UNIVERSITY OF TROMSØ UIT

FACULTY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF CHEMISTRY

Theoretical studies of natural and electromagnetically induced birefringences

Dmitry Shcherbin

A dissertation for the degree of
Philosophiae Doctor

May 2011

Contents

1 Preface **2**

2 Light in medium **3**
2.1 The Maxwell equations . . . 3
2.2 Observable quantities of a light beam: the Stokes parameters . . . 6
2.3 Polarization of light: ellipsoidal description . . . 7
2.4 Polarization of light via the Stokes parameters . . . 9
2.5 Cases of polarization . . . 10

3 Propagation of light in the medium: forward scattering theory **12**
3.1 A molecule in the external field . . . 12
3.2 A case study: microscopic and macroscopic polarizations in two electric fields . . . 13
3.3 Forward scattering and the Kerr effect . . . 15
3.4 Linear birefringence . . . 17

4 Response theory **18**
4.1 Response theory, propagator approach . . . 18
4.2 Important features of a propagator or two-time Green's functions . . . 20
4.2.1 Equation of motion for the propagator and its Fourier trasformation 21
4.2.2 Moment expansion . . . 21
4.2.3 Excitational manifold . . . 21
4.2.4 Sum-over-states expression (SOS) for the Fourier transformed propagator in the basis of exact ground and excited states . . . 22
4.2.5 Eigenvalue problem when exact ground and excited states are not known. . . . 23

5 The problem of origin dependence in response theory **26**

6 Polarizable continuum model (PCM) **29**
6.1 Electrostatic setup . . . 29
6.2 Quantum mechanical setup: with no time-dependent external perturbations 31

7 The list of papers, included in the thesis, with short descriptions **32**

8 Acknowledgements **34**

The weather was very cloudy. It was snowing. Holy Olaf the king sent out somebody to look around, but there was no clear point in the sky. Then he asked Sigurd to tell him where the Sun was. After Sigurd complied, he grabbed a sunstone, looked at the sky and saw from where the light came, from which he guessed the position of the invisible Sun. It turned out, that Sigurd was right

Ramskou T. 1967 Solstenen. Skalk 2, 1617. Ref.[17]

1 Preface

In life or in a scientific experiment, we do not observe light from a source unchanged. Light traverses some medium which causes scattering and absorption. Both scattering and absorption are referred to in the literature as light *attenuation* processes (e.g. Ref.[13]) or as *extinction* processes — which means that a light beam loses part of its energy via scattering or absorption while going through the medium. The observed light is thus already modified by its interaction with the medium.

In what follows it will be discussed which characteristics of light can be considered theoretically and experimentally, how the light affects the medium it traverses, and how the medium affects the light in return. In an experiment it is possible to measure the characteristics of the light before entering a medium as well as on exiting from the medium, and from this to deduce some properties of the medium. At the same time, there is a great demand for materials with desired optical properties, *i.e.* with some prescribed effect on the light.

This thesis introduction is organized in the following order:

- How to characterize light: the polarization and the Stokes parameters
- Molecules and atoms in an external electric field — a phenomenological approach
- Effect of the medium on light: forward scattering theory.
- The Kerr effect, as an example of an induced optical property.
- Linear birefringence
- The quantum-theoretical approach to molecules and atoms in external electric and magnetic fields: response theory.
- Polarizable continuum model.

2 Light in medium

In this section some very basic details of the theory of light will be presented. The main objective is to introduce the notation we use. We start with some details on the macroscopic Maxwell equations in matter. For more details the reader is referred to Refs. [13, 14, 15, 16].

2.1 The Maxwell equations

The macroscopic Maxwell equations (in SI units) and in vector form in the medium are

$$\nabla \cdot \boldsymbol{D}(\boldsymbol{r}) = \rho_{\mathrm{f}}(\boldsymbol{r}) \tag{2.1}$$

$$\nabla \times \boldsymbol{E}(\boldsymbol{r}) = -\frac{\partial \boldsymbol{B}(\boldsymbol{r})}{\partial t} \tag{2.2}$$

$$\nabla \cdot \boldsymbol{B}(\boldsymbol{r}) = 0 \tag{2.3}$$

$$\nabla \times \boldsymbol{H}(\boldsymbol{r}) = \boldsymbol{J}_{\mathrm{f}}(\boldsymbol{r}) + \frac{\partial \boldsymbol{D}(\boldsymbol{r})}{\partial t} \tag{2.4}$$

In these equations we have introduced a "free" charge density ρ_{f}, a "free" source current density $\boldsymbol{J}_{\mathrm{f}}$, the electric and magnetic fields in free space $\boldsymbol{E}$ and $\boldsymbol{B}$, and the electric and magnetic fields in the matter, $\boldsymbol{D}$ and $\boldsymbol{H}$. Also "bound" densities are accounted for in $\boldsymbol{D}$ and $\boldsymbol{H}$ (see Ref. [16] for more details).

"Macroscopic" means that there is some procedure of averaging of microscopic properties of the medium. On a macroscopic scale we are not interested in the "exact" behavior of individual particles and fields but rather in some averaged properties of the fields and the medium (*e.g.* Refs. [19, 16]). In this averaging procedure, it is customary to divide charged particles into two groups: "free", or conducting, and "bound". This division is not strict, but it has proven to be useful in devising physical models.

The relation between the electric field in matter $\boldsymbol{D}$, the free space electric field $\boldsymbol{E}$ and bound charge densities in the simple approximated form looks like:

$$\boldsymbol{D} = \epsilon_0 \boldsymbol{E} + \boldsymbol{\mathcal{P}} \tag{2.5}$$

In the same way we have for $\boldsymbol{H}$:

$$\boldsymbol{H} = \frac{1}{\mu_0}\boldsymbol{B} - \boldsymbol{\mathcal{M}} \tag{2.6}$$

In these relations $\boldsymbol{\mathcal{P}}$ and $\boldsymbol{\mathcal{M}}$ are the macroscopic polarization and magnetization of the matter, respectively (not to be confused with their microscopic counterparts $\boldsymbol{P}$ and $\boldsymbol{M}$, to be introduced later). The electromagnetic constants — ϵ_0 is the electric permittivity of free space and μ_0 is the magnetic permeability of free space.

Remark:
The rigorous definition of the microscopic polarization will be presented in the section on response theory.
The reader should be aware that in the subject of nonlinear optics, the word "polarization" is used in two ways. In the current context of the medium in an external field we have the (macro- and microscopic) polarization as a response of the medium to the external electromagnetic fields.
When considering electromagnetic waves, the polarization of the wave defines the orientation and motion of the electric field vector of the wave.

If polarization, magnetization and currents are assumed to be linear with respect to the free-space fields, we have:

$$\boldsymbol{\mathcal{P}} = \epsilon_0 \chi \boldsymbol{E} \tag{2.7}$$
$$\boldsymbol{D} = \epsilon \boldsymbol{E}, \qquad \epsilon = \epsilon_0(1+\chi) \tag{2.8}$$
$$\boldsymbol{B} = \mu \boldsymbol{H} \tag{2.9}$$
$$\boldsymbol{J} = \sigma \boldsymbol{E} \tag{2.10}$$

where we introduced parameters characterizing the case of the linear response of the medium to external fields: χ is the electric susceptibility, μ is the magnetic permeability and σ is the conductivity of the matter.

If we consider an infinite homogeneous medium with no "free" charges and with zero conductivity, then the Maxwell equations become:

$$\nabla \cdot \boldsymbol{D} = 0 \tag{2.11}$$
$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \tag{2.12}$$
$$\nabla \cdot \boldsymbol{B} = 0 \tag{2.13}$$
$$\nabla \times \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t} \tag{2.14}$$

which can be transformed into two wave-like equations for the electric and magnetic fields separately:

$$\nabla^2 \boldsymbol{E} = \mu\epsilon \frac{\partial^2 \boldsymbol{E}}{\partial^2 t} \tag{2.15}$$
$$\nabla^2 \boldsymbol{B} = \mu\epsilon \frac{\partial^2 \boldsymbol{B}}{\partial^2 t} \tag{2.16}$$

with a wave velocity $v = \frac{1}{\sqrt{\mu\epsilon}}$ and a free-space velocity $c = \frac{1}{\sqrt{\mu_0\epsilon_0}}$. The *refractive index* of the medium is then:

$$n = \sqrt{\frac{\epsilon\mu}{\epsilon_0\mu_0}} = c\sqrt{\epsilon\mu} \tag{2.17}$$

These wave equations allow for a solution in the form of plane waves. In a complex form, the solution is:

$$\boldsymbol{E} = \boldsymbol{E}_0 \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t) \tag{2.18}$$
$$\boldsymbol{H} = \boldsymbol{H}_0 \exp(i\,\boldsymbol{k}\cdot\boldsymbol{r} - i\omega t) \tag{2.19}$$

with complex constant vectors $\boldsymbol{E}_0$,$\boldsymbol{H}_0$ and wave vector $\boldsymbol{k}$. The wave is characterized by the amplitude and the phase, for an electric field the amplitude is $\boldsymbol{E}_0 e^{\mathrm{Im}(\boldsymbol{k})\cdot\boldsymbol{r}}$ and the phase is $\mathrm{Re}(\boldsymbol{k})\cdot\boldsymbol{r} - \omega t$.

With substitution of this plane-wave solution into the homogeneous Maxwell equations 2.11 can be transformed to the following form:

$$\boldsymbol{k}\cdot\boldsymbol{E}_0 = 0 \tag{2.20}$$
$$\boldsymbol{k}\cdot\boldsymbol{H}_0 = 0 \tag{2.21}$$
$$\boldsymbol{k}\times\boldsymbol{E}_0 = \omega\mu\boldsymbol{H}_0 \tag{2.22}$$
$$\boldsymbol{k}\times\boldsymbol{H}_0 = -\omega\epsilon\boldsymbol{E}_0 \tag{2.23}$$

If the constants are real, these relations allow for a simple interpretation — the transversity of the wave. In this case, both electric and magnetic fields are perpendicular to the wave vector and mutually perpendicular to each other.

In the case when the wave is homogeneous (see Ref.[14]), which is the case when the imaginary and real parts of the complex wave vectors are parallel to each other, we have:

$$\boldsymbol{k}\cdot\boldsymbol{k} = \omega^2\epsilon\mu,\ \boldsymbol{k} = k\hat{\boldsymbol{n}},\ k = \mathrm{Re}(k) + i\,\mathrm{Im}(k) = \omega\frac{n}{c} \tag{2.24}$$

where $\hat{\boldsymbol{n}}$ is a unit vector of propagation (in the plane perpendicular to this vector we have constant phase and amplitude). Let us write $\boldsymbol{n} = n\hat{\boldsymbol{n}}$. For the homogeneous plane wave we have:

$$\boldsymbol{E} = \boldsymbol{E}_0 \exp\left(-\frac{\omega}{c}\mathrm{Im}(\boldsymbol{n})\cdot\boldsymbol{r}\right)\exp\left(i\frac{\omega}{c}\mathrm{Re}(\boldsymbol{n})\cdot\boldsymbol{r} - i\omega t\right) \tag{2.25}$$

For this wave, the so called *Poynting vector* [14, 15, 16] can be defined:

$$\boldsymbol{S}(\boldsymbol{r}) = \frac{1}{2}(\boldsymbol{E}\times\boldsymbol{H}^*) \tag{2.26}$$

This vector characterizes the transfer of energy in space. The time-averaged Poynting vector for the homogeneous plane wave is

$$\langle\boldsymbol{S}(\boldsymbol{r})\rangle = \frac{1}{2}\hat{\boldsymbol{n}}\,\mathrm{Re}\left(\sqrt{\frac{\epsilon}{\mu}}\right)|\boldsymbol{E}_0|^2\exp\left(-2\frac{\omega}{c}\mathrm{Im}(n)\,\hat{\boldsymbol{n}}\cdot\boldsymbol{r}\right) \tag{2.27}$$

so we see that the direction of this vector is the propagation direction, and the absolute value of it is called *the intensity.*

We can see that if the imaginary part of the vector $\boldsymbol{n}$ is non-zero, we have an exponential decay of the intensity:

$$I(\boldsymbol{r}) = I_0\exp\left(-2\frac{\omega}{c}\mathrm{Im}(n)\,\hat{\boldsymbol{n}}\cdot\boldsymbol{r}\right) \tag{2.28}$$

In other words, the attenuation of the beam (wave) is related to the imaginary part of the refractive index.

