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The Physical Origin of Anomalous Scattering

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THE PHYSICAL ORIGIN OF ANOMALOUS SCATTERING

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Owing to the availability of synchrotron radiation, anomalous scattering of X-rays plays an increasing role in crystallography. This makes full understanding of the underlying principles necessary.

The first part of the article explains anomalous scattering in terms of the classical theory of scattering by a damped oscillator. The damping accounts for the action of the emitted radiation on the oscillator itself. It causes a phase shift with respect to the motion of an undamped oscillator. This phase shift is the characteristic of anomalous scattering and is represented by adding an imaginary component to the real scattering factor. The relations to the macroscopic index of refraction and the absorption coefficient are discussed. To bridge the gap between classical and quantum theory, the harmonic oscillator model is explained in terms of atomic wave functions and their deformation under influence of the electric field.

The nonrelativistic quantum theoretical treatment of X-ray scattering is based on perturbation theory whereby use is made of Feynman-type diagrams and their mathematical translations. The origin of Thomson and Rayleigh scattering are given. The second one is characterized by virtual transitions to intermediate states. When the incident radiation corresponds with an absorption edge, the virtual transitions become real ones and decay of the intermediate state sets in. This decay leads to a phase shift of the probability amplitude of the path, the quantum mechanical equivalent of the scattering factor.

The relation between the position of the target and the phase of the scattered beam is a matter of convention. This convention also dictates the sign of the phase shift mentioned above. Mathematical tools and detailed derivations are given in an appendix.

Keywords: Anomalous scattering; Quantum theory; Scattering

CONTENTS

1. INTRODUCTION 96

2. CLASSICAL THEORY OF SCATTERING 98

2.1. Introduction 98

2.2. Emission of Radiation by a Charged Oscillator 104

2.3. Scattering by a One-electron Atom 108

2.4. Scattering by a Molecule 109

2.5. Anomalous Scattering and Polarity 110

2.6. Wave Scattered by a Thin Slab of
Charged Particles 112

2.7. Refractive Index 116

2.8. Absorption and the Optical Theorem 119

2.9. Some Atomic Quantum Theory 121

3. QUANTUM THEORY OF SCATTERING 124

3.1. Introduction 124

3.2. Quantum Mechanical Description of the
Interacting Systems 125

3.3. Time Dependence of the Interacting System 131

3.4. Perturbation Theory 133

3.5. Interaction Between X-rays and Matter 135

3.6. Scattering 141

3.7. Scattering Factor 150

References 156

4. APPENDICES 157

4.1. The Dirac Delta Function and Related
Mathematical Identities 157

4.2. Fields from Charges and Currents 162

4.3. Energy Levels of Interacting Systems 169

4.4. Elementary Processes and Matrix Terms 178

Subject Index 184

1. INTRODUCTION

Soon after the discovery of X-ray diffraction, the basic mechanism of the scattering of X-rays by electrons could be understood on the basis

of the electron theory of Lorentz. This theory was able to explain dispersion and the effects that have to be taken into account when the frequency of the X-rays is close to one of the resonance frequencies of the scattering system, i.e. anomalous dispersion.

The term anomalous scattering suggests that we are dealing with an abnormal phenomenon. This is not true at all: the obvious fact that a plane wave of X-rays gets weaker when it passes through matter is accounted for by 'anomalous scattering'. Immediately when we take interaction between light and matter into account, it shows up. However, since both von Laue and Bragg were able to account for the most important aspects of X-ray diffraction by crystals without going into the nature of this interaction, it did not receive much attention for a long time.

In 1930 Koster *et al.* [1] showed that anomalous scattering allows the determination of the polarity of a crystal and twenty years later Bijvoet *et al.* [2] were able to determine the absolute configuration of enantiomorphs by using the small differences in intensity between reflection and counter reflection that are due to anomalous scattering.

Since anomalous scattering has only appreciable values close to the absorption edge of a scattering system, it did not play a very large role in X-ray diffraction as long as only a limited number of wavelengths were available.

Synchrotron radiation has changed this situation drastically and anomalous scattering has fulfilled the promise to be a major tool in synchrotron radiation studies. This fact makes it desirable, if not mandatory, that the basis or physical origin of anomalous scattering is well understood by the main body of crystallographers. In the present situation, unfortunately, the various concepts that play a role in the scattering of X-rays by atoms or molecules are inundated by large amounts of mathematics that allows only a limited number of experts to grasp the main ideas. In fact, the absence of a sound knowledge of the origin of anomalous scattering made it possible for a contribution at the Kyoto meeting of the IUCr [3] (1972) that claimed an error in the existing theory, to cause such a havoc among the people determining the absolute configuration of compounds. Since then the basic features have been amply discussed at conferences, in books and in articles [4–6]. Nevertheless the complicated physics of the scattering process has

made access to the field and understanding of the subtle features difficult.

The present article intends to show the main line of reasoning that leads to anomalous scattering. Most parts of the treatment can be found in textbooks; collecting it in a single article and keeping the level of required knowledge as low as possible should make the effort worthwhile. One of the reasons for the confusion in the field is the multitude of concepts involved. It is good to keep in mind the following statement of an anonymous author: "Scientific knowledge grows like the accumulation of bric-a-brac in a vast and disorderly closet in a house kept by a sloven. Few are the attempts at ridding the closet of rusty or obsolete gear, at throwing out redundant equipment, at putting things in order. For example, spurious distinctions are still made between reflection, refraction, scattering, interference, and diffraction despite centuries of accumulated knowledge about the nature of light and matter".

In Chapter 2 the article will treat the classical theory of X-ray scattering in order to introduce the basic concepts of harmonic motion and damping in scattering by atomic systems. A number of the concepts used do not fit in present day atomic theory, so an addendum to this chapter introduces some quantum concepts that illuminates the basic ideas of the classical theory. Chapter 3 presents the quantum mechanical treatment of both Thomson and Rayleigh scattering and it will be shown that the latter contains the origin of damping. Where detailed derivations tend to fragment the line of reasoning, much material was moved to the appendix, given as last chapter.

2. CLASSICAL THEORY OF SCATTERING

2.1. Introduction

In the present chapter we start with the well-known theory of scattering of electromagnetic radiation by charged particles. The alternating electric field causes these particles to oscillate. The oscillating particles, in turn, radiate. The phase relation between the incident and the emitted radiation plays an important role in our discussion. The much smaller magnetic effects are neglected.

2.1.1. Motion of a Charged Particle in an External Electromagnetic Field – Response Function

A particle with mass m and charge q is placed at the origin. It is tied to its rest position by an harmonic force $-\mathbf{g}\mathbf{r}$. For future purposes we replace the force constant g by $m\omega_s^2$, leading to a restoring force

$$-m\omega_s^2\mathbf{r} \quad (2.1)$$

The particle is irradiated by an electromagnetic wave coming from an external source. The electric component is:

$$\mathbf{E} = \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_0 \cdot \mathbf{r})} \quad (2.2)$$

of which only the real part is implied. The wave vector \mathbf{k} has the direction of the wave while its magnitude is inversely proportional to the wavelength: $|\mathbf{k}| = 2\pi/\lambda$. The ratio of the angular frequency ω_0 and the magnitude of the wave vector \mathbf{k} is given by the velocity of light:

$$c = \frac{\omega_0}{|\mathbf{k}_0|} \quad (2.3)$$

The field exerts a force $q\mathbf{E}$ on the particle. Finally there is a damping force

$$-\gamma m \dot{\mathbf{r}} \quad (2.4)$$

The mass is included for practical purposes.

Newton's law relates these forces to acceleration according to

$$-m\omega_s^2\mathbf{r} + q\mathbf{E} - \gamma m \dot{\mathbf{r}} = \mathbf{F} = m\ddot{\mathbf{r}} \quad (2.5)$$

We assume that the result is a steady oscillation with the frequency of the external field:

$$\mathbf{r} = \mathbf{r}_0 e^{i\omega_0 t} \quad (2.6)$$

Substituting (2.2) and (2.6) in (2.5) yields for \mathbf{r}_0

$$\mathbf{r}_0 = \frac{q}{m(\omega_s^2 - \omega_0^2 + i\gamma\omega_0)} \mathbf{E}_0 \quad (2.7)$$

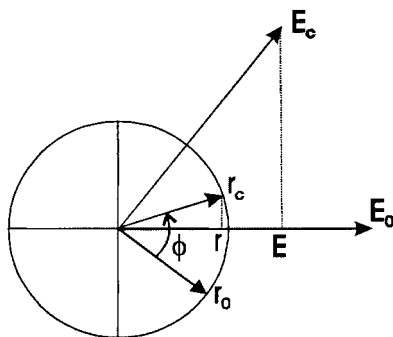


FIGURE 1 Argand diagram showing the electric field \mathbf{E} and the displacement of the charged particle \mathbf{r} along the horizontal axis as projections of the rotating vectors \mathbf{E}_c and \mathbf{r}_c respectively. The angles are defined in the text.

It is clear from this equation that when we choose \mathbf{E}_0 to be real, \mathbf{r}_0 has to be complex. In general the particle does not move in phase with the electric wave. The phase relation between the two can be shown in an *Argand* diagram. Along the horizontal axis we find the real value, while the imaginary value is displayed along the vertical axis. Both the real and the imaginary components can be vectors in three-dimensional space, such as fields and displacements.

In Figure 1 the electric field \mathbf{E} is given by a projection of a vector \mathbf{E}_c on the horizontal axis. The angle between \mathbf{E}_c and \mathbf{E}_0 , the latter chosen along the horizontal axis, is given by the phase angle of \mathbf{E}_c , $\phi(t) = \omega_0 t$. With time progressing, \mathbf{E}_c rotates counter clockwise with constant angular velocity. \mathbf{r} can be represented as the projection of \mathbf{r}_c on the horizontal axis, where the angle between \mathbf{r}_c and \mathbf{r}_0 is also given by $\phi(t)$. Expression (2.7) gives the relation between \mathbf{E}_0 and \mathbf{r}_0 , the so-called *response function* R .

$$R = \frac{q}{m(\omega_s^2 - \omega_0^2 + i\gamma\omega_0)}. \quad (2.8)$$

When the incident field has a vanishing frequency a positively charged, bonded particle moves in phase with the field. When the particle is free, i.e. when the harmonic force is absent and no friction occurs, i.e. $\omega_s = 0$, $\gamma = 0$, the displacement of the particle has a phase opposite to the field.

