From classical to quantum optical dispersion, after Bohr
Initial approach

Focus of interest:

- Different ways in which optical phenomena became intimately connected to certain models of matter at the beginning of the XX century.

- Difficulties from combining a picture of matter with oscillating electrons and a picture of matter of rotating electrons, in interaction with light. Profound tensions in the coexistence of both quantum and classical hypotheses. Optical dispersion a special paradigmatic example in this sense.

Dissertation’s outline:

Mechanical and electromagnetic models, particles oscillating with ether

1870.

1906. Drude’s classical synthesis

1913. Bohr

Debye-Sommerfeld model

1921. Quantum optical dispersion

HQ3 talk
Outline

1. Drude’s 1906 classical theory of optical dispersion.

2. Bohr’s 1913 atom and the building of molecules.

3. Debye-Sommerfeld’s model of $\text{H}_2$ molecule and optical dispersion.

What is optical dispersion?

Normal dispersion

Anomalous dispersion, discovered in the 1870s

Kundt, 1871, by means of crossed prisms

At anomalous dispersion frequencies, light was absorbed!!
Drude’s classical picture, 1906

Elastically-bound electrons, vibrating at proper frequencies $\nu_s$. Vibrations of charges = polarization.

1. Light disturbs proper vibrations of electrons and set them in motion at frequency $\nu$.
2. Charges reemit radiation of frequency of light.
3. Outgoing radiation = interference of primary and reemitted radiation
Optics and electrons, 1906

\[ n^2 = 1 + \sum_s \frac{\theta_h}{1 - \frac{\tau_h}{\tau^2}} \]

\( \tau_h \) are the proper frequencies

![Graph showing anomalous dispersion and normal dispersion](image)

Charged particles \( \rightarrow \) electrons. Number of "dispersion electrons" (characterized by e/m) \( \rightarrow \) number of valence electrons

\[ \theta_h = 4\pi N_h \frac{e^2}{m_h} \tau_h \]

\( N_s \) is the number of "dispersion electrons"

- **Remarkable discrepancies**, Wood (1904), vapor of sodium, \( N_{\text{s exp}} \ 4 \cdot 10^{12}; N_{\text{drude}} \ 2 \cdot 10^{17} \)
- **Small discrepancies**, Koch (1912), Hydrogen \( H_2 \), \( \lambda = 92.5 \) nm: \( N_{\text{s exp}} = 0.75N_{s \text{Drude}} \)

What about the constitution of matter we can know from optical dispersion experiments?

1. Good description of data \( \rightarrow \) Optical dispersion as a support of a model of atom with oscillating electrons.

2. Number of "dispersion electrons" \( \rightarrow \) discrepancies with valence electrons.
Niels Bohr’s model of atom, 1913

Niels Bohr (1885-1962)
Bohr molecule, 1913

How many electrons?

The actual number of electrons in a neutral atom (...) is equal to the number which indicates the position of the corresponding element in the series of elements arranged in order of increasing atomic weight. (Bohr, 1913II, 477)

Stability?

The stability (...) is secured through the introduction of the hypothesis of the universal constancy of the angular momentum of the electrons. (Bohr, 1913II, 480)

Ordinary mechanics can be used to calculate the vibrations of the electrons perpendicular to the plane of the ring - contrary to the case of vibrations in the plane of the ring. In addition it will be shown later that the assumption seems to be in agreement with experiments on dispersion. (Bohr, 1913II: 482).
Bohr optical dispersion, 1913

Optical dispersion not a quantum phenomena, contrary to emission of light?

The objection as to the emission of the radiation in quanta will not have reference to the calculations in question –coronal spectrum–, if we assume that we are not dealing with a true emission but only with a scattering of radiation. (Bohr, 1913I, 23).

Model of hydrogen molecule $H_2$ (Bohr, 1913III):

\[ v_1 = \frac{E}{h} \]

\[ v_1 \text{ (quantum)} = 3.7 \times 10^{15} \text{ 1/sec} \]

\[ v_2 \text{ (mechanics)} = 3.8 \times 10^{15} \text{ 1/sec} \]

\[ v_{\text{disp}} \text{ (exp)} = 3.5 \times 10^{15} \text{ 1/sec} \]

\[ v_{\text{disp}} \approx v_2 \approx v_1 !! \]

However, for Helium, $v_{\text{disp}} \approx v_1 \approx 3 \times v_2$!!!! This could explain disagreements regarding the number of “dispersion electrons”.
Debye, Sommerfeld and Davisson

Arnold Sommerfeld (1868-1951), Annie Schrödinger and Peter Debye (1884-1966) in Zürich 1926.

Clinton Davisson (1881-1958)
Debye, 1915
“The constitution of hydrogen molecule”

Model of hydrogen molecule $H_2$, already proposed by Bohr:

"A connection was missing between the required quasi-elastically bound electrons—Drude’s theory— and the electrons in rotatory motion—Bohr’s model. “ (Debye, 1915:1)

"The hydrogen atom should look like that—Bohr’s model,—only this can yield the known series spectrum. In contrast, we make use of the diatomic hydrogen molecule for dispersion measurements. This model also appears in Bohr“. (Debye, 1915:2)
Debye, 1915
“The constitution of hydrogen molecule”

1. Quantum restriction:

\[ ma^2 \omega_{orb} = \frac{h}{2\pi} \]

1. Mechanical procedure: Perturbation of orbits on the basis of a planetary model. Assumption: such perturbations of orbits can emit radiation, according to classical electrodynamics.

\[ v_2 = 0.56 \quad \omega_{orb} \]

\[ v_3 = 1.41 \quad \omega_{orb} \]

New resonance frequencies \( v_2, v_3, v_4 \) are mechanical frequencies!
Sommerfeld, 1915

Sommerfeld’s extension of Debye’s model to any molecule with axial symmetry. More accurate analysis of possible contradictions:

1. Debye’s model as an example of compatibility between quantum and mechanics.

2. Contradictions regarding electrodynamics: stationary orbits could not radiate.

How to solve the contradiction?