2.2 Observable quantities of a light beam: the Stokes parameters

An interesting feature of quantum mechanics is that not all objects entering the equations of quantum mechanics can be observed directly in experiment. The so-called observables define quantities which are measured in experiments.

An analogous situation is present in optics — the electric and magnetic fields of the light beam cannot be measured directly, but certain real-valued linear combinations of products of the components of the fields can be measured.

The most standard set of parameters which connect theory and experiment is the set of Stokes parameters. In what follows we will use the notation from Ref.[14].

In homogeneous non-absorbing medium (thus all constants in Eq. (2.20) are real) we have electric and magnetic fields in a plane perpendicular to the unit vector of propagation $\hat{\boldsymbol{n}}$. This vector is specified by two angles (see fig.1): ϑ is a polar coordinate with the range $[0, \pi]$ and φ is an azimuthal angle with the range $[0, 2\pi)$.

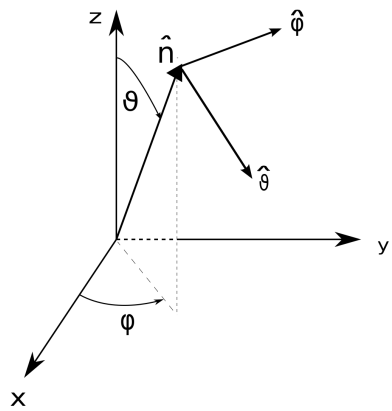

Figure 1: Spherical coordinates

The plane perpendicular to the unit vector $\hat{\boldsymbol{n}}$ is also characterized by these two polar angles. Two vectors are therefore introduced: a unit vector $\hat{\vartheta}$ which lies in the plane containing the z-axis (the meridional plane) and $\hat{\boldsymbol{n}}$, and a vector $\hat{\varphi}$ which is perpendicular to this meridian plane, and thus $\hat{\boldsymbol{n}} = \hat{\vartheta} \times \hat{\varphi}$. In this coordinate system it is possible to define the components of the fields of the light beam by only two components:

$$\boldsymbol{E} = \boldsymbol{E}_\vartheta + \boldsymbol{E}_\varphi = E_\vartheta \hat{\vartheta} + E_\varphi \hat{\varphi} \tag{2.29}$$

It is customary (Refs.[14, 13]) to introduce a density or a coherence matrix composed of products of these two components:

$$\frac{1}{2}\sqrt{\frac{\epsilon}{\mu}} \begin{pmatrix} E_\vartheta E_\vartheta^* & E_\vartheta E_\varphi^* \\ E_\varphi E_\vartheta^* & E_\varphi E_\varphi^* \end{pmatrix} \tag{2.30}$$

This is already a complete set that characterizes the monochromatic beam, so any observable can be expressed as a linear combination of these matrix elements. However, it

is more suitable to use real-valued quantities, *the Stokes parameters*, which are written as a column-vector $\boldsymbol{I}$:

$$\boldsymbol{I} = \begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix} = \frac{1}{2}\sqrt{\frac{\epsilon}{\mu}} \begin{pmatrix} E_\vartheta E_\vartheta^* + E_\varphi E_\varphi^* \\ E_\vartheta E_\vartheta^* - E_\varphi E_\varphi^* \\ -E_\vartheta E_\varphi^* - E_\varphi E_\vartheta^* \\ i(E_\varphi E_\vartheta^* - E_\vartheta E_\varphi^*) \end{pmatrix} = \frac{1}{2}\sqrt{\frac{\epsilon}{\mu}} \begin{pmatrix} E_\vartheta E_\vartheta^* + E_\varphi E_\varphi^* \\ E_\vartheta E_\vartheta^* - E_\varphi E_\varphi^* \\ -2\mathrm{Re}(E_\vartheta E_\varphi^*) \\ 2\mathrm{Im}(E_\vartheta E_\varphi^*) \end{pmatrix} \tag{2.31}$$

The first parameter I is an intensity, introduced previously (Eq.(2.28)), the other three parameters characterize the *polarization state*. These four parameters are not independent because of the quadratic relation:

$$I^2 = Q^2 + U^2 + V^2 \tag{2.32}$$

In order to see what information about a light beam that can be deduced from these parameters — we introduce the *ellipsoidal description* of the light.

2.3 Polarization of light: ellipsoidal description

Let us write the electromagnetic field in a non-absorbing homogeneous medium as

$$\boldsymbol{E} = \boldsymbol{E}_0 \exp\left(i\frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r} - i\omega t\right) \tag{2.33}$$

and write its complex amplitudes as

$$E_{0\vartheta} = a_\vartheta \exp(i\Delta_\vartheta) \tag{2.34}$$

$$E_{0\varphi} = a_\varphi \exp(i\Delta_\varphi) \tag{2.35}$$

where we have real-valued non-negative amplitudes a_ϑ and a_φ, and real phases Δ_ϑ and Δ_φ. With the factor $\frac{1}{2}\sqrt{\frac{\epsilon}{\mu}}$ omitted the Stokes parameters then are:

$$I = a_\vartheta^2 + a_\varphi^2 \tag{2.36}$$

$$Q = a_\vartheta^2 - a_\varphi^2 \tag{2.37}$$

$$U = -2a_\vartheta a_\varphi \cos(\Delta) \tag{2.38}$$

$$V = 2a_\vartheta a_\varphi \sin(\Delta) \tag{2.39}$$

where we have introduced the phase difference

$$\Delta = \Delta_\vartheta - \Delta_\varphi \tag{2.40}$$

From these equations we see that the wave can be uniquely identified up to the phase difference, whereas the phases of the components cannot be identified and thus measured. In an experiment, two waves with the same phase difference (the same Stokes parameters) but with different phases, are identical.

Now let us express the $\hat{\vartheta}$ and $\hat{\varphi}$ real-valued components as:

$$E_\varphi(\boldsymbol{r},t) = a_\varphi \cos\left(\Delta_\varphi + \frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r} - \omega t\right) \tag{2.41}$$

$$E_\vartheta(\boldsymbol{r},t) = a_\varphi \cos\left(\Delta_\vartheta + \frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r} - \omega t\right) \tag{2.42}$$

For a fixed space coordinate, these equations are parametric equations in t. In general the tip of the electric field describes an ellipse, depending on a relative phase difference of two components (meridian and azimuthal) of the light beam (see Fig.2).

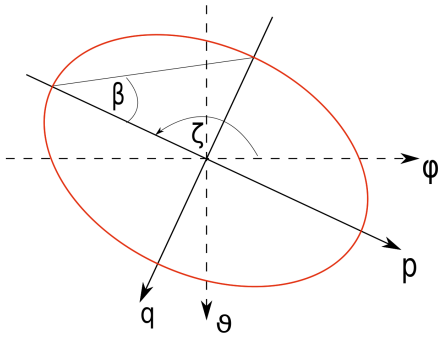

Figure 2: Ellipse drawn by the tip of the electric vector of the wave

If we fix the time coordinate, then we obtain an elliptic helix in space (see Fig.3)

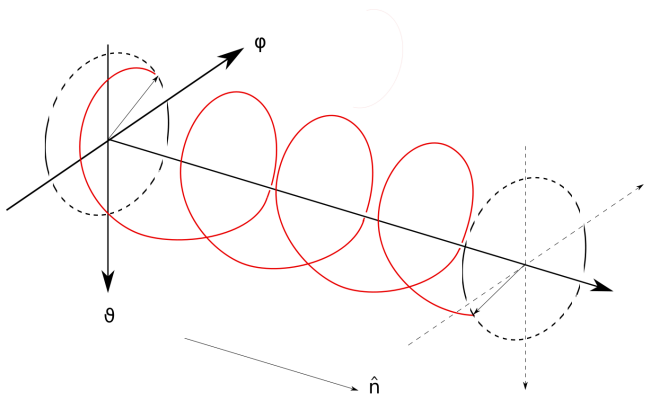

Figure 3: General elliptic polarization of the light beam

The orientation of the ellipse (Fig.2) is characterized by the orientation angle ζ, which is derived by rotation of the ϕ-axis clock-wise (with respect to the direction of the propagation) until ϕ coincides with the major axis of the ellipse. Thus we introduce the coordinate system (p, q) as in the Fig.2, the axes of which coincide with the minor and major elliptical axes. This coordinate system is rotated with respect to (ϑ, φ) by an angle ζ.

The ratio of the major and the minor axis, a so-called *ellipticity*, is expressed as $|\tan(\beta)|$, where the range of β is $[-\frac{\pi}{4}, +\frac{\pi}{4}]$. The sign of β defines the *handedness* —

which specifies whether a point on the parametric curve moving in the clockwise (+) or counter-clockwise (−) direction with respect to the vector of propagation.

The lengths of the axes are defined as $a\cos\beta$ and $a\sin\beta$ where a is an elliptical "radius".

Taking these parameters of the ellipse into account, the components of the electromagnetic field in some space coordinate can be written in the form:

$$E_q(t) = a\sin\beta\,\sin(\delta-\omega t) \tag{2.43}$$
$$E_p(t) = a\cos\beta\,\cos(\delta-\omega t) \tag{2.44}$$

these parametric equations represent right- or left-hand rotation along the ellipse (Fig.2) of the electric vector, and it is customary to say that depending on β we have either right-hand polarization or left-hand polarization.

2.4 Polarization of light via the Stokes parameters

The orientation of the ellipse and ellipticity can be expressed via the Stokes parameters. For this purpose we transform the components of the field in (p,q) coordinates to components in the (ϑ,φ) coordinates.

$$E_\vartheta(\boldsymbol{r},t) = -E_q(\boldsymbol{r},t)\cos\zeta + E_p(\boldsymbol{r},t)\sin\zeta \tag{2.45}$$
$$E_\varphi(\boldsymbol{r},t) = -E_q(\boldsymbol{r},t)\sin\zeta - E_p(\boldsymbol{r},t)\cos\zeta \tag{2.46}$$

After some trigonometric manipulations (Ref.[14]), we get

$$a_\vartheta^2 = a^2(\sin^2\beta\cos^2\zeta+\cos^2\beta\sin^2\zeta) \tag{2.47}$$
$$a_\varphi^2 = a^2(\sin^2\beta\sin^2\zeta+\cos^2\beta\cos^2\zeta) \tag{2.48}$$
$$a_\vartheta a_\varphi\cos\Delta = -\frac{1}{2}a^2\cos 2\beta\sin 2\zeta \tag{2.49}$$
$$a_\vartheta a_\varphi\sin\Delta = -\frac{1}{2}a^2\sin 2\beta \tag{2.50}$$

and taking the Stokes parameters into account, we have:

$$I = a^2 \tag{2.51}$$
$$Q = -I\cos 2\beta\cos 2\zeta \tag{2.52}$$
$$U = I\cos 2\beta\sin 2\zeta \tag{2.53}$$
$$V = -I\sin 2\beta \tag{2.54}$$

Thus the lengths of the major and minor axes are expressed via the intensity and β as $\sqrt{I}|\cos\beta|$ and $\sqrt{I}|\sin\beta|$. The orientation angle ζ is defined by:

$$\tan 2\zeta = -\frac{U}{Q} \tag{2.55}$$

The *ellipticity*, the sign of which determines left- or right-hand rotation of the electric field vector, is:

$$\tan 2\beta = -\frac{V}{\sqrt{Q^2+V^2}} \tag{2.56}$$

from which we can see that we have the left-handed polarization for $V > 0$ and the right-hand polarization for $V < 0$. (Should be also noticed that the sign of $\cos 2\zeta$ is the same as that of $-Q$.)