This shift of the phase angle can easily be demonstrated with attaching three identical particles to the same horizontal bar with different lengths of string, making three pendulums with different natural frequencies. When one of the pendulums is excited, coupling via the bar imparts the motion to the other two. This takes the place of driving by an external electromagnetic field. The longer pendulum has a lower natural frequency (is 'bonded' weaker) than the excited one, hence it moves with opposite phase, while the shorter one will be in phase with it.

At high driving frequencies, commonly the case in X-ray diffraction, the effect of bonding becomes negligible and the phase becomes more or less the phase of a free particle, opposite to the phase of the EM-field.

At lower frequencies, the phase depends on the sign of γ , which is positive. This follows from general reasoning. Consider the oscillating charge after removal of the external electric field. Owing to inertia, the oscillation will continue for some time. Since the oscillating charge will emit radiation, the energy of which has to come from the oscillating system, the amplitude of the oscillator will decrease continuously.

Newton's law for the decaying oscillator reads as follows:

$$-m\omega_s^2 \mathbf{r} - \gamma m \dot{\mathbf{r}} = m \ddot{\mathbf{r}}$$

Assuming the damping to be small we get

$$-\omega_s^2 \mathbf{r}_0 e^{i\omega t} - \gamma i \omega \mathbf{r}_0 e^{i\omega t} = -\omega^2 \mathbf{r}_0 e^{i\omega t}$$

or

$$\omega^2 - i\gamma\omega - \omega_s^2 = 0$$

The solutions are:

$$\omega = \frac{i\gamma \pm \sqrt{-\gamma^2 + 4\omega_s^2}}{2} \quad (2.9)$$

With $\gamma \ll 2\omega_s$, we get $\omega = (i\gamma \pm 2\omega_s)/2$ and

$$\mathbf{r} = \mathbf{r}_0 e^{i\omega t} = \mathbf{r}_0 e^{\pm i\omega_s t} e^{-\gamma t/2} \quad (2.10)$$

Conclusion: for the oscillation to decay, γ has to be positive.

In Appendix 4.2.2. we calculate the value of γ from the intensity of the emitted radiation.

2.1.2. Dispersion Relations, First Encounter

There is a remarkable and most useful relation between the real and imaginary parts of the response function: if the real part is known at all frequencies, then the imaginary part can be determined, and conversely. The proof of this relation requires some advanced mathematics. Fortunately it is easy to show for a slightly modified form of (2.7). It is clear that the response function has only appreciable values where $\omega_0 \cong \omega_s$; hence its main characteristics remain when we replace ω_0 by ω_s everywhere, except where it occurs in the factor $(\omega_0 - \omega_s)$. We then get the new response function

$$R'(\omega_0) = \frac{q/m}{2\omega_s[(\omega_s - \omega_0) + i\gamma/2]} \quad (2.11)$$

In Figure 2 we show both the original and the modified response function.

Separating $R'(\omega_0)$ into real and imaginary components gives

$$R'(\omega_0) = \frac{q}{m} \left[\frac{2(\omega_s - \omega_0)}{\omega_s[4(\omega_s - \omega_0)^2 + \gamma^2]} + i \frac{-\gamma}{\omega_s[4(\omega_s - \omega_0)^2 + \gamma^2]} \right] \quad (2.12)$$

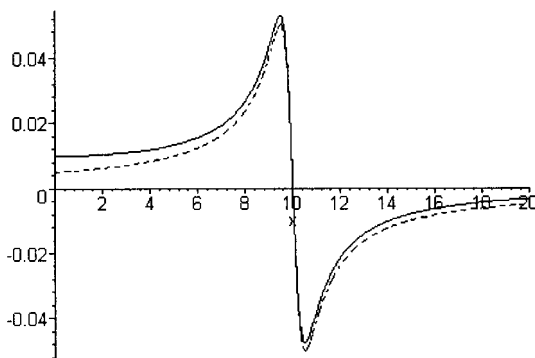


FIGURE 2 The real part of the original (solid) and the modified (dashed) response function in arbitrary units.

We shall now show that the value of the real part of the modified response function at some value ω' , $R'_r(\omega')$, is related to the values that the imaginary part of it, R'_i , takes for all frequencies ω from $-\infty$ to ∞ .

Consider $R_i(\omega)/(\omega' - \omega)$. When we integrate this function over ω , we encounter a singularity when $\omega' - \omega = 0$. We now integrate over the whole ω -range except for an infinite small region symmetrically about the singularity. In this narrow range $R_i(\omega_0)$ can be assumed to be constant. Within this narrow range the integrand is antisymmetric and the integral over that range vanishes accordingly. This procedure is known as taking Cauchy's *principal value* of the integral, represented by P. (See Section 4.1 for a discussion)

$$P \int_{-\infty}^{\infty} \frac{R'_i(\omega)}{(\omega' - \omega)} d\omega = \frac{q}{m} P \int_{-\infty}^{\infty} \frac{-\gamma}{4\omega_s[(\omega_s - \omega)^2 + \gamma^2/4](\omega' - \omega)} d\omega \quad (2.13)$$

The integral at the RHS is a standard one. Since we do not have to worry about the singularity anymore we can use the primitive of the integrand and evaluate it at the limits. The result is:

$$P \int_{-\infty}^{\infty} \frac{R'_i(\omega)}{\omega' - \omega} d\omega = \frac{q}{m\omega_s} \frac{2\pi(\omega_s - \omega')}{4(\omega_s - \omega')^2 + \gamma^2} \quad (2.14)$$

This is just $\pi \times$ the real part of the RHS of (2.12). Consequently

$$R'_r(\omega') = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{R_i(\omega)}{\omega' - \omega} d\omega \quad (2.15)$$

Similarly

$$R'_r(\omega') = \frac{-1}{\pi} P \int_{-\infty}^{\infty} \frac{R_r(\omega)}{\omega' - \omega} d\omega \quad (2.16)$$

One problem arises: the equations refer to negative frequencies, whereas only positive frequencies have physical meaning. Both $\mathbf{r}(t)$ and $\mathbf{E}(t)$ are physical quantities and, consequently, real. Their Fourier transforms, $\mathbf{r}(\omega)$ and $\mathbf{E}(\omega)$, thus satisfy the following rules: $\mathbf{E}_c(-\omega) = \mathbf{E}_c^*(\omega)$ and $\mathbf{r}_c(-\omega) = \mathbf{r}_c^*(\omega)$.

The relations (2.15) and (2.16) are known as the *dispersion relations*. The motion of the charged particle follows the changes in the electric field: the two are causally related. In that case quite general mathematical considerations lead to these relations in a very elegant way. It can be found in most standard texts on Mathematics for Physicists [7]. We shall encounter them again in the Kramers–Kronig relations in Chapter 3.

2.2. Emission of Radiation by a Charged Oscillator

According to the basic theory of electromagnetism an electromagnetic field is observed when a accelerated charged particle is present (Figure 3) [8]:

$$\mathbf{E}_{\text{sc}}(t) = \frac{-q}{4\pi\epsilon_0} \left[\frac{\mathbf{e}_{r'}}{r'^2} + \frac{r'}{c} \frac{d}{dt} \left(\frac{\mathbf{e}_{r'}}{r'^2} \right) + \frac{1}{c^2} \frac{d^2}{dt^2} \mathbf{e}_{r'} \right] \quad (2.17)$$

in which r' is the distance from the charged particle to the point P where the field is observed, $\mathbf{e}_{r'}$ is the unit vector pointing from P to the charge, c is the velocity of light and ϵ_0 is the permittivity of free space. The position of the particle, and thus also r' , has to be evaluated at an earlier time, $t' = t - |\mathbf{r}'|/c$, the so called retarded time. We assume the oscillation to be so small that r' remains constant.

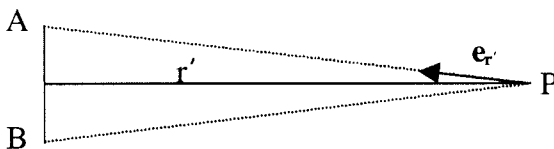


FIGURE 3 A charged particle is oscillating along AB and the field is observed at P .

When the velocity of the particle is small compared to the velocity of light and when P is far away from the charge, only the last term has to be retained and the field of the oscillating charge is given by

$$\mathbf{E}_{\text{sc}}(t) = \frac{-q}{4\pi\epsilon_0} \frac{1}{c^2} \frac{d^2}{dt^2} \mathbf{e}_{r'} \quad (2.18)$$

A derivation can be found in Appendix 4.2.

Since displacement along the line that connects the observer with the charge does not change the unit vector $\mathbf{e}_{r'}$, only the component perpendicular to it is important. The changes of $\mathbf{e}_{r'}$ are proportional to the component of motion of the particle perpendicular to this line with a proportionality constant of $1/r'$. Hence the field reduces with distance as $1/r'$, which implies that the intensity of the scattered electromagnetic wave diminishes with $1/r'^2$. Since the area of a spherical shell grows with r^2 , the energy passing through the shell per unit time is independent of the radius of the shell.

We now use these results to study a system in which an incident beam induces an oscillation of a particle with mass m and charge q . The beam is polarized along z , the axis perpendicular to the plane of the incident beam and the point P where the scattered radiation is observed (Figure 4).

The incident beam is described by

$$\mathbf{E}_{\text{inc}}(t, \mathbf{r}) = \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_0 \cdot \mathbf{r})} \quad (2.19)$$

in which \mathbf{k}_0 has the magnitude $2\pi/\lambda$ and the direction of the incident beam.

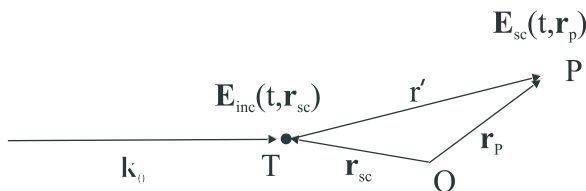


FIGURE 4 An incident wave causes the scatterer to oscillate. The oscillating particle emits a wave, observed at P . O is the origin, T the target.