„But we know from Bohr’s theory of spectral lines that the emission of atoms, and in particular that of monatomic molecules, in no way takes place according to the laws of mechanics, which is taken here as a basis. Thus our dispersion formula will only be valid at an adequate distance from the emission and absorption lines and for normal dispersion. How one should approach the anomalous dispersion and the related electron damping remains entirely obscure“. (Sommerfeld, 1915:577)
“In this way one methodological contradiction is also solved, which seemed formerly to misrepresent the quantum theory of atoms on the one side, and the quantum theory of molecules on the other. Of electron orbits in the atom (spectral theory) it is said that the orbits are determined by quantum laws and do not radiate. In contrast, of the electron motions in molecules (dispersion theory) it is claimed that only the natural orbits of electrons are determined by quantum laws and do not radiate; the orbits altered by light waves act in accordance with laws of mechanics and give out emissions. Does this varied treatment of atoms and molecules lead to a contradiction? We claim: “Nein!”” (Sommerfeld, 1917: 502)

New definition of “stationary states“:

- **Angular momentum is not conserved.**

- **Adiabatic principle**: All infinitely slow perturbations of orbits are „new stationary states“, referred to the same quantum state.

- From one to another „new stationary states“, emission!
Dispersion electrons and anisotropy

Approximation for infrared region = Drude’s formula.
- New resonance frequencies, due to oscillations of orbits, not electrons:

\[ n^2 = 1 + \sum_s \frac{\vartheta_h}{1 - \frac{\tau_h^2}{\tau^2}} \]

But!! The optical parameter related to the dispersion electrons depended on the anisotropy of the molecule, through the parameter \( C_h \). This explained experimental disagreements observed in the case of \( \text{H}_2 \):

\[ \vartheta_h = 4\pi N_h \frac{e^2}{m_h} \tau_h \rightarrow \vartheta_h = 4\pi C_h N_h \frac{e^2}{m_h} \tau_h \]

Experimental agreement was a support for this \( \text{H}_2 \)-model and Debye-Sommerfeld’s approach, generally accepted as the **Debye-Sommerfeld model**.

Perturbation method applied to \( \text{H}_2 \) extended in 1916 to the Faraday effect.
Debye-Sommerfeld approach

Necessity of making compatible a physical picture of oscillations and a picture of rotating electrons, in order to make compatible spectral results and optical dispersion. Translation of electron oscillations into orbit oscillations.

Contradictions regarding emission of light and Bohr’s “stationary states”

- Modification of certain basic Bohr’s assumptions and sharp distinction between treatment of atoms and of molecules.
- Shift of the problem: from “Optical phenomenon” in Drude’s “Textbook of optics” (1906) to “Phenomenon of Molecular Models” in Reiche’s textbook “The quantum theory” (1920). Agreement with experimental data on optical dispersion depends on building the most satisfactory mechanical model of molecules. No mention of mechanism of light-matter interaction.
Bohr’s atom model can in no way be reconciled with the fundamental assumptions of Lorentz’s electron theory. We have to make our choice between these two theories. (Oseen, 1915: 405)
Bohr, in a withdrawn paper for Philosophical Magazine, 1915:

Experiments...show that characteristic frequencies -of anomalous dispersion- coincide with the frequencies of the lines in the...spectra...[T]hese frequencies correspond with transitions between the normal states of the atom...On this view we must consequently assume that the dispersion...depends on the same mechanism as the transition between different stationary states, and that it cannot be calculated by application of ordinary electrodynamics from the configuration and motions of the electrons in these states.
Stern & Volmer, 1919: Fluorescence

How to explain in quantum terms the intensity decay of radiated energy in fluorescence?

\[ E = E_0 e^{-\frac{t}{\tau}} \]

They introduced the following analogy:

N classical resonators with mean energy \( h \nu_s \) and decay time \( \tau \):

\[ \rightarrow \]

N resonators in quantum state b, only \( N \exp \left(-\frac{t}{\tau} \right) \) move to state a.

\[ E_b - E_a = h \nu_s \]

Correspondence principle, Einstein 1916

Reorienting the question

If one does not have a monochromatic resonator, but instead an orbiting electron, then the above statement—an analogy between classical and quantum resonators—is not immediately transferable since in the classical system the frequencies change with energy, but not in the quantum system. That we obtain the same order of magnitude for with this analogy proves the approximate validity of the classical dispersion theory. (Stern and Volmer, 1919: 187)


1921. Rudolf Ladenburg’s interpretation of dispersion electrons in terms of probability transitions from different quantum states, on the basis of Stern&Volmer analogy.

New approach: resonance frequencies = spectral frequencies + correspondence principle and probabilities of transition ➔ counting dispersion electrons.
Final remarks

• Necessity of maintaining a physical picture of oscillators interacting with light (from classical physics) and putting it together with a physical picture of rotating electrons in Bohr’s model of atoms and molecules.

• Both interpretations solved the problem of dispersion electrons in different ways. But Debye-Sommerfeld’s model showed conceptual contradictions with basic quantum assumptions of Bohr’s model regarding light-matter interaction, as being at the border between classical and quantum approaches.