2.5 Cases of polarization

- In the case when $U = 0$, we have orientation angle ζ equal either to 0

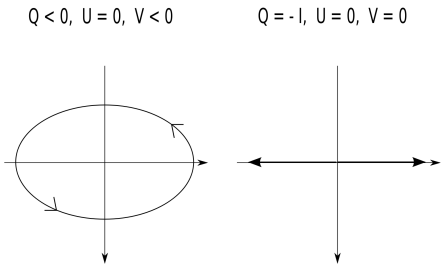

Figure 4:

or $\zeta = \frac{\pi}{2}$

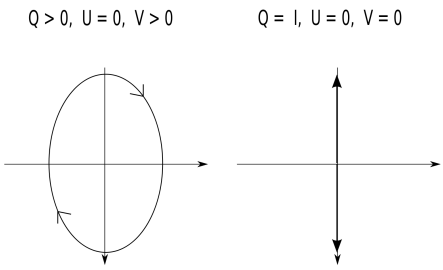

Figure 5:

From these figures we see that if V is non-zero it specifies the rotation (as shown by arrows in the figures). If V is zero we get linear polarization.

- In the case when $Q = 0$, we have orientation angle ζ equal either $\frac{\pi}{4}$

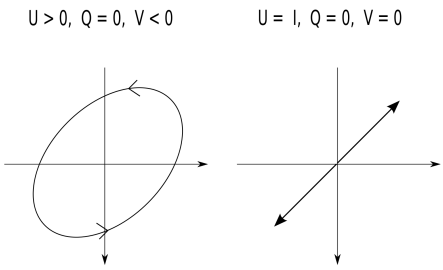

Figure 6:

or $\zeta = \frac{3\pi}{4}$

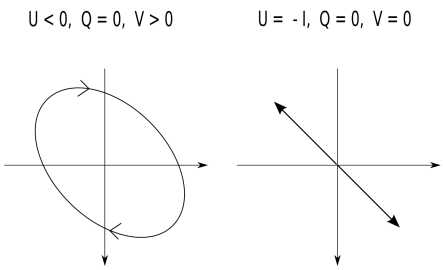

Figure 7:

- In the case when both Q and U are zero, it means we have $\beta = \pm\frac{\pi}{4}$. Thus we have circular polarization, the handedness being defined by the sign of V.

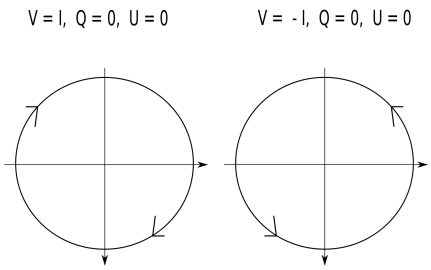

Figure 8:

3 Propagation of light in the medium: forward scattering theory

In the previous section we saw that the description of light traversing a medium is essentially macroscopic. We considered the macroscopic Maxwell equations, where all terms are macroscopically averaged (see Ref.[19]). In this subsection we consider the interplay between microscopic and macroscopic levels. External electromagnetic fields affect the medium, and the effect should firstly be considered on a single molecule level. To get from the molecular level to the macroscopic level, some procedure of averaging should be applied.

3.1 A molecule in the external field

To treat the interaction of the molecule with the electromagnetic field it is common to employ the so-called semi-classical approach. In this approach the external field is treated in classical electro-dynamical way, but the molecule subjected to the external electromagnetic field is treated as the quantum system. In this case it is said that the quantum system is subject to "mechanical" external time-dependent or static perturbations. The external semi-classical perturbation is expressed via components of the classical electromagnetic field and the multipole operators of the molecule.

The molecule is characterized by the expectation values of its electric and magnetic multipole moments, like dipole moment, quadruple moment, magnetic moment and diamagnetic susceptibility tensor defined as:

$$\boldsymbol{\mu} = -\sum_i \boldsymbol{r}_i + \sum_n Z_n \boldsymbol{R}_n \tag{3.1}$$

$$\begin{aligned} \Theta_{\alpha\beta} &= -\sum_i \frac{1}{2}(3r_{i\alpha}r_{i\beta} - \boldsymbol{r}_i^2\delta_{\alpha\beta}) + \\ &+ \sum_n \frac{1}{2}Z_n(3R_{n\alpha}R_{n\beta} - \boldsymbol{R}_n^2\delta_{\alpha\beta}) \end{aligned} \tag{3.2}$$

$$\boldsymbol{m} = -\sum_i \frac{1}{2}\boldsymbol{r}_i \times \boldsymbol{p}_i + \sum_n \frac{Z_n}{2M_n}\boldsymbol{R}_n \times \boldsymbol{P}_n \tag{3.3}$$

where the sum $\sum_i$ is over all electrons of the molecule, the sum $\sum_n$ over all nuclei of the molecule, $\boldsymbol{r}_i$ and $\boldsymbol{R}_n$ are the Cartesian coordinates of the ith electron and nth nucleus, M_n and Z_n are the mass and charge of the nth nucleus (mass and charge of electrons are taken as 1 and -1 respectively). $\boldsymbol{p}_i$ and $\boldsymbol{P}_n$ are the linear momenta of the ith electron and nth nucleus, respectively. We also assume Einstein sum convention.

The general multipole interaction dynamic Hamiltonian, which corresponds to the time-dependent electromagnetic field, in the Barron-Gray [1] gauge, which is the gauge chosen by Barron and Gray to derive a dynamical interaction Hamiltonian which would resemble a static one

$$V(\boldsymbol{r},t) = -\mu_\alpha(E_\alpha)_0(t) - \frac{1}{3}\Theta_{\alpha\beta}(E_{\alpha\beta})_0 - m_\alpha(B_\alpha)_0 - \frac{1}{2}\chi^{(d)}_{\alpha\beta}(B_\alpha)_0(B_\beta)_0 + \dots \tag{3.4}$$

where subscript 0 comes from the Taylor expansion[1] of the electromagnetic field potentials around the atomic nucleus or the center of mass of a molecule

$$E_\alpha(\boldsymbol{r},t) = (E_\alpha)_0(t) + r_\beta(E_{\beta\alpha})_0(t) + \dots \tag{3.5}$$

$$B_\alpha(\boldsymbol{r},t) = (B_\alpha)_0(t) + r_\beta(B_{\beta\alpha})_0(t) + \dots \tag{3.6}$$

which correspond to Taylor expansions of classical scalar and vector potentials of the external electromagnetic field:

$$\phi(\boldsymbol{r},t) = -r_\alpha(E_\alpha)_0(t) - \frac{1}{2}r_\alpha r_\beta(E_{\alpha\beta})_0 + \dots \tag{3.7}$$

$$A_\alpha(\boldsymbol{r},t) = \frac{1}{2}\epsilon_{\alpha\beta\gamma}(B_\beta)_0(t)r_\gamma + \frac{1}{3}\epsilon_{\alpha\gamma\delta}(B_{\beta\gamma})_0 r_\delta + \dots \tag{3.8}$$

If we stop the expansion at the spatially uniform (constant) term, we will get the well-known dipole-moment approximation, in which the molecule interacts with the external electric field via the simple perturbation operator:

$$V(t) = -\boldsymbol{\mu}\cdot\boldsymbol{E}(t) \tag{3.9}$$

3.2 A case study: microscopic and macroscopic polarizations in two electric fields

For illustration purposes we consider the case when the medium is considered to be subjected to a to a weak (probe) light wave field $\boldsymbol{E}(t)$ and a relatively strong static uniform field $\boldsymbol{\mathcal{E}}$. The induced dipole moment of the molecule (polarization)

$$\boldsymbol{P}(t,\boldsymbol{E},\boldsymbol{\mathcal{E}}) = \langle\Psi(t,\boldsymbol{r},\boldsymbol{E},\boldsymbol{\mathcal{E}})\,|\boldsymbol{\mu}|\,\Psi(t,\boldsymbol{r},\boldsymbol{E},\boldsymbol{\mathcal{E}})\rangle \tag{3.10}$$

for a quantum state $\Psi(t,\boldsymbol{r},\boldsymbol{E},\boldsymbol{\mathcal{E}})$ will in general be a complicated function of time and external perturbation fields.

Perturbation theories for cases where the frequencies of the external fields do not match internal frequencies of the molecule (so-called *non-resonant* cases) usually lead to expressions which are power series in the strengths of the perturbation fields. Such a rigorous theory will be presented in section 4.

In this section we will assume a very simplified and idealized approach. We assume that the expectation value of the dipole moment oscillates on the same frequency as the external field.

The polarization is written (using Buckingham's notation [15]) as a Taylor expansion in both external fields:

$$P_i = P_i^0 + \alpha_{ij}E_j + \alpha_{ij}^0\mathcal{E}_j + \frac{1}{2}\beta_{ijk}E_j\mathcal{E}_k + \frac{1}{2}\beta_{ijk}^0\mathcal{E}_j\mathcal{E}_k + \frac{1}{6}\gamma_{ijkl}E_j\mathcal{E}_k\mathcal{E}_l + \dots \tag{3.11}$$

where the superscript 0 identifies the terms corresponding to the static contribution, and where tensors β and γ, introduced by Buckingham and Pople, are so-called *hyperpolarizabilities*. In the theory described in Refs.[15, 16] it is assumed that the light field does not influence the molecular orientation, which means that the energy of the charges in

the external field is considered only for the static field. Thus we have standard static electrical energy as:

$$W = W^0 - P_i^0 \mathcal{E}_i - \frac{1}{2}\alpha_{ij}^0 \mathcal{E}_i \mathcal{E}_j - \frac{1}{6}\beta_{ijk}^0 \mathcal{E}_i \mathcal{E}_j \mathcal{E}_k - \dots \tag{3.12}$$

By considering the medium as consisting of molecules of the same kind, we should take an orientational average of the dipole moments. In the averaging procedure, we use the energy W depending on the static field $\boldsymbol{\mathcal{E}}$ as a Boltzmann weighting factor

$$\bar{P}_i(\boldsymbol{\mathcal{E}}, \boldsymbol{E}) = \frac{\int d\tau P_i(\tau, \boldsymbol{\mathcal{E}}, \boldsymbol{E}) \exp(-\frac{W(\tau, \boldsymbol{\mathcal{E}})}{kT})}{\int d\tau \exp(-\frac{W(\tau, \boldsymbol{\mathcal{E}})}{kT})} \tag{3.13}$$

where τ is an orientational parameter. This expression is then expanded as a Taylor series in powers of the static field. For this expansion we need an expansion of the Boltzmann factor and expansion of the dipole moment

$$P_i(\boldsymbol{\mathcal{E}}, \boldsymbol{E}, \tau) = P_i(\mathbf{0}, \boldsymbol{E}, \tau) + \left(\frac{\partial P_i}{\partial \mathcal{E}_j}\right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_j + \frac{1}{2}\left(\frac{\partial^2 P_i}{\partial \mathcal{E}_j \partial \mathcal{E}_k}\right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_j \mathcal{E}_k + \dots \tag{3.14}$$

Using Eq.(3.11) and omitting some intermediate calculations (see Refs.[15, 16] for details) we have for the averaged dipole moment up to second order in the static field:

$$\begin{aligned} \bar{P}_i(\boldsymbol{\mathcal{E}}, \boldsymbol{E}) &= \langle \alpha_{ij} \rangle E_j + \mathcal{E}_k [\langle \alpha_{ij}^0 \rangle + \frac{1}{kT} \langle P_i^0 P_k^0 \rangle] + \\ &+ \frac{1}{2} E_j \mathcal{E}_k \mathcal{E}_l [\frac{1}{3} \langle \gamma_{ijkl} \rangle + \frac{1}{kT} (\langle \alpha_{ij} \alpha_{kl}^0 \rangle - \langle \alpha_{ij} \rangle) \langle \alpha_{kl}^0 \rangle + \langle P_l^0 \beta_{ijk} \rangle] + \\ &+ \frac{1}{(kT)^2} [\langle P_k^0 P_l^0 \alpha_{ij} \rangle - \langle P_k^0 P_l^0 \rangle \langle \alpha_{ij} \rangle] \end{aligned} \tag{3.15}$$

In the following we are interested in the time-dependent (emitting) induced dipole moment, so we will write it as

$$\bar{P}_i = d_{ij} E_j \tag{3.16}$$

where d_{ij} can be derived from Eq.(3.15), omitting the purely static part. This is a pivotal crossroad point — from here we can either consider the macroscopic Maxwell equations in the medium with no currents (the approach considered in Ref.[16]), or to consider *forward scattering theory* (approach considered in Ref.[15]), taking each molecule as a center of forward scattering.

We will here consider forward scattering theory.