The particle with charge q at \mathbf{r}_{sc} oscillates according to

$$z(t) = \frac{q}{m(\omega_s^2 - \omega_0^2 + i\gamma\omega_0)} |\mathbf{E}_0| e^{i(\omega_0 t - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}})}$$

The field at P then is given by the use of (2.18):

$$\begin{aligned} \mathbf{E}_{\text{sc}}(t, \mathbf{r}_P) &= \frac{-q}{4\pi\epsilon_0 c^2 r'} \mathbf{1}_z \ddot{z}(t - r'/c) \\ &= \frac{-q}{4\pi\epsilon_0 c^2 r'} \mathbf{1}_z (-\omega_0^2) z(t - r'/c) \\ &= \frac{-q^2}{4\pi\epsilon_0 m c^2} \frac{1}{r'} \frac{-\omega_0^2}{(\omega_s^2 - \omega_0^2 + i\gamma\omega_0)} \mathbf{E}_0 e^{i(\omega_0(t-r'/c) - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}})} \end{aligned} \quad (2.20)$$

in which $\mathbf{1}_z$ is a unit vector in the z -direction.

The exponent can be simplified by using (2.3) and by defining the vectors \mathbf{k}_1 and \mathbf{r}' , both pointing from the scatterer to P with the magnitudes $2\pi/\lambda$ and r' respectively.

$$\begin{aligned} e^{i(\omega_0(t-r'/c) - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}})} &= e^{i(\omega_0 t - 2\pi r'/\lambda - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}})} \\ &= e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}' - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}})} \end{aligned} \quad (2.21)$$

Hence

$$\mathbf{E}_{\text{sc}}(t, \mathbf{r}_P) = \frac{-q^2}{4\pi\epsilon_0 m c^2} \frac{1}{r'} \frac{-\omega_0^2}{(\omega_s^2 - \omega_0^2 + i\gamma\omega_0)} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}' - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}})} \quad (2.22)$$

In the case of scattering by a cluster of scattering particles, all far removed from the detector at P , \mathbf{k}_1 can be assumed to be the same for all particles and the following form of the exponent is useful:

$$\begin{aligned} \omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}' - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}} &= \omega_0 t - \mathbf{k}_1 \cdot (\mathbf{r}_P - \mathbf{r}_{\text{sc}}) - \mathbf{k}_0 \cdot \mathbf{r}_{\text{sc}} \\ &= \omega_0 t + (\mathbf{k}_1 - \mathbf{k}_0) \cdot \mathbf{r}_{\text{sc}} - \mathbf{k}_1 \cdot \mathbf{r}_P \end{aligned} \quad (2.23)$$

We define the scattering vector as

$$\mathbf{K} \equiv \mathbf{k}_1 - \mathbf{k}_0 \quad (2.24)$$

Hence the electromagnetic field at P is given by

$$\mathbf{E}_{\text{sc}}(t, \mathbf{r}_P) = \frac{-q^2}{4\pi\epsilon_0 mc^2} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}_P)} \frac{1}{r'} \frac{-\omega_0^2}{(\omega_s^2 - \omega_0^2 + i\gamma\omega_0)} e^{i\mathbf{K} \cdot \mathbf{r}_{\text{sc}}} \quad (2.25)$$

When the particle is a completely free electron, ω_s vanishes and, neglecting damping, the scattered wave is given by

$$\begin{aligned} \mathbf{E}_{\text{sc}}^{\text{free}}(t, \mathbf{r}_P) &= -\frac{e^2/m}{4\pi\epsilon_0 c^2} \frac{1}{r'} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}_P)} e^{i\mathbf{K} \cdot \mathbf{r}_{\text{sc}}} \\ &\equiv -r_0 \frac{1}{r'} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}_P)} e^{i\mathbf{K} \cdot \mathbf{r}_{\text{sc}}} \end{aligned} \quad (2.26)$$

where r_0 is the so called classical electron radius ($= 2.817938 \times 10^{-15}$ m).

Notice the fact that in this case the scattering power is independent of the frequency. Thomson first derived this expression [9]; hence scattering by a free electron is known as *Thomson scattering*.

The scattering by an electron in an atom is usually expressed in terms of the scattering by a free electron, without damping.

$$\mathbf{E}_{\text{sc}} \equiv f \times \mathbf{E}_{\text{sc}}^{\text{free}} \quad (2.27)$$

in which f is called the scattering factor. Stated differently, the state of a free electron is the reference state and, by definition, the scattering factor for a free electron, denoted by f_0 , is unity (Figure 5).

From (2.25), (2.26) and (2.27) we get for f :

$$\begin{aligned} f &= \frac{-\omega_0^2}{\omega_s^2 - \omega_0^2 + i\gamma\omega_0} \\ &= \frac{\omega_0^2}{\omega_0^2 - \omega_s^2 - i\gamma\omega_0} \end{aligned} \quad (2.28)$$

In general f is complex and can be written as

$$\begin{aligned} f &\equiv f_{\text{re}} + if'' \equiv 1 + f' + if'' \\ &= |f| e^{i\theta} \end{aligned} \quad (2.29)$$

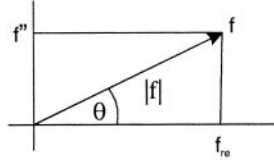


FIGURE 5 Argand diagram of the scattering factor f of an electron in an atom.

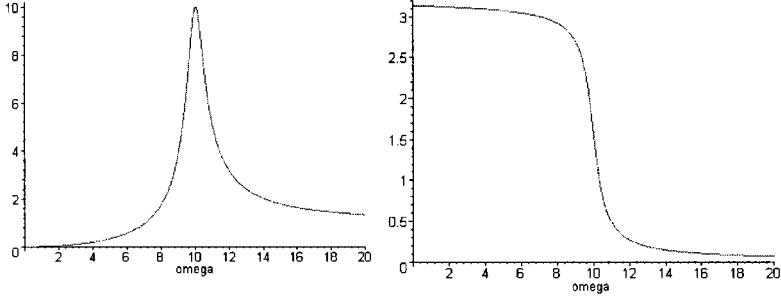


FIGURE 6 Magnitude $|f|$ and phase angle θ of the electronic scattering factor as function of the frequency ω_0 . All in arbitrary units with ω_s^2 chosen as 10. *N.B.* Since the scattering by an electron in the reference state has an angle opposite to the phase of the incident beam, radiation with a phase angle of 3.14 is in phase with the incident beam.

The magnitude and the phase angle are displayed in Figure 6.

2.3. Scattering by a One-electron Atom

In general an electron in an atom corresponds with many oscillators of different frequencies. Assuming the number of oscillators with frequency ω_s to be g_s , we can write for the situation far from resonance, i.e. when γ is negligible and the scattering factor is real:

$$\begin{aligned} f_{\text{re}} &= \sum_s \frac{-g_s \omega_0^2}{\omega_s^2 - \omega_0^2} = \sum_s g_s + \sum_s \frac{g_s \omega_0^2}{\omega_s^2 - \omega_0^2} \\ &\equiv f_0 + f' \end{aligned} \quad (2.30)$$

The number g_s is known as *the oscillator strength*. When more electrons are present, each with their own oscillators, their scattering

factors have to be added, since the electrons scatter independently. The result for atom A is the scattering factor f_A . In a strictly classical treatment it is difficult to assign physical meaning to the various oscillators and we shall defer the discussion to the end of the chapter where we shall introduce some quantum mechanical concepts. There we shall also learn that the uncertainty relation forbids point scatterers; they have to be replaced by charge clouds. The consequence is that not only f' and f'' , but also f_0 depends on \mathbf{K} and thus also on ω_0 :

$$f_A^{\text{atom}}(\omega_0) = f_0(\omega_0) + f'(\omega_0) + f''(\omega_0) \quad (2.31)$$

2.4. Scattering by a Molecule

In the hydrogen molecule we find an electron close to each nucleus. We use (2.26) to calculate the field at the detector at P :

$$\mathbf{E}_{\text{sc}}(t, \mathbf{r}_p) = -r_0 \frac{1}{r'} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}_p)} \left(f e^{i\mathbf{K} \cdot \mathbf{r}_{\text{sc}}^{(A)}} + f e^{i\mathbf{K} \cdot \mathbf{r}_{\text{sc}}^{(B)}} \right) \quad (2.32)$$

in which we have neglected the difference in distance r' in the denominator. The term between brackets is called the *structure factor*. For convenience we slightly change the notation: $\mathbf{r}_{\text{sc}}^{(A)} \equiv \mathbf{r}_A$, etc.

From Figure 7 we get

$$\begin{aligned} \mathbf{K} \cdot \mathbf{r}_B - \mathbf{K} \cdot \mathbf{r}_A &= \mathbf{K} \cdot \mathbf{r}_{BA} = (\mathbf{k}_1 - \mathbf{k}_0) \cdot \mathbf{r}_{BA} \\ &= 2\pi(AD - (-CA))/\lambda \end{aligned} \quad (2.33)$$

which states that the scattering with the shorter optical path length has the larger phase angle.

In a molecule with more scattering centers the structure factor is given by:

$$F(\mathbf{K}) = \sum_n f_A e^{i\mathbf{K} \cdot \mathbf{r}_n} \quad (2.34)$$

where the summation extends over the atoms in the molecule. The rather lengthy treatment is deemed to be necessary in view of the importance of the sign of the exponent in determining the absolute conformation of compounds.

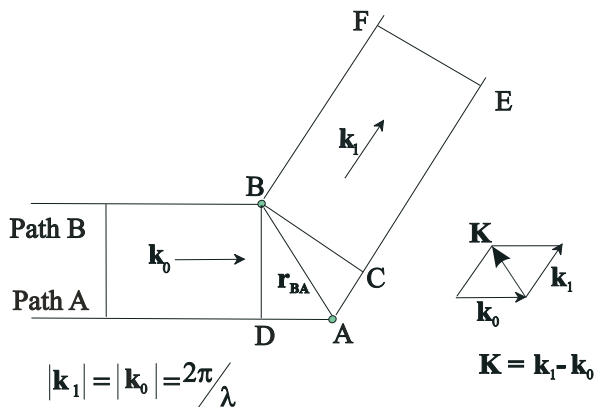


FIGURE 7 Two center scattering. The phase angle of the radiation scattered by B is positive compared with phase angle of the radiation scattered by A .

