameters of this model to fit the absorption spectrum and circular dichroism spectrum of a solution of non-aggregated bacteriochlorophyll molecules (monomers). Finally, using these parameters we calculate the spectra for the proposed geometries of dimer and compare them to measured spectra of dimers. This procedure may allow us to infer which of the proposed models of dimer describes best the actual dimers formed spontaneously in the solution and perhaps also in the chlorosome.

Chapter 2

Available data

2.1 Measured spectra

Our work is based on the experimental absorption spectra and circular dichroism spectra of a liquid solution of bacteriochlorophyll monomers, dimers and larger aggregates in an organic solvent.[10] The aggregation occurs spontaneously in non-polar solvents (such as hexane). The first figure shows the absorption spectra, the second figure shows the circular dichroism spectra (CD) of the same solutions.

For the lack of space on this page, the plots are given on the next page.

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[10] These data were made available to us by doc. Jakub Pšenčík, PhD.

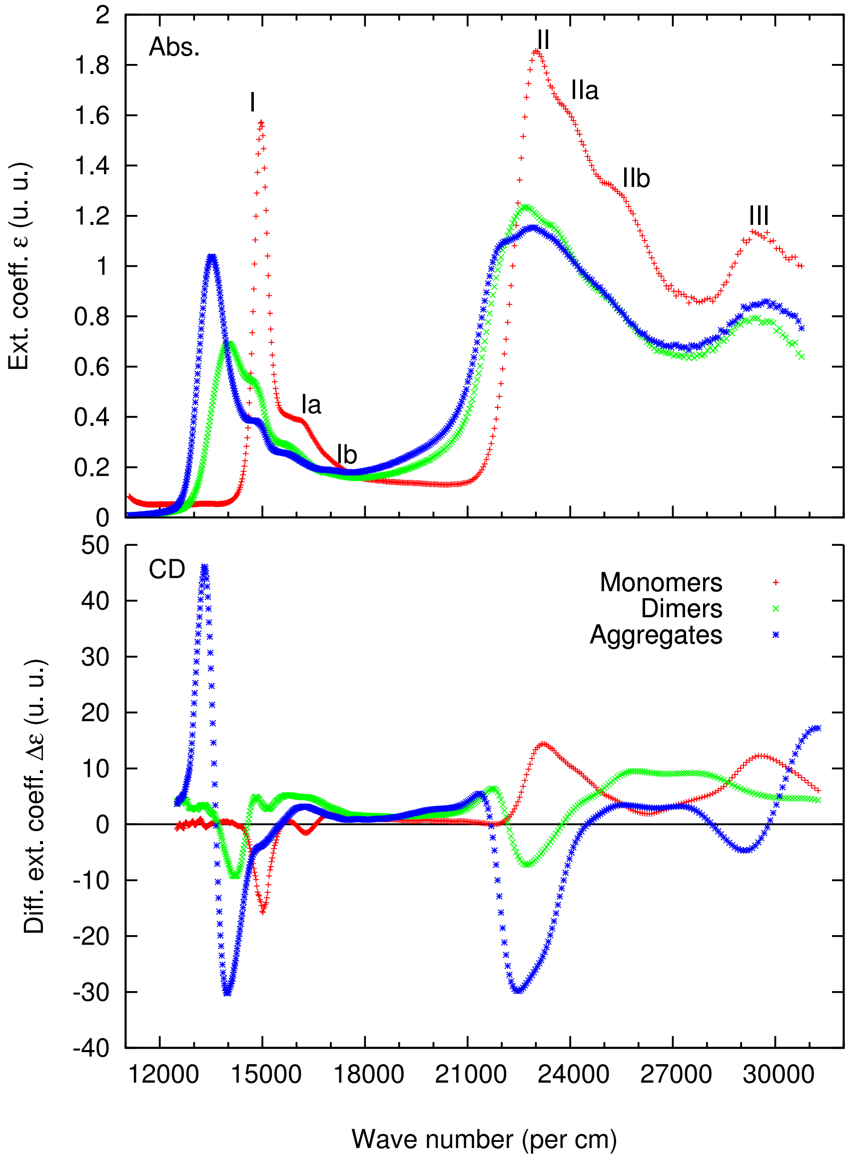

Figure 2.1: Absorption spectra of solution of monomers, dimers and larger aggregates. Both quantitites are in unknown units and the relation between the units is also unknown.

Both intensities are given in unknown units, which means that only the ratios of two intensities of the same quantity at different wave numbers have physical meaning. The values of circular dichroism and of absorption are in different unknown units so unfortunately we cannot infer anything as to how strong the circular dichroism is.

On the other hand, the wave number axis is common to both plots; they were created so as to facilitate the identification of the corresponding bands in both plots.

From the absorption spectra the basic observation is that as the molecules aggregate into dimers, their resonance frequencies decrease while the corresponding bands undergo broadening, and the same thing happens (albeit less strongly) when passing from dimers to even larger aggregates. The spectrum of monomer molecule (red) shows three main distinct bands I, II, III, at wave numbers 15000, 23000 and 29500 cm^{-1}.

Near the band I, there is another satellite band Ia at 15800 cm^{-1}. The band Ib is not visible well on the monomer spectrum, but is supposed to be present there since it gets more pronounced as the aggregation proceeds. Both satellite bands are only mildly pronounced and almost coalesce with the main band.

The band II has also two satellites with higher frequencies that are so close together that they coalesce together.

The band III does not have any further recognizable structure, and it does not change its position with aggregation either.

In the case of circular dichroism, few basic comments can also be made. The solution of monomer molecule (red) exhibits non-zero circular dichroism at the resonance frequencies corresponding to the above absorption bands. The band I at 15000 cm^{-1} has in CD spectrum characteristic glimmer, resulting from the subtraction of two bands of two different resonance frequencies (for left-handed and right-handed light). The negative part of the band has minimum at 15000 cm^{-1}, so the right-handed light is absorbed more strongly at this frequency. The positive part is at 15700 cm^{-1} but is much lower, which means the left-handed light has a band that is not so intense as that of right-handed light. The behaviour is converse for the two other bands II and III, which show stronger absorption of left-handed light.

As the aggregation proceeds towards dimers, great changes in the CD

Band	Position (cm^{-1}) / Peak intensity		
	monomer	dimer	aggregate
I	15000 / 1.57	14000 / 0.69	13500 / 1.04
Ia	15800 / 0.40	14700 / 0.55	14800 / 0.39
Ib	16200 / 0.39 ?	15600 / 0.29	15700 / 0.26
II	23000 / 1.86	22700 / 1.24	22100 / 1.10
IIa	23800 / 1.64	23400 / 1.16	22900 / 1.15
IIb	25200 / 1.33	25000 / 0.88	24900 / 0.91 ?
III	29500 / 1.14	29400 / 0.80	29800 / 0.86

Table 2.1: Positions and intensities of the most pronounced bands in the absorption spectrum. The question marks denote bands that were almost unrecognizable, so the corresponding numbers should be taken with a grain of salt.

spectrum take place. The peaks of the band I shift to lower frequencies and are less pronounced, which is consistent with the behaviour of this band in ordinary absorption spectrum. The changes in the peaks of the bands II and III are more pronounced - the circular dichroism reverts sign, which may be a sign of notable structure changes (such as formation of dimers).

2.2 Plan of the work

The plan of our work should be as follows. First we need to formulate the macroscopic theory of the absorption spectra. Then we need some microscopic model of the BChl molecule and its dimer. The model of a bacteriochlorophyll molecule will employ several parameters a_k describing its microscopic structure and behaviour under action of a light wave. We should choose their values in such a way that the model leads to spectra of one molecule as similar to the experimental spectra as possible. The best parameters a_k^* may be used to calculate the spectra of the simplest aggregates - dimers. Comparing them to the measured spectra, we may be able to infer which geometry of dimers occurs naturally.

Chapter 3

Macroscopic theory of light absorption

In this chapter we summarize macroscopic theory describing the phenomena of ordinary absorption and circular dichroism in isotropic liquids. This will be useful in later chapters when we will discuss microscopic model of the aggregate and seek its connection to the measured spectra.

3.1 Ordinary absorption

Linearly polarized light of angular frequency ω and constant intensity I_0 is led to pass through a translucent cuvette containing the investigated substance (e.g. bacteriochlorophylls) dissolved in a liquid solvent. Let us denote the light intensity by I. This intensity is a function of distance z the light wave has travelled in the liquid (we neglect the absorption in the walls of the cuvette and the air).

If the solution is rare, the Lambert-Beer law is known to hold true with good accuracy - the intensity of light decreases exponentially with distance:

$$I(z) = I_0 e^{-Az}. \tag{3.1}$$

Here A is the *absorption coefficient* of the solution. It depends on the frequency of the light wave and also on the composition of the solution.

As the pure solvent has also non-zero absorption in the studied interval of wave numbers, the quantity A cannot be regarded as a property of the solute molecules only.

In order to correct at least for the major part of the solvent absorption and thus obtain a quantity that characterizes the solute more faithfully, it is customary to assume that the total absorption in solution is described by the formula

$$I(z) = I_0 e^{-(\mathscr{N}_{\text{solute}}\epsilon_{\text{solute}} + \mathscr{N}_{\text{solvent}}\epsilon_{\text{solvent}})z}. \tag{3.2}$$

where $\mathscr{N}_{\text{solute}}$ is the concentration of the solute molecules and ϵ_{solute} is called *extinction coefficient* of the solute.[11] Similarly for the solvent.

When the solution in the cuvette is replaced by a pure solvent, we assume that the intensity behaves according to the formula

$$I'(z) = I_0 e^{-\mathscr{N}'_{\text{solvent}}\epsilon_{\text{solvent}} z} \tag{3.3}$$

where the extinction coefficient of the solute is the same as before and where the concentration of solvent molecules $\mathscr{N}'_{\text{solvent}}$ is slightly different than $\mathscr{N}_{\text{solvent}}$. However, if the solution was rare, with great accuracy the concentration of pure solvent can be approximated by the concentration of the solvent in solution $\mathscr{N}_{\text{solvent}}$.

Knowing both quantities for some $z = d$ (width of the cuvette), we can solve the above equations for the extinction coefficient of the solute:

$$\epsilon_{\text{solute}} = \frac{1}{\mathscr{N}_{\text{solute}}\, d} \ln \frac{I'(d)}{I(d)}. \tag{3.4}$$

In general, the extinction coefficient is a function of frequency of light, and this function or its plot is sometimes called *absorption spectrum.*

3.2 Circular dichroism

Another way to measure the ability of the medium to absorb light is to use circularly polarized light, of which there are two kinds: left-circularly polarized and right-circularly polarized (also called left-handed and right-handed). It turns out that most molecules absorb light with different intensity depending on the handedness of the light wave.

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[11] If we imagined that light was some kind of material substance, the density of which was proportional to the intensity of light I, and that the absorption of light was due to absorption of this substance upon its impact on small impenetrable absorption centres, the extinction coefficient would play role of average cross-section area of these centres. However, this picture is rather misleading if pushed too far, as the wavelength of light is much higher than the dimensions of such hypothetical absorption centers.

We can perform similar absorption measurement for the circularly polarized light as we described for linearly polarized light, only now the resulting extinction coefficient may depend, besides frequency, also on the handedness of the light wave. For *left-handed* light wave, we denote the corresponding extinction coefficient by $\epsilon_{\mathrm{L}}(\omega)$. For *right-handed* light wave, we have $\epsilon_{\mathrm{R}}(\omega)$.

In general, these two absorptions are not the same. Their difference

$$\Delta\epsilon(\omega) = \epsilon_{\mathrm{L}}(\omega) - \epsilon_{\mathrm{R}}(\omega) \tag{3.5}$$

is called *circular dichroism* (CD spectrum). We may call it also differential absorption coefficient. For common concentrations of organic molecules, it is a quantity of many orders of magnitude (6-8) smaller than the extinction coefficients themselves.

3.3 Electromagnetic theory of light

Let us consider the setup from previous section in the framework of electromagnetic theory. The light ray can be understood as an electromagnetic wave whose electric field obeys the general wave equation

$$\left(\frac{1}{c^2}\partial_t^2 - \Delta\right)\mathbf{E} = -\frac{K}{c^2}\partial_t\mathbf{j} - K\nabla\rho, \tag{3.6}$$

where $\mathbf{E}$ is the macroscopic electric field vector, $\mathbf{j}$ is the macroscopic current density and ρ is the macroscopic density of electric charge. The adjective "macroscopic" is used in the sense that these are the quantities from the macroscopic electromagnetic theory; they do not reflect the molecular structure of matter and thus give only an approximate description of the actual microscopic fields.

Since we are interested in dielectric liquid, we will neglect any possible conduction currents, and assume that the only current arises from the charged particles bound in the molecules. The term $K\nabla\rho$ can be dropped out in isotropic medium, because the molecules are oriented randomly and there is no systematic deviation from charge neutrality.[12] Finally, it is convenient to express $\mathbf{j}$ as a time derivative of another quantity, the polarization potential $\mathbf{P}$:

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[12] This will be better explained after the definition of the macroscopic average in terms of the microscopic quantities is given.

$$\mathbf{j}(z,t) = \partial_t \mathbf{P}(z,t), \tag{3.7}$$

We would like to note that the polarization potential $\mathbf{P}$ is only an auxiliary mathematical quantity without direct physical interpretation; despite its appearance, it is not necessarily the same as the macroscopic electric polarization.[13] The simplified wave equation governing the macroscopic electric field is

$$\left(\frac{1}{c^2}\partial_t^2 - \Delta\right)\mathbf{E} = -\frac{K}{c^2}\partial_t^2\mathbf{P}. \tag{3.8}$$

3.4 Linearly polarized wave

We assume that in the medium, our damped wave propagating along the axis z is described by the functions

$$\mathbf{E}(z,t) = \mathbf{e}_x E_0 e^{-rz}\cos(\Omega t - kz) \tag{3.9}$$

$$\mathbf{B}(z,t) = \mathbf{e}_y E_0 e^{-rz}\cos(\Omega t - kz) \tag{3.10}$$

with frequency Ω, wave number k and absorption coefficient r. On account of the absorption, the wave is assumed to fall down exponentially with distance travelled.

In order to be possible for such a damped wave to be a solution of the above wave equation, the polarization potential $\mathbf{P}$ has to oscillate with phase behind the electric field and the phase lag has to be in the interval $(0,\pi)$. The potential $\mathbf{P}$ can be written in the convenient form

$$\mathbf{P}(z,t) = \mathbf{e}_x \frac{1}{K}\chi E_0 \cos(\Omega t - kz - \varphi) \tag{3.11}$$

where χ is the coefficient of proportionality and φ is the phase lag of the oscillations of $\mathbf{P}$ behind the electric field.

Because the considered quantities are harmonic functions of time and space coordinates, the relation between them is conveniently handled by the method of phasors. In this method, each harmonically oscillating quantity

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[13] This is because the electric polarization refers to average electric moment of the molecules, which is not always sufficient to determine the current density $\mathbf{j}$. Actually, the current density $\mathbf{j}$ is the basic quantity. Nevertheless, it is useful to define the potential $\mathbf{P}$ and use it to define susceptibility $\tilde{\chi}$.

is supplemented by a new complex variable - phasor - with the property that the real part of the phasor gives the actual value of the quantity.

We introduce complex phasor for the electric field of dampe wave. For field polarized along the axis x, the phasor is

$$\tilde{\mathbf{E}} = \mathbf{e}_x E_0 e^{i\phi'}, \tag{3.12}$$

where

$$\phi' = \Omega t - (k - ir)z. \tag{3.13}$$

Similarly, the phasor for the polarization potential is

$$\tilde{\mathbf{P}} = \mathbf{e}_x \chi E_0 e^{i(\phi' - \varphi)}. \tag{3.14}$$

Introducing complex susceptibility

$$\tilde{\chi} = \chi e^{-i\varphi}, \tag{3.15}$$

we can write the relation between the electric field phasor and the polarization potential phasor as

$$\tilde{\mathbf{P}} = \frac{1}{K}\tilde{\chi}\tilde{\mathbf{E}}. \tag{3.16}$$

If the phase lag φ is in $(0, \pi)$, the time average $\overline{\mathbf{E} \cdot \mathbf{j}}$ is positive. This means that the macroscopic field does work on the moving charges and the Poynting energy of the field decreases.

On the other hand, if the phase is in the interval $(\pi, 2\pi)$, the above temporal average is negative; the medium does work on the field and the energy of source driving the oscillations of the medium is converted into the Poynting energy of the macroscopic wave.

Given the wave has frequency Ω and the medium has complex susceptibility $\tilde{\chi}$, what are the values of the angular wave number k and the damping constant r of the electromagnetic wave?

Inserting the above expressions into the wave equation, we obtain the equation:

$$-\frac{\Omega^2}{c^2} + (k - ir)^2 = \frac{\Omega^2}{c^2}\tilde{\chi}, \tag{3.17}$$

where

$$\tilde{\chi} = \chi e^{-i\varphi} = R + iI. \tag{3.18}$$

Introducing the index of refraction $n' = k/(\Omega/c)$, index of absorption $n'' = -r/(\Omega/c)$ and real (R) and imaginary (I) part of $\tilde{\chi}$, we obtain the equation

$$(n' + in'')^2 = 1 + R + iI. \tag{3.19}$$

The relevant solution is[14]

$$n' = \sqrt{\frac{1 + R + \sqrt{(1+R)^2 + I^2}}{2}}, \tag{3.20}$$

$$n'' = \mathrm{sgn} I \sqrt{\frac{-(1+R) + \sqrt{(1+R)^2 + I^2}}{2}}. \tag{3.21}$$

In case $I \ll 1 + R$, the last expression will contain difference of two close numbers and this may be problematic in computer calculations. In such case, it is convenient to re-express the corresponding quantity in a way better adapted to finite-precision arithmetics, for example by use of approximate Taylor's series:

$$n'' \approx \frac{I}{2}\sqrt{\frac{1}{(1+R)} - \frac{I^2}{4(1+R)^3}}. \tag{3.22}$$

The intensity of light is proportional to square of the electric field and decreases with distance as

$$I(z) = I_0 e^{-2rz}. \tag{3.23}$$

Comparing this to the Lambert-Beer law, we infer that the calculated extinction coefficient is

$$\epsilon(\Omega) = \frac{2r}{\mathscr{N}}, \tag{3.24}$$

or

$$\epsilon(\Omega) \approx |I|\sqrt{\frac{1}{(1+R)} - \frac{I^2}{4(1+R)^3}}\frac{\Omega}{\mathscr{N}c}. \tag{3.25}$$

The functions $R(\Omega)$ and $I(\Omega)$ describe the behaviour of the molecules under action of the light wave. These two functions can be found from a microscopic model of the medium (molecules).

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[14] The one giving positive index of refraction n'.

3.5 Circularly polarized wave

In certain media the above linearly polarized wave cannot propagate. For example, in a solution of chiral molecules (one stereoisomer of glucose) the light will constantly change direction of its polarization. This is explained as follows. The medium has such material properties that do not allow linearly polarized wave. However, it may be that circularly polarized wave is allowed.

There are two distinct kinds of circularly polarized light, which can behave differently in the medium. Both kinds can be visualized as a helical curve made of points to which the electric vectors originating on the z axis point at the same time.

3.6 Left circularly polarized light wave

If the shape of the helix is that of a left-handed screw, the light wave is called to be *left circularly polarized* (or shortly, *left-handed*) and its electric field can be described by the function

$$\mathbf{E}_L(z,t) = (\mathbf{e}_x \cos\phi_L + \mathbf{e}_y \sin\phi_L) E_0 e^{-r_L z}, \tag{3.26}$$

where

$$\phi_L = \Omega t - k_L z.$$

When the image of the electric vector of left-handed wave rotating in the xy plane is viewed by an eye placed at positive z (so that the light wave is propagating towards the eye), it rotates counter-clockwise (to the left). For left circularly polarized wave, $\mathbf{E} \cdot \dot{\mathbf{B}} < 0$.

The expression for the electric field and Maxwell's equations determine the expression for the magnetic field. From Faraday's law

$$\nabla \times \mathbf{E}_L = -\frac{1}{c}\frac{\partial \mathbf{B}_L}{\partial t}, \tag{3.27}$$

we infer that

$$\mathbf{B}_L = E_0 \frac{\sqrt{k_L^2 + r_L^2}}{\Omega/c} (\mathbf{e}_x \sin(\phi_L + \alpha_L) + \mathbf{e}_y \cos(\phi_L + \alpha_L)), \tag{3.28}$$

where

$$\alpha_L = \arctan\frac{k_L}{r_L} < \frac{\pi}{2}. \tag{3.29}$$

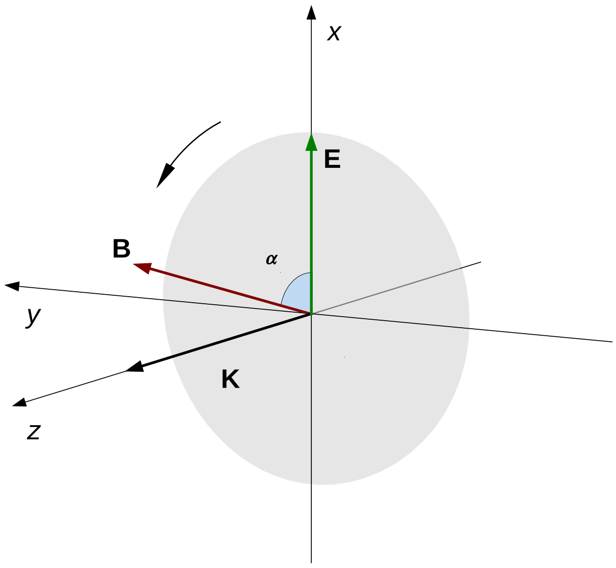

Figure 3.1: Electric and magnetic vector of left-handed light wave.

3.7 Right circularly polarized light wave

If the shape of the helix is that of a right-handed screw, the light wave is called to be *right circularly polarized* or right-handed and its electric field can be described by the function

$$\mathbf{E}_R(\mathbf{x},t) = (\mathbf{e}_x \cos\phi_R - \mathbf{e}_y \sin\phi_R) E_0 e^{-r_R z}. \tag{3.30}$$

where

$$\phi_R = \Omega t - k_R z.$$

When the image of the electric vector rotating in the xy plane is viewed by an eye placed at positive z (so that the light wave is propagating towards the eye), it rotates clockwise (to the right). For right circularly polarized wave, $\mathbf{E}\cdot\dot{\mathbf{B}} > 0$.

The expression for the electric field and Maxwell's equations determine the expression for the magnetic field. From Faraday's law

$$\nabla \times \mathbf{E}_R = -\frac{1}{c}\frac{\partial \mathbf{B}_R}{\partial t}, \tag{3.31}$$

we infer that

$$\mathbf{B}_R = E_0 \frac{\sqrt{k_R^2 + r_R^2}}{\Omega/c} (\mathbf{e}_x \sin(\phi_R + \alpha_R) - \mathbf{e}_y \cos(\phi_R + \alpha_R)), \tag{3.32}$$

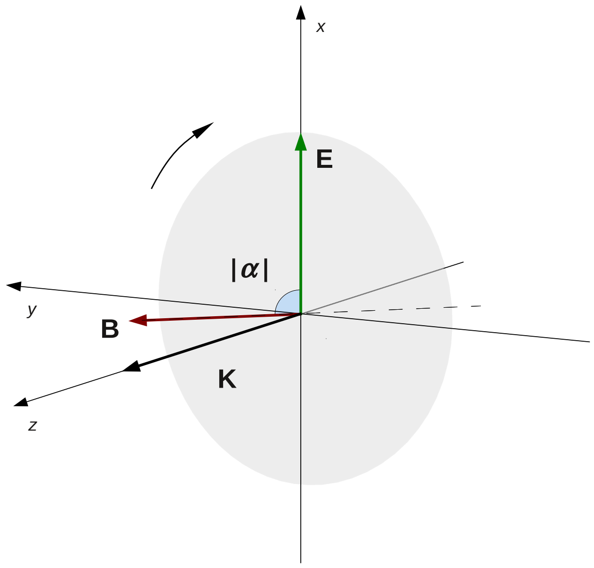

Figure 3.2: Electric and magnetic vector of right-handed light wave.

where

$$\alpha_R = \arctan \frac{k_R}{r_R} - \pi \tag{3.33}$$

and

$$-\pi < \alpha_R < -\frac{\pi}{2}. \tag{3.34}$$

3.8 Absorption of a circularly polarized wave

In the following text, the EM wave is supposed to have left circular polarization. In analogy with the case of linearly polarized light, we assume that the medium has such an effect that the amplitude of the electric field E decreases with distance z according to the formula

$$E(z) = E_0 e^{-r_R z},$$

where r_R quantifies the absorption of left-polarized light.