Remark:

We have everything at hands for the first approach. In one of the Maxwell macroscopic equations:

$$\nabla \times \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t} \tag{3.17}$$

the time-dependent $\boldsymbol{D}$ should be taken as:

$$D_i = (\epsilon_0 \delta_{ij} + N d_{ij}) E_j \tag{3.18}$$

where N is the so-called number density of molecules. The medium polarization is thus related to the orientational averaged polarization of the individual molecules as

$$\boldsymbol{\mathcal{P}} = N \bar{\boldsymbol{P}}$$

It is also assumed at this point that medium polarization is linear with respect to the time-dependent field (see Eq.(2.7)).

3.3 Forward scattering and the Kerr effect

In this subsection we will follow the exposition of the theory of the Kerr effect from Ref.[16], developed in Ref.[18]. The set up for the microscopic theoretical consideration of scattering is the following:

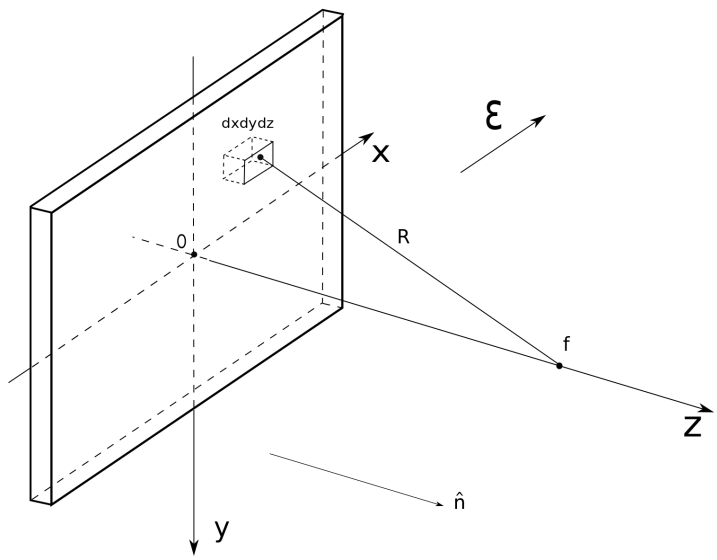

Figure 9: From [14]

A thin square (with lengths $2L$) lamina of width Δz is considered, with the center at the origin and positioned in the xy plane. A harmonic light beam is considered as propagating in the positive direction along the z. The external static field $\boldsymbol{\mathcal{E}}$ is considered

to be in the x direction, *i.e.* $(\mathcal{E}, 0, 0)$.
In Fig.9, R is a distance from the volume element of the lamina $dxdydz$ to the point f where the resulting field, consisting of incident and scattered light, will be calculated.

The electric field emitted by $dxdydz$ at the point f (we write the volume dipole moment as $\bar{\boldsymbol{P}}dxdydz$):

$$E_i^f(\boldsymbol{R}, t) = \frac{1}{4\pi\epsilon_0 c^2 R^3}(R_i R_j - R^2\delta_{ij})\ddot{\bar{P}}\left(t - \frac{R}{c}\right) dxdy\Delta z \tag{3.19}$$

because we consider light as harmonic and we consider the molecule as emitting at the same frequency, having in mind the relation of $\bar{\boldsymbol{P}}$ to the light field from Eq.(3.16):

$$\ddot{\bar{P}}\left(t - \frac{R}{c}\right) = -\omega^2\bar{\boldsymbol{P}}\left(t - \frac{R}{c}\right) = -\omega^2\bar{\boldsymbol{P}}_0 e^{-i\omega\left(t-\frac{R}{c}\right)} \tag{3.20}$$

The field from all the lamina at the point f with coordinate $(0, 0, z)$ is obtained by integration (for details see Refs.[16, 15]):

$$\delta E_x^f = i\frac{N\omega}{2\epsilon_0 c} d_{xx} E_x e^{-i\omega\left(t-\frac{z}{c}\right)}\Delta z\left(1 + O\left(\sqrt{\frac{\lambda}{z}}\right)\right) \tag{3.21}$$

$$\delta E_y^f = i\frac{N\omega}{2\epsilon_0 c} d_{yy} E_y e^{-i\omega\left(t-\frac{z}{c}\right)}\Delta z\left(1 + O\left(\sqrt{\frac{\lambda}{z}}\right)\right) \tag{3.22}$$

where we have $\lambda = \frac{2\pi c}{\omega}$ as the wave length, E_x and E_y are the amplitudes of the incident light.

In derivations of these equations it was assumed that z is of the same order as L and $z \ll \lambda$ (the so-called far-field assumption).

The only thing left to us to do is to consider the combined field E_x^{sum} at f as a sum of the incident light wave and the scattered wave from the lamina. For the x component we have:

$$E_x^{\text{sum}}(0, 0, z, t) = \left(1 + i\left(\frac{N\omega}{2\epsilon_0 c} d_{xx}\right)\Delta z\right) E_x \exp\left(-i\omega\left(t - \frac{z}{c}\right)\right) \tag{3.23}$$

The second term in the first brackets can be approximated into the exponent and thus becomes a phase factor:

$$E_x^{\text{sum}}(0, 0, z, t) \approx E_x \exp\left(-i\omega\left(t - \frac{N\omega}{2\epsilon_0 c} d_{xx}\Delta z - \frac{z}{c}\right)\right) \tag{3.24}$$

At f, we will therefore have a light beam with the same amplitude but with shifted phase, and the shift is proportional to the width of the lamina Δz. This equation implies that it takes additional time for the x-component of the wave to propagate from $(0, 0, 0)$ to f, and this can be considered as a slowing down of the wave in the lamina. Instead of $\frac{\Delta z}{c}$, it takes $\frac{\Delta z}{c}\left(1 + \frac{N\omega}{2\epsilon_0 c} d_{xx}\right)$, from which we have the refraction index:

$$n_x = 1 + \frac{N\omega}{2\epsilon_0} d_{xx} \tag{3.25}$$

and the same for y component:

$$n_y = 1 + \frac{N\omega}{2\epsilon_0} d_{yy} \tag{3.26}$$

Thus we see that x and y components are scattered differently by the lamina to which the static field is applied. The difference in the refractive indices is

$$n_x - n_y = \frac{N}{2\epsilon_0}(d_{xx} - d_{yy}) \tag{3.27}$$

We see from Eq.(3.16) that this difference is quadratic in the static field. If no static field is applied, it is shown in Refs.[16, 15], that $d_{xx} = d_{yy} = \frac{\alpha_{ii}}{3} = \alpha$, where α is the mean polarizability. Thus, in the absence of the external static field, the refractive index is isotropic:

$$n_x = n_y = n = 1 + \frac{N\alpha}{2\epsilon_0} \tag{3.28}$$

and x and y components of the light beam are retarded identically.

3.4 Linear birefringence

The formula (3.27) from the previous section shows us, that in the presence of the external static field $\boldsymbol{\mathcal{E}}$, perpendicular to the propagation of the probe light beam $\boldsymbol{E}$, there are different refractive indices for the components of the electric field of the light beam. And this is the case of so called the *linear birefringence*.

In the above case study we had the static field in the x direction, and we had the difference between refractive indices in the x and y directions. For linear birefringences it is customary to write refraction indices with respect to external field which induces the effect. Then we have the refractive index $n_{||}$ written for the direction parallel to the external field, and the refractive index $n_{\perp}$ in the direction perpendicular to the static field and propagation vector.

$$\Delta n = n_{||} - n_{\perp} \tag{3.29}$$

This birefringence is called *linear* because we decompose elliptically (in general) polarized light into its linear polarized components, parallel and perpendicular to the external field, as we did in the case study. These linear polarized components are propagating in the medium with different velocities, they have different retardation in the medium, because of the static field.

The result of propagation, in the case when there is no absorption in the medium, like we had in the above case — is the change in the phase difference of the linearly-polarized components of the probe light. This change is expressed as a gain in the *ellipticity* β (Eq.2.56). We see that the change of the phase factor in (Eq.3.24) is proportional to the increment Δz along the *optical path* we can write

$$\Delta\beta \propto (n_x - n_y)\Delta z \tag{3.30}$$

If there is no external static field (3.28), the ellipticity change would be zero in this case. The medium is then considered as optically *isotropic*.

4 Response theory

There exist several different formulations of response theory. For illustration purposes the polarization propagator approach will be briefly outlined, following Ref.[3].

4.1 Response theory, propagator approach

In response theory a quantum system is considered as being subjected to some time-dependent perturbation. It enters the Hamiltonian of a quantum system as an interaction between the quantum system and the perturbation, and we consider it as adiabatically switched on (the situation of instantaneous switching on can also be considered [4]):

$$V_t(\boldsymbol{r}) = \int_{-\infty}^{+\infty} d\omega V_\omega(\boldsymbol{r}) e^{-i\omega t + \epsilon t} \tag{4.1}$$

where the parameter ϵ ensures adiabaticity. For V_t to be hermitian $V_\omega^* = V_{-\omega}$. As an example of an external perturbation, we may consider the semi-classical dipole interaction of an atom or a molecule with an electric field. The perturbation operator entering the Hamiltonians is in this case:

$$V_t(\boldsymbol{r}) = -\boldsymbol{r} \cdot \boldsymbol{E}(t) = \int_{-\infty}^{+\infty} d\omega \boldsymbol{r} \cdot \boldsymbol{E}_\omega(\boldsymbol{r}) e^{-i\omega t + \epsilon t} \tag{4.2}$$

In response theory, we are interested in the evolution of expectation values of an operators which are related to some observables, when exposed to the external perturbation. An important step in the development of response theory, which started in the late 50s (*e.g.* Ref.[4]) was the change from the wave-function picture to the density matrix picture, allowing a far more economical approach to the quantum-mechanical many-body problem. A complete specification of the quantum state is usually intractable, and only limited knowledge (deduced from observables for example) is available about the state. The density matrix "interfaces" the wave function into observable quantities and it is widely used in quantum physics and quantum statistical physics [7].

For a state wave function which satisfies the time-dependent Schrödinger equation

$$i\frac{d}{dt}|\psi\rangle = (H_0 + V_t)|\psi\rangle \tag{4.3}$$

for $H_0\langle 0| = E_0\langle 0|$, the evolution of some operator P is

$$\langle \psi \,|P|\, \psi\rangle = \sum_\nu \langle \psi \,|P|\, \phi_\nu\rangle \langle \phi_\nu \mid \psi\rangle = \sum_\nu \langle \phi_\nu \,|P|\, \psi\rangle \langle \psi|\phi_\nu\rangle = \mathrm{Tr}(\rho P) \tag{4.4}$$

In this equation any complete basis of state vectors ϕ_ν can be used and the density matrix operator for the state ψ is defined in the standard way (Ref.[7]) as

$$\rho(t) = |\psi\rangle\langle\psi| \tag{4.5}$$

Instead of the Shrödinger equation for the wave function, we have the Liouville equation [3, 7] for the density matrix ρ_I in the *interaction representation* (Ref.[3]):

$$\begin{aligned} i\frac{d}{dt}e^{iH_0t}|\psi\rangle &= V_t e^{iH_0t}\psi\rangle \\ i\frac{d}{dt}\rho_I &= [V_t(t), \rho_I(t)] \\ \rho_I(t) &= e^{iH_0t}\rho(t)e^{-iH_0t} \\ V_{t'}(t) &= e^{iH_0t}V_{t'}e^{-iH_0t} \end{aligned} \tag{4.6}$$

Note that the perturbation operator is also used in the interaction picture, in a so-called *dressed* form as $V_{t'}(t)$. In the *equation-of-motion*, times t and t' are the same.