2.5. Anomalous Scattering and Polarity

2.5.1. Introduction

Anomalous scattering derives its fame from the ability to determine the handedness, or chirality, of the molecules in a crystal structure, such as we find in Figure 8. We shall see that the essence is the ability to distinguish two linear polar molecules related by inversion.

2.5.2. Polar Molecules

To simplify the discussion we rotate the molecules about the vertical axis through C over an angle $\pm\pi/4$ in such a way that the atoms A and B are in the plane of the paper and D in front. The origin is taken at C . We now consider a Bragg reflection against the plane defined by the atoms CDE , the plane perpendicular to the paper. The \mathbf{K} -vector of such a reflection is perpendicular to the CDE -plane, hence moving the atoms D and E in the plane to C does change the reflection.

In this way the system is reduced to scattering by the polar molecules ACB and BCA . We now plot in an Argand diagram the contributions of the various atoms to the structure factors according to (2.34).

When we assume that all atomic scattering factors are real, symmetry informs us that the two structure factors, $F^L(\mathbf{K})$ and

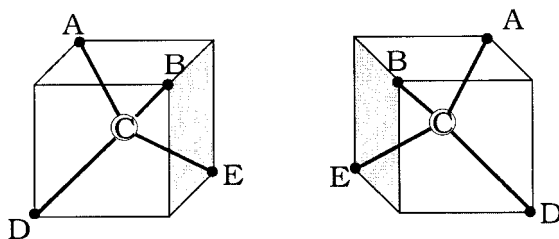


FIGURE 8 Two hypothetical enantiomorphs, related by a vertical mirror plane.

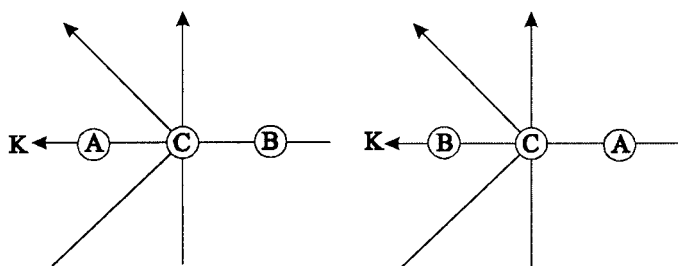


FIGURE 9 X-ray diffraction by two linear polar molecules oriented oppositely.

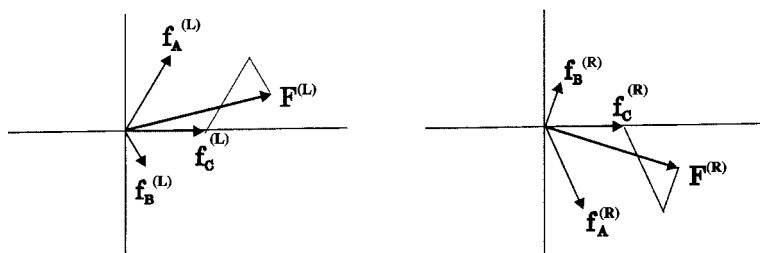


FIGURE 10 Structure factors of the two enantiomorphs.

$F^R(\mathbf{K})$, corresponding to the left and the right structure of Figure 9 respectively, have the same magnitude, as is shown in Figure 10. Since the intensity $I(\mathbf{K})$ of the diffracted beam is proportional to the square of the magnitude of the structure factor, $|F(\mathbf{K})|^2$, replacement of the left structure by the right one will not change the intensity.

We obtain the same Argand diagram as found in the right side of Figure 10 when we plot the atomic contributions to the structure factor $F(-\mathbf{K})$ of the reflection against the vertical plane through C of

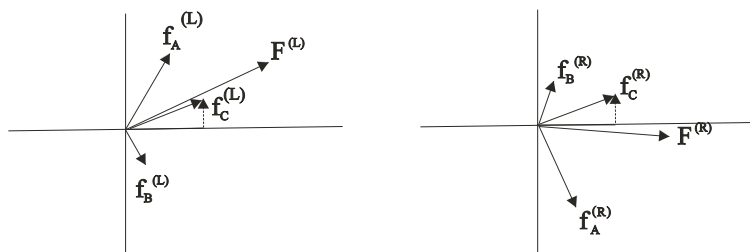


FIGURE 11 The same as Figure 10 with an anomalous component added to the scattering by atom C.

the left hand enantiomorph of Figure 8. Soon after the discovery of X-ray diffraction this identity was recognised by Friedel [10], who then stated: $|F(\mathbf{K})| = |F(-\mathbf{K})|$.

Several years later Koster *et al.* [1] realized that the symmetry in the Argand diagram is lost when one or more of the atoms show anomalous scattering. In Figure 11 we see that the magnitudes of the structure factors have become different. This enabled them to determine the polar direction in the ZnS crystal.

Bijvoet and his coworkers [2] realized that the problem of the absolute configuration, i.e. the choice between the two enantiomorphs of Figure 8, is essentially the same as the one of the polarity of the ZnS moiety in the crystal. Hence from the Bijvoet differences, defined as $F(\mathbf{K}) - F(-\mathbf{K})$, one can determine the absolute configuration of the molecule concerned.

2.6. Wave Scattered by a Thin Slab of Charged Particles

When radiation traverses a thin slab of matter, the atoms of this slab will scatter radiation in various directions. In the first instance the incident beam continues undimmed. An observer behind the slab, however, will simultaneously receive the incident beam and the beams scattered by the atoms in the slab. We shall show that the radiation coming from these other atoms is out of phase with the incident radiation.

A row of electrons is placed in a beam of EM-radiation with a wave vector normal to the row. Behind the row we find an observer at

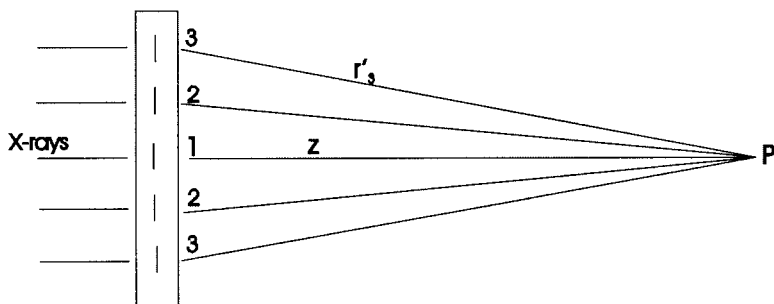


FIGURE 12 Scattering by a row of electrons placed along the x -axis, and observed at P . The incident beam is polarized in the x -direction. The origin is at atom 1.

point P . (see Figure 12). We assume the beam to be polarized in the direction of the row of electrons.

The radiation scattered by an electron on the origin, position 1 in Figure 12, observed at P at time t , is given by (2.22):

$$\mathbf{E}_{\text{sc}}^1(t, \mathbf{r}_p) = -r_0 f \frac{1}{r_1'} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_1 \cdot \mathbf{r}_1')} \quad (2.35)$$

where r_0 is the classical electron radius, introduced in (2.26).

We notice that for a free electron, where $f=1$, the scattered radiation is out of phase with the incident radiation. For particles in the row that are not on the z -axis, such as particle 3, we return to the first line of (2.35) and get

$$\mathbf{E}_{\text{sc}}^3(t, \mathbf{r}_p) = -r_0 f \frac{1}{r_3'} \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_3 \cdot \mathbf{r}_3')} * g_3 \quad (2.36)$$

where $g_3 < 1$ has been introduced to account for the fact the electrons do not oscillate perpendicular to r' .

We now extend the problem to a field scattered by a thin slab, made up of loosely bonded electrons, placed perpendicular to an incident field, see Figure 13. Nuclei are added to make the slab neutral, but we assume the frequency of the incident radiation to be too high for the nuclei to respond to it; hence they can be left out of consideration. The thickness of the slab is dz and the electron density is given by n_0 . All electrons in a ring with the z -axis as center have the same distance to P .

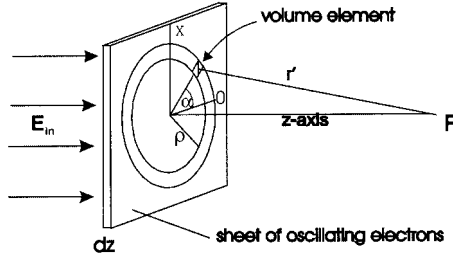


FIGURE 13 Radiation by a slab of oscillating electrons.

Rings with larger radii contain more electrons. At the same time the distance to P increases and consequently, the emitted field per electron as observed at P gets smaller. The two effects cancel one another. The origin is taken at the point where the z -axis meets the slab.

To get the total scattering by the slab we first calculate the scattering by the electrons in a volume element $\rho d\alpha \cdot d\rho \cdot dz$ of the ring with radius ρ at distance r' from the point P . Again a factor g has to be introduced to account for the fact that only for $\alpha=0$ and 2π the oscillation occurs perpendicular to \mathbf{r}' . For all other angles the factor depends on ρ as well.

Since the electrons are assumed to be free we can apply (2.36) with $f=1$ and get for the scattering by the volume element:

$$\mathbf{E}_{\text{sc}}^{\text{element, free}}(t, \mathbf{r}'_P) = -r_0 \frac{1}{r'} \rho d\alpha \cdot d\rho \cdot dz \cdot n_0 g(\alpha, \rho) \mathbf{E}_0 e^{i(\omega_0 t - \mathbf{k}_{\text{element}} \cdot \mathbf{r}')}$$

Since only the expression between brackets depends on α we first integrate over α :

$$\int_0^{2\pi} g(\alpha, \rho) d\alpha$$

Because we are not interested in its exact value we call the result $2\pi g(\rho)$ and remember it decreases with increasing ρ .