As in the case of linearly polarized light, we assume that the magnitude of the polarization potential is proportional to the electric field magnitude, but its phase has non-zero phase lag behind it:

$$\mathbf{P} = \frac{1}{K}\chi E[\mathbf{e}_x \cos(\phi - \varphi) + \mathbf{e}_y \sin(\phi - \varphi)]. \tag{3.35}$$

After inserting this expressions into the wave equation, we find out that χ, φ obey exactly the same relations as in the case of linearly polarized light. The solution of these equations - the expressions for r, k in terms of the real and imaginary part of susceptibility - are therefore the same. In phasor notation,

$$\tilde{\mathbf{E}}_L = (\mathbf{e}_x - i\mathbf{e}_y) E_0 e^{i\phi_L}, \tag{3.36}$$

$$\tilde{\mathbf{P}}_L = \frac{1}{K} \tilde{\chi}_L \tilde{\mathbf{E}}_L \tag{3.37}$$

and

$$\tilde{\mathbf{E}}_R = (\mathbf{e}_x + i\mathbf{e}_y) E_0 e^{i\phi_R}, \tag{3.38}$$

$$\tilde{\mathbf{P}}_R = \frac{1}{K} \tilde{\chi}_R \tilde{\mathbf{E}}_R. \tag{3.39}$$

The same calculations and results hold both for the left-handed and right-handed light wave. The susceptibilities for the two kinds of wave are denoted by χ_L, χ_R; they differ in general and so do the quantities r, k. We will denote those belonging to the left-handed wave by r_L, k_L and those belonging to the right-handed wave by r_R, k_R.

The difference between the absorption of left-handed and right-handed light as a function of frequency Ω is called circular dichroism (CD):

$$\Delta\epsilon = \epsilon_L - \epsilon_R. \tag{3.40}$$

The difference is usually a quantity of much lower order of magnitude than ϵ_L or ϵ_R; we have to do with difference of two very close numbers. Experimentally, CD may be 6-8 orders of magnitude smaller than the ordinary absorption ϵ_L. This means that if we want to use the above formula for CD, we should be careful enough to calculate the absorptions ϵ_L, ϵ_R accurately to more than 6-8 significant digits.

Chapter 4

Connections to microscopic theory

In order to infer some information on the microscopic structure of the molecules from the absorption spectra, we have to understand the process of absorption in terms of a microscopic mathematical model. Mathematically, we need to find the connection between the macroscopic current density $\mathbf{j}$ and microscopic current density $\mathbf{j}_\mu$.

4.1 Orientation of the molecule

Liquid solution contains many molecules placed and oriented in a random way. The orientation of the molecule has an important effect on the way the driving forces of light influence the oscillations of its electrons and also on the way these oscillations influence back the macroscopic light wave. We need to describe these orientations mathematically and be able to average over them.

In order to simplify the problem, we will assume that the molecule behaves as a rigid body, i.e. its configuration with respect to the laboratory is determined by 3 coordinates x, y, z of its central point and by 3 angles φ, ϑ, α. We want to define these angles in such a way that the probability distribution function of these angles, corresponding to random orientation, can be easily found.

The procedure of orienting the body into any orientation is, in few words, this. First we rotate the body around its Z axis by the angle φ in the positive sense. Then we rotate it around its axis Y by angle ϑ in the positive sense, so that the axis X ends up below the plane xy of the laboratory system. At this point, the position of the axis Z is given by the spherical angles φ, ϑ.

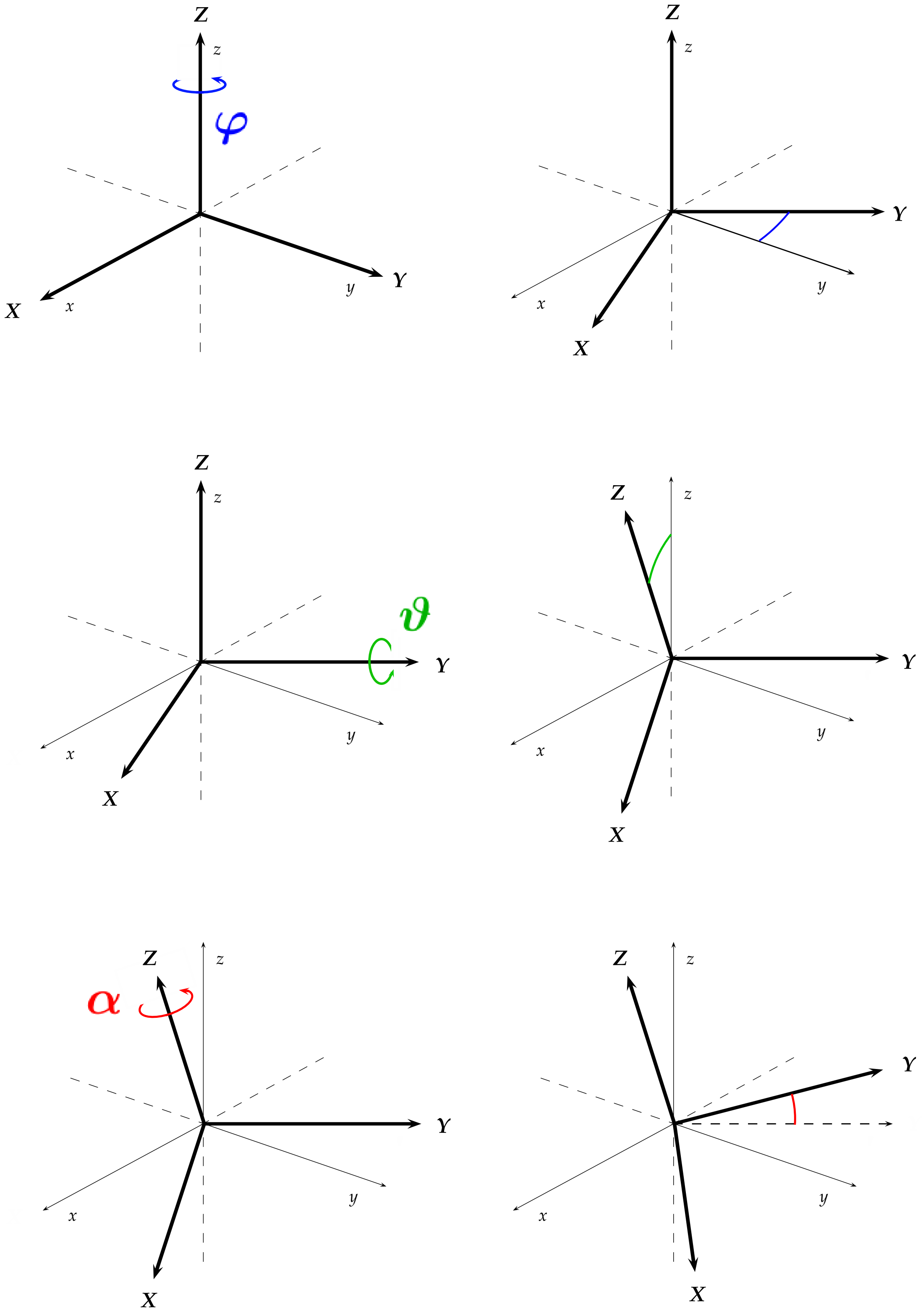

Figure 4.1: Used rotations.

Finally, we rotate the unit around its axis Z by angle α in the positive sense. From this it is clear that the angle φ takes values from $\langle 0, 2\pi)$, ϑ from $\langle 0, \pi)$ and α from $\langle 0, 2\pi)$.

The total effect of the three rotations can be written down as the matrix $\mathbf{R}$ that gives the new coordinates $\mathbf{r}'''$ of the point P in the final position as a function of the old coordinates $\mathbf{r}$:

$$\mathbf{r}''' = \mathbf{R}\mathbf{r}. \tag{4.1}$$

The rotation matrix $\mathbf{R}$ is a function of the rotation angles and can be written as the product

$$\mathbf{R}(\varphi, \vartheta, \alpha) = \mathbf{R}_{z''}(\alpha)\mathbf{R}_{y'}(\vartheta)\mathbf{R}_z(\varphi). \tag{4.2}$$

Here the matrix $\mathbf{R}_z(\varphi)$ rotates the vector around the axis z. The new rotated system is S' and its axes are $x'y'z'$.

The matrix $\mathbf{R}_y(\vartheta)$ rotates the vector around the axis y'. The new rotated system is S'' and its axes are $x''y''z''$.

The matrix $\mathbf{R}_z(\alpha)$ rotates the vector around the axis z''. The new rotated system is S''' and its axes are $x'''y'''z'''$.

We need these matrices expresed in the laboratory system. The mutual orientation of the laboratory system S and the system S' is described by the *matrix of transformation* $\mathbf{C}$. This matrix is such that

$$\mathbf{C}^{-1}\mathbf{r} = \mathbf{r}' \tag{4.3}$$

or

$$\mathbf{C}\mathbf{r}' = \mathbf{r}, \tag{4.4}$$

so obviously it is equal to the matrix of the first rotation:

$$\mathbf{C} = \mathbf{R}_z(\varphi). \tag{4.5}$$

Next, the second rotation consists of rotation around the axis y' of the system S'. We can express the rotation in the coordinates of S' and transform back to S:

$$\mathbf{R}_{y'}(\vartheta) = \mathbf{C}\mathbf{M}_2(\vartheta)\mathbf{C}^{-1}. \tag{4.6}$$

The mutual orientation of the laboratory system S and the system S'' is described by the matrix of transformation $\mathbf{D}$. This matrix is equal to the matrix of the first two rotations:

$$\mathbf{D} = \mathbf{R}_{y'}(\vartheta)\mathbf{R}_z(\varphi). \tag{4.7}$$

The third rotation consists of rotation around the axis z'' of the system S''. Again, we express it in the coordinates of S'' and transform back to S:

$$\mathbf{R}_{z''}(\alpha) = \mathbf{D}\mathbf{M}_3(\alpha)\mathbf{D}^{-1}. \tag{4.8}$$

Putting all pieces together, we obtain slightly surprising result

$$\mathbf{R} = \mathbf{M}_3(\varphi)\mathbf{M}_2(\vartheta)\mathbf{M}_3(\alpha), \tag{4.9}$$

since the order of the angles is exactly the opposite to the one given in the definition of the rotations.

The basic matrices are

$$\mathbf{M}_3(\varphi) = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{4.10}$$

$$\mathbf{M}_2(\vartheta) = \begin{pmatrix} \cos\vartheta & 0 & \sin\vartheta \\ 0 & 1 & 0 \\ -\sin\vartheta & 0 & \cos\vartheta \end{pmatrix}, \tag{4.11}$$

$$\mathbf{M}_3(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{4.12}$$

We would like to find the matrix of the whole operation in the laboratory frame. This matrix has components

$$\mathbf{R} = \begin{pmatrix} \cos\varphi\cos\vartheta\cos\alpha - \sin\varphi\sin\alpha & -\cos\varphi\cos\vartheta\sin\alpha - \sin\varphi\cos\alpha & \cos\varphi\sin\vartheta \\ \sin\varphi\cos\vartheta\cos\alpha + \cos\varphi\sin\alpha & -\sin\varphi\cos\vartheta\sin\alpha + \cos\varphi\cos\alpha & \sin\varphi\sin\vartheta \\ -\sin\vartheta\cos\alpha & \sin\vartheta\sin\alpha & \cos\vartheta \end{pmatrix}. \tag{4.13}$$

The transformation of coordinates to the system S''' is effected by

$$\mathbf{r}''' = \mathbf{R}^{-1}\mathbf{r} \tag{4.14}$$

where

$$\mathbf{R}^{-1} = \mathbf{M}_3(-\alpha)\mathbf{M}_2(-\vartheta)\mathbf{M}_3(-\varphi), \tag{4.15}$$

$$\mathbf{R}^{-1} =$$

$$\begin{pmatrix} \cos\alpha\cos\vartheta\cos\varphi - \sin\alpha\sin\varphi & \cos\alpha\cos\vartheta\sin\varphi + \sin\alpha\cos\varphi & -\cos\alpha\sin\vartheta \\ -\sin\alpha\cos\vartheta\cos\varphi - \cos\alpha\sin\varphi & -\sin\alpha\cos\vartheta\sin\varphi + \cos\alpha\cos\varphi & \sin\alpha\sin\vartheta \\ \sin\vartheta\cos\varphi & \sin\vartheta\sin\varphi & \cos\vartheta \end{pmatrix}. \tag{4.16}$$

4.2 Averaging

What probability distribution function $f(\varphi,\vartheta,\alpha)$ is the most appropriate one to describe the fact that the molecule has random orientation?

Considering briefly the above definition of the angles, it follows quite naturally that the pairs of angles φ, ϑ have to be chosen from uniform distribution on a sphere $\frac{1}{4\pi}\sin\vartheta$, since this is the only distribution that gives equal density of probability for the final position of the axis Z. The remaining angle α does not influence the position of Z and has to be chosen from uniform distribution $\frac{1}{2\pi}$ on the interval $\langle 0, 2\pi)$, since there is no preferred orientation of the axes X, Y for the already fixed orientation of Z. The total probability distribution is therefore product of these two distributions:

$$f(\varphi,\vartheta,\alpha) = \frac{1}{8\pi^2}\sin\vartheta. \tag{4.17}$$

4.3 Macroscopic electric current density

From the viewpoint of the molecular theory of matter, it is not clear at once why the older theory of smooth fields works so well; the electromagnetic fields between the molecules are not smooth, slowly varying functions of position as the macroscopic theory assumes. What is the connection between the smooth macroscopic field and the fluctuating microscopic field ?

Often the macroscopic quantities like current density $\mathbf{j}$ are thought to be generalized spatial averages of the corresponding microscopic quantities, as explained, for example, in the paper by Russakoff.[15] In this approach, the macroscopic quantity $\mathbf{E}$ is defined as an integral of the corresponding microscopic quantity $\mathbf{E}_\mu$ with some bell-like weighing function $w(\boldsymbol{\rho})$:

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[15] G. Russakoff, *A Derivation of the Macroscopic Maxwell equations*, Am. J. Phys. 38, 1188 (1970).

$$\langle \mathbf{E}_\mu(\mathbf{x}) \rangle = \int \mathbf{E}_\mu(\mathbf{x} + \boldsymbol{\rho})\, w(\boldsymbol{\rho})\, d^3\boldsymbol{\rho}. \tag{4.18}$$

This integral is over the whole space and the weighing function $w(\boldsymbol{\rho})$ has support extending in all directions and is usually isotropic and smooth. This definition can be used for any other microscopic field - electric charge density, elecric field, etc. It has the advantage that the formal derivation of the relation

$$\nabla \cdot \mathbf{P} = -\rho_p, \tag{4.19}$$

between macroscopic polarization $\mathbf{P}$ and macroscopic density of the bound or "polarization" charge ρ_p, known from the macroscopic electromagnetic theory of dielectric, is straightforward provided both of these quantities are defined as the above integrals of certain microscopic quantities.

However, this approach has also its disadvantages and there are reasons which make it unsatisfactory for the description of dispersion phenomena. For example, the above integral depends on the choice of the weighing function and is thus arbitrary, so we cannot expect to have a definite relation between the microscopic and the macroscopic field, like the one considered in the Lorentz local field theory. Also, the integration seems to be a reversible transformation for most regular functions $w(\boldsymbol{\rho})$, so the microscopic field $\mathbf{E}_\mu$ can be reconstructed back from the so defined macroscopic field $\langle \mathbf{E}_\mu \rangle$ by inverting the integral operator, while the macroscopic field $\mathbf{E}$ used in the dispersion theory carries no such information.

The weighing function is often imagined to be such that non-zero contributions come from places having distances much greater than the typical dimension of a molecule in every direction. This is to make the result not vary appreciably over the molecular distances. However, the variation of the macroscopic electric field over the length of the molecule in the direction of the wave propagation is a necessary part of the very explanation of the phenomenon of optical activity and circular dichroism in particular. It does not seem advisable to define macroscopic electric field by averaging microscopic field from places with different coordinates z, which have different expected phases. What is the purpose of macroscopic electric field on the plane $z = z_0$, where z is the coordinate along the axis of wave propagation? In the theory of dispersion, the macroscopic electric field on the plane z is used to calculate the driving forces acting on the molecules.

The average field thus has the role of estimate of the actual microscopic field acting on the molecule at z. It makes no sense to spoil the quality of this estimation by using macroscopic field defined as average of quantities belonging to different z. Also from the numerical point of view, adding numbers with different expected values (due to different z) would spoil the speed of convergence of the averaging process.

For these reasons, we introduce different averaging method, which is free of the above mentioned objections. Instead of averaging over the whole space with arbitrary weighing function, the macroscopic electric field at z_0 is defined as an average of the microscopic electric field *over a large square* lying in the plane $z = z_0$ perpendicular to the direction of wave propagation:

$$\mathbf{E}(z_0, t) = \frac{1}{L^2} \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \mathbf{E}_\mu(x, y, z_0, t)\, dx dy. \tag{4.20}$$

Similarly for the current density and other quantities whose macroscopic version depends only on the coordinate z and time t.

However, should we use this formula for electric current density, we would have to consider individually many different molecules at random positions with random orientations and numerically integrate microscopic current density due to them on a large plane, a task which is very demanding since great many molecules would be required to obtain average comparable to the measurements. It would be better to estimate the result of such averaging by some faster and more convenient method.

This can be achieved by replacing the spatial integration of current density of *many* molecules by integration of the current density of *one* molecule $\mathbf{J}$ over a probability distribution of its position and orientation.

Consider a molecule whose configuration s – its position and orientation with respect to the laboratory – is given by three coordinates of its centre and three angles of rotation (we assume that the molecule is a rigid body) as written in the list

$$s = (x_c, y_c, z_c, \varphi, \vartheta, \alpha). \tag{4.21}$$

The set of all such configurations forms a *configuration space* of the molecule.

Let the microscopic current density due to this molecule at the point x, y, z_0 at time t be denoted as

$$\mathbf{J}(x, y, z_0, t|x_c, y_c, z_c, \varphi, \vartheta, \alpha), \tag{4.22}$$

or simply as

$$\mathbf{J}(x, y, z_0, t|s). \tag{4.23}$$

In a liquid solution, there are many molecules that contribute to the total microscopic current density $\mathbf{j}_\mu$. We will assume that these molecules can have any orientation and position with equal probability, but for the sake of simplicity we will restrict their position to be inside of a box B of dimensions $L \times L \times L$.

We introduce density function $\rho(s)$ such that the expression

$$\int_I \rho(s)\, ds \tag{4.24}$$

gives the expected number of molecules that have their configuration within the subset I of the just introduced configuration space. The total expected number of molecules in the box is

$$\int_0^{2\pi} d\alpha \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi \int\limits_{-L/2}^{L/2} dz_c \int\limits_{-L/2}^{L/2} dy_c \int\limits_{-L/2}^{L/2} dx_c\, \rho = \tag{4.25}$$

$$= \mathscr{N} L^3 \tag{4.26}$$

where $\mathscr{N}$ is the concentration of the molecules. From this and from the definition of the angles we infer that the density function is

$$\rho(s) = \mathscr{N} \frac{1}{8\pi^2} \sin\vartheta. \tag{4.27}$$

We now come back to averages. Instead of the actual spatial average suggested above, we propose this formula for the average current density at any point xyz_0:

$$\mathbf{j}(x, y, z_0, t) = \int \mathbf{J}(x, y, z_0, t|s)\, \rho(s)\, ds. \tag{4.28}$$

Note that instead of the spatial averaging of the actual current density $\mathbf{j}_\mu$ at different points of space, here we average different currents at one point of space due to many possible, differently spaced and oriented molecules.

Because the box is finite, the points with the same z_0 but different x, y are not entirely equivalent and the resulting average will slightly vary with x, y. However, because we consider plane waves, we are interested only in the variation of macroscopic quantities in the direction of the axis z. It is therefore useful to simplify the next considerations by extending the box and the corresponding integration to infinity in all directions. This way, the arbitrary L is removed as well. Then we write the integral as

$$\mathbf{j}(x, y, z_0, t) = \int \mathbf{J}(x, y, z_0, t|s)\, \rho(s)\, ds, \tag{4.29}$$

or in more detail,

$$\mathbf{j}(x, y, z_0, t) = \int_0^{2\pi} d\alpha \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi \int\limits_{-\infty}^{\infty} dz_c \int\limits_{-\infty}^{\infty} dy_c \int\limits_{-\infty}^{\infty} dx_c$$

$$\mathbf{J}(x, y, z_0, t|x_c, y_c, z_c, \varphi, \vartheta, \alpha, [\Omega t - kz_c])\, \mathscr{N} \frac{1}{8\pi^2} \sin\vartheta. \tag{4.30}$$

The quantity in the brackets [ ] reminds the relevant phase of the wave of the macroscopic electric field at the position of the molecule z_c at time t; k is the wave number of the macroscopic wave.

Since the integration has been extended to the whole space and the concentration $\mathscr{N}$ is uniform in space, the result should be independent of the coordinates x, y. The resulting current density should depend only on the coordinate z_0. It is expected to behave as a wave with the same wavelength as the macroscopic electric field.

The last expression is more promising than the original definition, since it refers to one function $\mathbf{J}$ describing the kind of molecule considered, not many different functions due to many molecules. Still, it has one apparent disadvantage. When the integration is expressed as a large sum, it requires repetition of the calculation of the microscopic current density for many molecules of different configuration s and then uses only a thin slice of the molecule's current density at plane $z = z_0$; the rest of the current density at planes $z \neq z_0$ is discarded. Since the numerical calculations of the molecular current density in their simplest form will yield the current distribution in the whole space already, this is not a very efficient use of the calculated data. It is desirable to find a way to use the results of these calculations more efficiently.

We do this by "displacing all the molecules into the origin" and "adding the currents at different positions at correspondingly different times".

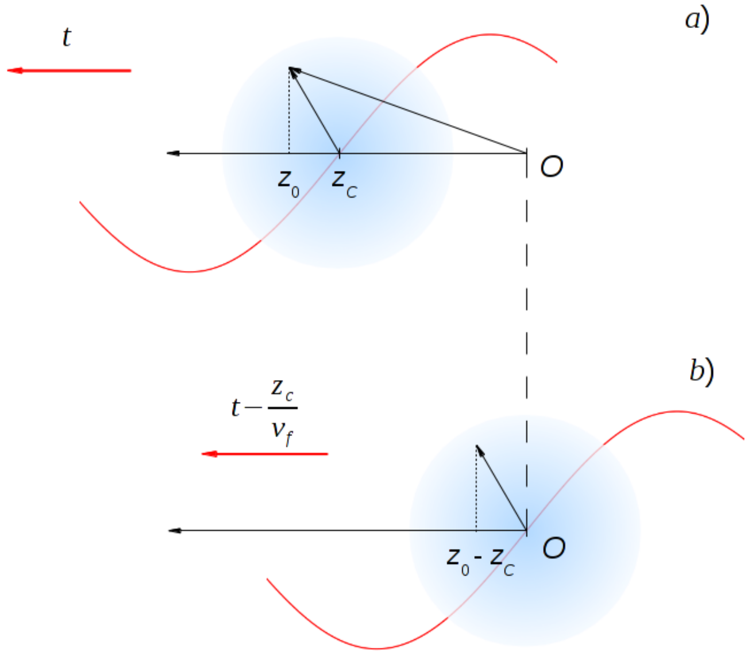

Figure 4.2: Schematic picture of electric current density of the molecule (blue) in two equivalent situations: a) at the point x, y, z_0 at time t; b) at the point $x, y, z_0 - z_c$ at time $t - \frac{z_c}{v_f}$. The red line pictures the phase of the macroscopic electromagnetic wave and the arrow its direction of propagation.