The Liouville equation can be integrated using the limit

$$\lim_{t\to-\infty}\rho_I(t) = \rho_0 = |0\rangle\langle 0| \tag{4.7}$$

to yield

$$\rho_I(t) = \rho_0 - i\int_{-\infty}^{t}[V_{t'}(t'), \rho_I(t')]dt' \tag{4.8}$$

which is to be solved iteratively via substitution. To get *the linear response*, one should substitute in the integral ρ_I with ρ_0, to get *the second-order response* one should substitute ρ_I with the result of the previous iteration for the linear response, and so forth. For the linear response, we therefore have:

$$\rho_I(t) = \rho_0 - i\int_{-\infty}^{t}[V_{t'}(t'), \rho_0(t')]dt' \tag{4.9}$$

The evolution of the density matrix $\rho(t)$:

$$\rho(t) = \rho_0 - i\int_{-\infty}^{t}[V_{t'-t}(t'), \rho_0(t')]dt' \tag{4.10}$$

Equation (4.10) can now be substituted into Eq.(4.4) and we have:

$$\langle\psi\,|P|\,\psi\rangle = \langle 0\,|P|\,0\rangle + \int_{-\infty}^{+\infty}\langle\langle P(t); V_{t'}(t')\rangle\rangle^{\mathrm{r}}dt' \tag{4.11}$$

where we have introduced a key object of response theory — the retarded two-time Green's function (see Ref.[4]), or propagator:

$$\langle\langle P(t); Q(s)\rangle\rangle^{\mathrm{r}} = -i\Theta(t-s)\langle 0|[P(t), Q(s)]|0\rangle \tag{4.12}$$

Here both operators are in the interaction representation

$$A(t) = e^{iH_0t}Ae^{-iH_0t} \tag{4.13}$$

In the case when there is no external time-dependent perturbation — this is just the Heisenberg representation of the operators (*e.g.* Ref.[20]).

In Eq.(4.12) Θ is the Heaviside step function: $\Theta(s) = 1$ for $s > 0$ and $\Theta(s) = 0$ for $s < 0$. If we insert equation (4.1) into equation (4.11), we get the following expression:

$$\langle \psi | P | \psi \rangle = \langle 0 | P | 0 \rangle + \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} dt' \langle\langle P(t); V_\omega(t') \rangle\rangle^{\mathrm{r}} e^{(\epsilon - i\omega)t'} \tag{4.14}$$

To illustrate this equation we can consider the polarization of a molecule or an atom by a dipole interaction (e.g. Refs.[3, 4]) with an external time-dependent electric field (Eq.(4.2)). For the α component of the dipole moment $\langle \psi | \boldsymbol{r} | \psi \rangle$ we can write:

$$\mu_\alpha(t) = \langle \psi | r_\alpha | \psi \rangle = \mu_\alpha(-\infty) - \int_{-\infty}^{+\infty} d\omega \sum_\beta \int_{-\infty}^{+\infty} dt' \langle\langle r_\alpha(t); r_\beta(t') \rangle\rangle^{\mathrm{r}} E_{\omega\beta} e^{(\epsilon - i\omega)t'} \tag{4.15}$$

Here the first term $\boldsymbol{\mu}(-\infty)$ is the static dipole moment and the second term is the induced dipole moment. The frequency-dependent part of the integral expression for the induced dipole can be written as:

$$\alpha_{\alpha\beta}(\omega) = -\int_{-\infty}^{+\infty} dt \langle\langle r_\alpha(0); r_\beta(t) \rangle\rangle^{\mathrm{r}} e^{(\epsilon - i\omega)t} \tag{4.16}$$

for which we have:

$$\mu_\alpha(t) = \mu_\alpha(-\infty) - \int_{-\infty}^{+\infty} d\omega \alpha(\omega)_{\alpha\beta} E_{\omega\beta} e^{(\epsilon - i\omega)t} \tag{4.17}$$

where we have introduced the dynamic polarizability tensor $\boldsymbol{\alpha}$ as an example of a so-called *polarization propagator* — $\langle\langle r_\alpha(0) : r_\beta(t) \rangle\rangle^{\mathrm{r}}$. This kind of propagators (or correlators) appeared in statistical quantum physics in the 50s (see Refs.[21, 4] for details).

4.2 Important features of a propagator or two-time Green's functions

In order to derive the above formulas one must use the following property of a propagator:

$$\langle\langle P(t); Q(s) \rangle\rangle^{\mathrm{r}} = \langle\langle P(0); Q(s-t) \rangle\rangle^{\mathrm{r}} \tag{4.18}$$

From this we can see that a two-time Green function actually depends not on absolute times, but rather on the difference of times.
To get more insight into the properties of the propagators, one can consider the spectral representation by making a Fourier transform of the propagator:

$$\langle\langle P; Q \rangle\rangle^{\mathrm{r}}_\omega = \lim_{\epsilon \to +0} \int_{-\infty}^{+\infty} \langle\langle P(0); Q(t) \rangle\rangle^{\mathrm{r}} e^{-i\omega t + \epsilon t} \tag{4.19}$$

In what follows we will try to deduce some properties of this Fourier-transformed propagator.

4.2.1 Equation of motion for the propagator and its Fourier trasformation

The equation-of-motion (EOM) for two-times propagator is:

$$i\frac{d}{dt}\langle\langle P(0);Q(t)\rangle\rangle = -\delta(t)\,\langle 0\,|[P,Q]|\,0\rangle + \langle\langle P(0);[Q(t),H_0]\rangle\rangle \tag{4.20}$$

where EOM for operator $P(t)$ in the interaction (Heisenberg) picture was used:

$$i\frac{d}{dt}P = [P(t),H_0] \tag{4.21}$$

For the propagator in the frequency domain $\langle\langle P;Q\rangle\rangle_\omega$, the EOM (see [6, 3]) is:

$$-E\langle\langle P;Q\rangle\rangle_\omega = -\,\langle 0\,|[P,Q]|\,0\rangle + \langle\langle P;[Q,H_0]\rangle\rangle_\omega \tag{4.22}$$

4.2.2 Moment expansion

Equation-of-motion Eq.(4.22) can iterated in the following way:

$$\langle\langle P;Q\rangle\rangle_\omega = \frac{\langle 0\,|[P,Q]|\,0\rangle}{\omega} + \frac{\langle 0\,|[P,[H_0,Q]]|\,0\rangle}{\omega^2} + \frac{\langle 0\,|[P,[H_0,[H_0,Q]]]|\,0\rangle}{\omega^3} + \dots \tag{4.23}$$

which is the so-called *moment expansion* of the energy-dependent propagator, introduced by Goscinski (Ref.[9])). This expression is usually written down in the so-called super-operator resolvent formulation, where operators form a super-operator space (e.g. Refs. [8, 10]), in which a binary product $(P|Q) = \left\langle 0\,\middle|[P^\dagger,Q]\middle|\,0\right\rangle$ is defined, and the super-operator Hamiltonian $\hat{H}$ acts on elements of the super-operator space via the commutation relation $\hat{H}P = [H,P]$ and the identity operator is defined as $\hat{I}P = P$. Within this formulation, the moment expansion is:

$$\langle\langle P;Q\rangle\rangle_\omega = \frac{(P^\dagger|Q)}{\omega} + \frac{(P^\dagger|\hat{H}_0Q)}{\omega^2} + \frac{(P^\dagger|\hat{H}_0^2Q)}{\omega^3} + \dots \tag{4.24}$$

With the super-operator resolvent operator:

$$(\omega\hat{I} - \hat{H}_0)^{-1} = \frac{1}{\omega}[\hat{I} + \sum_{n=1}^{\infty}(\frac{\hat{H}_0}{\omega})^n] \tag{4.25}$$

we arrive at:

$$\langle\langle P;Q\rangle\rangle_\omega = (P^\dagger|(\omega\hat{I} - \hat{H}_0)^{-1}|Q) \tag{4.26}$$

4.2.3 Excitational manifold

Another trick (originating from Ref.[8]) has been extensively used with respect to this super-operator approach. Instead of using the operator form, the matrix form is introduced via introduction of the *complete operator manifold* (Ref.[8]) $\boldsymbol{h}$ and usage of the binary product in the super-operator space:

$$(\omega\hat{I} - \hat{H}_0)^{-1} = |\tilde{\boldsymbol{h}})(\boldsymbol{h}|\omega\hat{I} - \hat{H}_0|\tilde{\boldsymbol{h}})^{-1}(\boldsymbol{h}| \tag{4.27}$$

here $\boldsymbol{h}$ is arranged as a column vector, and $\tilde{\boldsymbol{h}}$ is its transposed - the row vector. For the energy-dependent propagator:

$$\langle\langle P^{\dagger}; Q\rangle\rangle_{\omega} = (P|\tilde{\boldsymbol{h}})(\boldsymbol{h}|\omega\hat{I} - \hat{H}_0|\tilde{\boldsymbol{h}})^{-1}(\boldsymbol{h}|Q) \tag{4.28}$$

The meaning of the complete operator manifold is in the action on the reference state $|0\rangle$, which should generate the basis for evaluation of the propagator in frequency domain. If the reference state is taken as an SCF state, then we should have an operator manifold comprised of number-conserving operators (see details in Ref.[3, 28]):

$$\boldsymbol{h} = \boldsymbol{h_2}, \boldsymbol{h_4}, \boldsymbol{h_6}, \ldots \tag{4.29}$$

where $\mathbf{h_2}$ generate so-called single excitations, $\mathbf{h_4}$ generate double excitations and so forth. (More details on this subject will be given in the subsection 4.2.5)

4.2.4 Sum-over-states expression (SOS) for the Fourier transformed propagator in the basis of exact ground and excited states

If we know exact ground and excitation states $|n\rangle$ for the Hamiltonian H_0

$$H_0|n\rangle = E_n|n\rangle \tag{4.30}$$

we can construct the excitation manifold consisting of excitation and de-excitation operators

$$\{|n\rangle\langle 0|, |0\rangle\langle n|\}$$

. The evaluation of Eq.(4.28) in this basis set of exact excitation operators will lead to so-called Sum-over-state expression:

$$\langle\langle P; Q\rangle\rangle_{\omega}^{r} = \lim_{\epsilon\to+0}\sum_{n\neq 0}\{\frac{\langle 0\,|P|\,n\rangle\,\langle n\,|Q|\,0\rangle}{\omega - (E_n - E_0) + i\epsilon} - \frac{\langle 0\,|Q|\,n\rangle\,\langle n\,|P|\,0\rangle}{\omega - (E_n - E_0) + i\epsilon}\} \tag{4.31}$$

where SOS is a common abbreviation for "sum-over-states".

From this SOS expression we can see that Fourier transformation of a linear response function gives us unperturbed excitation energies and transition moments from the reference state $|0\rangle$ to excited states $|n\rangle$ — $\langle 0\,|P|\,n\rangle\,\langle n\,|Q|\,0\rangle$ and $\langle 0\,|Q|\,n\rangle\,\langle n\,|P|\,0\rangle$.

Remark:

From Eq.(4.31) we can see that the Green's function approach is giving us more physical approach then wave-function picture.
The time-independent Schrödinger equation can be reformulated in a so-called *resolvent* operator form, which depends on the absolute energies of the system, while energy-dependent propagators depend not on the absolute energies of the quantum system, but on its energy differences.
For a quantum system, we know from experiment what energy it can absorb or emit, so experiments provide us with information related to differences in the energy levels, not to its absolute values.