The total scattering coming from the rings is, with $|\mathbf{k}| = 2\pi/\lambda$:

$$\mathbf{E}_{\text{sc}}^{\text{free}}(t, P) = -r_0 \mathbf{E}_0 e^{i\omega_0 t} n_0 dz \int_0^\infty \frac{1}{r'} e^{-2\pi i r' / \lambda} g(\rho) 2\pi \rho d\rho \quad (2.37)$$

Since $(r')^2 = z^2 + \rho^2$, we get $\rho d\rho = r' dr'$.

We now change the integration variable from ρ to r' . It implies the change of the lower integration limit from $\rho=0$ to $r'=z$. The function $g(\rho)$ turns into $g(r')$ that slowly decreases with increasing r' from $g(z)=1$ to $g(\infty)=0$. The scattering by the plane becomes:

$$\mathbf{E}_{\text{sc}}^{\text{free}}(t, P) = -r_0 \mathbf{E}_0 e^{i\omega_0 t} n_0 dz 2\pi \int_z^\infty e^{-2\pi i r' / \lambda} g(r') dr' \quad (2.38)$$

We can integrate this in the formal way, but to contribute to understanding we integrate graphically by adding the contributions of the zones: $\sum_i g(r'_i) e^{-2\pi i r'_i / \lambda} \Delta r'_i$. The contribution of the central zone is

$$\mathbf{E}_{\text{sc}}^c(t, P) = -r_0 \mathbf{E}_0 e^{i\omega_0 t} n_0 dz 2\pi [e^{-2\pi i z / \lambda}] \Delta r'_1$$

where we used the fact that for an element on the axis, $g(r)=1$. As expected, the contribution of the center ring is out of phase with respect to the incident beam as observed at P (Figure 14), which is given by

$$\begin{aligned} \mathbf{E}_{\text{inc}}(t, \mathbf{r}_p) &= \mathbf{E}_0 e^{i(\omega t - \mathbf{k}_0 \cdot \mathbf{r}_p)} \\ &= \mathbf{E}_0 e^{i[\omega t - (2\pi z / \lambda)]} \end{aligned} \quad (2.39)$$

To simplify the expressions we evaluate the sum at the time that makes the exponent vanish. Hence in an Argand diagram the contribution of the center ring, \mathbf{E}_{sc}^c , is represented by a vector along the horizontal axis in the negative direction, thus making an angle π with the incident

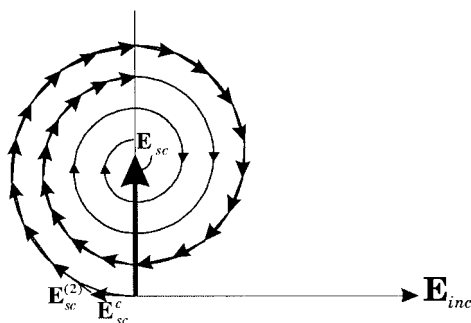


FIGURE 14 Graphic summation of the contributions of the consecutive rings to the total radiation observed at point P , drawn at an arbitrary scale. The phase angles are with respect to the phase of the incident beam.

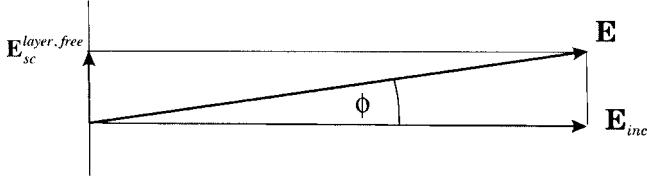


FIGURE 15 The electromagnetic field observed at a point behind the thin slab of electrons is the sum of the incident beam and the field emitted by the oscillating electrons.

beam. The vector corresponding with the next ring, \mathbf{E}_{sc}^2 , makes a smaller angle with \mathbf{E}_{in} and is slightly shorter, owing to the factor $g(r_2)$. The result of all additions is shown in Figure 14. The contributions are seen to spiral down to the center of the circle. We notice that the line from the origin to the center makes a right angle to the first contribution.

$$\begin{aligned}
 \mathbf{E}_{sc}^{\text{slab, free}}(t, P) &= -2\pi r_0 \mathbf{E}_0 e^{i\omega_0 t} n_0 dz * \left(-i \frac{c}{\omega_0} e^{-2\pi i z/\lambda} \right) \\
 &= i r_0 2\pi \frac{c}{\omega_0} n_0 dz \mathbf{E}_{inc}(t, \mathbf{r}_p) \\
 &= i r_0 \lambda n_0 dz \mathbf{E}_{inc}(t, \mathbf{r}_p)
 \end{aligned} \tag{2.40}$$

The radiation observed at P is the sum of the incident beam and the radiation scattered by the slab. Since the contribution of the thin slab is very small, its effect on the observed radiation is mainly an increase of phase (Figure 15).

When the radiation is observed in a direction different from the incident beam the situation becomes more complicated and this beam cannot be used as a reference. The construction of rings with the same scattering power is still possible and the phase difference between the resulting scattered beam and the beam due to a free electron at the origin remains $\pi/2$.

2.7. Refractive Index

2.7.1. Free Electrons

In the treatment of the previous section we assumed that the incident beam passed through the thin slab with the velocity c and wave vector

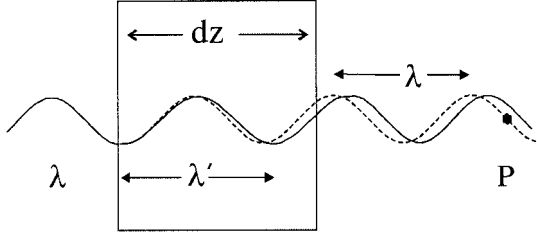


FIGURE 16 X-ray wave passing through matter. The diagram shows the plane wave (solid line) before and behind the thin slab. To connect the two fields the wavelength inside the slab has to increase. The incident wave is shown as a dashed line.

k. Adding to it the scattering coming from all the charged particles in the slab we obtained the total field \mathbf{E} , as observed in a point P behind the slab. Owing to symmetry, the same field is observed in all points in a plane at a distance z from the thin slab. Hence, the total field behind the slab is a plane wave. The crossing through the slab results in a change of phase compared with the original plane wave. This change of phase is equivalent to a shift of the incident wave in space (Figure 16).

We now have two expressions for the field behind the slab. For practical purposes we take the origin at the left side of the slab and write the field as sum of the incident field and the field scattered by the electrons of the slab:

$$\begin{aligned}\mathbf{E}(t, z) &= \mathbf{E}_{\text{inc}}(t, z) + \mathbf{E}_{\text{sc}}^{\text{slab, free}}(t, z) \\ &= (1 + ir_0\lambda n_0 dz)\mathbf{E}_{\text{inc}}(t, z) \\ &\approx \mathbf{E}_{\text{inc}}e^{ir_0\lambda n_0 dz} \equiv \mathbf{E}_{\text{inc}}e^{i\phi}\end{aligned}\quad (2.41)$$

Since $\mathbf{E}(t, z)$ is still a plane wave, we can also write it as:

$$\begin{aligned}\mathbf{E}(t, z) &= \mathbf{E}_0 e^{i(\omega_0 t - k' dz - k(z - dz))} \\ &= \mathbf{E}_{\text{inc}} e^{-i(k' - k)dz}\end{aligned}\quad (2.42)$$

where k' is the apparent wave vector inside the slab with magnitude k' .

Both expressions must yield the same field, so comparison of (2.41) and (2.42) yields

$$(k' - k)dz = -r_0\lambda n_0 dz \quad (2.43)$$

So passing through a slab causes a decrease of k and, consequently, an increase of λ .

The phase velocity v of a wave is given by the product of frequency and wavelength. Increase of wavelength implies that v becomes larger than c , the phase velocity of the incident beam:

$$v = \frac{\omega_0}{2\pi} \lambda' > c \quad (2.44)$$

The fact that $v > c$, does not violate relativity theory that states that no signal can propagate with a velocity larger than c . The velocity of a signal depends on the group velocity rather than on the phase velocity we have been talking about.

The index of refraction n is given by

$$n = \frac{c}{v} = \frac{k'}{k} = \frac{\lambda}{\lambda'} \quad (2.45)$$

from which we derive with the help of (2.43)

$$\begin{aligned} n - 1 &= \frac{k' - k}{k} = \frac{-r_0 \lambda n_0}{k} \\ &= \frac{-2\pi r_0 n_0}{k^2} \end{aligned} \quad (2.46)$$

Hence the index of refraction is smaller than the one in the present case.

2.7.2. Bonded Electrons with Damping

The treatment above is based on a thin slab of free electrons that do not experience damping: $\gamma=0$. In reality electrons are not free and damping occurs and their scattering is given by $r_0 f$ rather than by r_0 . The contribution, \mathbf{E}_{sc}^c , from the center region of the thin slab is no longer opposite to the incident beam, but has a phase angle that is larger than π , as is shown in Figure 17. In fact the phase angle of \mathbf{E}_{sc}^c is given by $\pi + \theta$, as follows from Figure 5. \mathbf{E}_{sc} will rotate over the same angle and will get components along and perpendicular to \mathbf{E}_{inc} . In addition to the phase shift, \mathbf{E}_1 , we get weakening of the incident beam by \mathbf{E}_2 , observed as absorption.

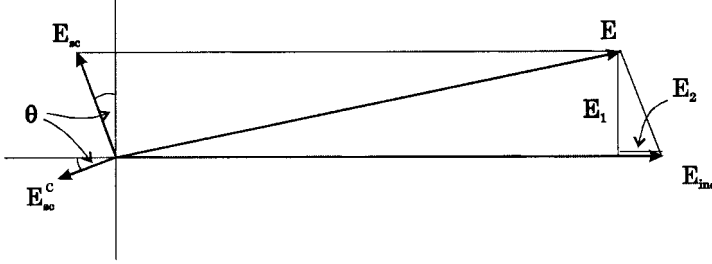


FIGURE 17 Argand diagram of the field observed at a point P behind the slab. Absorption and phase shift are the result when the harmonic motion of the electrons is damped.