Since we deal with wave propagation, the microscopic current density at the point x, y, z_0 at time t due to a molecule centred at x_c, y_c, z_c is the same as the microscopic current density at the point $x - x_c, y - y_c, z_0 - z_c$ due to molecule centred at $x = y = z = 0$ at time $t - \frac{z_c}{v_f}$. The quantity v_f is the phase velocity of the macroscopic wave.

In this way, we can move all the molecules to the same place with coordinates $x, y, z = (0, 0, 0)$ and rewrite the integral as

$$\int_0^{2\pi} d\alpha \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi \int\limits_{-\infty}^{\infty} dz_c \int\limits_{-\infty}^{\infty} dy_c \int\limits_{-\infty}^{\infty} dx_c$$

$$\mathbf{J}(x - x_c, y - y_c, z_0 - z_c, t - \frac{z_c}{v_f}|0, 0, 0, \varphi, \vartheta, \alpha, [\Omega t])\, \mathscr{N} \frac{1}{8\pi^2} \sin\vartheta. \quad (4.31)$$

Now we introduce new coordinates x', y', z' referring to the coordinate system centred in the molecule:

$$x' = x - x_c, \quad (4.32)$$

$$y' = y - y_c, \quad (4.33)$$

$$z' = z_0 - z_c. \quad (4.34)$$

The macroscopic current density is given by

$$\mathbf{j}(z_0, t) = \int_0^{2\pi} d\alpha \int_0^{\pi} d\vartheta \int_0^{2\pi} d\varphi \int\limits_{-\infty}^{\infty} dz' \int\limits_{-\infty}^{\infty} dy' \int\limits_{-\infty}^{\infty} dx'$$

$$\mathbf{J}(x', y', z', t - \frac{z_0 - z'}{v_f}|0, 0, 0, \varphi, \vartheta, \alpha, [\Omega t])\, \mathscr{N} \frac{1}{8\pi^2} \sin\vartheta. \quad (4.35)$$

This expression has the advantage that the whole calculated current density is used. It suffices to calculate it for the molecules that are centred at the same point 0,0,0; however, we still need to calculate it for different orientations of the molecule and average over them.

4.4 Acting field and effective field

In order to find the microscopic current density of a molecule, we need to find electromagnetic fields acting on the molecule - the "acting" fields. Now we will consider only the electric field.

In stationary regime, when the molecule oscillates under action of harmonically oscillating external forces, we know that the current density is an harmonic function of time too.[16] But to describe optical activity the time dependence of the acting field is no longer sufficient; we need also the spatial dependence of this acting field.

Although the acting field will have the same angular frequency at any fixed point of space, spatially it will vary in a complicated manner, since other randomly spaced molecules scattering the primary wave are present.

We do not want to consider many molecules individually, so we will not attempt to find this acting field from the configurations of those many molecules. Rather we would like to use a simple function of spatial coordinates - the effective field $\mathbf{E}_{\text{eff}}$ - to describe approximately the actual acting field.

We assume that the macroscopic field of a left-circularly polarized wave at the point O is given by

$$\mathbf{E}(0,0,0,t) = E_0\Big(\mathbf{e}_x \cos\Omega t + \mathbf{e}_y \sin\Omega t\Big). \tag{4.36}$$

The effective field $\mathbf{E}_{\text{eff}}$ which we shall use has the following properties. Its oscillation at the point of the molecular centre is in phase with the oscillations of the macroscopic field at that point; when the molecule is at $z = 0$, we assume that the effective field at that point can be written as

$$\mathbf{E}_{\text{eff}}(0,t) = \kappa \mathbf{E}(0,t) \tag{4.37}$$

with some constant κ.[17]

For the calculation of the molecular oscillations we need also the spatial dependence of the effective field. One may think that similar relation holds true for any point on the axis z, in other words that the equation

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[16] At least in the first approximation.

[17] This assumption is taken from the theory of ordinary absorption and dispersion, where it is quite fruitful.

$$\mathbf{E}_{\text{eff}}(z,t) = \kappa \mathbf{E}(z,t) \tag{4.38}$$

is true. However, this cannot be so, since $\mathbf{E}(z,t)$ is a wave with phase velocity of macroscopic wave which does not obey Maxwell's equations for vacuum, while the effective field is in vacuum. Since the particles forming the molecule are in vacuum, the most appropriate expected field acting on them seems to be that of a plane wave in *vacuum*, which has phase velocity c. That is, the appropriate wave number to be used seems to be $k_0 = \frac{\Omega}{c}$, not the wave number k of the macroscopic wave. For the left-handed light wave, the effective field around the point (0,0,0) is assumed to be

$$\mathbf{E}_{\text{eff}}(z',t) = \kappa E_0 \bigg(\mathbf{e}_x \cos(\Omega t - k_0 z') + \mathbf{e}_y \sin(\Omega t - k_0 z') \bigg). \tag{4.39}$$

In reality, of course, due to the other molecules, the acting field varies with the coordinates x', y' as well; and for each different molecule, this field will be different. However, the method of effective plane wave works quite well in the theory of ordinary dispersion and absorption. We will use it for circular dichroism as well and assume it describes the average acting field.

If the synchronization of $\mathbf{E}$ and $\mathbf{E}_{\text{eff}}$ occurs at the centre of the molecule, it cannot occur at the other points on the z-axis, since the wavelength of the fields is not the same. The choice of the centre to be the point of synchronization seems to be somewhat arbitrary and unsatisfactory. Here we will simply assume that it does not cause any significant troubles.

4.5 Application to point-like particles bound to immovable centers

We consider a rigid aggregate of many interacting localized oscillators a. The radius vector of the a-th immovable center is denoted by $\mathbf{R}_a$; the aggregate is placed into the point (0,0,0) of the laboratory coordinate system. The position of the a-th negatively charged particle is $\mathbf{R}_a + \mathbf{u}_a(t)$. The microscopic current density is given by

$$\mathbf{j}_\mu(\mathbf{x},t) = \sum_a q_a \mathbf{v}_a(t) \delta(\mathbf{x} - \mathbf{R}_a - \mathbf{u}_a(t)). \tag{4.40}$$

We find the macroscopic current density as a function of z by applying the general formula derived above. The result of spatial integration is approximately

$$\mathbf{j}(0,t|\varphi,\vartheta,\alpha) = \mathscr{N}\sum_a q_a\mathbf{v}_a\left(t+\frac{\mathbf{R}_{a,z}}{v_f}\right). \tag{4.41}$$

where the possible higher harmonics were discarded.[18] In order to obtain the macroscopic current density, this expression has to be further averaged over all orientations.

4.6 Vanishing of $\nabla\rho$ in isotropic dielectric liquid

Now we can explain why we could drop out the term $K\nabla\rho$ from the macroscopic wave equation in the previous chapter. In microscopic theory, the wave equation is

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)\mathbf{E}_\mu = -\frac{K}{c^2}\frac{\partial \mathbf{j}_\mu}{\partial t} - K\nabla\rho_\mu. \tag{4.42}$$

The term $K\nabla\rho_\mu$ is present and is nonzero at places where the charged particles are present. The passage to macroscopic theory is made by the procedure we indicated in previous sections. The charge density ρ_μ is integrated over large sheet to give macroscopic charge density:

$$\rho(z_0) = \frac{1}{L^2}\int_{-L}^{L}\int_{-L}^{L}\rho_\mu(x,y,z_0)dx\,dy. \tag{4.43}$$

Since the EM field oscillates in the plane xy and the molecules are oriented randomly, the systematic oscillations of the charges occur also in the plane xy. There is no systematic loss or increase of charge at one such plane $z = z_0$, so the above average is to be assigned value 0 for all z_0.[19] Consequently, the wave equation for averaged quantities is

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)\mathbf{E} = -\frac{K}{c^2}\frac{\partial \mathbf{j}}{\partial t}. \tag{4.44}$$

4.7 On the microscopic model

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[18] We assume that the amplitude of oscillation of $\mathbf{u}_a$ is much lower than the typical distance between the oscillators.

[19] This is not true in crystals, where the molecules are oriented in one direction and EM oscillations in one plane can excite systematic oscillations of charges in other plane.

In order to calculate the spectrum of the solution of the BChl molecules, we have to formulate a microscopic model that will enable us to calculate the microscopic current density due to these molecules. We have to go to such a level of sophistication that the resulting model will be capable to account for different behaviour of the molecule in the presence of left-handed and right-handed light wave.

There have been many distinct attempts to formulate such microscopic model. The basic two approaches are 1) models based on the Schrödinger equation and 2) models based on the Newtonian equations of motion.

The Schrödinger equation has been very successful in explaining various properties of molecules and there also exists significant literature on the theory of optical activity based on it. An introduction to these theories can be found in the review by Moscowitz[20] and Tinoco.[21] They express the circular dichroism spectrum as a function of (theoretically infinite number of) matrix elements of molecular electric moment and magnetic moment. These models pose certain difficulties. For example, they do not allow simple inclusion of the phenomenon of damping (line broadening). This is usual for any Hamiltonian model; the necessary irreversibility is often put in the model by theoretically not very satisfactory application of the ”golden rule”, or better, it is simulated by connecting the system to another, much larger system that acts as a source of noise and, on average, also as a source of damping.

In contrast, a model based on the Newtonian equations of motion can be easily supplemented by a damping term with no need to simulate another complicated system. That being said, the Schrödingerian model is still very useful even without ability to describe the damping, as it provides a general method for predictions of resonance frequencies of the molecules.

However, when we pass to calculations of circular dichroism and optical rotatory dispersion, another drawback of the Hamiltonian formalism appears. As is generally known, the difference in the response of the system to left-handed and right-handed wave arises because the driving field is not constant throughout the molecule, but varies harmonically in space along

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[20] A. Moscowitz, *Theoretical aspects of optical activity, Part One: Small molecules*, Advances in Chemical Physics, Vol. IV, p. 67-112 (1962).

[21] I. Tinoco, *Theoretical aspects of optical activity, Part Two: Polymers*, Advances in Chemical Physics, Vol. IV, p. 113-160, (1962).

the direction of propagation of the wave. It is the difference in the field at different parts of the molecule that enables it to "feel" the chiral character of the driving wave. If the wave number of the wave propagating along the axis z is $k = \frac{2\pi}{\lambda}$, the electric field strength amplitude E_0 and the dimension of molecule in the direction of propagation R, the actual field values differ from the value at the center of the molecule by quantity of order of magnitude of $2\pi\frac{R}{\lambda}E_0$.

This quantity is much smaller than the amplitude E_0, so it can be said that circular dichroism is a quantity very sensitive to small variations of the driving wave. However, the driving electric field is not the total field affecting the internal motions in the molecule. There are also interaction electromagnetic fields acting on one part of the molecule due to its other parts. These fields oscillate at the same frequency as the driving wave, and may have amplitude F_0 comparable or even higher than E_0, if the test point is close enough to the charged electrons. From the point of view of charged particle, it does not matter whether the field originates in distant source or nearby part of the molecule; for calculation of circular dichroism, a systematic account of the wave-like character of the EM field seems to be necessary.

For this reason we cannot replace the interaction fields by the electrostatic dipole fields as is done in ordinary absorption spectroscopy; such approximation may give value for the interaction field that differs from the actual one by quantity comparable to $2\pi\frac{R}{\lambda}F_0$ and the calculation of the CD spectrum may be spoiled by too great errors.

This point of view will perhaps appear less strange after some numerical estimates are made. We will estimate the various corrections needed to correct the approximate electrostatic dipole field to give exact retarded electromagnetic field of an oscillating charge.

Let the position, velocity and acceleration of the charged particle b in an inertial reference frame be described by functions of time $\mathbf{r}_b(t)$, $\mathbf{v}_b(t)$ and $\mathbf{a}_b(t)$. We now state the exact retarded electromagnetic fields at the point $\mathbf{x}, t$ due to this particle. We will need the radius vector $\mathbf{r}_b$, velocity $\mathbf{v}_b$ and acceleration $\mathbf{a}_b$ at a past time such that the light signal from $[\mathbf{r}_b]$ will arrive at position $\mathbf{x}$ at time t. We denote these *retarded* quantities by $[\mathbf{r}_b], [\mathbf{v}_b], [\mathbf{a}_b]$. If we introduce the retarded distance

$$\mathbf{R} = \mathbf{x} - [\mathbf{r}_b], \tag{4.45}$$

and its magnitude R, from the above definition we obtain the condition defining $\mathbf{R}$:

$$\mathbf{R} = \mathbf{x} - \mathbf{r}_b \left(t - \frac{R}{c} \right). \tag{4.46}$$

We also introduce the quantities

$$\mathbf{n} = \frac{\mathbf{R}}{R}, \tag{4.47}$$

$$\boldsymbol{\beta}_b = \frac{[\mathbf{v}_b]}{c}, \tag{4.48}$$

$$\boldsymbol{\gamma}_b = \frac{[\mathbf{a}_b]}{c}. \tag{4.49}$$

The retarded electric field at the position $\mathbf{x}$ and time t can be written as a sum of two parts

$$\mathbf{E}_b = \mathbf{E}_{b,near} + \mathbf{E}_{b,far}, \tag{4.50}$$

which we may call the "near" field and the "far" field.[22] The near field is

$$\mathbf{E}_{b,near}(\mathbf{x},t) = \frac{Kq_b}{4\pi} \frac{\left(1 - \boldsymbol{\beta}_b^2\right)}{\left(1 - \boldsymbol{\beta}_b \cdot \mathbf{n}\right)^3} \frac{\mathbf{n} - \boldsymbol{\beta}_b}{R^2}, \tag{4.51}$$

and the far field is

$$\mathbf{E}_{b,far}(\mathbf{x},t) = \frac{Kq_b}{4\pi} \frac{1}{\left(1 - \boldsymbol{\beta}_b \cdot \mathbf{n}\right)^3} \frac{\mathbf{n} \times \{(\mathbf{n} - \boldsymbol{\beta}_b) \times \boldsymbol{\gamma}_b\}}{cR}. \tag{4.52}$$

The far field seems negligible in the vicinity of the molecule, but falls off more slowly with distance, so it becomes important for the interaction of more distant molecules. The electromagnetic field (light) from distant sources is given almost entirely by the far field.

We remind that all the quantities right of the constant prefactor are to be taken at the retarded time. Derivation of these formulae can be found in Jackson's textbook.[23]

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[22] These names are already in use in the antenna theory, where they have somewhat different meaning.

[23] J. D. Jackson, *Classical Electrodynamics*, John Wiley & Sons, 3rd ed., 2001, sec. 14.1 .

Let us estimate the magnitudes of the contributions to the field due to electron oscillating under action of an oscillating external field. For moderate fields the amplitude of the electron will be very small and we can simplify the expression for the retarded field by linearization in the electronic position vector $\mathbf{u}_b$. The result is

$$\mathbf{E}(\mathbf{r}_b,t) = \frac{Kq_b}{4\pi}\Bigg[\ \frac{\mathbf{n}_0}{R_0^2} + \frac{1}{R_0^3}\Big([\mathbf{u}_b] - 3([\mathbf{u}_b]\cdot\mathbf{n}_0)\mathbf{n}_0\Big) + \tag{4.53}$$

$$+ \frac{1}{cR_0^2}\Big([\dot{\mathbf{u}}_b] - 3([\dot{\mathbf{u}}_b]\cdot\mathbf{n}_0)\mathbf{n}_0\Big) + \tag{4.54}$$

$$+ \frac{1}{c^2R_0}\Big([\ddot{\mathbf{u}}_b] - ([\ddot{\mathbf{u}}_b]\cdot\mathbf{n}_0)\mathbf{n}_0\Big)\qquad\Bigg], \tag{4.55}$$

where R_0 is the distance from the average position of the electron to the test point $\mathbf{x}$ and $\mathbf{n}_0$ is unit vector pointing from the average position towards the test point. We may call the various terms Coulomb field, dipole field, velocity field and acceleration field. The three last of them are functions of past motion of the electron.

We will assume that the electron oscillates under driving wave of optical wavelength $\lambda = 600$ nm described by $\mathbf{E}(t) = \mathbf{e}_z E_0 \cos\Omega t$ with $E_0 = 10^{-15}$ N/e.[24] The electron will perform oscillations in antiphase described approximately by

$$\mathbf{u}_b(t) = -\mathbf{e}_z x_0 \cos\Omega t$$

with amplitude

$$x_0 = \frac{qE_0}{m\Omega^2}. \tag{4.56}$$

We can easily evaluate the magnitude of all of the interaction terms. For each term, we also calculate the correction to its instantaneous simplification due to retardation. Since all the terms oscillate at angular frequency $2\pi c/\lambda$ and we consider distances $R \ll \lambda$, the retardation correction is always $2\pi\frac{R}{\lambda}$ times the contributing term. The resulting values in the above table show that on the atomic and molecular scale $R \approx 1 - 10$ Å the retardation correction to the electrostatic dipole field and the velocity field

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[24] Intensity corresponding to light of a pocket laser with mW power and light ray cross-section in orders of mm^2.

Field term	magnitude (N/e)	$R = 1$ Å	$R = 10$ Å	$R = 100$ Å
E_{ext}	E_0	10^{-15}	10^{-15}	10^{-15}
δE_{ext}	$\frac{2\pi R}{\lambda} E_0$	$1.0 \cdot 10^{-18}$	$1.0 \cdot 10^{-17}$	$1.0 \cdot 10^{-16}$
E_{dip}	$Kq^2 E_0 \frac{\lambda^2}{16\pi^3 mc^2 R^3}$	$2.6 \cdot 10^{-14}$	$2.6 \cdot 10^{-17}$	$2.6 \cdot 10^{-20}$
δE_{dip}	$Kq^2 E_0 \frac{\lambda}{8\pi^2 mc^2 R^2}$	$2.7 \cdot 10^{-17}$	$2.7 \cdot 10^{-19}$	$2.7 \cdot 10^{-21}$
E_{vel}	$Kq^2 E_0 \frac{\lambda}{8\pi^2 mc^2 R^2}$	$2.7 \cdot 10^{-17}$	$2.7 \cdot 10^{-19}$	$2.7 \cdot 10^{-21}$
δE_{vel}	$Kq^2 E_0 \frac{1}{4\pi mc^2 R}$	$2.8 \cdot 10^{-20}$	$2.8 \cdot 10^{-21}$	$2.8 \cdot 10^{-22}$
E_{acc}	$Kq^2 E_0 \frac{1}{4\pi mc^2 R}$	$2.8 \cdot 10^{-20}$	$2.8 \cdot 10^{-21}$	$2.8 \cdot 10^{-22}$
δE_{acc}	$Kq^2 E_0 \frac{1}{2mc^2 \lambda}$	$3.0 \cdot 10^{-23}$	$3.0 \cdot 10^{-23}$	$3.0 \cdot 10^{-23}$

Table 4.1: Magnitudes of various contributions to the electric field at test point $\mathbf{x}$ separated from the electron by distance R. The quantities denoted by the symbol δ denote the corrections due to retardation.

are of the same order of magnitude as the correction δE_{ext} to the external field necessary for the calculation of circular dichroism.

Based on these arguments, it seems important for circular dichroism to model the interactions in the system in such a way that these relativistic effects are taken into account. However, both the Hamiltonian description and the Schrödinger equation describe the interaction of the particle of the system with the internal fields due to other particles of the system as if the interaction was a function of instantaneous position and possibly velocity of the other particles (if the Darwin terms or the Breit equation is used); no acceleration-dependent terms or retardation of interaction can be easily incorporated into such models.

When we want to account for these effects, we have to either formulate non-Hamiltonian equations for the particles or augment the Hamiltonian description by the field variables.

It is perhaps possible in principle to do the latter in the framework of quantum electrodynamics where the field variables are taken into account, but due to complexity of this theory, the formulation and evaluation of such a model would be most probably a very difficult task.

On the other hand, similarly to the case with damping, the general equations of motion do not suffer the limitations of the Hamiltonian formalism for particles; the interaction forces can be prescribed as due to retarded electromagnetic fields of the other particles and eventually expressed as functions of their past state of motion. This leads to a system of delayed differential equations which can be simplified into linear differential equations. These have the advantage that for periodic driving term they can be easily solved with the help of the computer. We will present this model in the next chapters.

Chapter 5

Microscopic theory: general considerations

One reasonable model of a molecule is a system that consists of heavy point-like nuclei of positive charge and light point-like electrons of negative charge. The nuclei maintain their mutual configuration and move only very little, while the electrons move erratically from one to another and around them.[25]

We will begin our considerations with the electromagnetic theory of point-like particles proposed by J. Frenkel.[26] This theory is the simplest consistent electromagnetic theory of charged particles, but unfortunately it is virtually unknown, so we take some place here to explain its basics.

5.1 Electromagnetic theory of point-like particles.

Let us consider a system of N charged particles contained inside a simple, non-moving and closed surface Σ of volume V. The equation of motion of the charged particle a is

$$\frac{d\mathbf{p}_a}{dt} = \mathbf{F}_{-a}, \tag{5.1}$$

where $\mathbf{p}_a = \gamma_a m_a \mathbf{v}_a$ is the momentum of the particle and $\mathbf{F}_{-a}$ is the force acting on it. We assume that this force is a sum of contributions due to all other particles except for the particle itself; there is no "self-force" in this theory.

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[25] Discussion regarding the applicability of the idea of a point-like charge can be found in the Appendix.

[26] J. Frenkel, *Zur Elektrodynamik punktförmiger Elektronen*, Zeits. f. Phys., 32 (1925), p. 518-534.

The electromagnetic field of each particle is assumed to obey the Maxwell-Lorentz equations with localized sources:

$$\nabla \cdot \mathbf{E}_a = K\rho_a, \tag{5.2}$$

$$\nabla \cdot \mathbf{B}_a = 0, \tag{5.3}$$

$$\nabla \times \mathbf{E}_a = -\frac{1}{c}\frac{\partial \mathbf{B}_a}{\partial t}, \tag{5.4}$$

$$\nabla \times \mathbf{B}_a = \frac{K\mathbf{j}_a}{c} + \frac{1}{c}\frac{\partial \mathbf{E}_a}{\partial t}, \tag{5.5}$$

where

$$\rho_a(\mathbf{x}) = q_a\delta(\mathbf{x} - \mathbf{r}_a), \tag{5.6}$$

$$\mathbf{j}_a(\mathbf{x}) = q_a\mathbf{v}_a\delta(\mathbf{x} - \mathbf{r}_a). \tag{5.7}$$

If only electromagnetic forces are present, the total force acting on a particle a is a sum of the Lorentz forces due to fields of all other charged particles:

$$\frac{d\mathbf{p}_a}{dt} = \sum_b{}' q_a\mathbf{E}_b(\mathbf{r}_a) + q_a\frac{\mathbf{v}_a}{c} \times \mathbf{B}_b(\mathbf{r}_a). \tag{5.8}$$

The prime $'$ after the summation sign reminds that the summation is over all charged particles b except the particle a. We will call this equation the *Newton - Lorentz equation.*

These equations of motion allow us to derive the following theorem similar to the Poynting theorem from the macroscopic theory:

$$\sum_a\sum_b{}'\mathbf{E}_a \cdot \mathbf{j}_b =$$

$$-\nabla \cdot \left(\frac{c}{K}\sum_a\sum_b{}'\mathbf{E}_a \times \mathbf{B}_b\right) - \partial_t\left(\frac{1}{2K}\sum_a\sum_b{}'\mathbf{E}_a \cdot \mathbf{E}_b + \mathbf{B}_a \cdot \mathbf{B}_b\right). \tag{5.9}$$

This theorem can be used to define energy of the system and formulate a law describing its change in time. The total power of forces acting on the particles within the volume V consists of two contributions: the internal power of forces due to particles belonging to the region V, and the driving power $\mathscr{F}$ due to all other forces. These other forces can be either electromagnetic forces from the particles outside the region V or non-electromagnetic forces. The power being transmitted to the particles can be written as

$$P = \int_V \sum_a {\sum_b}' \mathbf{E}_a \cdot \mathbf{j}_b \, dV + \mathscr{F}. \tag{5.10}$$

At the same time, this power is equal to the rate of change of the total energy of the particles:

$$P = \frac{d}{dt} \left(\gamma_a m_a c^2 \right). \tag{5.11}$$

Combining the last two expressions and taking advantage of the above theorem, we arrive at the equation

$$\frac{d}{dt} \left(\sum_a \gamma_a m_a c^2 + \int_V w dV \right) + \oint_\Sigma \mathbf{s} \cdot d\mathbf{\Sigma} = \mathscr{F}, \tag{5.12}$$

where

$$w = \frac{1}{2K} \sum_a {\sum_b}' \mathbf{E}_a \cdot \mathbf{E}_b + \mathbf{B}_a \cdot \mathbf{B}_b \tag{5.13}$$

can be interpreted as a density of electromagnetic energy of the system and

$$\mathbf{s} = \frac{c}{K} \sum_a {\sum_b}' \mathbf{E}_a \times \mathbf{B}_b \tag{5.14}$$

can be interpreted as a surface density of flux of electromagnetic energy of the system.