4.2.5 Eigenvalue problem when exact ground and excited states are not known.

In case when we don't have complete set of exact eigenvalue states for the unperturbed Hamiltonian H_0 we need to use some approximations. The most important approximate functions for us are those which are derived via self-consistent-field (SCF) procedures, such as HF (Hartree–Fock) and MCSCF (multi-configurational) wave functions. The HF SCF function is defined as a Slater product. The Slater determinant for a system consisting of N electrons (fermions) is the anti-symmetric product of N orthonormal orbitals $\phi_1(\boldsymbol{r}), \ldots, \phi_N(\boldsymbol{r})$, . In matrix form, the Slater product is just a determinant of the following matrix:

$$\frac{1}{\sqrt{N!}} \begin{bmatrix} \phi_1(\boldsymbol{r}_1) & \phi_2(\boldsymbol{r}_1) & \ldots & \phi_N(\boldsymbol{r}_1) \\ \phi_1(\boldsymbol{r}_2) & \phi_2(\boldsymbol{r}_2) & \ldots & \phi_N(\boldsymbol{r}_2) \\ . & . & \ldots & . \\ . & . & \ldots & . \\ . & . & \ldots & . \\ \phi_1(\boldsymbol{r}_N) & \phi_2(\boldsymbol{r}_N) & \ldots & \phi_N(\boldsymbol{r}_N) \end{bmatrix} \tag{4.32}$$

This representation of the electronic wave-function ensures the Pauli principle for multi-fermion system, which postulates that a wavefunction for a system of fermions should be anti-symmetric. Anti-symmetricity means that the wavefunction changes sign if two fermions are interchanged:

$$\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_k, \ldots, \boldsymbol{r}_n, \ldots, \boldsymbol{r}_N) = -\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \ldots, \boldsymbol{r}_k, \ldots, \boldsymbol{r}_N) \tag{4.33}$$

The permutational properties of the matrix determinant ensures that this condition is automatically fulfilled. The factor $\frac{1}{\sqrt{N!}}$ gives a normalized wave-function.
The determinant closed-shell function $|\mathrm{CSF}\rangle$ can be represented with the help of fermionic creation and annihilation operators, acting on a 'vacuum' state (see Ref.[28]):

$$|\mathrm{CSF}\rangle = \prod_i a^\dagger_{i\alpha} a^\dagger_{i\beta} |\mathrm{vac}\rangle \tag{4.34}$$

where $\langle \mathrm{vac}|\mathrm{vac}\rangle = 1$ and operators $a^\dagger$ and a satisfy the anticommutation relations:

$$[a^\dagger_i, a^\dagger_j]_+ = a^\dagger_i a^\dagger_j + a^\dagger_j a^\dagger_i = 0 \tag{4.35}$$

$$[a_i, a_j]_+ = 0 \tag{4.36}$$

$$[a^\dagger_i, a_j]_+ = \delta_{ij} \tag{4.37}$$

and their actions on the vacuum state is specified by:

$$a_i|\mathrm{vac}\rangle = 0, \quad \langle \mathrm{vac}|a^\dagger_i = 0 \tag{4.38}$$

The addition subscripts α and β appearing in Eq.(4.34) specify the spin state. Doubly occupied state i is represented by $a^\dagger_{i\alpha} a^\dagger_{i\beta}|\mathrm{vac}\rangle$.

A wavefunction taken as a Slater determinant can be used as the ansatz to solve the time-independent Schrödinger equation in the Born-Oppenheimer approximation. An ansatz can be represented in the parametrized form:

$$|\mathrm{CSF}\rangle(\boldsymbol{k}) = e^{\hat{k}}|\mathrm{CSF}\rangle \tag{4.39}$$

where the exponent of an anti-Hermitian operator $\hat{k}$ produces unitary transformations of the Slater determinant

$$\hat{k} = \sum_{i<j} k_{ij}(\hat{E}_{ij} - \hat{E}_{ji}), \quad \hat{E}_{ij} = a^\dagger_{i\alpha} a_{j\alpha} + a^\dagger_{i\beta} a_{j\beta}, \tag{4.40}$$

The Hartree–Fock (HF) function is a solution of the variational problem, where variations are performed by means of parameters $\boldsymbol{k}$ (for details see Ref.([28])):

$$\delta \langle \mathrm{CSF}(\boldsymbol{k}) \, |H| \, \mathrm{CSF}(\boldsymbol{k}) \rangle = 0 \tag{4.41}$$

The Hartree–Fock state $|\mathrm{HF}\rangle$ is thus a stationary state for this variational problem. There exist more complicated approximations, e.g. MCSCF wave-function approximation, which is a multi-configuration SCF approach, where instead of one Slater determinant, the linear combination of determinants is considered and taken as an ansatz to solve the Schrödinger equation (e.g. Ref.[28]).
The approximations are thus based on the choice of the reference state and how big an operator manifold we consider. If we take the reference state as a Hartree–Fock wave function and restrict the complete operator manifold to single excitations, we get the *random phase approximation* (RPA) Ref.[6, 3, 2].

We need to evaluate Eq.(4.28) in the basis of an operator manifold generated by number-conserving excitation and de-excitation operators, acting on some ground state. Let us consider as an example SCF ground-state function and the restricted manifold consists of the infinite set of single excitation and de-excitation operators.

$$\{\boldsymbol{q}^\dagger, \boldsymbol{q}\}$$

Then matrix, raw and column vector in Eq.(4.28) can be written as:

$$\begin{aligned} \langle\langle P^\dagger; Q \rangle\rangle_\omega &= \begin{bmatrix} (P|\tilde{\boldsymbol{q}}^\dagger) & (P|\tilde{\boldsymbol{q}}) \end{bmatrix} \times \\ &\times \begin{bmatrix} (\boldsymbol{q}^\dagger|\omega\hat{I} - \hat{H}_0|\tilde{\boldsymbol{q}}^\dagger) & (\boldsymbol{q}^\dagger|\omega\hat{I} - \hat{H}_0|\tilde{\boldsymbol{q}}) \\ (\boldsymbol{q}|\omega\hat{I} - \hat{H}_0|\tilde{\boldsymbol{q}}^\dagger) & (\boldsymbol{q}|\omega\hat{I} - \hat{H}_0|\tilde{\boldsymbol{q}}) \end{bmatrix}^{-1} \begin{bmatrix} (\boldsymbol{q}^\dagger|Q) \\ (\boldsymbol{q}|Q) \end{bmatrix} \end{aligned} \tag{4.42}$$

which can be written:

$$\langle\langle P^\dagger; Q \rangle\rangle_\omega = \begin{bmatrix} \tilde{\boldsymbol{P}} & -\tilde{\boldsymbol{P}} \end{bmatrix} \begin{bmatrix} \omega\boldsymbol{I} - \boldsymbol{A} & -\boldsymbol{B} \\ -\boldsymbol{B} & \omega\boldsymbol{I} - \boldsymbol{A} \end{bmatrix}^{-1} \begin{bmatrix} \boldsymbol{Q} \\ -\boldsymbol{Q} \end{bmatrix} \tag{4.43}$$

where:

$$\boldsymbol{P} = \{(P|\boldsymbol{q}^\dagger_\nu)\}, \; \boldsymbol{Q} = \{(Q|\boldsymbol{q}^\dagger_\nu)\}, \; \boldsymbol{A}_{\nu\nu'} = \{(\boldsymbol{q}^\dagger_\nu|\hat{H}|\boldsymbol{q}^\dagger_{\nu'})\}, \; \boldsymbol{B}_{\nu\nu'} = \{(\boldsymbol{q}_\nu|\hat{H}|\boldsymbol{q}^\dagger_{\nu'})\} \tag{4.44}$$

where subscript ν runs all over operators of the manifold. For more details and notation see Ref.[3].
The problem of finding the poles E_λ of the propagator reduces to solving the *non-Hermitian eigenvalue problem*:

$$\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} \\ \boldsymbol{Y} \end{bmatrix}_\lambda = E_\lambda \begin{bmatrix} \boldsymbol{1} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{1} \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} \\ \boldsymbol{Y} \end{bmatrix}_\lambda \tag{4.45}$$

we have also:

$$\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{bmatrix} \begin{bmatrix} \boldsymbol{Y} \\ \boldsymbol{Z} \end{bmatrix}_{-\lambda} = -E_\lambda \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \boldsymbol{Y} \\ \boldsymbol{Z} \end{bmatrix}_{-\lambda} \tag{4.46}$$

These equations give us the poles for the propagator, and the eigenvectors together with operator vectors give us *residues* — approximate transition moments.
To get the transition moments we need to get back to SOS kind of expression. For this we arrange the set of the eigenvectors $\begin{bmatrix} \boldsymbol{Z} \\ \boldsymbol{Y} \end{bmatrix}_\lambda$ into column vector $\begin{bmatrix} \boldsymbol{Z} \\ \boldsymbol{Y} \end{bmatrix}$, where each eigenvector should be normalized (see Ref.[3]) and write:

$$\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{Z} \end{bmatrix} = \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{Z} \end{bmatrix} \begin{bmatrix} \boldsymbol{E} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{E} \end{bmatrix} \tag{4.47}$$

By adding to the left and right side of this equation the energy-dependent terms we have:

$$\begin{aligned} &\begin{bmatrix} \omega\mathbf{1} - \boldsymbol{A} & -\boldsymbol{B} \\ -\boldsymbol{B} & \omega\mathbf{1} - \boldsymbol{A} \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{Z} \end{bmatrix} = \\ &= \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{Z} \end{bmatrix} \begin{bmatrix} \omega\mathbf{1} - \boldsymbol{E} & \mathbf{0} \\ \mathbf{0} & \omega\mathbf{1} + \boldsymbol{E} \end{bmatrix} \end{aligned} \tag{4.48}$$

From this we can get the inverse of the matrix from Eq.(4.43) (normalization condition should be used, see Ref.[3])

$$\begin{aligned} &\begin{bmatrix} \omega\mathbf{1} - \boldsymbol{A} & -\boldsymbol{B} \\ -\boldsymbol{B} & \omega\mathbf{1} - \boldsymbol{A} \end{bmatrix}^{-1} = \\ &= \begin{bmatrix} \boldsymbol{Z} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{Z} \end{bmatrix} \begin{bmatrix} \omega\mathbf{1} - \boldsymbol{E} & \mathbf{0} \\ \mathbf{0} & \omega\mathbf{1} + \boldsymbol{E} \end{bmatrix}^{-1} \begin{bmatrix} \tilde{\boldsymbol{Z}} & \tilde{\boldsymbol{Y}} \\ -\tilde{\boldsymbol{Y}} & -\tilde{\boldsymbol{Z}} \end{bmatrix} \end{aligned} \tag{4.49}$$

This matrix can be substituted in Eq.(4.43), and we get:

$$\begin{aligned} \langle\langle P; Q \rangle\rangle_E = &\begin{bmatrix} (P|\hat{\boldsymbol{q}}^\dagger) & (P|\hat{\boldsymbol{q}}) \end{bmatrix} \begin{bmatrix} \boldsymbol{Z} & \boldsymbol{Y} \\ \boldsymbol{Y} & \boldsymbol{Z} \end{bmatrix} \times \\ \times &\begin{bmatrix} \omega\mathbf{1} - \boldsymbol{E} & \mathbf{0} \\ \mathbf{0} & \omega\mathbf{1} + \boldsymbol{E} \end{bmatrix}^{-1} \begin{bmatrix} \hat{\boldsymbol{Z}} & \hat{\boldsymbol{Y}} \\ -\hat{\boldsymbol{Y}} & -\hat{\boldsymbol{Z}} \end{bmatrix} \begin{bmatrix} (\boldsymbol{q}^\dagger|Q) \\ (\boldsymbol{q}|Q) \end{bmatrix} \end{aligned} \tag{4.50}$$

To get the spectral representation this equation should be rewritten by introducing the excitation state vectors. For a state λ with excitation energy E_λ (as in Ref.[3]):

$$O_\lambda^+ = \begin{bmatrix} \tilde{\mathbf{q}}^\dagger & \tilde{\mathbf{q}} \end{bmatrix} \begin{bmatrix} \mathbf{Z} \\ \mathbf{Y} \end{bmatrix}_\lambda \tag{4.51}$$

$$O_\lambda = \begin{bmatrix} \tilde{\mathbf{q}}^\dagger & \tilde{\mathbf{q}} \end{bmatrix} \begin{bmatrix} \mathbf{Y} \\ \mathbf{Z} \end{bmatrix}_\lambda \tag{4.52}$$

so we get the SOS expression:

$$\langle\langle P; Q \rangle\rangle_\omega = \sum_\lambda \left[\frac{(P \mid O_\lambda^+)(O_\lambda^+ \mid Q)}{\omega - E_\lambda} - \frac{(P \mid O_\lambda)(O_\lambda \mid Q)}{\omega + E_\lambda} \right] \tag{4.53}$$

where transition moments are expressed in term of the infinite excitational manifold.

5 The problem of origin dependence in response theory

In physical theories special care should be taken regarding the origin independence of all observable values derived (see [16, 25, 26]). When we solve equations approximately it is desirable that all values we get in these approximations keep the property of origin independence.

In the previous subsections we considered a perturbation theory, approach in which we had an expansion in the strength of the perturbing field. Truncation of such an expansion gave us the linear response theory, the quadratic response theory and so forth. Each level of truncation should be investigated with respect to origin dependence. Moreover — we had the following approximations:

1. The approximated state wave-function and the excitation manifold were introduced.
2. Truncated basis sets are applied in practical computer calculations.

Each step should be physically reasonable.

Let us consider as an example the case of optical activity of the chiral medium - the *optical rotation.*

Chiral molecules (or a medium which is chiral because of the orientation of the molecules, which may be induced by applied magnetic or electric fields) scatter left- and right-circularly polarized light differently (see Fig.8). A linearly polarized light (also named as plane-polarized light) can be decomposed into a sum of two circularly polarized lights, left and right-circular components. When passing through the chiral medium, these components develop phase shift. As the result of this phase shift — the vector of the linear polarized vector becomes rotated, or, in other words, its plane of polarization is rotated.