From Figure 17 we derive

$$\frac{|E_2|}{|E_1|} = \frac{\text{Im}(E_{sc}^c)}{\text{Re}(E_{sc}^c)} = \frac{f''}{f_{re}} \quad (2.47)$$

where the last identity follows from (2.27) and (2.29). The triangles defined by (E_1, E_2) and (f_{re}, f'') are congruent and with (2.41) we get:

$$\frac{|E_2|}{f''} = \frac{|E_1|}{f_{re}} = \frac{|E_{sc}|}{|f|} = r_0 \lambda n_0 dz E_{inc}(t, z) \quad (2.48)$$

Notice that the decrease in amplitude, represented by E_2 , is proportional to the imaginary part of the scattering factor. This takes us to the next section.

2.8. Absorption and the Optical Theorem

We can account for the decrease in amplitude, E_2 , by assuming the refractive index n inside the slab to be complex. First we introduce two new quantities, n' and n'' by

$$n - 1 = -n' - in'' \quad (2.49)$$

Replacing r_0 by fr_0 in (2.46) yields

$$\begin{aligned} n - 1 &= -fr_0 \frac{2\pi n_0}{k^2} \\ -n' - in'' &= -(f_{re} + if'')r_0 \frac{2\pi n_0}{k^2} \end{aligned}$$

from which we derive

$$\begin{aligned} n' &= f_{\text{re}} r_0 \frac{2\pi n_0}{k^2} \\ n'' &= f'' r_0 \frac{2\pi n_0}{k^2} \end{aligned} \quad (2.50)$$

n' accounts for the shift in phase, while n'' yields the decrease in amplitude.

When X-rays pass through matter, the intensity decreases (attenuates) according to

$$I(z) = I_{\text{inc}} e^{-\kappa z} \quad (2.51)$$

with κ the absorption coefficient.

Crossing the thin slab reduces the beam to

$$= I_{\text{inc}}(1 - \kappa dz) \quad (2.52)$$

With $I(z) \propto |\mathbf{E}(z)|^2$ we get

$$\begin{aligned} |\mathbf{E}(z)| &= |\mathbf{E}_{\text{inc}}| e^{-\kappa dz/2} \\ &= |\mathbf{E}_{\text{inc}}|(1 - \kappa dz/2) \end{aligned}$$

Hence

$$|\mathbf{E}_2| = |\mathbf{E}| - |\mathbf{E}_{\text{inc}}| = -|\mathbf{E}_{\text{inc}}|\kappa dz/2$$

From (2.48) we get

$$|\mathbf{E}_2| = -f'' r_0 \lambda n_0 dz \mathbf{E}_{\text{inc}}$$

and

$$\kappa = 2r_0 \lambda n_0 f''(0) \quad (2.53)$$

To stress the fact that the whole derivation is based on the scattering in forward direction by the electron on the z -axis, we write $f''(0)$. The relation expressed in (2.53) is known as *the optical theorem* in

scattering theory. It tells us that the imaginary component of the scattering factor can be derived from absorption measurements.

2.9. Some Atomic Quantum Theory

The harmonic model and atomic theory The simple model of the harmonic oscillator is very useful in explaining the basic phenomena of scattering X-rays. When the theory was derived no sound model of atoms was available. At first sight, the model seems difficult to incorporate into the models for atoms presently in use: the Coulomb forces between electron and nucleus are quite different from the harmonic forces used in the model. Even more difficult to fit in seems to be the fact that light carries momentum. Consequently, scattering is accompanied by transfer of momentum and it is difficult to see how this can be combined with elastic scattering.

Before a full quantum-theoretical treatment of scattering is given, it is shown that to a large extent the various aspects of the model can be given a basis in quantum theory.

Harmonic forces The Bohratom consists of a positive nucleus in the center and pointlike electrons moving in orbits. A better model is the one that represents each electron by a density cloud. At this stage we limit ourselves by considering a one-electron atom, hydrogen. In quantum theory the ground state of the electron of the hydrogen atom is described by the spherical $1s$ orbital or wave function (in atomic units) [11]:

$$\psi(\mathbf{r}) = 1s = N_1 e^{-r} \quad (2.54)$$

in which N_1 is a constant. The origin is chosen on the nucleus and r is the distance from the point \mathbf{r} , see Figure 18.

The density cloud is given by

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2 = N_1^2 e^{-2r} \quad (2.55)$$

Other stationary states are possible, such as the $2p_z$ -state, described by the (real) orbital

$$2p_z = N_2 z e^{-r/2} \quad (2.56)$$

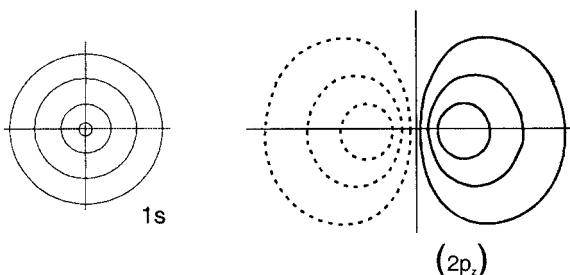


FIGURE 18 Some hydrogen wave functions or orbitals: $1s$, $2p_z$. The solid contours denote a positive density, the dashed lines a negative one. All are in arbitrary units.

The corresponding electron cloud is no longer spherical but still contains many symmetry elements, among which an inversion center at the origin (Figure 18).

This spherical cloud corresponding with the ground state becomes deformed when we place the atom in a (static) electric field. The inversion center has disappeared and we need a linear combination of orbitals to describe the state of the electron:

$$\psi(\mathbf{r}) = a(1s(\mathbf{r})) + b(2p_z(\mathbf{r})) \quad (2.57)$$

This wave function with $a = b = 1/\sqrt{2}$ is depicted in Figure 19.

The corresponding electron cloud is given by:

$$\begin{aligned} \rho(\mathbf{r}) &= |1s(\mathbf{r}) + 2p(\mathbf{z})|^2 \\ &= a^2 |1s(\mathbf{r})|^2 + b^2 |2p(\mathbf{z})|^2 + 2ab(1s(\mathbf{r}) * 2p(\mathbf{z})) \end{aligned} \quad (2.58)$$

It is easy to see that squaring the diagram of Figure 19 yields an electron cloud that has its maximum at the right hand side of the diagram: the atom is polarized.

When the electric field is removed, the deformed atom is not stationary anymore and the electron cloud starts to move. To know this motion we have to include the time-dependent part of the wave

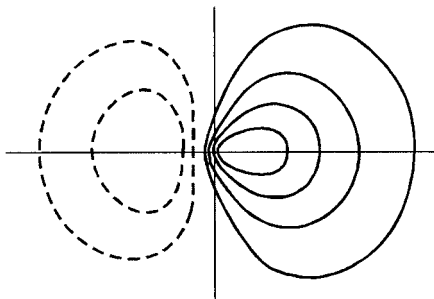


FIGURE 19 An orbital describing a polarized hydrogen atom. The solid contours denote a positive density, the dashed lines a negative one. All in arbitrary units.

functions:

$$\begin{aligned} 1s(\mathbf{r}, t) &= 1s(\mathbf{r})e^{iE_1t/\hbar} \\ 2p_z(\mathbf{r}, t) &= 2p_z(\mathbf{r})e^{iE_2t/\hbar} \end{aligned} \quad (2.59)$$

Expression (2.58) becomes:

$$\begin{aligned} \rho(\mathbf{r}, t) &= a^2 * 1s(\mathbf{r})e^{iE_1t/\hbar} * 1s(\mathbf{r})e^{-iE_1t/\hbar} + b^2 * 2p_z(\mathbf{r})e^{iE_2t/\hbar} * 2p_z(\mathbf{r})e^{-iE_2t/\hbar} \\ &\quad + ab * 1s(\mathbf{r})e^{iE_1t/\hbar} * 2p_z(\mathbf{r})e^{-iE_2t/\hbar} + ab * 2p_z(\mathbf{r})e^{iE_2t/\hbar} * 1s(\mathbf{r})e^{-iE_1t/\hbar} \\ &= a^2 * (1s(\mathbf{r}))^2 + b^2 * (2p_z(\mathbf{r}))^2 \\ &\quad + 2ab * 1s(\mathbf{r}) * 2p_z(\mathbf{r})[e^{i(E_2-E_1)t/\hbar} + e^{i(E_1-E_2)t/\hbar}] \end{aligned} \quad (2.60)$$

The exponential part of which can be written as

$$\begin{aligned} [e^{i(E_2-E_1)t/\hbar} + e^{i(E_1-E_2)t/\hbar}] &= 2 \cos(E_2 - E_1)t/\hbar \\ &\equiv 2 \cos \omega_{21} t \end{aligned}$$

We notice a stationary part that is the average of the electron clouds of the two states involved and a time-dependent part, an electron cloud that oscillates with a frequency that is proportional to the energy difference between the two states. It is this frequency that

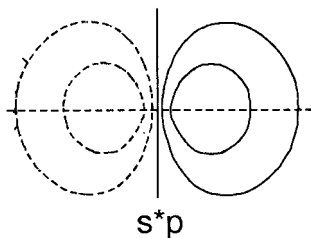


FIGURE 20 The oscillating electron cloud derived from the superposition of the $1s$ and the $2p_z$ orbitals.

was introduced as ω_s in (2.1). The oscillating electron cloud is shown in Figure 20.

For practical purposes the linear combination of (2.57) consists of equal contributions by the $1s$ and the $2p_z$ orbitals. Owing to the energy loss by radiation the contribution of the $2p_z$ orbital diminishes slowly and finally the hydrogen atom is back in its ground state.

Up to now the polarization of the hydrogen atom was accomplished by adding $2p_z$ character to the $1s$ orbital. The same effect, albeit weaker, can be obtained by mixing in p_z functions with a higher principle quantum number n . In fact even the orbitals corresponding with a free electron have to be taken into account. This explains the need of many oscillators to describe the behavior of just one electron in an atom.

We notice that in the polarized state, orbitals that were unoccupied before are used to describe the state of the electron. We say the orbitals get populated by (partial) transitions to those orbitals.