The equation for energy can be stated in this way: the power being transmitted to the particles inside Σ by the external or other non-electromagnetic forces is equal to the sum of rate of change of the total energy inside the surface and the power radiated away by the system through the surface.

Note that the quantities $w, \mathbf{s}$ *do not* give the *total* electromagnetic energy and radiation power; the corresponding expressions contain only the fields due to the particles of the system, not all the fields. The integral

$$\int_V w \, dV \tag{5.15}$$

should therefore be called electromagnetic energy *of the system* in the volume V. This distinction seems natural and useful, since usually we are not interested or knowledgeable about the electromagnetic energy of distant particles. Also, the inertial mass of our system of particles can be shown to be given by this energy alone; the electromagnetic energy of the extraneous particles is present in the region V too, but it does not influence the inertia of the system.

In the first decades of 20th century, Niels Bohr and other physicists who attempted to explain properties of atoms came to conclusion that the Rutherford planetary model of atom cannot be stable in classical electromagnetic theory. The main argument was that the accelerating electrons would radiate energy away from the atom, so the atom should lose its internal energy, the electron should fall on the nucleus and the atom should collapse. This lead many scientists to abandon such pictorial concept of atoms and molecules in favor of more abstract concepts.

However, from the standpoint of the presented theory, the basic argumentation seems to be based on unwarranted assumptions: that the atom is left undisturbed by other bodies and that the energy it radiates comes from its internal energy. In other words, the power of driving forces $\mathscr{F}$ figuring on the right-hand side of the above energy equation was assumed to be zero. However, it seems much more realistic to assume that the atom is under action of myriads of different elementary fields from other particles that can supply or withdraw energy from it. If the average energy of the atom remains constant, it is an indication that the radiated power is supplied by forces other than the internal electromagnetic forces. This conclusion is similar to the picture suggested by T. Boyer in the framework of stochastic electrodynamics.[27]

The stability of a molecule and the empirical laws governing its chemical behaviour are not apparent from the basic laws of this electromagnetic theory, but they are not in direct contradiction to them either.[28]

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[27] T. H. Boyer, *Random electrodynamics: The theory of classical electrodynamics with classical electromagnetic zero-point radiation*, Phys. Rev. D 11, 790–808 (1975). Approximate numerical calculations of the trajectory of the electron in fluctuating electromagnetic field seem to support this picture. For example, see the paper: D. C. Cole, Yi Zou, *Quantum mechanical ground state of hydrogen obtained from classical electrodynamics*, Physics Letters A 317 (2003), p. 14–20.

[28] They are contradicted by Larmor's formula for the power of energy radiation from accelerated particle, but this formula is not valid in the present theory. To the best of our knowledge, all "confirmations" of this formula were based on measurements of radiation due to great num-

5.2 Electromagnetic fields

In order to use the above theory to analyze the motion of the particle a, we need to have the fields $\mathbf{E}_b, \mathbf{B}_b$ due to other particles expressed explicitly and substituted into the equations of motion. The Maxwell-Lorentz equations for these fields admit an infinity of different solutions for the same motion of charged particles. One solution differs from another by a solution of the homogeneous Maxwell equations.

Which solution is realized on the microscopic level is not an easy question to answer; usually we think in terms of retarded fields (fields are determined by the past motion of the charged particles) but there are theories that come close to recovering the familiar behaviour of the charged bodies from the macroscopic theory with the use of mixed half-retarded, half-advanced fields (determined by both the past and the future positions of the particles).[29]

In stochastic electrodynamics one assumes the presence of fluctuating background fields with no definite connection to past of future motion of charge bodies and this seems to help to explain the stability of atoms and also many other phenomena involving charged particles and thermal radiation.

In this work, we will assume that the best fields to work with are the retarded fields. These solutions provide the most natural picture. The background fields can be regarded as retarded fields of distant sources, but for simplicity and focus on our goals we will not consider them.

The retarded electric field was already given in the previous chapter, but for readability we give it again here. The near field is

$$\mathbf{E}_{b,near}(\mathbf{x},t) = \frac{Kq_b}{4\pi} \frac{\left(1-\boldsymbol{\beta}_b^2\right)}{\left(1-\boldsymbol{\beta}_b\cdot\mathbf{n}\right)^3} \frac{\mathbf{n}-\boldsymbol{\beta}_b}{R^2}, \tag{5.16}$$

and the far field is

$$\mathbf{E}_{b,far}(\mathbf{x},t) = \frac{Kq_b}{4\pi} \frac{1}{\left(1-\boldsymbol{\beta}_b\cdot\mathbf{n}\right)^3} \frac{\mathbf{n}\times\{(\mathbf{n}-\boldsymbol{\beta}_b)\times\boldsymbol{\gamma}_b\}}{cR}. \tag{5.17}$$

The magnetic field is given by

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ber of particles in correlated motion, for which the present theory gives virtually the same radiation power per electron as the Larmor formula.

[29] J. A. Wheeler, R. P. Feynman, *Interaction with the Absorber as the Mechanism of Radiation*, Rev. Mod. Phys. 17, p. 157–181 (1945).

$$\mathbf{B}_b(\mathbf{x}, t) = \mathbf{n} \times \mathbf{E}_b. \tag{5.18}$$

and is non-zero only if the particle was moving at the retarded time.

5.3 Model of the molecule

The total force acting upon the negative particle a consists of more contributions. These are the forces due to nuclei and electrons co-forming the molecule, due to other molecules in the solution and farther away, due to source of light (laser, lamp), the forces of the background fields of distant sources and possibly also non-electromagnetic forces:

$$\mathbf{F}_{-a} = \mathbf{F}_{-a}^{\text{nuclei}} + \mathbf{F}_{-a}^{\text{electrons}} + \mathbf{F}_{-a}^{\text{molecules}} + \mathbf{F}_{-a}^{\text{source}} + \mathbf{F}_{-a}^{\text{background}} + \mathbf{F}_{-a}^{\text{NE}}. \tag{5.19}$$

Chapter 6

Lorentzian model

We will not attempt to use the exact theory from the previous chapter directly to describe the complex system of many particles forming the molecule. The reason is that the number of particles in the BChl molecules is very large and an exact mathematical treatment of such system would be numerically too demanding.

Instead of insisting on the exact formulae for fields given above, we will use the corresponding theory in a more liberal way. We use it as an inspiration for the formulation of a model which will include the most important phenomena - the stability of configuration and damping of electronic oscillations - more easily. Hopefully it may be made both simple and faithful enough to allow to connect to the spectroscopic measurements.

The first important thing to consider when simplifying the above equations is the fact that for the description of low intensity monochromatic light, the behaviour of the medium seems to be quite well described by simple harmonic oscillation equal to that of the primary wave. Deviations from the harmonic oscillation seem to be unimportant for the shape of ordinary absorption spectra. Perhaps the same is true also for the circular dichroism, although due to smallness of this effect the small non-linearities perturbing the harmonic motion may have important contributions.

Similar harmonic behaviour is found in the stationary solutions of systems of linear differential equations with periodic right-hand side (driving term). Such system has stationary solutions that perform harmonic oscillations at the frequency of the driving term, albeit with a possible phase shift.

Hence it seems to be a good idea to simplify the exact scheme from the previous chapter and base the model of molecule and its interaction with light on linear differential equations, in the spirit of the classical Lorentz-Drude model of atomic oscillator.

In order to do that, we imagine the molecule as a rigid system of point-like immovable nuclei a of positive electric charge Q_a placed at positions $\mathbf{R}_a$ of the laboratory coordinate system. Each nucleus has attached to it by elastic force one negatively charged point-like particle of mass $Z_a m_e$ and negative charge q_a which has equilibrium position at the position of the nucleus and can move in its vicinity. The radius vector of the negative charge with respect to the nucleus will be denoted by $\mathbf{u}_a$. The couple nucleus-negative particle will be called (physical) *oscillator*.

We will assume that the various contributions to the force can be separated into groups of distinct character.

The electrons are bound to the molecule and the main part of the bonding force is presumably the electrostatic field of the nuclei. This attracts the electrons and contributes to the stability of the system. However, this field is not the only one relevant for the stability; as explained above, there are many other fields from the other particles both near and far from the molecule which probably contribute in an important way; they balance the radiative loss of energy. Instead of dealing with such complex interacting many-particle system, we will introduce an effective attractive force to substitute for this combined effect of many stabilizing forces. Since the spectra of atoms and molecules show high preference for harmonic motions, we will use linear elastic force $\mathbf{F}_{-a}^{\text{elastic}} = -m_a \omega_a^2 \mathbf{u}_a$ that leads to elliptic orbits with coordinates oscillating harmonically in time.

Similarly, another part of the combined action of all the particles leads to effective damping of the oscillations set by the external field. We will model this by force $\mathbf{F}_{-a}^{\text{damping}} = -m_a \gamma_a \mathbf{v}_a$. There is also the residual fluctuating force $\mathbf{F}_{-a}^{\text{fluct}}$ from the same agents, which however we will neglect. Different electrons interact among each other, so there is also the sum of forces due to all other neutral pairs (nucleus - negative charge) $\mathbf{F}_{-a}^{\text{coupling}}$. Finally, there is the force due to combined action of the molecules of the solution and of the primary source of light $\mathbf{F}_{-a}^{\text{driving}}$ that drives the oscillating motion of the molecule. Overall the total force can be written as

$$\mathbf{F}_{-a} = \mathbf{F}_{-a}^{\text{elastic}} + \mathbf{F}_{-a}^{\text{damping}} + \mathbf{F}_{-a}^{\text{fluct}} + \mathbf{F}_{-a}^{\text{coupling}} + \mathbf{F}_{-a}^{\text{driving}}. \tag{6.1}$$

We will look into the two last forces more closely.

6.1 Forces of interaction

Here we take an inspiration from the above exact theory of electromagnetic fields. We imagine that the negative particles oscillate only a little around their equilibrium positions. The force on the negative particle a from all other oscillators b is given by the Lorentz formula with the retarded fields given above. We will approximate these by expressions linear in the displacement vector $\mathbf{u}_a$ and its derivatives.

The notation used in the following text requires some explanation. Since the force considered is due to b on a, the important quantities are the position $\mathbf{u}_a$ of the a-th particle at the present time t and the position $[\mathbf{u}_b]$ of b at the retarded time. The quantity $\mathbf{u}_{ab}$ denotes their difference:

$$\mathbf{u}_{ab} = \mathbf{u}_a - [\mathbf{u}_b]. \tag{6.2}$$

We also define the vector

$$\mathbf{R}_{ab} = \mathbf{R}_a - \mathbf{R}_b \tag{6.3}$$

and denote its magnitude by R_{ab}. The symbol $\mathbf{n}_{ab}$ denotes unit vector in the same direction:

$$\mathbf{n}_{ab} = \frac{\mathbf{R}_{ab}}{R_{ab}}. \tag{6.4}$$

Using this notation, the retarded radius vector of b is approximately equal to

$$[\mathbf{u}_b] = \mathbf{u}_b \left(t - \frac{R_{ab}}{c} \right). \tag{6.5}$$

The main static part of the field of the negative particle cancels the electrostatic field of the nucleus, so the remaining linear part of the field due to the negative particles is

$$\begin{aligned}
\mathbf{F}_{-a}^{\text{coupling}} = {\sum_b}' \frac{K q_a q_b}{4\pi} \Bigg[\quad & \frac{\mathbf{u}_{ab} - 3(\mathbf{u}_{ab} \cdot \mathbf{n}_{ab})\mathbf{n}_{ab}}{R_{ab}^3} - & (6.6)\\
& - \frac{[\dot{\mathbf{u}}_b] - 3([\dot{\mathbf{u}}_b] \cdot \mathbf{n}_{ab})\mathbf{n}_{ab}}{cR_{ab}^2} - & (6.7)\\
& - \frac{[\ddot{\mathbf{u}}_b] - ([\ddot{\mathbf{u}}_b] \cdot \mathbf{n}_{ab})\mathbf{n}_{ab}}{c^2 R_{ab}} \quad \Bigg]. & (6.8)
\end{aligned}$$

We will need the negative acceleration due to this force. We write this as

$$-\frac{1}{m_a}\mathbf{F}^{\text{coupling}}_{-a} = \sum_c{}' - \ K_{ac}\frac{1}{R^3_{ac}}\Big(\mathbf{u}_{ac} - 3(\mathbf{u}_{ac}\cdot\mathbf{n}_{ac})\mathbf{n}_{ac}\Big) + \tag{6.9}$$

$$+ \ K_{ac}\frac{1}{cR^2_{ac}}\Big([\dot{\mathbf{u}}_c] - 3([\dot{\mathbf{u}}_c]\cdot\mathbf{n}_{ac})\mathbf{n}_{ac}\Big) + \tag{6.10}$$

$$+ \ K_{ac}\frac{1}{c^2R_{ac}}\Big([\ddot{\mathbf{u}}_c] - ([\ddot{\mathbf{u}}_c]\cdot\mathbf{n}_{ac})\mathbf{n}_{ac}\Big), \tag{6.11}$$

where

$$K_{ac} = \frac{Kq_aq_c}{4\pi m_a}. \tag{6.12}$$

6.2 Driving force

We will assume that the driving force is the electromagnetic force due to fields of the source of light and the molecules in the path of the light ray:

$$\mathbf{F}^{\text{driving}}_{-a} = q_a\mathbf{E}^{\text{driving}}(\mathbf{r}_a) + q_a\frac{\mathbf{v}_a}{c}\times\mathbf{B}^{\text{driving}}(\mathbf{r}_a). \tag{6.13}$$

The magnetic term is linear in the displacement of the particle and thus should be included into our scheme on the linear level of approximation. However, since the term oscillates at double the frequency of the source, it would complicate the procedure of solving the equations of motion. The term is small when compared to the electric term, but again, for circular dichroism it may still be important. We will leave the investigation of the effect of this contribution on circular dichroism to other works and neglect it here for the sake of simplicity.

The driving field is much more complicated than the smooth macroscopic field and cannot be faithfully described by a plane wave. The scattering of the primary wave from the other molecules leads to a total microscopic field that has quite complicated spatial pattern, albeit the same frequency. The driving field acting on any molecule will be similar in this respect - almost no molecule will experience driving field in the direction or amplitude of the macroscopic field.

Nevertheless, we will replace this complicated driving field by field of a plane wave and assume that it still is a useful approximate representation of the driving field, at least on the average. What amplitude and wave number should this idealized wave have?

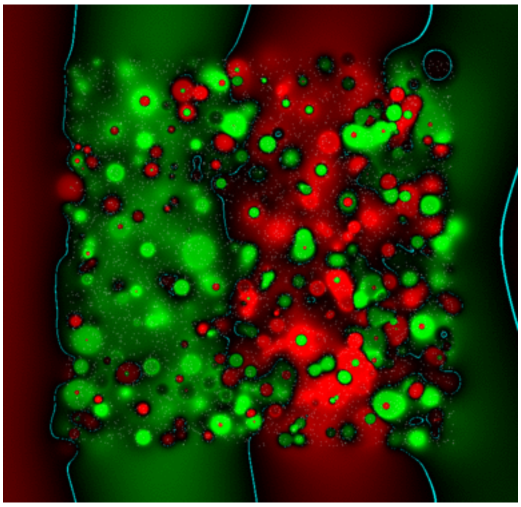

Figure 6.1: Depiction of the total electric field passing through a cube of oscillators interacting with the primary wave and among each other. The electric field is polarized linearly in the direction z normal to the plane of the paper, green color shows regions where the value of E_z is positive, red those where the value negative, and the cyan lines shows the node surface where E_z is zero. Notice how the total field deforms due to random positions of the scatterers and that it differs from the simple plane wave one uses in macroscopic theory.

The microscopic field that acts on the molecule propagates in vacuum and obeys source-free Maxwell equations. For this reasons, it seems that the wave number $k_0 = \frac{\Omega}{c}$ suits it much better than the macroscopic wave number k (which is usually higher but changes significantly with frequency near the absorption bands).

As for the amplitude, for simplicity we will assume that the best amplitude to use for the driving field is a one proportional to the amplitude of the macroscopic field E_0:

$$E_0 = \kappa E. \tag{6.14}$$

This seems like a reasonable assumption within linear theory. We have already shown how the macroscopic field amplitude may be obtained from the microscopic one: by averaging, which is a linear operation.

According the the macroscopic theory of optical activity of liquid solution, we have two distinct fields to consider.

Left-circularly polarized light. The macroscopic field is described by the electric vector

$$\mathbf{E}_{\mathrm{L}}(\mathbf{x},t) = \left\{\mathbf{e}_x \cos(\Omega t - \mathbf{k}_{\mathrm{L}}\cdot\mathbf{x}) + \mathbf{e}_y \sin(\Omega t - \mathbf{k}_{\mathrm{L}}\cdot\mathbf{x})\right\} E. \tag{6.15}$$

We assume that the microscopic driving field is given by

$$\mathbf{E}_{\mathrm{L}}^{\mathrm{driving}}(\mathbf{x},t) = \left\{\mathbf{e}_x \cos(\Omega t - \mathbf{k}_0\cdot\mathbf{x}) + \mathbf{e}_y \sin(\Omega t - \mathbf{k}_0\cdot\mathbf{x})\right\} E_0. \tag{6.16}$$

In the complex phasor notation,

$$\mathbf{E}_{\mathrm{L}}^{\mathrm{driving}}(\mathbf{x},t) = \mathrm{Re}\bigg\{(\mathbf{e}_x - i\mathbf{e}_y)e^{i(\Omega t - \mathbf{k}_0\cdot\mathbf{x})}E_0\bigg\}. \tag{6.17}$$

Right-circularly polarized light. The macroscopic field is described by the electric vector

$$\mathbf{E}_{\mathrm{R}}(\mathbf{x},t) = \left\{\mathbf{e}_x \cos(\Omega t - \mathbf{k}_{\mathrm{R}}\cdot\mathbf{x}) - \mathbf{e}_y \sin(\Omega t - \mathbf{k}_{\mathrm{R}}\cdot\mathbf{x})\right\} E. \tag{6.18}$$

We assume that the microscopic driving field is given by

$$\mathbf{E}_{\mathrm{R}}^{\mathrm{driving}}(\mathbf{x},t) = \left\{\mathbf{e}_x \cos(\Omega t - \mathbf{k}_0\cdot\mathbf{x}) - \mathbf{e}_y \sin(\Omega t - \mathbf{k}_0\cdot\mathbf{x})\right\} E_0. \tag{6.19}$$

In the complex phasor notation,

$$\mathbf{E}_{\mathrm{R}}^{\mathrm{driving}}(\mathbf{x},t) = \mathrm{Re}\bigg\{(\mathbf{e}_x + i\mathbf{e}_y)e^{i(\Omega t - \mathbf{k}_0\cdot\mathbf{x})}E_0\bigg\}. \tag{6.20}$$

6.3 Equation of motion

Finally we come to formulation of the equation of motion for the oscillators. Since we are restricting the description to linear terms, we approximate relativistic momentum

$$\mathbf{p}_a = \frac{m_a \mathbf{v}_a}{\sqrt{1 - \frac{v_a^2}{c^2}}} \tag{6.21}$$

by the main part linear in coordinates, which is $m_a\mathbf{v}_a$. We introduce the radius vector with respect to nuclei $\mathbf{u}_a$. The equations of motion are then as follows. For left circular polarization:

$$\ddot{\mathbf{u}}_a + \gamma_a \dot{\mathbf{u}}_a + \omega_a^2 \mathbf{u}_a - \frac{1}{m_a}\mathbf{F}_{-a}^{\mathrm{coupling}} =$$

$$= \frac{q_a E_0}{m_a} \left(\mathbf{e}_x \sin(\Omega t - \mathbf{k}_0 \cdot \mathbf{R}_a)) + \mathbf{e}_y \cos(\Omega t - \mathbf{k}_0 \cdot \mathbf{R}_a)\right). \tag{6.22}$$

For right circular polarization:

$$\ddot{\mathbf{u}}_a + \gamma_a \dot{\mathbf{u}}_a + \omega_a^2 \mathbf{u}_a - \frac{1}{m_a} \mathbf{F}_{-a}^{\text{coupling}} =$$

$$= \frac{q_a E_0}{m_a} \left(\mathbf{e}_x \sin(\Omega t - \mathbf{k}_0 \cdot \mathbf{R}_a)) - \mathbf{e}_y \cos(\Omega t - \mathbf{k}_0 \cdot \mathbf{R}_a)\right). \tag{6.23}$$

Notice that the two cases differ only by different sign in the driving term on the right-hand side of the equation.

6.4 Solution by the method of phasors

Since we are interested in stationary oscillating solutions the equations admit, we can neglect the effect of initial conditions and seek the solution in the form of harmonic oscillations. This is most efficiently handled by the complex phasor method. We focus on the new complex equations of motion

Left c.p.:

$$\ddot{\tilde{\mathbf{U}}}_a + \gamma_a \dot{\tilde{\mathbf{U}}}_a + \omega_a^2 \tilde{\mathbf{U}}_a - \frac{1}{m_a} \tilde{\mathbf{F}}_{-a}^{\text{coupling}} = \frac{q_a E_0}{m_a} (\mathbf{e}_x - i\mathbf{e}_y)\, e^{i(\Omega t - \mathbf{k}_0 \cdot \mathbf{R}_a)}. \tag{6.24}$$

Right c.p.:

$$\ddot{\tilde{\mathbf{U}}}_a + \gamma_a \dot{\tilde{\mathbf{U}}}_a + \omega_a^2 \tilde{\mathbf{U}}_a - \frac{1}{m_a} \tilde{\mathbf{F}}_{-a}^{\text{coupling}} = \frac{q_a E_0}{m_a} (\mathbf{e}_x + i\mathbf{e}_y)\, e^{i(\Omega t - \mathbf{k}_0 \cdot \mathbf{R}_a)}. \tag{6.25}$$

It is easy to see that the real part of both equations gives the actual equations of motion from above. We seek stationary solutions (for all a):

$$\tilde{\mathbf{U}}_a = \mathbf{U}_a e^{i\Omega t} \tag{6.26}$$

where $\mathbf{U}_a$ is a complex vector describing the amplitude and phase of oscillations of the a-th oscillator. The retarded quantities $[\mathbf{u}_c]$ in the coupling terms are replaced by $\mathbf{U}_c e^{i(\Omega t - \varphi_{ac})}$. The time-dependent term $e^{i\Omega t}$ drops out of the equation and we arrive at the system of equations for $\mathbf{U}_a$:

Left c.p.:

$$(-\Omega^2 + i\gamma_a\Omega + \omega_a^2)\mathbf{U}_a + \mathbf{I}_a = \frac{q_a E_0}{m_a}\left(\mathbf{e}_x - i\mathbf{e}_y\right)e^{-i\mathbf{k}_0\cdot\mathbf{R}_a}.$$

Right c.p.:

$$(-\Omega^2 + i\gamma_a\Omega + \omega_a^2)\mathbf{U}_a + \mathbf{I}_a = \frac{q_a E_0}{m_a}\left(\mathbf{e}_x + i\mathbf{e}_y\right)e^{-i\mathbf{k}_0\cdot\mathbf{R}_a}.$$

where the interaction is described by the vectors

$$\mathbf{I}_a = -\frac{1}{m_a}\tilde{\mathbf{F}}^{\text{coupling}}_{-a}e^{-i\Omega t}, \tag{6.27}$$

which has expression

$$\begin{aligned}
\mathbf{I}_a = {\sum_c}' -\frac{K_{ac}}{R_{ac}^3}\left(\mathbf{U}_a - 3\mathbf{U}_a\cdot\mathbf{n}_{ac}\mathbf{n}_{ac}\right) + & \qquad (6.28)\\
+\ \frac{K_{ac}e^{-i\varphi_{ac}}}{R_{ac}^3}\left(\mathbf{U}_c - 3\mathbf{U}_c\cdot\mathbf{n}_{ac}\mathbf{n}_{ac}\right) + & \qquad (6.29)\\
+\ \frac{K_{ac}i\Omega e^{-i\varphi_{ac}}}{cR_{ac}^2}\left(\mathbf{U}_c - 3\mathbf{U}_c\cdot\mathbf{n}_{ac}\mathbf{n}_{ac}\right) + & \qquad (6.30)\\
+\ \frac{K_{ac}(-\Omega^2)e^{-i\varphi_{ac}}}{c^2R_{ac}}\left(\mathbf{U}_c - \mathbf{U}_c\cdot\mathbf{n}_{ac}\mathbf{n}_{ac}\right), & \qquad (6.31)
\end{aligned}$$

and

$$\varphi_{ac} = \Omega\frac{R_{ac}}{c} \tag{6.32}$$

is the phase shift due to retardation of the field acting on a due to c.