The result of measurements of optical rotation is reported as the specific optical rotation $[\alpha]$, defined as:

$$[\alpha] = \frac{\alpha V}{ml} \tag{5.1}$$

where α is the rotation of the linearly polarized light, l is the optical path, m is the mass of the optically active sample and V is its volume.

The specific optical rotation is proportional to the trace of the so-called Rosenfeld tensor $\beta_{\alpha\beta}$, which is expressed in terms of the linear response function (see Refs.[24, 23]):

$$\beta_{\alpha\beta} = -\omega^{-1} G'_{\alpha\beta}(\omega) \tag{5.2}$$

$$G'_{\alpha\beta}(\omega) = -\omega \, \mathrm{Im}(\langle\langle \mu_\alpha; m_\beta \rangle\rangle_\omega) \tag{5.3}$$

The behavior of the trace of this tensor with respect to the translation of the origin should be tested (*e.g.* [26, 25]).

Let us take the mass and charge of the electron as 1 and -1, respectively (atomic units). The contribution $\boldsymbol{\mu}$ to the dipole moment is then $-\boldsymbol{r}$, and the magnetic moment $\boldsymbol{m}$ is $-\frac{1}{2}\boldsymbol{r} \times \boldsymbol{p}$. We now shift the origin with respect to which the position of the electron is defined by a vector $\boldsymbol{a}$. Noting that a shift leaves the momentum operator $\boldsymbol{p} = -i\nabla$ unchanged, the trace of G' changes by [26, 25]:

$$\mathrm{Tr}\langle\langle \boldsymbol{r} - \boldsymbol{a}; (\boldsymbol{r} - \boldsymbol{a}) \times \boldsymbol{p} \rangle\rangle_\omega = \mathrm{Tr}\langle\langle \boldsymbol{r}; \boldsymbol{r} \times \boldsymbol{p} \rangle\rangle_\omega - \mathrm{Tr}\langle\langle \boldsymbol{r}; \boldsymbol{a} \times \boldsymbol{p} \rangle\rangle_\omega \tag{5.4}$$

The last term can be written out component-wise as:

$$\begin{aligned}\mathrm{Tr}\langle\langle \boldsymbol{r}; \boldsymbol{a}\times\boldsymbol{p}\rangle\rangle_\omega &= a_x(\langle\langle r_z; p_y\rangle\rangle_\omega - \langle\langle r_y; p_z\rangle\rangle_\omega) + \\ &\quad a_y(\langle\langle r_x; p_z\rangle\rangle_\omega - \langle\langle r_z; p_x\rangle\rangle_\omega) + \\ &\quad a_z(\langle\langle r_x; p_y\rangle\rangle_\omega - \langle\langle r_y; p_x\rangle\rangle_\omega) \end{aligned} \tag{5.5}$$

If we take into account the equation-of-motion (4.22) for the dipole moment:

$$-\omega\langle\langle r_\alpha; r_\beta\rangle\rangle_\omega = -\langle 0\,|[r_\alpha, r_\beta]|\,0\rangle + \langle\langle r_\alpha, [r_\beta, H_0]\rangle\rangle_\omega \tag{5.6}$$

which is satisfied for the approximate wave functions HF, MCSCF and Kohn–Sham DFT, among others.

The unperturbed electronic Hamiltonian H_0 satisfies the standard commutator identity

$$[\boldsymbol{r}, H_0] = i\boldsymbol{p}$$

which also holds for the second-quantization representations of these operators for a complete basis.

Thus for the complete basis we can replace $\langle\langle r_\alpha; p_\beta\rangle\rangle_\omega$ in Eq.(5.5) with $i\omega\langle\langle r_\alpha; r_\beta\rangle\rangle_\omega$ and find that the "origin-dependent" last term of Eq.(5.4) vanishes.

Remark:
With the help of the commutator identities $[\boldsymbol{r}, H_0] = i\boldsymbol{p}$, $[r_\alpha, (\boldsymbol{r}\times\boldsymbol{p})_\alpha] = 0$ and the equation-of-motion (4.22) we can arrive at the equivalence of the so-called length- and velocity-gauge representations of the response function (e.g. Ref.[26]):

$$\mathrm{Im}(\mathrm{Tr}\langle\langle r_\alpha; (\boldsymbol{r}\times\boldsymbol{p})_\beta\rangle\rangle_\omega) = \frac{1}{\omega}\mathrm{Re}(\mathrm{Tr}\langle\langle p_\alpha; (\boldsymbol{r}\times\boldsymbol{p})_\beta\rangle\rangle_\omega) \tag{5.7}$$

This relation does not hold for the truncated basis. In principle, we can choose to use response functions in the velocity gauge (on the right) which are then origin independent even for the finite basis. Unfortunately, for a given truncated basis, a velocity-gauge based implementation does not perform as well as the length gauge, thus a length-gauge formulation is preferred, which is origin dependent for an incomplete basis, as Eq.(5.4) shows.

The approach from Ref. [27] (and references therein), which aims to overcome origin-dependence problems for finite basis sets, will be schematically reviewed here. The detailed review of this approach would require the introduction of some extra tools, thus only the outline of their approach will be presented here, without details.

The following steps are made to get response functions being origin independent, even for the finite basis sets, and with good convergence behavior with increasing of size of the basis set.

1. The so-called LAO — London atomic orbitals (or GIAO for gauge-including atomic orbitals) are used (Ref.[29]):

$$\chi_\mu^{\mathrm{LAO}}(\boldsymbol{A}_\mu, \boldsymbol{R}_\mu, \boldsymbol{r}) = e^{-i\boldsymbol{A}_\mu\cdot\boldsymbol{r}}\chi_\mu(\boldsymbol{r}-\boldsymbol{R}_\mu) \tag{5.8}$$

where the gauge of the magnetic vector potential is:

$$\boldsymbol{A}_\mu = \frac{1}{2}\boldsymbol{B} \times (\boldsymbol{R}_\mu - \boldsymbol{O}) \tag{5.9}$$

where subscript μ specifies the basis function, $\boldsymbol{R}_\mu$ is the position of the nucleus at which AO χ_μ is centered, $\boldsymbol{r}$ is an electronic coordinate, $\boldsymbol{O}$ is the so-called gauge origin and χ_μ is an ordinary atomic orbital basis function. This type of atomic orbitals were originally introduced by F. London [29].

2. The magnetically perturbed (time-independent) Hamiltonian in a gauge shown above is introduced.

3. The Hamiltonian and other operators can be expressed in the second-quantization formulation (*e.g.* [28]) in a basis set derived from LAOs.

4. The crucial point of the approach taken in Ref.[27] is to use instead of the one-electron (in second-quantization picture) magnetic dipole $\boldsymbol{m} = -\frac{1}{2}\boldsymbol{r} \times \boldsymbol{p}$ — the "effective" magnetic dipole derived as a minus the first derivative of the magnetic Hamiltonian in the second quantization picture. This "LAO" magnetic dipole operator $\boldsymbol{m}^{LAO}$ differs from the standard magnetic dipole, the most drastic feature is that it is a two-electron operator.

5. The justification of the introduction of such an 'effective' magnetic moment is that it was proved (Ref.[27]) that in the limit of a complete basis set — these two operators coincide.

6. The bonus for the introduction of a such magnetic moment is that the response functions defined for this operator, in the length gauge, are origin independent even for a finite basis.

6 Polarizable continuum model (PCM)

In this section we briefly review the case of a liquid solvent surrounding the molecule (the *solute*). This solution is then considered as a system: *"bath" + molecule*, and there are a plethora of different models which aim to describe the interaction of a molecule and the solvent. Usually the solvent is considered as a dielectric continuous medium with a dielectric constant ϵ.

The electric field of the molecule induces polarization on the solution, and the solution reacts back via a so-called *reaction* (electromagnetic) field. Thus the solute can be considered as being subjected to the reaction field produced by the polarized solution and its properties are modified.

Originally (see [30]), the solution was modeled in the following way: the molecule is surrounded by a spherical cavity, which excludes the solvent. Currently, in numerical studies, cavity is considered of a complex shape, which follows the shape of the molecule. The cavity is divided into the set of spheres, where each sphere is centered on an atom of the molecule or group of atoms. The radii of a sphere is specified by the atom or group it is assigned (usually it is of order of Van der Waals radius).

6.1 Electrostatic setup

The classical electrostatic problem is considered in Refs.[32, 31]. The Poisson equation inside the cavity is:

$$-\nabla^2 V(\boldsymbol{r}) = 4\pi\rho_M(\boldsymbol{r}) \tag{6.1}$$

where $V(\boldsymbol{r})$ is the total electrostatic potential generated by the solute, ρ_M is the charge density of the solute. In isotropic dielectric medium, outside the cavity, we have:

$$-\epsilon\nabla^2 V(\boldsymbol{r}) = 0 \tag{6.2}$$

The boundary conditions are:

$$V_e - V_i|_\Sigma = 0 \tag{6.3}$$

$$(\frac{\partial V}{\partial \boldsymbol{n}})_i - \epsilon(\frac{\partial V}{\partial \boldsymbol{n}})_i|_\Sigma = 0 \tag{6.4}$$

where Σ specifies the cavity surface, subscripts i and e define interior and exterior regions with respect to the cavity, $\frac{\partial}{\partial \boldsymbol{n}}$ is the directional derivative along the normal (with respect to the cavity surface) vector $\boldsymbol{n}$ pointing outward. These conditions ensures continuous behavior of the electrostatic potential and its gradient on Σ.

The solution to the above equations is sought in the integral form (Green function approach):

$$V(\boldsymbol{r}) = \int_C \frac{\rho_M(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\boldsymbol{dr}' + \int_\Sigma \frac{\sigma(\boldsymbol{s})}{|\boldsymbol{r}-\boldsymbol{s}|}\boldsymbol{ds} \tag{6.5}$$

where integral $\int_C \boldsymbol{dr}'$ specifies the volume integration inside the cavity (C) and integral $\int_\Sigma \boldsymbol{ds}$ specifies the surface integration on Σ. The surface charge density σ is due to polarization of the medium, and it is called the apparent (or screening) surface charge density. This potential automatically satisfies the Poisson equations, and we are left with the task of determining a surface charge density that satisfies the boundary conditions.

In the Ref.[33] it was shown that σ satisfies the following equation in the integral-operator form:

$$A \cdot \sigma = B \cdot V \tag{6.6}$$

where operator A is defined as:

$$\begin{aligned}
A &= (\frac{I}{2} - D_e)S_i + S_e(\frac{I}{2} + D_i^*) && (6.7)\\
(S_i \cdot u)(\boldsymbol{r}) &= \int_\Sigma G_i(\boldsymbol{r}, \boldsymbol{r}')u(\boldsymbol{r}')\boldsymbol{dr}' && (6.8)\\
G_i(\boldsymbol{r}, \boldsymbol{r}') &= \frac{1}{4\pi|\boldsymbol{r} - \boldsymbol{r}'|} && (6.9)\\
(D_i \cdot u)(\boldsymbol{r}) &= \int_\Sigma \frac{\partial G_i(\boldsymbol{r}, \boldsymbol{r}')}{\partial \boldsymbol{n}(\boldsymbol{r}')}u(\boldsymbol{r}')\boldsymbol{dr}' && (6.10)\\
(D_i^* \cdot u)(\boldsymbol{r}) &= \int_\Sigma \frac{\partial G_i(\boldsymbol{r}, \boldsymbol{r}')}{\partial \boldsymbol{n}(\boldsymbol{r})}u(\boldsymbol{r}')\boldsymbol{dr}' && (6.11)\\
(S_e \cdot u)(\boldsymbol{r}) &= \int_\Sigma G_e(\boldsymbol{r}, \boldsymbol{r}')u(\boldsymbol{r}')\boldsymbol{dr}' && (6.12)\\
G_e(\boldsymbol{r}, \boldsymbol{r}') &= \frac{1}{4\pi\epsilon|\boldsymbol{r} - \boldsymbol{r}'|} && (6.13)\\
(D_e \cdot u)(\boldsymbol{r}) &= \int_\Sigma \frac{\partial G_e(\boldsymbol{r}, \boldsymbol{r}')}{\partial \boldsymbol{n}(\boldsymbol{r}')}u(\boldsymbol{r}')\boldsymbol{dr}' && (6.14)
\end{aligned}$$

where $\boldsymbol{r} \in \Sigma$. The integro-differential operator B is defined by the equation:

$$(B \cdot V)(\boldsymbol{r}) = ((\frac{I}{2} + D_e) \cdot V)(\boldsymbol{r}) + (S_e \cdot \left(\frac{\partial V}{\partial \boldsymbol{n}}\right)_i)(\boldsymbol{r}) \tag{6.15}$$

where $\left(\frac{\partial V}{\partial \boldsymbol{n}}\right)_i$ is the normal coordinate (with respect to the surface of cavity) of the electric field in the interior region.