3. QUANTUM THEORY OF SCATTERING

3.1. Introduction

It is clear that scattering of radiation by an atomic or molecular system requires the use of quantum mechanics to describe the system. In many cases the classical wave description of radiation, from infrared to X-rays, is adequate to handle interaction processes as absorption, emission and scattering. Combination of this method with quantum theory of matter yields the widely used semiclassical theory of radiative processes [12]. A flaw of this method is the inability to handle

spontaneous emission in a direct way. Since the anomalous part of the scattering factor depends on spontaneous emission and subsequent absorption of radiation, the semiclassical method does not suffice and quantization of the electromagnetic field and the use of the concept of photons is called for [13,14]. In the following we closely follow the introduction into the theory of X-ray scattering as described by Feil [15]. An excellent comprehensive treatment is given by Roy *et al.* [16].

The experimental situation encountered in X-ray diffraction is a parallel beam of X-rays moving in the direction of vector \mathbf{k}_0 , a second beam, parallel to \mathbf{k}_1 , and a target. In principle more beams \mathbf{k} can occur (see Figure 21). The detector is placed in such a position that it measures the photons in the scattered beam \mathbf{k}_1 .

In the second section we give the quantum mechanical description of the interacting systems, the X-ray beams and the target. Section three describes how interacting systems change with time. In the original state photons can only be found in the incident beam \mathbf{k}_0 , but owing to the interaction, the probability to find one in the beam \mathbf{k}_1 increases. The fourth section introduces perturbation theory, a method suitable for weakly interacting systems. In section five we find how the interaction between target and X-rays leads to absorption, emission and scattering, and finally section six discusses the various types of scattering.

3.2. Quantum Mechanical Description of the Interacting Systems

3.2.1. Description of the X-ray Beams

In the classical treatment of Chapter 2 the incident beam was described by the electromagnetic field \mathbf{E} . A more fundamental description is by

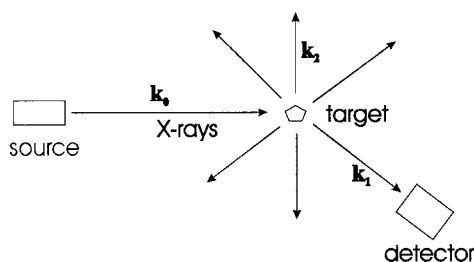


FIGURE 21 Target, incident beam k_0 , scattered beams k_1 and k_2 .

means of the vector potential \mathbf{A} and the potential ϕ , from which the electric component \mathbf{E} and the magnetic component \mathbf{B} can be derived:

$$\mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} - \nabla \phi(\mathbf{r}, t), \quad \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \quad (3.1)$$

The vector potential has a basic uncertainty: one can add $\nabla F(\mathbf{r}, t)$ to it, where F is an arbitrary function of \mathbf{r} and t , without \mathbf{B} being changed. By assuming $\nabla \cdot \mathbf{A} = 0$ (Coulomb gauge), we remove this uncertainty. The choice of gauge is dictated by reasons of expediency: many gauges remove the uncertainty, but some give a larger simplification of the mathematical treatment than others. In the classical theory $\nabla \cdot \mathbf{A} = (-1/c^2)/(\partial \phi / \partial t)$ is widely used as is shown in Appendix 4.2.

In vacuum, with charges and currents far away, the scalar potential $\phi(\mathbf{r})$ is zero and the vector potential $\mathbf{A}(\mathbf{r}, t)$ can be written as a linear combination of plane waves or modes. A monochromatic, polarized, incident beam is an example of such a plane wave:

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 e^{i(\omega t - \mathbf{k}_0 \cdot \mathbf{r})} \quad (3.2)$$

A consequence of our choice of gauge is that \mathbf{A} can have only two independent directions, both perpendicular to \mathbf{k}_0 . When necessary we use μ to distinguish between the two directions of polarization; often we just omit it.

Quantum mechanics informs us that the energy of the plane waves is quantized, i.e. it can only change by discrete amounts $\hbar\omega$, which in turn means that the amplitude of these waves can only change by discrete amounts. When the energy of mode (or wave) \mathbf{k} increases by $\hbar\omega$ the mode is said to have increased its number of photons, $n_{\mathbf{k}}$, by one.

We now describe the state of the EM field by listing the number of photons in each mode. The monochromatic, polarized incident beam, for example, is described by:

$$|n_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, 0_{\mathbf{k}_3}, \dots\rangle \quad (3.3)$$

Such a state, with a fixed number of photons in each plane wave, is an eigenvector of the radiation Hamiltonian H_{rad} :

$$\hat{H}_{\text{rad}} |n_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots\rangle = |n_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots\rangle E_{\text{rad}} \quad (3.4)$$

When diffraction has transferred m photons from the incident beam \mathbf{k}_0 to the plane wave \mathbf{k}_1 heading to the detector, the system is in a different eigenstate:

$$|n_{\mathbf{k}_0} - m, n_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, 0_{\mathbf{k}_3}, \dots\rangle \quad (3.5)$$

The processes in which the number of photons is increased or decreased are represented by the operations of the *creation* and *annihilation* operators respectively. The creation operator works as follows:

$$\hat{a}_{\mathbf{k}_0, \mu}^+ |n_{\mathbf{k}_0, \mu}, n_{\mathbf{k}_1}, \dots\rangle = |n_{\mathbf{k}_0, \mu} + 1, n_{\mathbf{k}_1}, \dots\rangle (n_{\mathbf{k}_0, \mu} + 1)^{1/2} \quad (3.6)$$

A photon is created in mode \mathbf{k}_0 , with polarization μ .

The annihilation operator has the opposite effect:

$$\hat{a}_{\mathbf{k}_0, \mu} |n_{\mathbf{k}_0, \mu}, n_{\mathbf{k}_1}, \dots\rangle = |n_{\mathbf{k}_0, \mu} - 1, n_{\mathbf{k}_1}, \dots\rangle n_{\mathbf{k}_0, \mu}^{1/2} \quad (3.7)$$

Notice the difference in constants between the two! When no photons in the particular mode are present, the result of the operation is zero.

$$\hat{a}_{\mathbf{k}_0, \mu} |0_{\mathbf{k}_0, \mu}, n_{\mathbf{k}_1}, \dots\rangle = 0 \quad (3.8)$$

In Section 3.5, we shall meet these operators again when describing the interaction between radiation and electrons.

3.2.2. Target: Atom, Molecule or Crystal

Owing to their large mass the nuclei do not play a role in the scattering process, so we can limit ourselves to a discussion of the electrons and assume the nuclei to be at the equilibrium positions. This is equivalent to the Born–Oppenheimer approximation [17]. Of course nuclei show thermal motion and electrons are dragged along, thus affecting X-ray scattering [18]. Since we concentrate on anomalous scattering we simplify our model as much as possible without losing essential features. Therefore, we assume the target to contain one electron. In the absence of interaction between radiation and electrons, this electron is described by the state function or state vector $|\varphi_p^{\text{el}}\rangle$ with

$$\hat{H}_{\text{el}} \left| \varphi_p^{\text{el}} \right\rangle = \left| \varphi_p^{\text{el}} \right\rangle \varepsilon_p^{\text{el}} \quad (3.9)$$

in which \hat{H}_{el} is the Hamiltonian of the electronic system:

$$\hat{H}_{\text{el}} = - \sum_i \frac{\hbar}{2m} \nabla_i + v(\mathbf{r}_i).$$

3.2.3. Total System: Photons and Electrons

When no interaction occurs, the Hamiltonian of the total system, consisting of the EM field and the crystal, is the sum of the Hamiltonians of the separate parts:

$$\hat{H}^{(0)} = \hat{H}_{\text{rad}} + \hat{H}_{\text{el}} \quad (3.10)$$

The state function of the total, noninteracting, system is the product of the two state functions:

$$\left| \varphi_p^{\text{el}} \right\rangle \otimes \left| n_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2} \right\rangle \quad (3.11)$$

and its energy is the sum of the energies of the EM field and the electron.

However, electrons and radiation do interact and the Hamiltonian is not $\hat{H}^{(0)}$ but \hat{H} :

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \quad (3.12)$$

in which the amount of interaction is given by \hat{H}' .

The eigenfunctions of \hat{H} describe stationary states of the interacting system. They satisfy the Schrödinger equation

$$\hat{H} \Psi_I = \Psi_I E_I \quad (3.13)$$

The eigenstates of the interacting system have energy levels that differ only slightly from the levels of the combining noninteracting states since the interaction is very weak. Each atomic level spreads out into a narrow band of levels of the interacting state. Whereas the

level spacing is of the order of 1 eV, the band width is about 10^{-7} eV. We illustrate the situation by working out a simplified example of an atom with two levels, interacting with three radiation modes. With the small number of interacting states we can use the variation method to calculate the eigenstates of the interaction system. In the calculation it is assumed that the interaction energy is substantially smaller than the excitation energy of the atom. Thus the ground state of the atom is omitted from the diagram shown in Figure 22. The case is worked out more extensively in Appendix 4.3.

The next diagram (Figure 23) shows the participation of the electronically excited state in each of the new eigenstates.

In reality the levels of the radiation state form a continuum and the four levels $E_I \dots E_{IV}$ turn into a band: line broadening of the electronic excited state.

Since the eigenfunctions of the noninteracting system, described in (3.11), form a complete set, we can use this set as the basis set and expand the wave function of the interacting state in terms of these

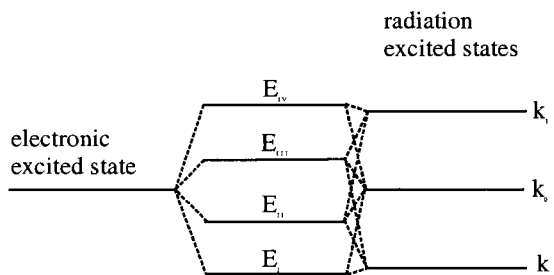


FIGURE 22 The energy diagram of an atom interacting with a radiation field. The levels $E_I \dots E_{IV}$ are the energy levels of the combined state.

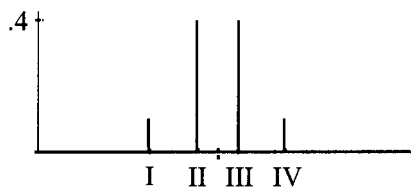


FIGURE 23 The participation of the original atomic excited state in eigenstates of the combined system.

eigenfunctions of $\hat{H}^{(0)}$:

$$\begin{aligned} |\Psi(t)\rangle &= \sum_p \sum_k \left| \varphi_p^{\text{el}}(t) \right\rangle \left| \text{rad}_k(t) \right\rangle c_{p,k}(t) \\ &\equiv \sum_m \left| \Psi_m^{(0)}(t) \right\rangle c_m(t) \end{aligned} \quad (3.14)$$

The coefficients can be determined by either variation or perturbation methods.