We can see that the equations are linear and thus easy to solve. In order to solve them, we would like to rewrite the system of equations into the matrix form

$$\sum_{b,l} M_{a,k|b,l}U_{b,l} = b_{a,k}. \tag{6.33}$$

After some manipulations, we arrive at this expression for the matrix M:

$$M_{a,k|b,l} = \sigma_a\delta_{ab}\delta_{kl} + \sum_c A_{ac}\delta_{ab}(\delta_{kl} - 3n_{ac,k}n_{ac,l}) + B_{ab}\delta_{kl} + C_{ab}n_{ab,k}n_{ab,l} \tag{6.34}$$

where

$$\sigma_a = -\Omega^2 + i\gamma_a\Omega + \omega_a^2, \tag{6.35}$$

and

$$A_{ac} = -\frac{K_{ac}}{R_{ac}^3}, \tag{6.36}$$

$$B_{ac} = K_{ac}e^{-i\varphi_{ac}}\left(\frac{1}{R_{ac}^3} + \frac{i\Omega}{cR_{ac}^2} - \frac{\Omega^2}{c^2R_{ac}}\right), \tag{6.37}$$

$$C_{ac} = K_{ac}e^{-i\varphi_{ac}}\left(-\frac{3}{R_{ac}^3} - \frac{3i\Omega}{cR_{ac}^2} + \frac{\Omega^2}{c^2R_{ac}}\right) \tag{6.38}$$

for $a \neq c$ and $A_{aa} = B_{aa} = C_{aa} = 0$ for the diagonal elements. The right-hand sides are
Left c.p.:

$$b_{b,l}^{\mathrm{L}} = \frac{q_bE_0}{m_b}(a_l - ib_l)e^{-ik\sum_m c_mR_{b,m}}, \tag{6.39}$$

Right c.p.:

$$b_{b,l}^{\mathrm{R}} = \frac{q_bE_0}{m_b}(a_l + ib_l)e^{-ik\sum_m c_mR_{b,m}}, \tag{6.40}$$

where we introduced the symbols a_l, b_l, c_l for the l-th coordinate of the unit vectors $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ in the laboratory system. In the following text, we will calculate only the case of left-handed light wave and will drop the superscript L to make the text more readable.

Once we have the matrix $\mathbf{M}$ and the right-hand side $\mathbf{b}$, we can solve for the quantities $\mathbf{U}$ formally by means of an inverse matrix. In order to do so, we introduce new indices α, β by

$$\alpha = 3(a-1) + k, \tag{6.41}$$

$$\beta = 3(b-1) + l. \tag{6.42}$$

The inverse transformation is, for the indices a and k, given by

$$a = (\alpha + 2) \text{ div } 3, \tag{6.43}$$

$$k = [(\alpha + 2) \bmod 3] + 1 \tag{6.44}$$

and similarly for b and l. We introduce the notation

$$U_\alpha = U_{a,k}, \tag{6.45}$$

$$M_{\alpha\beta} = M_{a,k|b,l}, \tag{6.46}$$

$$b_\beta = b_{b,l}. \tag{6.47}$$

The equations to be solved are

$$\sum_\beta M_{\alpha\beta} U_\beta = b_\alpha. \tag{6.48}$$

We write the solution in terms of an inverse matrix :

$$U_\alpha = \sum_\beta M^{-1}_{\alpha\beta} b_\beta. \tag{6.49}$$

In the laboratory frame, both the matrix $\mathbf{M}$ and the right-hand side $\mathbf{b}$ depend on the angles of rotation $\varphi, \vartheta, \alpha$. The inverse matrix will depend also on these angles in a somewhat complicated way and averaging U analytically over all orientations would be quote difficult.

However, the same equations of motion and the same linear algebraic equations hold also in the coordinate frame of the molecule, where we write

$$U'_\alpha = \sum_\beta M'^{-1}_{\alpha\beta} b'_\beta. \tag{6.50}$$

The matrix M' referring to the molecular coordinate system remains the same for all its orientations, and only the right-hand side b'_β depends on the angles $\varphi, \vartheta, \alpha$.

6.5 Susceptibility

According to the general definition of the macroscopic current density derived in the chapter on the connection to the macroscopic theory, in the laboratory coordinate system the current density is given by

$$\mathbf{j}(0,t) = \mathscr{N} \left\langle \sum_a q_a \dot{\mathbf{u}}_a \left(t + \frac{\mathbf{R}_a \cdot \mathbf{e}_z}{v_f} \right) \right\rangle \tag{6.51}$$

where the angles $\langle \ \rangle$ denote rotational averaging. This expression equals to

$$\mathbf{j}(0,t) = \frac{\partial}{\partial t}\left[\mathscr{N}\left\langle \sum_a q_a \mathbf{u}_a \left(t + \frac{\mathbf{R}_a \cdot \mathbf{e}_z}{v_f}\right)\right\rangle\right]. \tag{6.52}$$

The polarization potential is thus given by the expression

$$\mathbf{P}(t) = \mathscr{N}\left\langle \sum_a q_a \mathbf{u}_a \left(t + \frac{\mathbf{R}_a \cdot \mathbf{e}_z}{v_f}\right)\right\rangle. \tag{6.53}$$

In order to find an expression for the complex susceptibility $\tilde{\chi}$, and then the absorption spectrum from it, we pass to complex phasors. Since the quantities $\mathbf{u}_a$ oscillate harmonically in time, the phasor for the polarization potential is[30]

$$\tilde{\mathbf{P}}(t) = \mathscr{N}\left\langle \sum_a q_a \mathbf{U}_a e^{i\mathbf{k}\cdot\mathbf{R}_a} v_f \right\rangle e^{i\Omega t}, \tag{6.54}$$

where

$$\mathbf{k} = k\mathbf{e}_z \tag{6.55}$$

is the wave vector of the macroscopic wave. The macroscopic electric field for the left-handed light has the phasor

$$\tilde{\mathbf{E}}(t) = E(\mathbf{e}_x - i\mathbf{e}_y)e^{i\Omega t}. \tag{6.56}$$

According to the macroscopic theory of absorption and dispersion, these two quantities are related by

$$\tilde{\mathbf{P}}(t) = \frac{\tilde{\chi}}{K}\tilde{\mathbf{E}}(t). \tag{6.57}$$

Calculating dot product of both sides of this equation with $\mathbf{e}_x + i\mathbf{e}_y$ (for left-handed wave), we obtain the expression for the complex susceptibility

$$\tilde{\chi} = \frac{K\mathscr{N}}{2E}\sum_a q_a \left\langle \mathbf{U}_a \cdot (\mathbf{e}_x + i\mathbf{e}_y) e^{i\mathbf{k}\cdot\mathbf{R}_a}\right\rangle. \tag{6.58}$$

This expression contains the molecular quantities in dot products, which are invariant quantities with respect to change of coordinates. We can therefore quite as well express the susceptibility via the coordinates in the molecular coordinate frame:

---

[30] Once again we can see that the polarization potential is not the same as density of electric moment (electric polarization). The two differ by the factor $e^{i\mathbf{k}\cdot\mathbf{R}_a}$ in every term which is in the summation.

$$\tilde{\chi} = \frac{K\mathscr{N}}{2E}\sum_a q_a \left\langle \mathbf{U}'_a \cdot (\mathbf{e}'_x + i\mathbf{e}'_y) e^{i\mathbf{k}'\cdot\mathbf{R}'_a} \right\rangle \tag{6.59}$$

or

$$\tilde{\chi} = \frac{K\mathscr{N}}{2E}\sum_{\alpha\beta} q_a \left\langle M'^{-1}_{\alpha\beta} b'_\beta (a'_k + ib'_k) e^{i\mathbf{k}'\cdot\mathbf{R}'_a} \right\rangle . \tag{6.60}$$

However, we do not know the wave number k before we have the susceptibility $\tilde{\chi}$. We will therefore approximate k by $k_0 = \frac{\Omega}{c}$:

$$\tilde{\chi} \approx \frac{K\mathscr{N}}{2E}\sum_{\alpha} q_a M'^{-1}_{\alpha\beta} \left\langle b'_\beta (a'_k + ib'_k) e^{i\mathbf{k}'_0\cdot\mathbf{R}'_a} \right\rangle . \tag{6.61}$$

The matrix M^{-1} does not depend on the rotation angles and thus can be put in front of the averaging bracket. Since

$$b'_\beta = \frac{q_b E_0}{m_b}(a'_l - ib'_l) e^{-i\mathbf{k}'_0\cdot\mathbf{R}'_b}, \tag{6.62}$$

we obtain

$$\tilde{\chi} \approx \frac{1}{2}\kappa K\mathscr{N}\sum_{\alpha\beta} M'^{-1}_{\alpha\beta} T'_{\beta\alpha}. \tag{6.63}$$

For left-handed light, we obtain

$$T'^{\mathrm{L}}_{\beta\alpha} = \frac{q_b q_a}{m_b}\left\langle (a'_l - ib'_l)(a'_k + ib'_k) e^{-i\mathbf{k}'_0\cdot\mathbf{R}'_{ba}} \right\rangle \tag{6.64}$$

Similarly, for right-handed light, we obtain

$$T'^{\mathrm{R}}_{\beta\alpha} = \frac{q_b q_a}{m_b}\left\langle (a'_l + ib'_l)(a'_k - ib'_k) e^{-i\mathbf{k}'_0\cdot\mathbf{R}'_{ba}} \right\rangle . \tag{6.65}$$

The value of rotational average seems difficult to evaluate exactly. We therefore expand the exponential term into the Taylor series of 1st order and calculate

$$T'_{\beta\alpha} \approx \frac{q_b q_a}{m_b}\left\langle (a'_l - ib'_l)(a'_k + ib'_k) \left(1 - ik_0 \sum_m R'_{ba,m} c'_m\right) \right\rangle , \tag{6.66}$$

After the expansion, the averaged expression for left-handed light is

$$\left\langle a'_l a'_k + i a'_l b'_k - i b'_l a'_k + b'_l b'_k - ik_0 \sum_m R'_{ba,m} (a'_l a'_k + i a'_l b'_k - i b'_l a'_k + b'_l b'_k) c'_m \right\rangle . \tag{6.67}$$

This can be calculated with help of the matrix $\mathbf{R}^{-1}$ given in the section on rotations in the chapter on the connections to the macroscopic theory. It turns out that most terms vanish after averaging and the quantities T' can be written as

$$T'^{\mathrm{L}}_{\beta\alpha} \approx \frac{q_b q_a}{m_b}\left(\frac{2}{3}\delta_{lk} + \sum_m \frac{1}{3}\epsilon_{lkm} k_0 R_{ba,m}\right) \tag{6.68}$$

for left-handed light and

$$T'^{\mathrm{R}}_{\beta\alpha} \approx \frac{q_b q_a}{m_b}\left(\frac{2}{3}\delta_{lk} - \sum_m \frac{1}{3}\epsilon_{lkm} k_0 R_{ba,m}\right) \tag{6.69}$$

for right-handed light. If the susceptibilities are written as

$$\tilde{\chi}_L = R_L + iI_L, \tag{6.70}$$

$$\tilde{\chi}_R = R_R + iI_R, \tag{6.71}$$

the extinction coefficients are

$$\epsilon_{\mathrm{L}}(\Omega) \approx |I_L|\sqrt{\frac{1}{(1+R_L)} - \frac{I_L^2}{4(1+R_L)^3}}\,\frac{\Omega}{\mathscr{N}c}. \tag{6.72}$$

$$\epsilon_{\mathrm{R}}(\Omega) \approx |I_R|\sqrt{\frac{1}{(1+R_R)} - \frac{I_R^2}{4(1+R_R)^3}}\,\frac{\Omega}{\mathscr{N}c}. \tag{6.73}$$

The spectrum of circular dichroism is the difference between these two spectra:

$$\Delta\epsilon(\Omega) = \epsilon_{\mathrm{L}}(\Omega) - \epsilon_{\mathrm{R}}(\Omega). \tag{6.74}$$

Chapter 7

Control calculations

Before we try to apply our theory to such complicated molecules as bacteriochlorophylls, we use it to make some control calculations on simpler systems.

7.1 Pair of undamped oscillators

The system of two oscillators has its nuclei on a line and thus is not chiral. We thus expect that CD of such a system vanishes. The parameters of the system are given in the table. We prescribe positions of both oscillators (in Angströms), their resonance wave numbers and damping constants (both in cm^{-1}), effective electronic charge (in e) and mass (in kg). In the first example, the oscillators have zero damping constants.

Key	No.	x	y	z	ν_0	γ	q	m
OSC	1	0	1	0	13000	0	-0.000025	9.1E-31
OSC	2	0	-1	0	15000	0	-0.000025	9.1E-31

Table 7.1: Parameters of a pair of oscillators.

The results of calculations are presented in the form of self-explanatory plots of absorption spectra and circular dichroism. Each plot has a title giving the information on which parameters were used to calculate the interaction forces. The first number signifies inclusion of retardation, the second inclusion of velocity fields, and the third inclusion of the acceleration fields. If the number is 1, the effect was included, if 0, it was neglected. The purpose of this is to show the effect of the new non-electrostatic terms we introduced in the previous chapter.

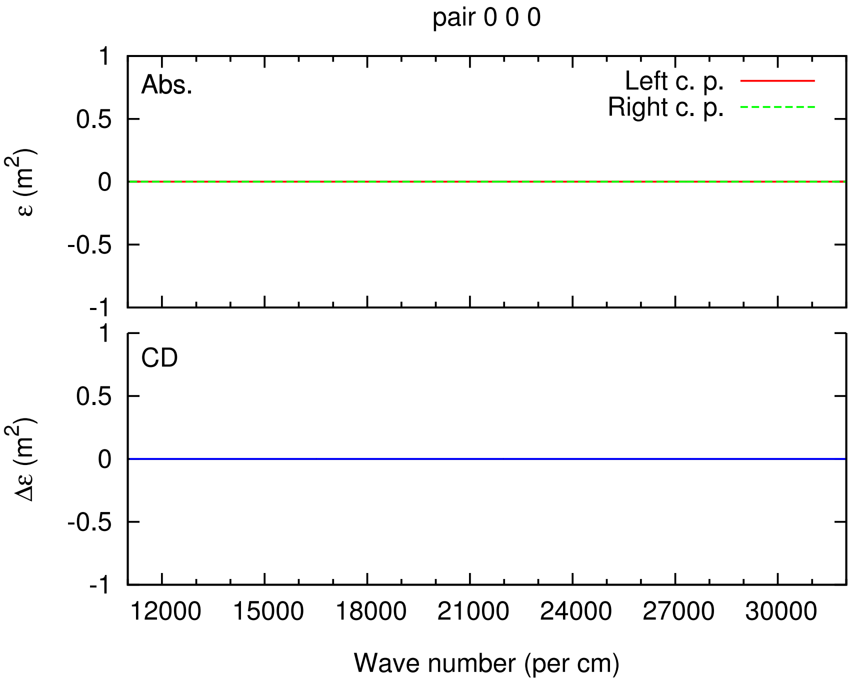

Figure 7.1: Absorption spectra of pair of oscillators.

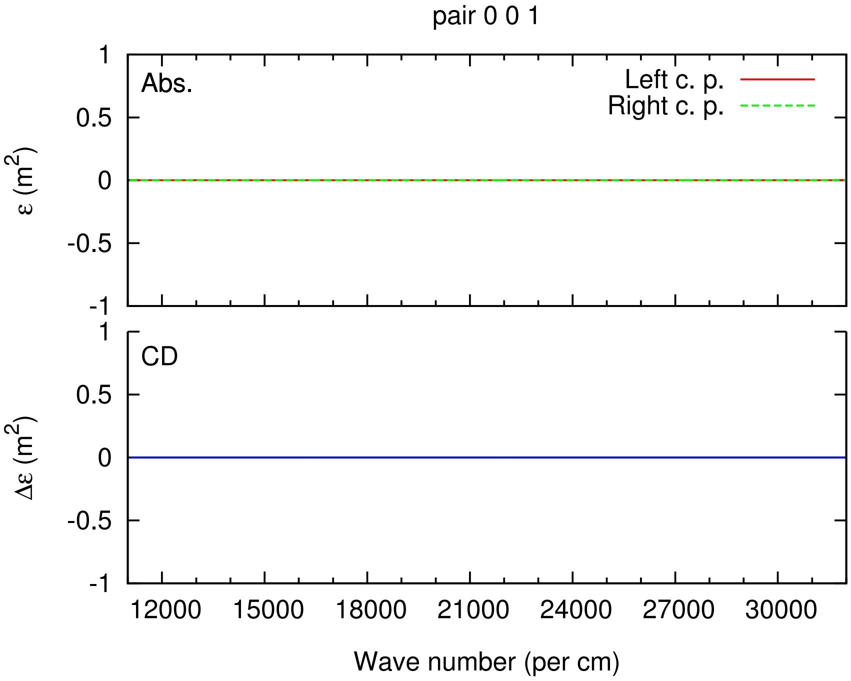

Figure 7.2: Absorption spectra of pair of oscillators.

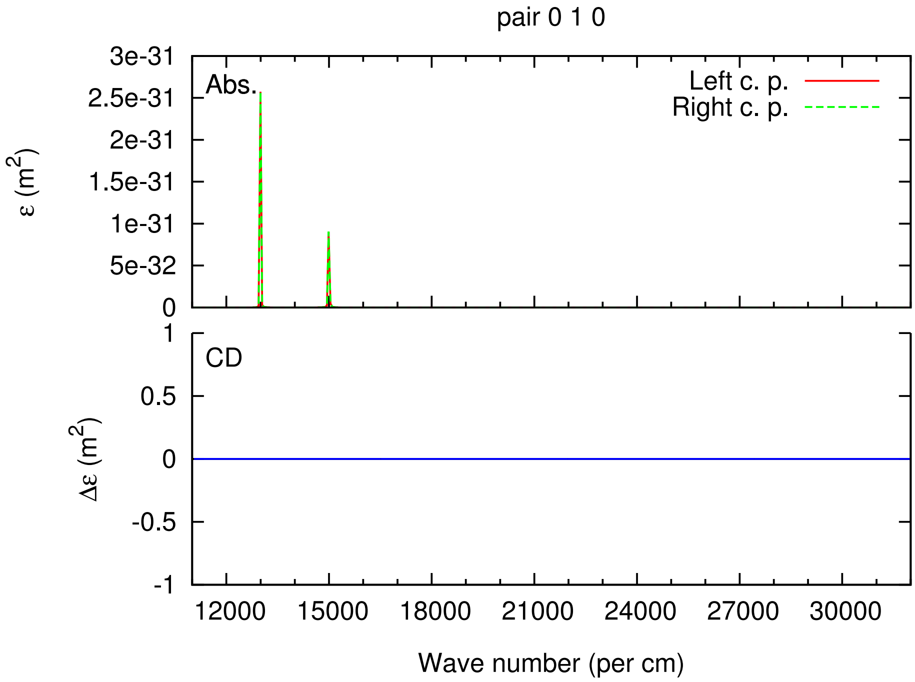

Figure 7.3: Absorption spectra of pair of oscillators.

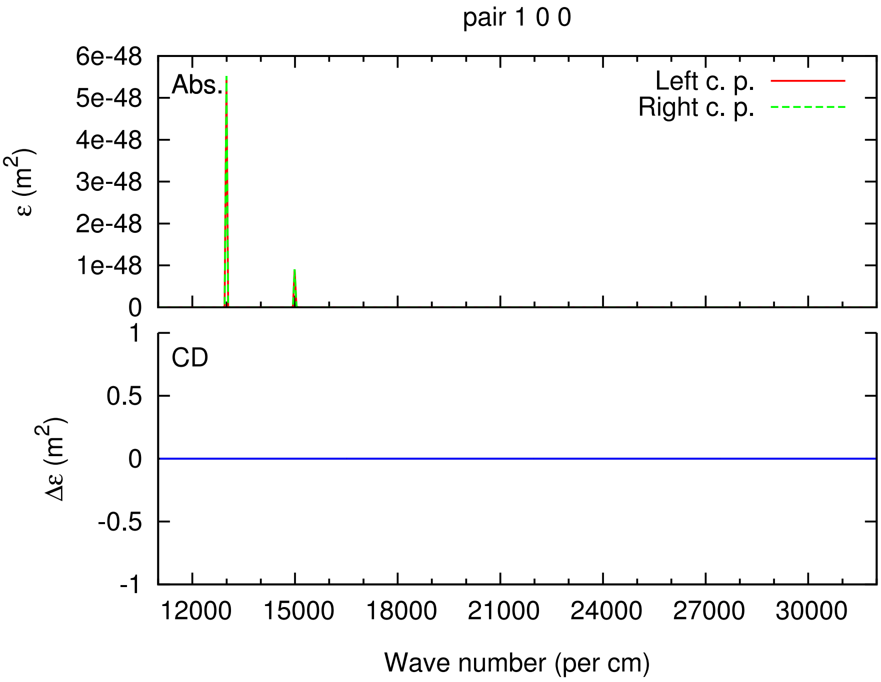

Figure 7.4: Absorption spectra of pair of oscillators.

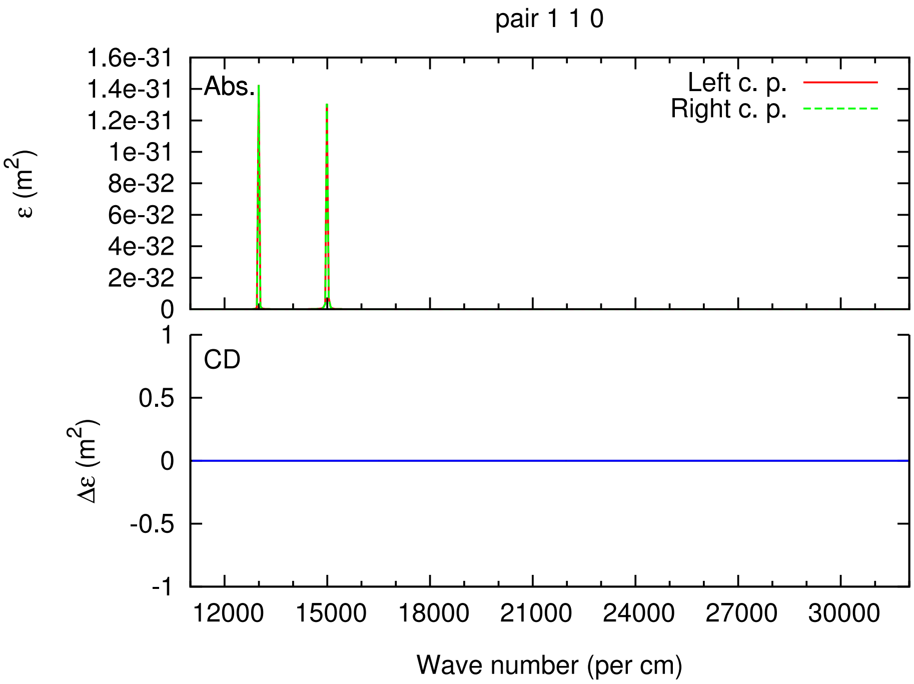

Figure 7.5: Absorption spectra of pair of oscillators.