Eq.(6.6) is to be solved numerically, via the so-called boundary element method. In this method, the cavity surface is partitioned into K tesserae (mosaic pieces), of known area. On each tessera the charge density is considered to be constant. Equation (6.6) can be written in the matrix form, for the vector $[\sigma]$ of size K:

$$[A] \cdot [\sigma] = [B \cdot V] \tag{6.16}$$

The matrices are to be evaluated using the partition of Σ. The system of linear equations (6.16) is solved:

$$[\sigma] = [A]^{-1}[B \cdot V] \tag{6.17}$$

The vector $[\sigma]$ can be taken as the vector $[q]$ — the vector of charges on each tessera. The matrix equation (6.17) can be rewritten as:

$$[q] = [Q][V] \tag{6.18}$$

6.2 Quantum mechanical setup: with no time-dependent external perturbations

In the polarizable continuum model (PCM) the quantum-mechanical formulation is introduced by defining a free energy functional $G(|\psi\rangle)$ which is applied to the solute wavefunction. This functional incorporates interactions between the molecule and the *apparent charges* due to the solvent. In general form it is defined as:

$$G(|\psi\rangle) = \left\langle \psi \left| \hat{G} \right| \psi \right\rangle = \left\langle \psi \left| H_0 + \frac{1}{2}\hat{V}_\sigma \right| \psi \right\rangle \tag{6.19}$$

The operator $\hat{V}_\sigma$ is defined through electrostatic interaction between charge distribution of a molecule (electronic and nuclear) and apparent charges on the cavity surface Σ. For details see Ref.([31]).

7 The list of papers, included in the thesis, with short descriptions

I The use of Coulomb-attenuated methods for the calculation of electronic circular dichroism spectra,
Dmitry Shcherbin and Kenneth Ruud
Chemical Physics, Volume 349, Issues 1-3, 16 June 2008, Pages 234-243

In this paper, a benchmark computational study was performed, where we tested different parametrizations of the commonly used exchange-correlation functional Coulomb-attenuated B3LYP (CAM-B3LYP) on a level of the DFT (Density Functional Theory) with respect to the more accurate but at the same time more time-consuming CC2 and CCSD theories. In additional to benchmarking the excitation energies, we also explored the rotational strengths that determine the phenomenon of *circular dichroism*, which is the differential absorption of right- and left-polarized light by chiral medium. A set of chiral molecules was considered. As the result of the study we concluded that if we want to achieve good result for both properties of interest — excitation energies and rotatory strengths — we cannot find a CAM-B3LYP parametrization which gives both types of quantities right. The observation was made that it is possible to consider the lowest excited state as the reference state, which suggests a uniform shift of all excitational energies. In this case, some of the CAM-B3LYP functionals work well both for excitational energies and rotatory strengths.

II Analytic calculations of nonlinear mixed electric and magnetic frequency-dependent molecular properties using London atomic orbitals: Buckingham birefringence,
Dmitry Shcherbin, Andreas J. Thorvaldsen, Kenneth Ruud, Sonia Coriani and Antonio Rizzo
Phys. Chem. Chem. Phys., 2009, 11, 816-825

In Paper I, the property considered can be classified as *natural* circular dichroism, which means that we do not need to put the medium in some external field observe the effect, although the effect is only non-zero for molecules that are optically active, that is, chiral molecules. In Paper II the property of interest can be classified as electromagnetically induced. This means that without some specific external field the effect can not be observed, but once a field is present, all molecules will display this birefringence. The property we studied is referred to in the literature as *Buckingham birefringence* or EFGB — *electric field gradient-induced birefringence* . The optical activity is induced by the electric field gradient, and different components of the light field propagate differently in this medium, leading to an anisotropy in the refractive index.
In the study we also tested our new response code at the Hartree-Fock theory level, where London atomic orbitals (LAOs) were used in the calculation. In this LAO implementation — the basis set depends both on the external perturbations and the frequency. The study shows that the new implementation performs very well, meaning that basis set convergence is very fast in comparison with conventional basis sets.

In the paper we also reported and compared our results with available experimental data for the observables. An interesting feature of the EFGB measurements is that they allow us to calculate the quadruple moment of the molecule.

III Jones and magnetoelectric birefringence of pure substances A computational study, Antonio Rizzo, Dmitry Shcherbin and Kenneth Ruud
Canadian Journal of Chemistry, Volume 87, Number 10, 1 October 2009 , pp. 1352-1361(10)

Another induced birefringence is considered in this paper — the Jones birefringence. The anisotropy of the medium is in this case a result of the application of two external static fields, electric and magnetic, which are parallel to each other and perpendicular to the direction of light propagation. The anisotropy of the refractive index is thus bilinear with respect to these fields. In the study we tested the implementation of the PCM theory in the context of the TD-DFT level of theory. PCM results were compared with respect to experimental data and with respect to an earlier non-PCM response implementation.

IV Gauge-origin independent calculations of Jones birefringence,
Dmitry Shcherbin, Andreas J. Thorvaldsen, Dan Jonsson and Kenneth Ruud

In this paper the new response theory implementation is tested. As in the Paper II LAO orbitals are used to get origin independent results for the Jones birefringence. One of the advantages of using these basis functions is that we get physically meaningful results even for small basis-sets (i.e. the results are indepenent of the choice of gauge origin).Another advantage is that we obtain better basis-set convergence for the LAO basis set in comparison to conventional basis sets.

8 Acknowledgements

I would like to thank my supervisor Prof. Kenneth Ruud, for his advice, patience and encouragement in the course of the work leading to this thesis.

I would like to thank my co-authors Andreas J. Thorvaldsen, Antonio Rizzo, Sonia Coriani and Dan Jonsson, I have learnt a lot from them during our work on our papers.

I would like to thank all the people in CTCC who make this place friendly and comfortable.

I am very grateful to my family, which became much bigger during these years, for support and happiness.

References

[1] L D Barron and C G Gray 1973 J. Phys. A: Math. Nucl. Gen. 6 59

[2] E. Dalgaard, Quadratic response functions within the time-dependent Hartree–Fock approximation, Phys. Rev. A 26, 4252 (1982)

[3] J.Oddershede, P.Jørgensen and D.L.Yeager, Computer Physics Reports 2 (1984) 33-92

[4] D.N.Zubarev, Double-time green functions in statistical physics, Soviet Physics Uspekhi, vol. 3, 3

[5] Esper Dalgaard, Timedependent multiconfigurational HartreeFock theory, J. Chem. Phys. 72, 816 (1980)

[6] J.Linderberg, Y. Öhrn, Propagators in quantum chemistry, Academic Press, London 1973.

[7] U. Fano, Description of States in Quantum Mechanics by Density Matrix and Operator Techniques, Rev. Mod. Phys. 29, 7493 (1957)

[8] P.-O. Löwdin, Phys. Rev. A 139 (1967) 357

[9] O. Goscinski and B. Lukman, Moment-conserving decoupling of green functions via pade approximants, Chemical Physics Letters Volume 7, Issue 6, 15 December 1970, Pages 573-576

[10] H. Primas, Generalized Perturbation Theory in Operator Form Rev.Mod. Phys. vol.35, N2, 710-12, 1963

[11] J. Frenkel, Wave Mechanics, Advanced General Theory (Clarendon, Oxford, 1935)

[12] P. W. Langhoff, S. T. Epstein, and M. Karplus, Aspects of Time-Dependent Perturbation Theory, Rev. Mod. Phys. 44, 602 (1972).

[13] H. C. Van De Hulst , Light Scattering by Small Particles, Dover Publications, 1981

[14] Mishchenko, M. I., L. D. Travis, and A. A. Lacis (2002): Scattering, Absorption, and Emission of Light by Small Particles, Cambridge University Press, Cambridge.

[15] L. Barron, Molecular Light Scattering and Opitical Activity, Cambridge University Press, 2004

[16] R. E. Raab and O. L. de Lange, Multipole Theory in Electromagnetism, Oxford University Press, 2004

[17] Gbor Horvth, Andrs Barta, Istvn Pomozi, Bence Suhai1, Ramn Hegeds, Susanne kesson, Benno Meyer-Rochow and Rdiger Wehner, On the trail of Vikings with polarized skylight: experimental study of the atmospheric optical prerequisites allowing polarimetric navigation by Viking seafarers, Phil. Trans. R. Soc. B 12 March 2011 vol. 366 no. 1565 772-782

[18] A D Buckingham and J A Pople, Theoretical Studies of the Kerr Effect I: Deviations from a Linear Polarization Law, 1955 Proc. Phys. Soc. A 68 905

[19] G. Russakoff, A derivation of the macroscopic Maxwell equations, Am. J. Phys. 38, 1188 (1970)

[20] Cohen-Tannoudji, Claude; Bernard Diu, Frank Laloe (1977). Quantum Mechanics (Volume One). Paris: Wiley. pp. 312314.

[21] R. Kubo, Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems, J. Phys. Soc. Jpn. 12 (1957), pp. 570586

[22] O. Christiansen, P. Jørgensen and C. Hättig, Int. J Quant. Chem. 68 (1998), p. 1.

[23] A. Rizzo, S. Coriani "Birefringences: A challenge for both Theory and Experiment " Adv. Quant. Chem., 50 143-184 (2005)

[24] M. Pecul, K. Ruud The Ab Initio Calculation of Optical Rotation and Electronic Circular Dichroism, Adv. Quantum. Chem., 50 185 (2005)

[25] T.D. Crawford, Ab Initio Calculation of Molecular Chiroptical Properties, Theor. Chem. Acc. 115, 227-245 (2006).

[26] Thomas Bondo Pedersen, Henrik Koch, Linus Boman, Alfredo M. J. Sanchez de Meras, Origin invariant calculation of optical rotation without recourse to London orbitals, Chemical Physics Letters, Volume 393, Issues 4-6, 1 August 2004, Pages 319-326

[27] Keld L. Bak, Aage E. Hansen, Kenneth Ruud, Trygve Helgaker, Jeppe Olsen and Poul Jørgensen, Ab initio calculation of electronic circular dichroism for trans-cyclooctene using London atomic orbitals, Theoretica Chimica Acta, Volume 90, Numbers 5-6, 441-458

[28] T. Helgaker, P. Jørgensen, J. Olsen: Molecular electronic-structure theory Wiley, New York, 2000. 938 pp

[29] F. London, The quantic theory of inter-atomic currents in aromatic combinations, J. Phys. Radium, 1937, 8, 397.

[30] Onsager, L. J. Am. Chem. Soc. 1936, 58, 1486

[31] Roberto Cammi, Luca Frediani, Benedetta Mennucci, Jacopo Tomasi, Kenneth Ruud, and Kurt V. Mikkelsen, A second-order, quadratically convergent multiconfigurational self-consistent field polarizable continuum model for equilibrium and nonequilibrium solvation, J. Chem. Phys. 117, 13 (2002)

[32] B. Mennucci, E. Cancés and J. Tomasi, Evaluation of Solvent Effects in Isotropic and Anisotropic Dielectrics and in Ionic Solutions with a Unified Integral Equation Method: Theoretical Bases, Computational Implementation, and Numerical Applications, J. Phys. Chem. B, 1997, 101 (49), pp 1050610517

[33] E. Cancés and B. Mennucci, New applications of integral equations methods for solvation continuum models: ionic solutions and liquid crystals, J. Math. Chem. 23, 309 (1998)

ISBN xxx-xx-xxxx-xxx-x