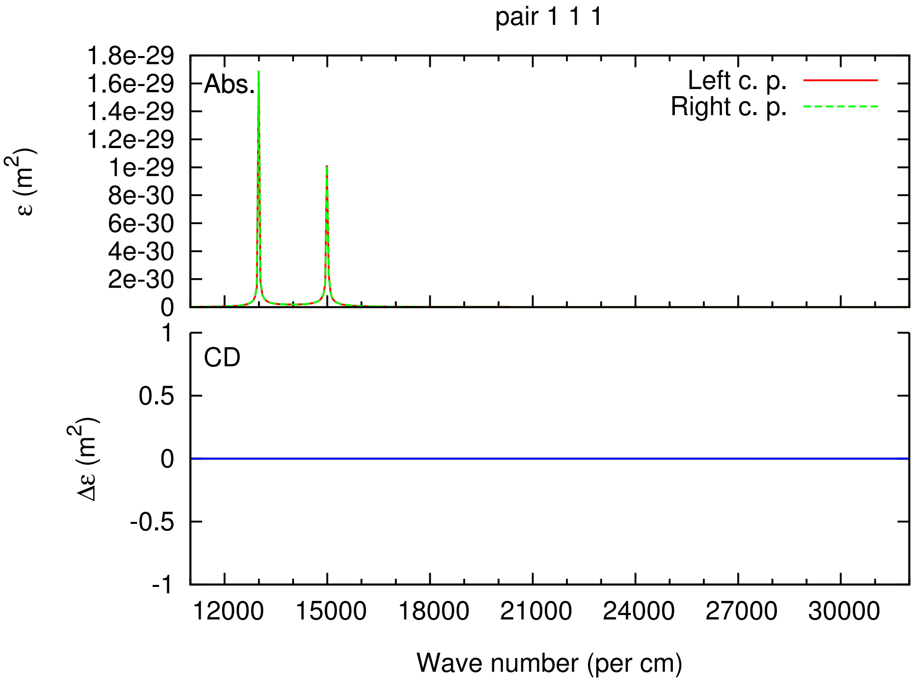

Figure 7.6: Absorption spectra of pair of oscillators.

From these plots we can see that if all non-electrostatic contributions are neglected, there is no absorption, which is natural since we prescribed zero external damping. However, if the retardation is turned on, the system exhibits absorption on both resonance frequencies. This is because the inclusion of retardation to the interaction forces introduces effective damping of the motion of the oscillators, since the differential equation has delayed terms. As the oscillator loses energy, the energy of the electromagnetic field increases, since the two oscillators move with acceleration in a correlated way. The delayed terms therefore provide a model of de-excitation accompanying the phenomenon of *spontaneous emission.*

Further inclusion of the velocity and acceleration fields leads to further broadening of the spectral line and notable increase in its intensity.

7.2 Pair of damped oscillators

Even with inclusion of all interaction terms, the absorption lines are very sharp and if the system interacts with surroundings, we expect it to have much broader spectral bands. This can be modelled by inclusion of a descriptive damping constant. An example of damped pair of oscillators with damping constants $\gamma = 1000$ cm^{-1} follows.

Key	Name	x	y	z	ν_0	γ	q	m
OSC	1	0	1	0	13000	1000	-0.000025	9.1E-31
OSC	2	0	-1	0	15000	1000	-0.000025	9.1E-31

Table 7.2: Parameters of a damped pair of oscillators.

We can see that the non-electrostatic effects have notable influence even on the ordinary absorption spectrum.

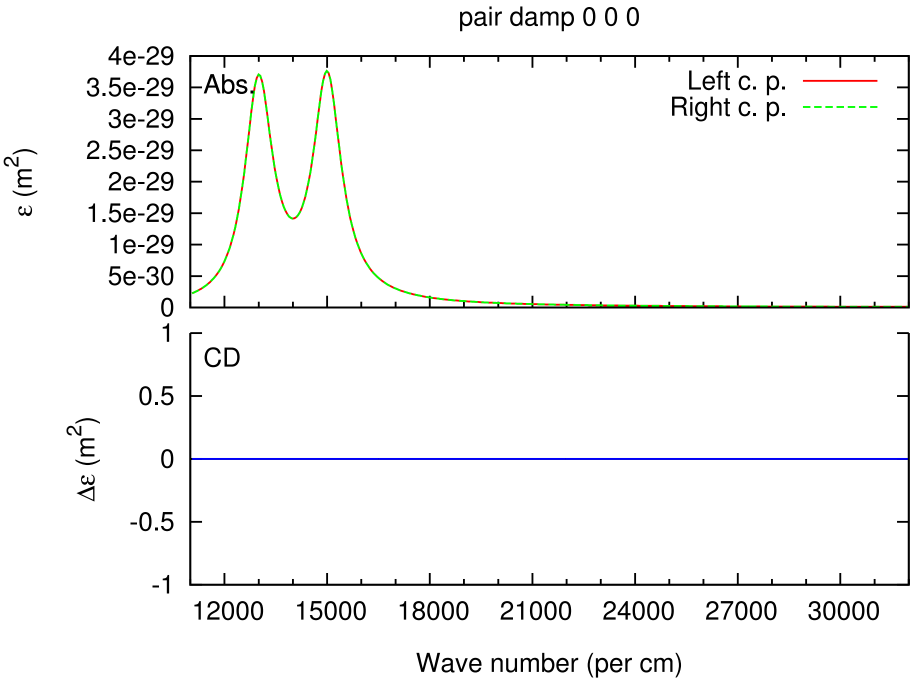

Figure 7.7: Absorption spectra of pair of oscillators.

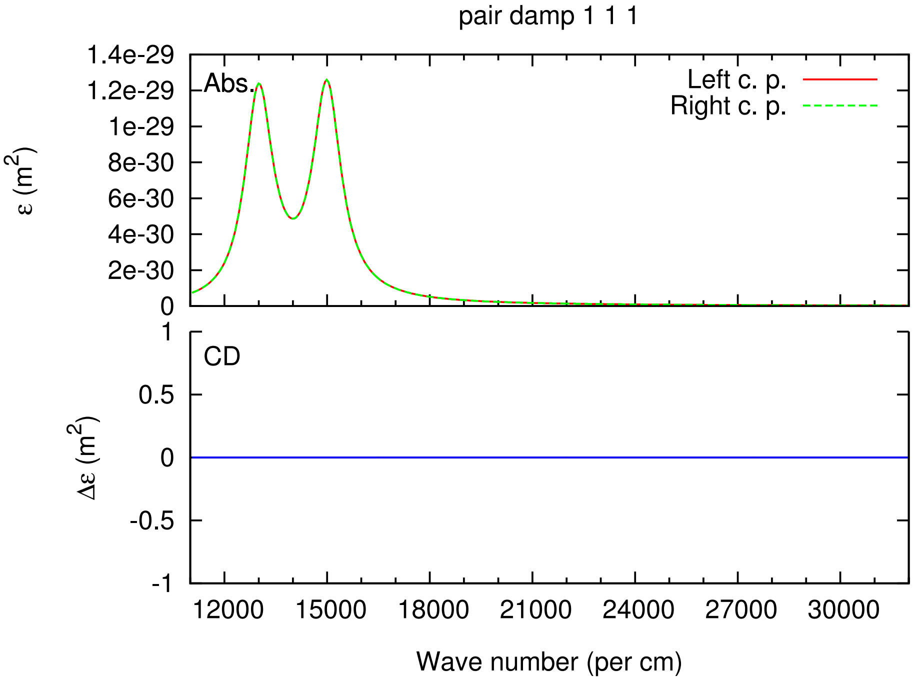

Figure 7.8: Absorption spectra of pair of oscillators.

7.3 Tetrahedron system

The simplest system that can exhibit non-zero circular dichroism consists of 4 distinct atoms, since simpler systems are not chiral in three-dimensional space. We use 4 distinct oscillators placed at vertices of a regular tetrahedron, with non-zero damping constants. The oscillators have mutual distance 2 Å .

Key	Name	x	y	z	ν_0	γ	q	m
OSC	A	1.732	0	0	13000	1000	-0.00000025	9.1E-31
OSC	B	0	1	0	15000	1000	-0.00000025	9.1E-31
OSC	C	0.577	0	1.633	17000	1000	-0.00000025	9.1E-31
OSC	D	0	-1	0	19000	1000	-0.00000025	9.1E-31

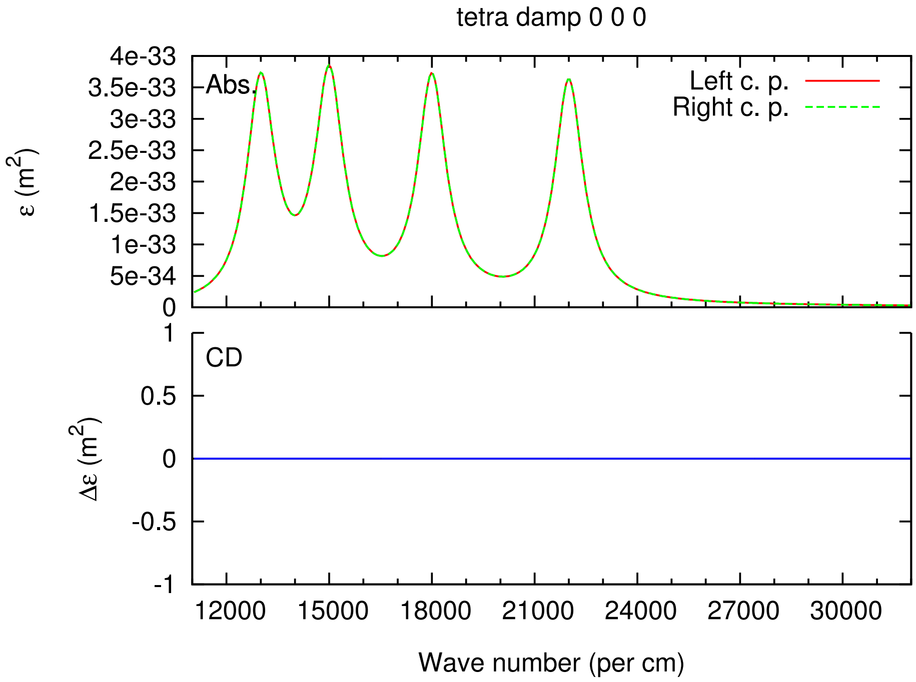

Figure 7.9: Absorption spectra of a chiral tetrahedron.

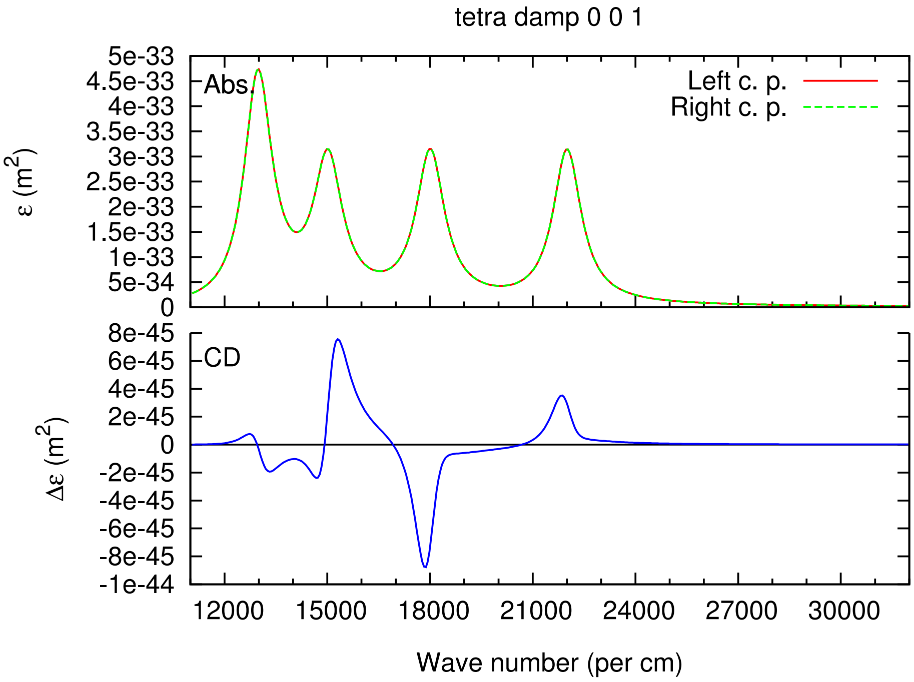

Figure 7.10: Absorption spectra of a chiral tetrahedron.

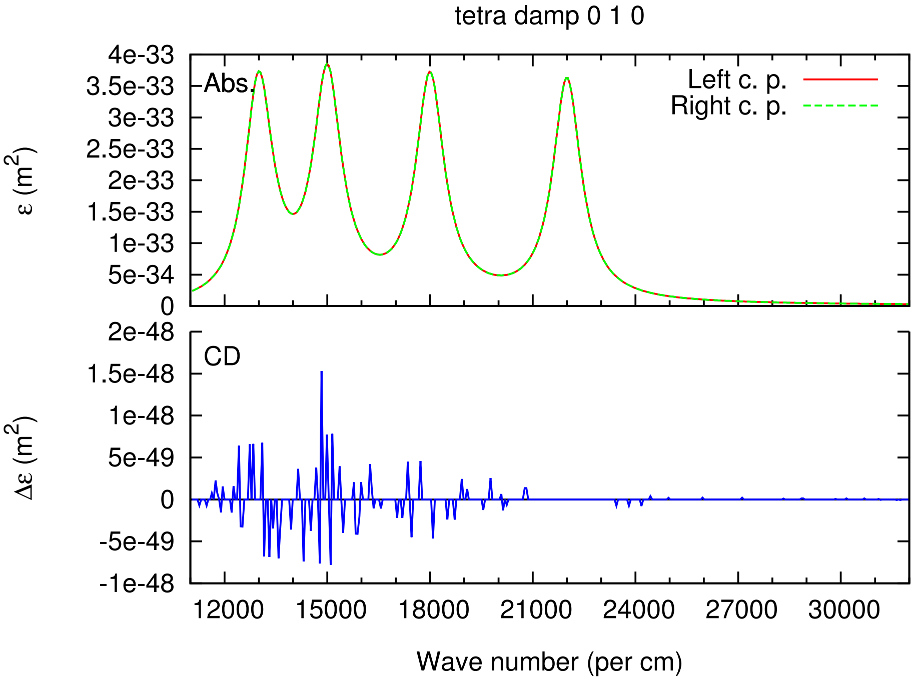

Figure 7.11: Absorption spectra of a chiral tetrahedron.

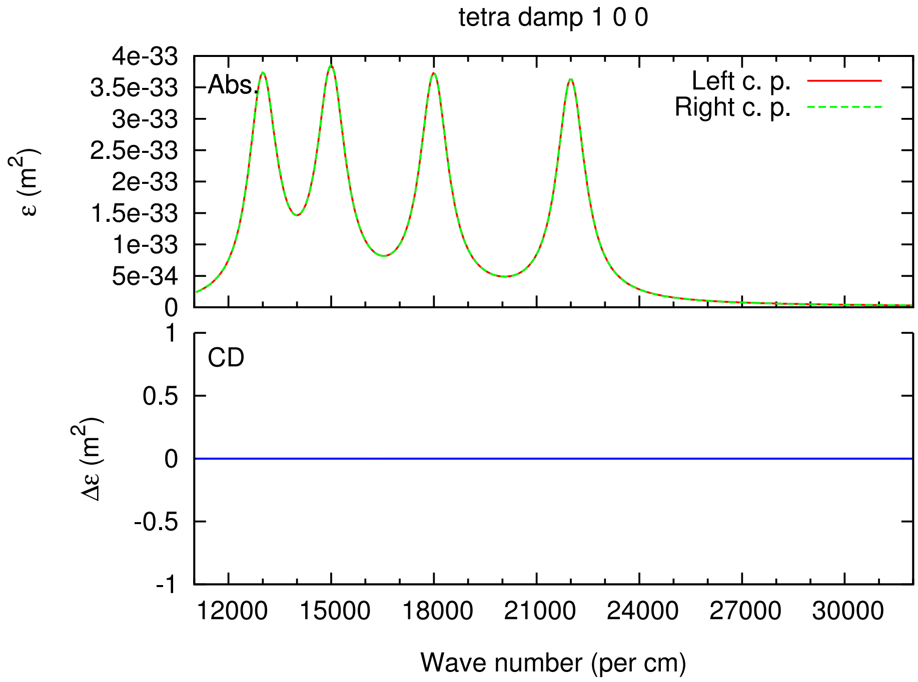

Figure 7.12: Absorption spectra of a chiral tetrahedron.

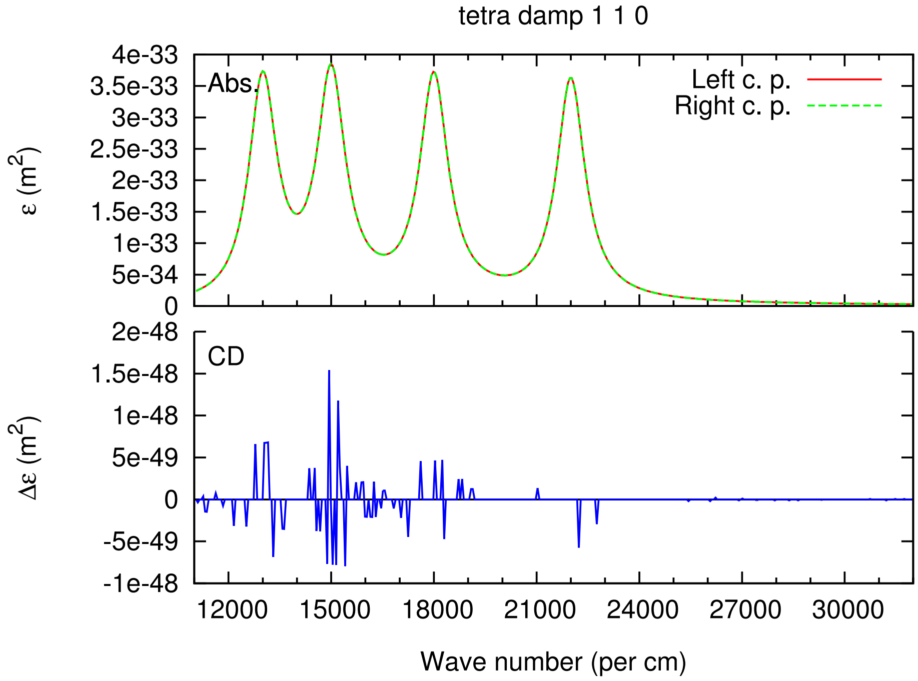

Figure 7.13: Absorption spectra of a chiral tetrahedron.simple chiral system.

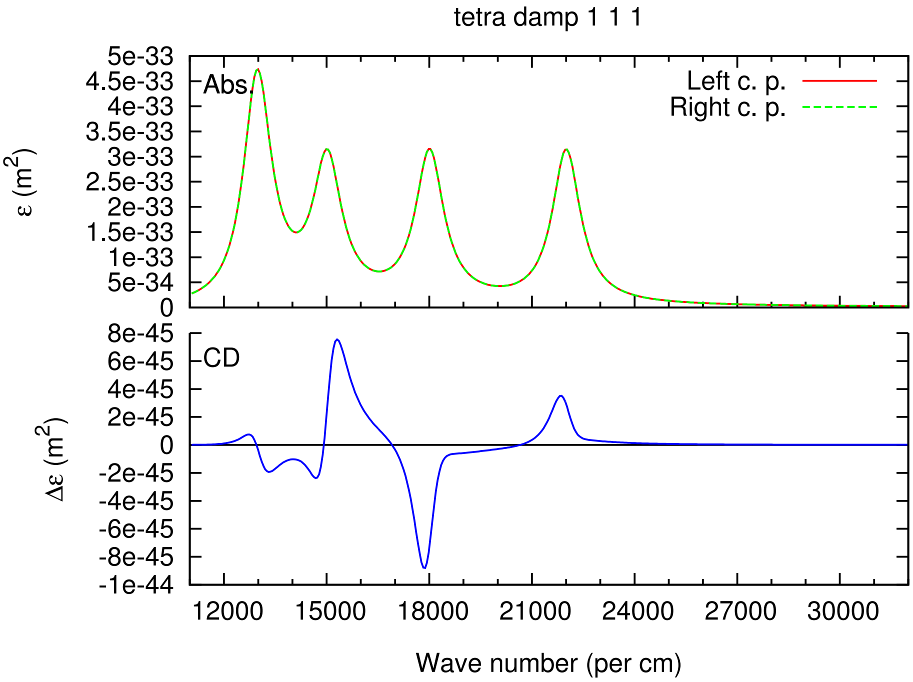

Figure 7.14: Absorption spectra of simple chiral system.

The calculation has shown very surprising result: the acceleration fields are necessary to obtain non-zero circular dichroism. The noisy CD curves on the plots without acceleration fields are numerical artifacts of finite precision arithmetics, since the maximum value of CD they give is 15 orders smaller than the extinction coefficient.

The necessity of the acceleration term in the interaction is very surprising and unexpected, since many calculations exist which apparently do not use such relativistic description yet still give non-zero circular dichroism for simple systems, and also since the acceleration terms are the smallest. Whether the acceleration fields really play such a great role in the spectra of interesting molecules requires another careful study.

7.4 Tetrahedron of same atoms

If the oscillators are taken all the same, the tetrahedron loses chiral asymmetry and the circular dichroism should vanish. We take two systems according to the following tables; the first is loosely a regular tetrahedron, while the second is much closer to regularity (it is impossible to prescribe exact coordinates of a regular tetrahedron due to finite precision arithmetics.) Otherwise the systems are same.

Key	Name	x	y	z	ν_0	γ	q	m
OSC	A	1.732	0	0	15000	1000	-0.00000025	9.1E-31
OSC	B	0	1	0	15000	1000	-0.00000025	9.1E-31
OSC	C	0.577	0	1.633	15000	1000	-0.00000025	9.1E-31
OSC	D	0	-1	0	15000	1000	-0.00000025	9.1E-31

Table 7.3: Parameters of tetrahedron system with same oscillators.

Key	Name	x	y	z	ν_0	...
OSC	A	1.73205080756887730	0	0	15000	...
OSC	B	0	1	0	15000	...
OSC	C	0.57735026918962576	0	1.63299316185545210	15000	...
OSC	D	0	-1	0	15000	...

Table 7.4: Parameters of precise tetrahedron system with same oscillators.

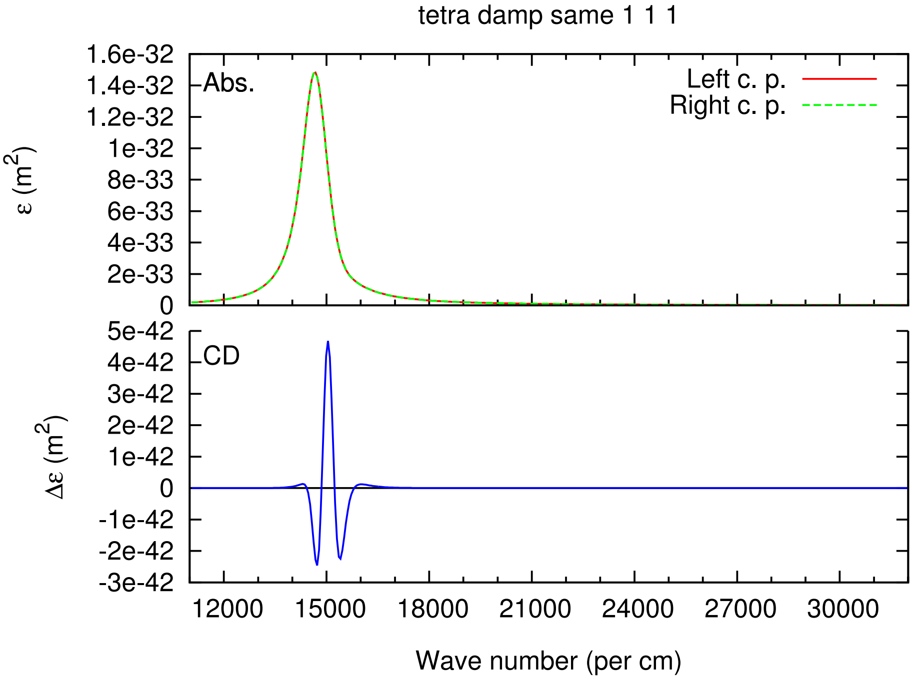

Figure 7.15: Absorption spectra of tetrahedron made of 4 same atoms.

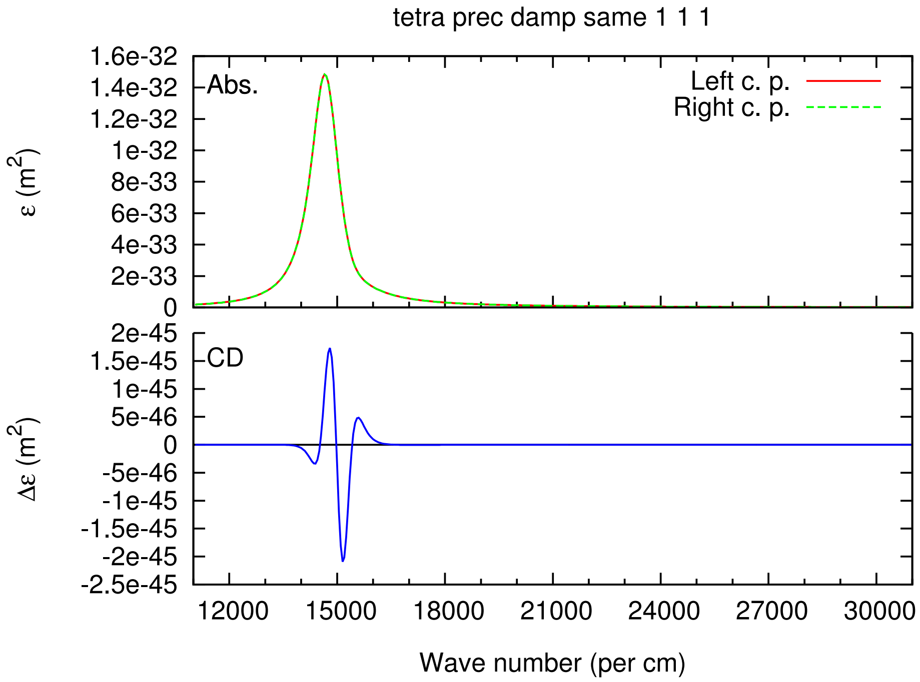

Figure 7.16: Absorption spectra of precise tetrahedron made of 4 same atoms.

These two cases have the same absorption spectra, as could be expected. The CD spectra do not vanish, which may seem strange at first, since the system is supposed to be achiral. However, the prescribed coordinates are not exactly those of a regular tetrahedron, but of a configuration very close to it, which is most probably chiral. As the shape of the quadruple comes closer to perfect tetrahedron, the intensity of the CD spectrum decreases. From this we see that the shape of the CD spectrum is a very sensitive quantity which can be affected by the slightest changes in the arrangement of the atoms.

The reader has indubitably noticed that the effective charge of oscillators is unusually small considering that one electron has charge 1. Such small charges were chosen to prevent the interaction terms from "taking over", which exhibits itself as complete extension of the absorption over all wave numbers. We are not sure why this occurs or what it means, but partial reason may be that our description of the bonding of electrons to nuclei is rather too approximate and in many ways flawed; it may allow the interaction effects to grow unrealistically strong. Further analysis of this behaviour is needed, but clearly something has to be done to make the description of bonding and electronic motion more realistic.

Chapter 8

Calculations for BChl

In order to calculate the spectra of BChl molecule and its dimers, we need the coordinates of their atoms. The data on bacteriochlorophyll *c* molecule seem to be hard to find, but the coordinates of atoms in bacteriochlorophyll *a* are easily found in many PDB files available on the Protein Data Bank site http://www.pdb.org. We extracted a smaller PDB file with skeletal atoms of such BChl *a* molecule and edited it into the skelet of BChl *c* molecule. The hydrogen atoms were added by means of the service *MolProbity* accessible on http://molprobity.biochem.duke.edu/index.php,[31] and in case of the methyl group attached to carbon C-20, the hydrogens were added manually.

The resulting structure consists of 135 atoms. Each atom has its own name in the PDB file. The pictures of the molecule with atoms and their names follow.[32].

Description of the meaning of the various entries in the PDB file can be found on http://deposit.rcsb.org/adit/docs/pdb_atom_format.html and also at "Protein Data Bank Contents Guide: Atomic Coordinate Entry Format Description" on

http://www.wwpdb.org/documentation/format33/v3.3.html

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[31] V. B. Chen et al., *MolProbity: all-atom structure validation for macromolecular crystallography*, Acta Crystallographica D66:12-21 (2010).

[32] The pictures were created by the program VMD, available on https://www-s.ks.uiuc.edu/Research/vmd/

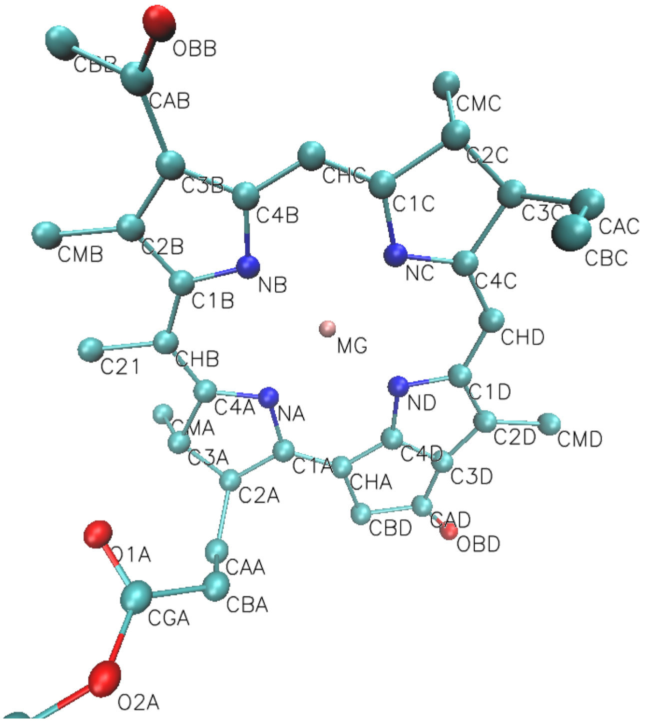

Figure 8.1: Names of atoms in the head part of the BChl *c* molecule.

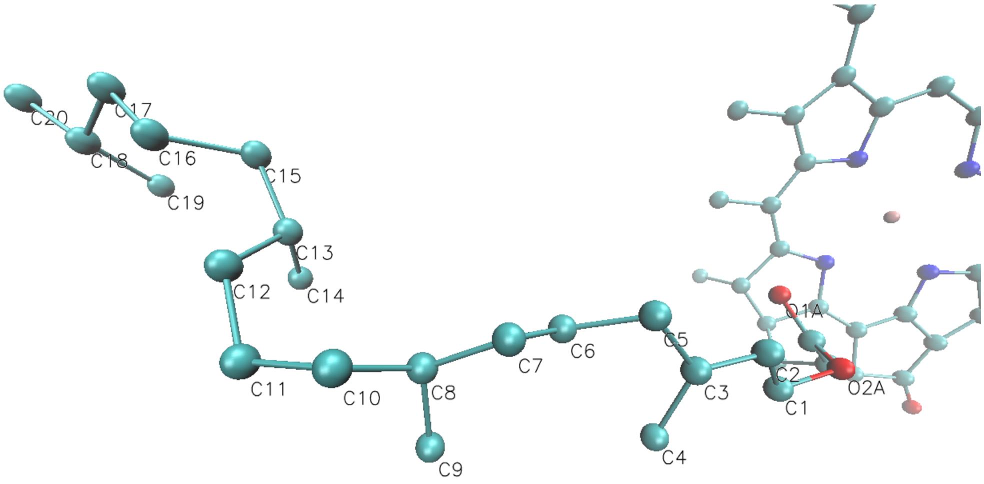

Figure 8.2: Names of the atoms in the tail part of the BChl *c* molecule.

8.1 Definition of the molecular axes of BChl c

We define the orientation of the molecular cartesian axes according to Blankenship (2002).[33] The orientation is shown on the following figures. For the purposes of calculations, we need to define the exact position of the axes with respect to the equilibrium positions of the atoms given in the PDB file. The nitrogen atoms do not need to lie exactly on the vertices of a rhombus, so it may not be possible to put the perpendicular axes through them.

We define the X axis of the molecule as the oriented line passing from the atom NA to the atom NC. The center of the molecule is defined as the point half-way from the nitrogen NA to the nitrogen NC.

Next, the Y axis is defined as the oriented line obtained by orthonormalization of the vector NB$-$ND with respect to the axis X. The axis Z is chosen perpendicular to the axes X, Y so that the resulting system is right-handed.

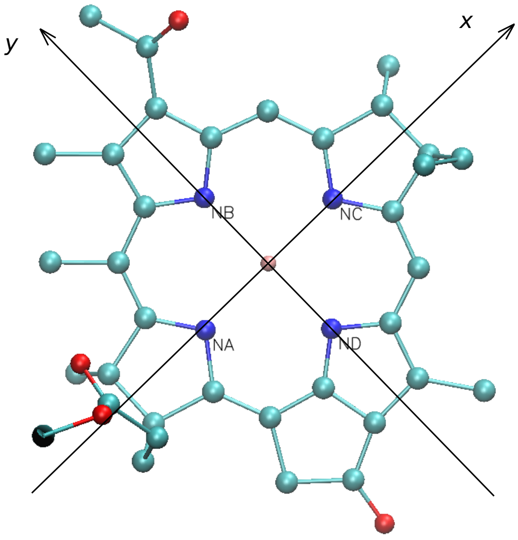

Figure 8.3: Coordinate system of the BChl c molecule; plane of the ring.

The calculation of absorption spectra require the coordinates of the atoms and also certain parameters describing the electronic properties of the molecule. Our model uses three such free parameters: resonance fre-

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[33] R. E. Blankenship, *Molecular Mechanisms of Photosynthesis*, Blackwell Science 2002, Fig. 4.9.

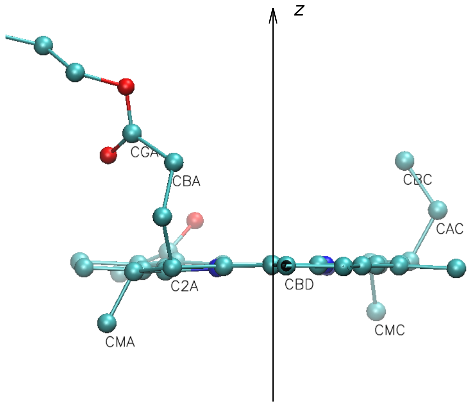

Figure 8.4: Coordinate system of the BChl *c* molecule; plane perpendicular to the ring.

quency, damping constant and effective charge for each oscillator (atom), so there is potentially as much as 3 × 135 = 405 parameters. Of course, such number of parameters allows one to produce almost any spectrum one wants with suitable choice of the parameter values. It makes no sense to attempt to fit all these parameters as independent, since the spectrum shows only few distinct bands. The number of distinct elements is much smaller: there is carbon, nitrogen, oxygen, hydrogen, magnesium; overall 5 different elements. For the sake of simplicity and also due to time constraints, we tried to introduce system of parameters describing these elements; each atom is ascribed properties based on which element is it; in other words, the oscillators assigned to carbon atoms have the same resonance wave number, damping constant, effective charge and mass.

Such procedure seems rather ad hoc and without physical justification. Our main motivation behind this procedure is that it provides a simple way to parametrize a system with many degrees of freedom. Other ways are possible, for example, we could attempt to introduce parameters for distinct kinds of chemical bonds occurring between the atoms. Admittedly, the parametrization model is rather simplistic and unrealistic, but nevertheless it is interesting to see what kind of spectrum it can lead to.

We attempted to assign elements resonance wave numbers based on the positions of the peaks in the experimental spectra, damping constants based on their broadening and effective charges based on the total area below the peak. We did not spend much time doing this, as the parametrization model is of very limited interest. We show the resulting spectrum mainly as the demonstration of the capabilities of the model and of the developed program.

Key	Element	ν_0	γ	f
ELEMENT	O	15000	1000	12E-8
ELEMENT	C	16000	1000	3E-8
ELEMENT	N	23000	5000	18E-8
ELEMENT	MG	17000	1000	3E-8
ELEMENT	H	29000	2000	3E-8

Table 8.1: Parameters of elements chosen for the calculations.

The parameter f is a factor which multiplies the actual negative charge of the atom corresponding to its atomic number. The mass of the oscillator is assigned as the total mass of all the electrons of the element.

8.2 Spectra of the BChl molecule

The actual molecule of Bacteriochlorophyll *c* contains large number of atoms (cca 130) which may make the calculations of spectra time-demanding. One is therefore lead to think about which atoms are the most important for the calculation of the spectrum, and which can perhaps be neglected.

Since the circular dichroism is thought to be a result of mirror asymmetry of the nuclear skelet of the molecule, an since the most pronounced asymmetry arises on atoms with chiral arrangement of substituents, it seems that we can neglect many atoms that are not a part of such locally chiral structure.[34]

In particular, we will neglect the unsaturated hydrocarbon chain and also the hydrogens that are not substituents of any chiral center. We are left with the C, N, O atoms forming the BChl head, the magnesium atom and the hydrogens H3C, H2C, H3A, H2A. That is 48 atoms for monomer.

Key	Element	x	y	z	nu_0	gamma	q	m
OSC	MG	0.007	0.030	-0.027	17000	1000	-3.60E-007	1.09E-029
OSC	CHA	-2.433	-2.399	0.050	16000	1000	-1.80E-007	5.47E-030
OSC	CHB	-2.320	2.450	0.004	16000	1000	-1.80E-007	5.47E-030
OSC	CHC	2.443	2.420	0.108	16000	1000	-1.80E-007	5.47E-030
OSC	CHD	2.283	-2.449	0.019	16000	1000	-1.80E-007	5.47E-030
OSC	NA	-2.045	0.000	0.000	23000	5000	-1.26E-006	6.38E-030
OSC	C1A	-2.906	-1.087	0.043	16000	1000	-1.80E-007	5.47E-030
OSC	C2A	-4.350	-0.627	0.037	16000	1000	-1.80E-007	5.47E-030
OSC	C3A	-4.263	0.864	-0.049	16000	1000	-1.80E-007	5.47E-030
OSC	C4A	-2.792	1.153	-0.037	16000	1000	-1.80E-007	5.47E-030
OSC	CMA	-4.786	1.375	-1.379	16000	1000	-1.80E-007	5.47E-030
OSC	CAA	-5.082	-1.025	1.357	16000	1000	-1.80E-007	5.47E-030
OSC	CBA	-4.450	-0.861	2.769	16000	1000	-1.80E-007	5.47E-030
OSC	CGA	-4.658	0.444	3.551	16000	1000	-1.80E-007	5.47E-030
OSC	O1A	-4.458	1.525	2.997	15000	1000	-9.60E-007	7.29E-030
OSC	O2A	-4.893	0.402	4.768	15000	1000	-9.60E-007	7.29E-030
OSC	NB	0.059	2.084	0.037	23000	5000	-1.26E-006	6.38E-030
OSC	C1B	-1.017	2.903	0.054	16000	1000	-1.80E-007	5.47E-030
OSC	C2B	-0.665	4.228	0.169	16000	1000	-1.80E-007	5.47E-030
OSC	C3B	0.749	4.256	0.219	16000	1000	-1.80E-007	5.47E-030
OSC	C4B	1.138	2.915	0.120	16000	1000	-1.80E-007	5.47E-030
OSC	CMB	-1.721	5.331	0.261	16000	1000	-1.80E-007	5.47E-030
OSC	CAB	1.601	5.363	0.495	16000	1000	-1.80E-007	5.47E-030
OSC	OBB	2.533	5.280	1.295	15000	1000	-9.60E-007	7.29E-030
OSC	CBB	1.195	6.743	-0.025	16000	1000	-1.80E-007	5.47E-030
OSC	NC	2.045	0.000	0.000	23000	5000	-1.26E-006	6.38E-030
OSC	C1C	2.869	1.097	0.045	16000	1000	-1.80E-007	5.47E-030
OSC	C2C	4.321	0.667	0.103	16000	1000	-1.80E-007	5.47E-030
OSC	C3C	4.257	-0.848	0.116	16000	1000	-1.80E-007	5.47E-030
OSC	C4C	2.786	-1.156	0.029	16000	1000	-1.80E-007	5.47E-030
OSC	CMC	5.015	1.163	-1.167	16000	1000	-1.80E-007	5.47E-030
OSC	CAC	4.750	-1.422	1.428	16000	1000	-1.80E-007	5.47E-030

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[34] Of course, this is only an approximation based on the idea that the interactions between closest neighbours are the most important, while those over larger distances can be neglected. Whether this is valid or not does not seem to easily answered in general, but we will assume it is, since we want to simplify the system to lower number of subsystems.

OSC	CBC	4.094	-0.895	2.728	16000	1000	-1.80E-007	5.47E-030
OSC	ND	-0.054	-2.000	0.037	23000	5000	-1.26E-006	6.38E-030
OSC	C1D	0.963	-2.859	0.012	16000	1000	-1.80E-007	5.47E-030
OSC	C2D	0.496	-4.158	-0.029	16000	1000	-1.80E-007	5.47E-030
OSC	C3D	-0.885	-4.162	-0.016	16000	1000	-1.80E-007	5.47E-030
OSC	C4D	-1.125	-2.795	0.027	16000	1000	-1.80E-007	5.47E-030
OSC	CMD	1.338	-5.421	-0.133	16000	1000	-1.80E-007	5.47E-030
OSC	CAD	-2.134	-4.708	-0.035	16000	1000	-1.80E-007	5.47E-030
OSC	OBD	-2.355	-5.895	-0.178	15000	1000	-9.60E-007	7.29E-030
OSC	CBD	-3.211	-3.680	0.015	16000	1000	-1.80E-007	5.47E-030
OSC	C21	-3.376	3.554	0.096	16000	1000	-1.80E-007	5.47E-030
OSC	C1	-6.138	1.023	5.163	16000	1000	-1.80E-007	5.47E-030
OSC	H3C	4.800	-1.219	-0.597	29000	2000	-3.00E-008	9.11E-031
OSC	H3A	-4.774	1.276	0.665	29000	2000	-3.00E-008	9.11E-031
OSC	H2C	4.806	1.015	0.868	29000	2000	-3.00E-008	9.11E-031
OSC	H2A	-4.847	-1.031	-0.690	29000	2000	-3.00E-008	9.11E-031

Table 8.2: Data for the essential part of the BChl molecule used to calculate the absorption spectra.

8.3 Monomer of BChl c

The following figures give spectra of simplified monomer molecules (ess as from "essential") calculated with electrostatic dipole forces only (000) and with all contributions discussed above (111), compared to suitably normalized experimental spectra.

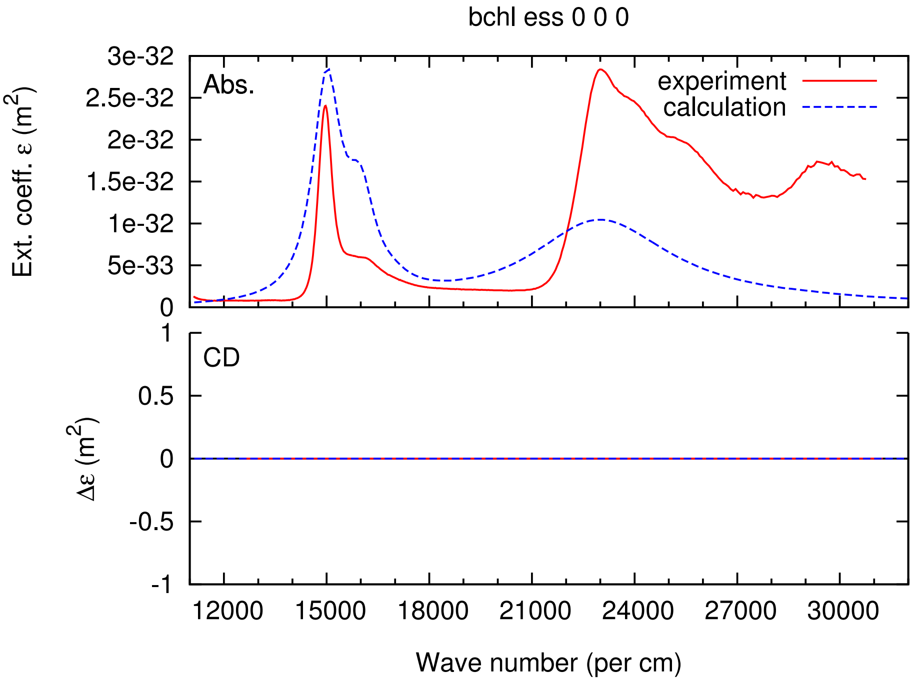

Figure 8.5: Absorption spectra of a simplified Bchl *c* molecule.

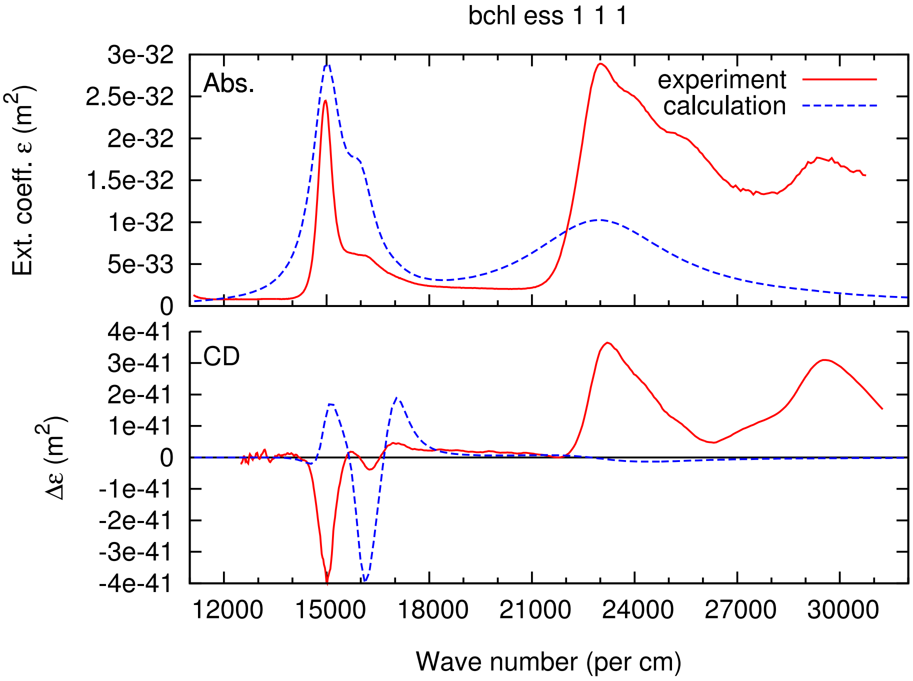

Figure 8.6: Absorption spectra of a simplified Bchl *c* molecule.

We can see once again that in order to obtain non-zero circular dichroism, description in terms of electrostatic dipole forces is not sufficient. The calculated spectra only remotely resemble the measured ones, as we chose the parameters only by an estimate and did not perform any systematic fitting.

8.4 Parallel dimer of BChl c

In the parallel dimer, the second molecule is put below the first and translated by a vector from the projection of the atom OBB on the XY plane to projection of the atom MG on the XY plane, so that the atom OBB of the 2nd molecule ends up below the MG atom of the first molecule. The distance of the rings is assumed to be the average distance 3.8 Å.

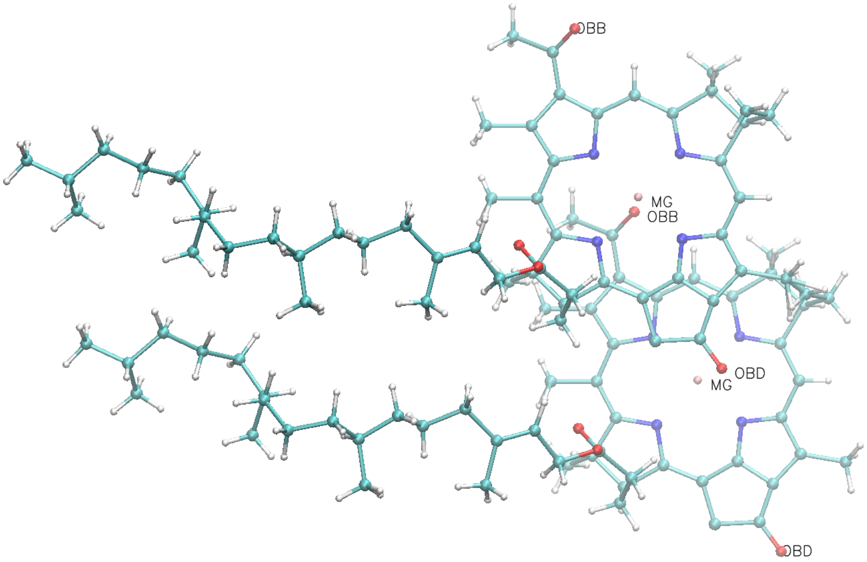

Figure 8.7: Parallel dimer of the BChl c molecules.

8.5 Anti-parallel dimer of BChl c

In the anti-parallel dimer, the second molecule is put below the first, rotated in the plane of the ring around the MG atom by 180° and translated by a vector from the projection of the atom MG on the plane XY to projection of the OBB atom on the plane XY (both atoms belonging to the first molecule), so that the MG atom of the 2nd molecule ends up below the

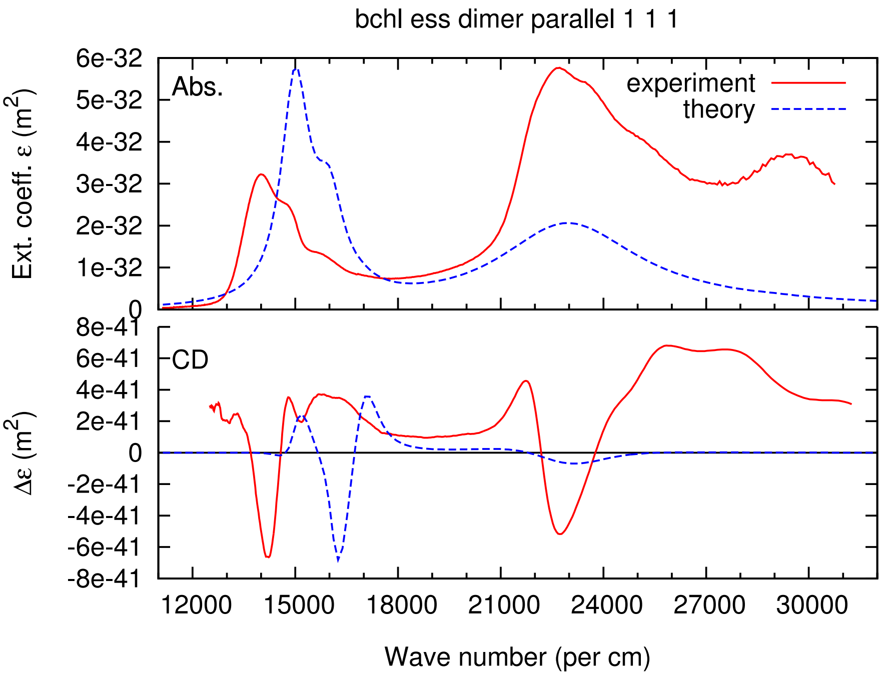

Figure 8.8: Absorption spectra of the parallel dimer of simplified Bchl *c* molecules.

OBB atom of the 1st molecule and the OBB atom of the second molecule ends up under the MG atom of the 1st molecule. The distance of the rings is assumed to be the average distance 3.8 Å .

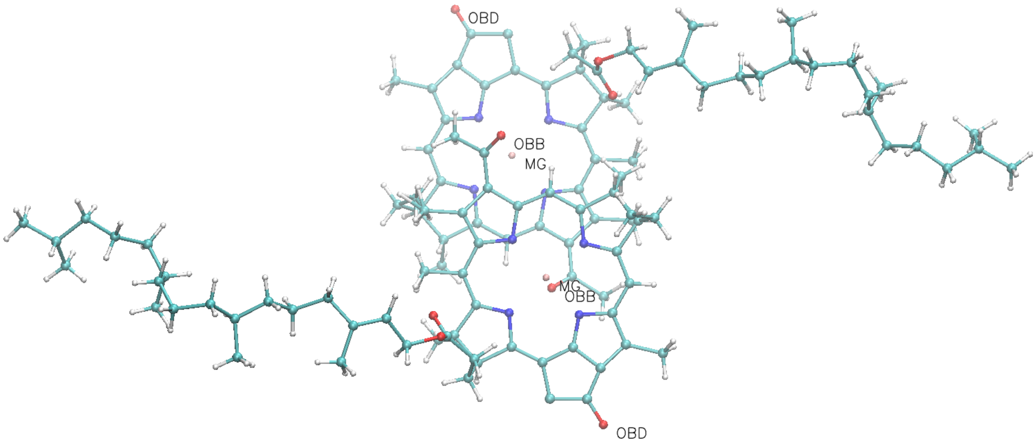

Figure 8.9: Anti-parallel dimer of the BChl *c* molecules.

Finally we give a plot comparing the spectra of parallel and anti-parallel dimers.

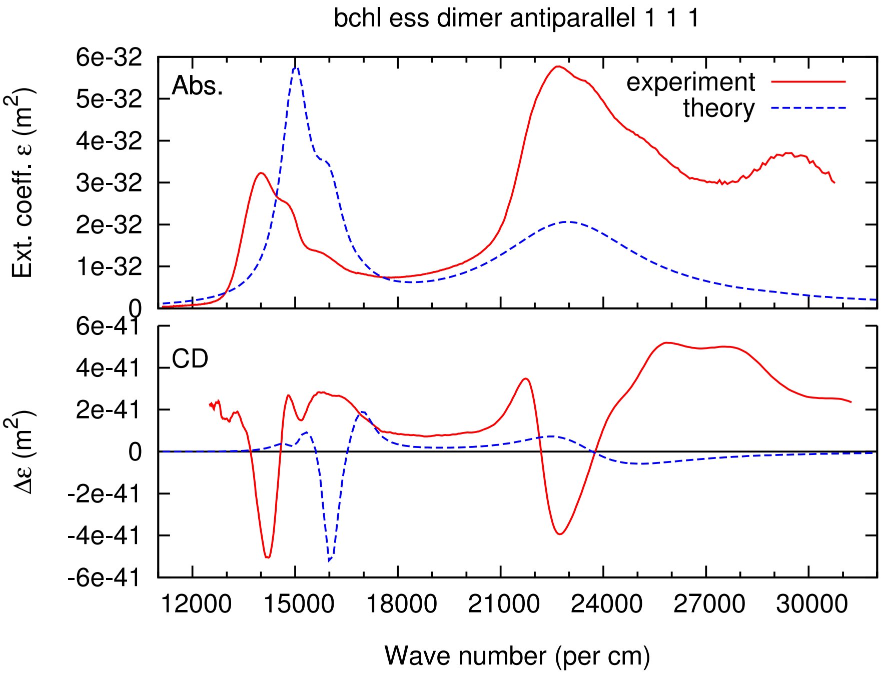

Figure 8.10: Absorption spectra of the anti-parallel dimer of simplified Bchl *c* molecules.

We can see that the aggregation into dimer increases the intensity of absorption by a factor of 2. Oddly enough, the circular dichroism which we would expect to change with aggregation a lot does not do so.

We can see that the spectra of parallel and anti-parallel dimers differ much less in calculation than in the measurements. The reason behind this is most probably too weak interaction between the molecules due to their low charges. Adjusting their values we could most probably make the changes more pronounced, but we will not attempt this here.

From the above plots we can derive these conclusions: that the model of circular dichroism responds to changes in the structure of the aggregate and that the non-electrostatic forces seem to be important for circular dichroism. Due to the preliminary character of the description of bonding of electrons and the simplistic way the model is parametrized, systematic fitting of the model to the experimental spectra does not seem very useful at this point. The obvious question is, how to develop and parameterize the model in a more compelling way? One possible way we see is to de-

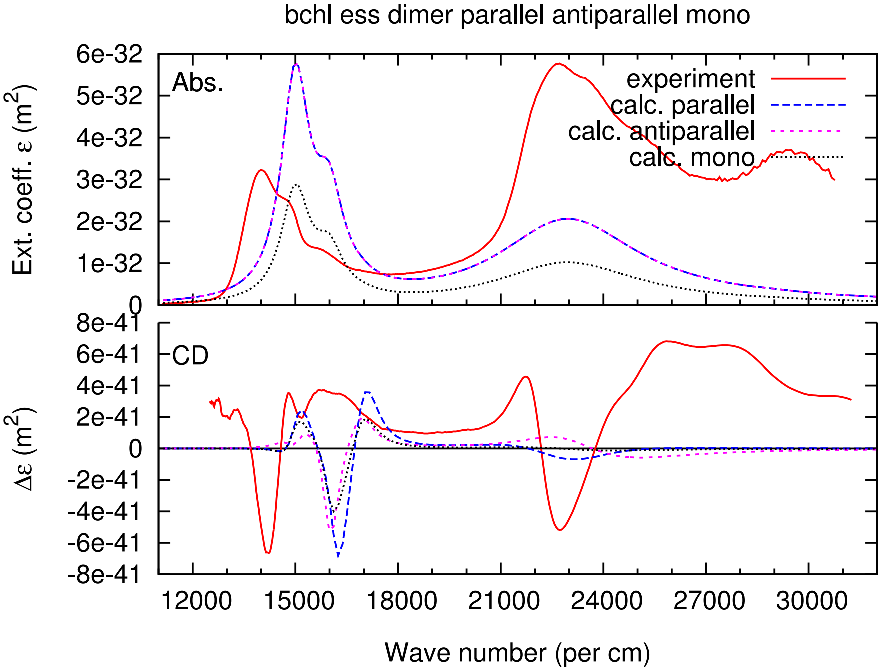

Figure 8.11: Absorption spectra of parallel and anti-parallel dimer and monomer of the simplified Bchl *c* molecules.

fine electronic oscillators for various kinds of chemical bonds (for example, for each pair of atoms one different oscillator) instead of nuclei and thus make some connection to the models based on the Schrödinger equation that have electrons moving more freely in between the nuclei. The most realistic approach compatible with relativistic interactions seems to be the calculation of the stochastic motion of the electrons around the nuclei in a way similar to that used by Cole and Zou in 2005 for the hydrogen atom, but such calculations are computationally very demanding and for large molecules such as bacteriochlorophyll are at present out of our reach.

Chapter 9

Conclusion

At the time of assignment, this work had two main goals.

The first one was to develop a theory of absorption that would enable us to predict absorption spectra and circular dichroism spectra for given geometries of atoms in a molecule and aggregate and for given spectral properties of one molecule. In particular, it was our intention to arrive at a model which would be able to account for the optical activity due to chirality of the molecule itself and also due to chirality introduced by the aggregation of the molecules.

The second goal was to apply such model to bacteriochlorophyll molecules and attempt to infer which one of the proposed models of aggregates lead to predicted spectra that are most similar to those experimentally measured.

The model we developed uses for the description of interactions within the aggregate relativistic expression for electric field that contains contributions due to non-zero velocity and acceleration of the charged particles and due to finite speed of propagation of EM signals. These effects are negligible for the calculations of ordinary absorption spectrum, but they seem to be important for satisfactory calculation of CD spectrum for theoretical reasons. The few calculations we performed seem to suggest that the acceleration fields play much greater role in circular dichroism than one would expect from their magnitude.

We applied our model to simple geometries of interacting oscillators and verified its physical behaviour. However, modelling of complicated BChl molecules stumbled on the imperfections of the model, the main of which is too simplistic description of the bonding of the electrons and the lack of compelling parametrization procedure for the electronic properties of the model. As a result, we cannot provide any insight on which model of the proposed models of bacteriochlorophyll dimer corresponds best to the measured absorption spectra of aggregated bacteriochlorophyll molecules. Perhaps some other work will try to develop the theory of circular dichroism further and accomplish this goal. May this work provide a good starting point and inspiration for similar endeavours.

Chapter 10

Appendix

Here we give remarks that did not fit well in the main text.

10.1 Point-like electron

In our work we assumed that the electron is a point-like particle, i.e. a particle with negligible or zero spatial extension. Unfortunately, some scientists seriously doubt that the electron can be regarded as point-like particle, so it seems good here to discuss this question. We do not know of any compelling argument falsifying the applicability of point-like model of the electron. Perhaps one of the most pronounced arguments goes as follows: *the ψ function describing the electron in hydrogen atom has substantial spatial extension of orders of Ångströms and (almost) never localizes at one point of space. Ergo the electron is not a point and has no definite spatial extension.*

This kind of argument seems to be based on the idea that the ψ function is the electron, or that the description of its state in terms of the ψ function requires us to reject description by means of a time-dependent radius vector. Let us look how the ψ function is used in the theory of atoms and molecules to see whether this idea is reasonable.

Let us consider a system of N particles. We can describe it with help of the Schrödinger equation for *one* ψ. This object ψ is by definition complex-valued, and is a function of spatial coordinates of all N particles and time, similarly to the Hamilton principal function $S(q_1, q_2, ..., t)$. For example, the function describing the pair of electrons in the helium atom may be written as

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t), \tag{10.1}$$

where $\mathbf{r}_1, \mathbf{r}_2$ are 3+3 real Cartesian coordinates. But coordinates of what? One triple of coordinates refers to a point. Since we have as many triples of coordinates as there are particles, it is clear that the configuration space on which the ψ function is defined refers to possible mutual configuration of N particles and Cartesian system of coordinates in physical space.

According to the Born interpretation, the meaning of the ψ function is that it gives probability that the system of particles is in certain configuration. More accurately,

$$\Delta P = \int_I |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 \, d^3\mathbf{r}_1 d^3\mathbf{r}_2 \tag{10.2}$$

is the probability that at time t, the system of the particles has the configuration belonging to the subset I of the configuration space. We see that the function ψ describes *probabilistically the whole system* of N electrons, not one electron.

Mathematically, the extension of support of ψ is as little evidence for extended nature of the electron as the extension of probability distribution function $\rho(\mathbf{r})$ in 3D space is evidence for the extended nature of the Brownian particle.

If the particle had some extension, it would be composed of parts, and these parts would require introduction of new coordinates (as in atom: it is composed of parts and hence its ψ function contains their coordinates). The appropriate ψ function would then be a function of these internal coordinates as well. We do not know whether the electron has such parts. Scattering experiments attempting to probe such internal parameters of the electron did not reveal any evidence of them; according to quantum field theory, recent experiments pose limit on the effective radius of the electron $R < 10^{-18}$ m.[35,36] For the purposes of chemical physics where typical scale of interest is 10^{-10} m and larger, the point-like model of electron seems quite adequate.

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[35] H. Dehmelt, *A Single Atomic Particle Forever Floating at Rest in Free Space: New Value for Electron Radius*, Physica Scripta, Vol. T22, 102-110, 1988.

[36] G. Gabrielse, D. Hanneke, T. Kinoshita, M. Nio, and B. Odom, *New Determination of the Fine Structure Constant from the Electron g Value and QED*, Phys. Rev. Lett. 97, 030802 (2006)

10.2 On the electric polarization P and magnetization M

In the quasi-stationary theory of dielectric materials, it is common to use the electric polarization **P**

The quantity **P** here is an average electric moment of neutral molecules per unit volume.

The macroscopic current density in dielectric is often written as

$$\mathbf{j} = \partial_t \mathbf{P}. \tag{10.3}$$

For most common dielectric materials this is a good approximation.[37]

Similarly, in quasi-stationary theory of magnetic materials, it is customary to use the magnetization **M** and express the macroscopic current density as

$$\mathbf{j} = \nabla \times \mathbf{M}. \tag{10.4}$$

The quantity **M** is an average magnetic moment of neutral molecules per unit volume. Such description does not allow current divergent current density, but for common insulating magnetic materials this is again quite well-working approximation.

The expression of the electric current via densities of electric and magnetic moment is a rather practical procedure of limited validity: detailed microscopic derivations show that the current density contains also contributions that are not expressible as functions of **P** and **M**. Some of these contributions may be expressed as functions of the electric quadrupole moment density and other higher moments of microscopic charge and current density. The contribution due to electric quadrupole moment of the molecules and similar higher moments are often neglected on the grounds that they are small enough, but in the case of circular dichroism, we should not neglect them without careful evaluation of their effect.

In our approach, instead of introducing new moments of higher order, we use directly the current density **j** and its conjugate polarization potential **P** such that

$$\mathbf{j} = \partial_t \mathbf{P}. \tag{10.5}$$

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[37] **P** is defined via average electric moment, which is only an approximate description of state of large collection of charged particles.

This **P** is not polarization in the above sense, but simply an auxiliary quantity whose time derivative is current density **j**. Provided that the average value of **j** is zero (we do no expect static current in dielectric), description in terms of the quantity **P** should be sufficient. The advantage of this approach is that no higher moment densities are necessary.

10.3 System of units

In a memoir of larger extent, it seems helpful to explain the habits and views adopted by the author, especially if they might differ from those expectable from the general interested reader.

The main difference to adopted practice in theoretical spectroscopy is that we use slightly customized system of units. We use the MKS system of units due to its simplicity and also because it is familiar to all scientists across disciplines. The great advantages of this system are that the basic units - kilogram, meter, second - are close to length and mass of common bodies and to duration of daily events, and that all other units are defined in terms of these three basic units in the simplest possible way, so that various conversion factors known from the older systems are avoided.

We will work mainly in the framework of the electromagnetic theory and thus we will need to use also units for the basic electromagnetic quantities such as electric charge and electric strength.

In the SI system, the fourth quantity to be taken as basic was chosen to be electric current and its unit was chosen Ampère. This choice was most probably based on practical grounds - electric current is easily measured and maintained quantity. It also lead to an immensely large unit of electric charge called the Coulomb - it corresponds approximately to charge of $6.24 \cdot 10^{18}$ electrons. Unfortunately, as a result the Coulomb does not share the above advantage of the MKS units.

On the other hand, according to accepted ideas of electromagnetic theory, any accumulated electric charge and electric charge in molecules consists of a whole number of certain indivisible units, called particles. These particles have electric charge of small quantity called *elementary charge*. We will denote it by symbol e. The electron has a negative charge -1 e, and the proton has positive charge of $+1$ e. One elementary charge is equal to $e_{\mathrm{C}} = 1.6022 \cdot 10^{-19}$ Coulombs. In the part of theoretical physics where we are dealing closely with electrons and other charged particles of likely small charge, it is much more reasonable to express electric charges in multiples of this elementary charge. The basic system of units is then m, kg, s, e.

For example, the mutual electrostatic force on any one of two bodies with charges q_1, q_2 separated by distance r can be written, according to the Coulomb law, in this way:

$$F = \frac{K}{4\pi}\frac{q_1 q_2}{r^2},$$

where the force F is in newtons, distance r is in meters, charges q_1, q_2 in elementary charges and

$$K = \frac{e_{\mathrm{C}}^2}{\epsilon_0} \approx 2.900 \cdot 10^{-27}\ \mathrm{N} \cdot \mathrm{m}^2 \cdot \mathrm{e}^{-2}$$

is a convenient constant expressing the strength of electromagnetic interaction in our units.

The good thing about the SI system is that it put the cumbersome factor 4π away from the Maxwell equations to their solutions; we will retain this convention.

There is another difficulty with the use of SI system in theoretical physics, namely that the Maxwell equations in terms of ϵ_0, μ_0 are quite cumbersome for the purposes of microscopic theory; also in SI the quantities $\mathbf{E}, \mathbf{B}$ have different units which makes direct comparison of electric and magnetic forces cumbersome.

The old Gauss system seems much better in this respect; the electric and magnetic field have the same units and instead of cumbersome ϵ_0, μ_0, there is only one factor c and it appears where expected. However, the Gauss system contains the factor 4π in the Maxwell equations, which is again cumbersome.

Instead of using pure SI or Gauss convention, we think it best to use combined convention and write the general Maxwell equations for the macroscopic fields in the form

$$\nabla \cdot \mathbf{E} = K\rho, \tag{10.6}$$

$$\nabla \cdot \mathbf{B} = 0, \tag{10.7}$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}, \tag{10.8}$$

$$\nabla \times \mathbf{B} = \frac{K\mathbf{j}}{c} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}. \tag{10.9}$$

The factor c appears always where expected - next to the time coordinate or in a fraction giving the velocity v/c - and the factor K always appears as a factor multiplying the sources $\rho, \mathbf{j}$. The factor 4π does not appear in the Maxwell equations, but in denominators of their (retarded) solutions. The latter are less often manipulated. They are usually obtained through the Green function of the wave equation, which already quite naturally contains the factor $1/(4\pi)$.

The Newton-Lorentz equations of motion of a charged particle in an external field are written

$$\frac{d\mathbf{p}}{dt} = q\mathbf{E}_{ext} + q\frac{\mathbf{v}}{c} \times \mathbf{B}_{ext}. \tag{10.10}$$

Overall, this convention combines the advantages of the SI system and the Gauss system; the basic equations are written transparently without cumbersome factors of 4π and the electric and the magnetic field have the same units, which gives more clarity to their use and helps to compare the corresponding forces. Also for estimating the importance of various relativistic corrections, natural appearance of the ratios $\mathbf{v}/c$ in this convention is very helpful.

10.4 List of used symbols

Symbol	Quantity	Unit
q	electric charge	e
ρ	electric charge density	$\mathrm{e} \cdot \mathrm{m}^{-3}$
$\mathbf{j}$	electric current density	$\mathrm{e} \cdot \mathrm{m}^{-2} \cdot \mathrm{s}^{-1}$
$\mathbf{E}$	electric field	$\mathrm{N} \cdot \mathrm{e}^{-1}$
$\mathbf{B}$	magnetic field	$\mathrm{N} \cdot \mathrm{e}^{-1}$
φ	scalar potential	$\mathrm{J} \cdot \mathrm{e}^{-1}$
$\mathbf{A}$	vector potential	$\mathrm{J} \cdot \mathrm{e}^{-1}$
ω	proper angular frequency of an oscillator	s^{-1}
Ω	angular frequency of an external wave	s^{-1}
v_f	phase velocity of the macroscopic wave	$\mathrm{m} \cdot \mathrm{s}^{-1}$
i, j	index of a Cartesian component	
a, b, c	index of a particle	
k, l, m, n	index of an eigenfunction	
m_a	mass of the a-th particle	
q_a	electric charge of the a-th particle	e
$\mathbf{r}_a$	radius vector of the a-th electron	m
$\mathbf{v}_a$	velocity vector of a-th electron	$\mathrm{m} \cdot \mathrm{s}^{-1}$
γ_a	gamma factor $\gamma_a = \frac{1}{\sqrt{1-\frac{v_a^2}{c^2}}}$	
$\mathbf{R}_a$	radius vector of the a-th nucleus	m
ν	wave number - number of periods that fit into unit length	m^{-1}
$\rho_\mu, \mathbf{j}_\mu, ...$	microscopic charge and current density varying on the atomic scale	
$\delta(\mathbf{x} - \mathbf{r}_a)$	delta distribution localized at point $\mathbf{r}_a$ of 3D coordinate space	
$\mathbf{E}_a$	electric field of the a-th particle	
$\mathbf{E}_{-a}, \mathbf{F}_{-a}$	electric field, force acting on the a-th particle	
$\mathrm{Sp}\ \mathbf{M}$	trace of the matrix $\mathbf{M}$	

Table 10.1: Used symbols, their meaning and units.

Chapter 11

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