The X-rays are generated by atomic de-excitation (tube) or by magnetic deflection (of a bunch) of electrons (synchrotron), followed by monochromatization. Hence the radiation arrives in wave packets that do not show mutual phase relations. Here we consider one packet and calculate its contribution to the diffracted beam.

It takes some time before such a wave packet reaches the target. In that time the photon and electrons do not interact yet. Then, at time t_0 interaction starts and the wave function changes according to Schrödinger's equation:

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = \hat{H} |\Psi(t)\rangle \quad (3.15)$$

The wave packet consists of a number of polarized, monochromatic waves with closely related wavelengths. Since these waves interact in almost the same way with the target, we can assume that at time t_0 the radiation field consists of one wave only, the quasi-monochromatic approach. To simplify the treatment, we further assume that this wave contains one photon. The initial state i of the system is then given by

$$\left| \Psi_i^{(0)} \right\rangle \equiv |i\rangle = \left| \psi_0^{\text{el}} \right\rangle \left| 1_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots \right\rangle \quad (3.16)$$

In crystallography we are interested in the *intensity* of the diffracted beam \mathbf{k}_1 . This intensity is proportional to the rate at which photons \mathbf{k}_1 are created, which is equal to the increase with time of the probability to find the system in the state

$$|f\rangle \equiv \left| \psi_0^{\text{el}} \right\rangle \left| 0_{\mathbf{k}_0}, 1_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots \right\rangle \quad (3.17)$$

with the electron in the ground state and the photon in \mathbf{k}_1 . Quantum mechanics states that the *probability* to find the system in this state f at time t is given by $|c_f(t)|^2$. The intensity that is measured by the detector is proportional to

$$I(\mathbf{k}_1) \simeq \sum_f |c_{f \in \mathbf{k}_1}|^2 \quad (3.18)$$

where the summation extends over all modes that are within the solid angle subtended by the detector opening.

3.3. Time Dependence of the Interacting System

To calculate the coefficient c_f we start from the fact that at $t = t_0$ the system is in the initial state: $c_i(t_0) = 1$, with all other coefficients zero. We express this by stating that of all states only state i is populated. With the Schrödinger equation (3.15) we calculate how the coefficients evolve in time. To do this we write the time dependent part of the base vectors explicitly:

$$|\Psi_m^{(0)}\rangle \equiv |m\rangle e^{-iE_m t/\hbar} \quad (3.19)$$

with

$$H^{(0)}|m\rangle = |m\rangle E_m \quad (3.20)$$

The energy E_m is the sum of the energies of the electromagnetic field and the electrons.

With

$$|\Psi(t)\rangle = \sum_m |m\rangle e^{-iE_m t/\hbar} c_m(t) \quad (3.21)$$

the right-hand side of (3.15) becomes, at $t > t_0$.

$$\begin{aligned} \hat{H}|\Psi(t)\rangle &= \sum_n (\hat{H}^{(0)} + H')|m\rangle e^{-iE_m t/\hbar} c_m(t) \\ &= \sum_m \left[|m\rangle e^{-iE_m t/\hbar} E_m c_m(t) + \hat{H}'|m\rangle e^{-iE_m t/\hbar} c_m(t) \right] \end{aligned} \quad (3.22)$$

The left-hand side is

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = i\hbar \sum_m \left[|m\rangle \frac{E_m}{i\hbar} e^{-iE_m t/\hbar} c_m(t) + |m\rangle e^{-iE_m t/\hbar} \dot{c}_m(t) \right] \quad (3.23)$$

Dropping the identical terms of (3.22) and (3.23) we get

$$(i\hbar) \sum_m |m\rangle e^{-iE_m t/\hbar} \dot{c}_m(t) = \sum_m \hat{H}' |m\rangle e^{-iE_m t/\hbar} c_m(t) \quad (3.24)$$

To calculate c_f as function of time, both sides of expression (3.24) are multiplied by $\langle \Psi_f(t) |$, one of the eigenstates of $H^{(0)}$, and integrated. We use the notation

$$\langle f|m\rangle \equiv \int_{-\infty}^{\infty} [\Psi_f^{(0)*} \Psi_m^{(0)}]_{t=0} dv$$

and

$$\langle f|H'|m\rangle \equiv \int_{-\infty}^{\infty} [\Psi_f^{(0)*} H' \Psi_m]_{t=0} dv$$

and get

$$(i\hbar) \sum_m e^{iE_f t/\hbar} \langle f|m\rangle e^{-iE_m t/\hbar} \dot{c}_m(t) = \sum_n e^{iE_f t/\hbar} \langle f|H'|m\rangle e^{-iE_m t/\hbar} c_n(t) \quad (3.25)$$

Owing to the orthogonality of the eigenstates, ($\langle f|m\rangle = 0$, $f \neq m$), the sum on the left-hand side reduces to one term:

$$\dot{c}_f(t) = (i\hbar)^{-1} \sum_m \langle f|H'|m\rangle e^{i(E_f - E_m)t/\hbar} c_m(t) \quad (3.26)$$

The RHS only contributes when $\langle f|H'|m\rangle \neq 0$. This implies that $H'|m\rangle$ must yield a term that is proportional to f . In words: the contribution does not vanish when H' causes a (partial) transition from m to f .

The following abbreviations

$$E_f - E_m \equiv \hbar\omega_{fm}, \quad \langle f|H'|m\rangle \equiv H_{fm} \quad (3.27)$$

lead to the most important expression:

$$\dot{c}_f(t) = (i\hbar)^{-1} \sum_m e^{i\omega_{fm} t} H_{fm} c_m(t) \quad (3.28)$$

3.4. Perturbation Theory

When the wave packet reaches the target, the coefficients are given by:

$$c_i(t_0) = 1, \quad c_f(t_0) = 0, \quad c_m(t_0) = \delta_{im} \quad (3.29)$$

In principle the value of these coefficients at a later time can be obtained by integration of (3.28):

$$\begin{aligned} c_i(t) &= c_i(t_0) + (i\hbar)^{-1} \sum_m \int_{t_0}^t dt' e^{i\omega_{im}t'} H_{fi} c_m(t') \\ c_f(t) &= (i\hbar)^{-1} \sum_m \int_{t_0}^t dt' e^{i\omega_{fm}t'} H_{fm} c_m(t') \end{aligned} \quad (3.30)$$

Expression (3.30) does not seem to take us far since we have to know all the coefficients c_m as functions of time just to calculate one of them. Of course, expression (3.30) can be used to describe $c_m(t')$ in the right-hand side of itself. We then get, using (3.29):

$$\begin{aligned} c_f(t) &= (i\hbar)^{-1} \sum_m \int_{t_0}^t dt' e^{i\omega_{fm}t'} H_{fm} \left[c_m(t_0) + \sum_k \int_{t_0}^{t'} dt'' e^{i\omega_{mk}t''} H_{mk} c_k(t'') \right] \\ &= (i\hbar)^{-1} \int_{t_0}^t dt' e^{i\omega_{fi}t'} H_{fi} c_i(t_0) + (i\hbar)^{-1} \sum_m \int_{t_0}^t dt' e^{i\omega_{fm}t'} H_{fm} \\ &\quad \times \sum_k \int_{t_0}^{t'} dt'' e^{i\omega_{mk}t''} H_{mk} c_k(t'') \end{aligned} \quad (3.31)$$

Repeating this procedure we get:

$$\begin{aligned} c_f(t) &= (i\hbar)^{-1} \int_{t_0}^t dt' e^{i\omega_{fi}t'} H_{fi} c_i(t_0) \\ &\quad + (i\hbar)^{-2} \sum_m \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{i\omega_{fm}t'} H_{fm} e^{i\omega_{mi}t''} H_{mi} c_i(t_0) + \dots \end{aligned} \quad (3.32)$$

The first term corresponds with a direct transition from the initial state i to the state f . The second term corresponds with the transition from state i to state m and, subsequently, from m to f . So state f is populated via intermediate states m , etc. The states m include excited

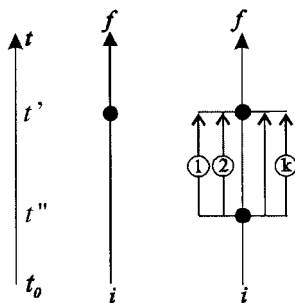


FIGURE 24 Diagram representing second-order perturbation. At the left side we find the time axis. The middle line expresses the first term of the right-hand side of (3.32). This term represents the sum of transitions from the state i to the state f at time t' , where t' takes on the values between t_0 and t . The heavy dot represents the operation of H' . The right hand part of the figure shows transitions at t'' from i to the states $1, 2, \dots, k$, followed by transitions at time t' from these states to state f . It is clear that t'' can take any value between t_0 and t' .

states of the electrons (bonded and free states) as well as states corresponding to photons moving in other directions. The result is the famous Born-series. We represent the first two terms of the series graphically in Figure 24.

The transitions from i to the intermediate states $1, 2, \dots, k$ are not observed. In fact they have no physical reality, but are the result of writing the state of the system as a linear combination of eigenstates of the noninteracting system. We therefore call them *virtual transitions*.

The *first Born approximation* limits the series to the first term. The kinematical theory of diffraction is based on this approximation. It assumes that the interaction between the radiation and the molecule is so weak that terms with products of matrix terms H_{mk} can be neglected. In other words, the states m hardly get populated and, consequently, we do not have to take into account transitions from those states to state f . It implies that the state i is hardly depopulated. Hence the contribution of state i to c_f is given by:

$$c_{fi}^{(1)}(t) = (i\hbar)^{-1} \int_{t_0}^t dt' e^{i\omega_{fi}t'} H_{fi} c_i(t_0) \quad (3.33)$$

and

$$c_f^{(1)} \equiv c_{fi}^{(1)} \quad (3.34)$$

3.5. Interaction Between X-rays and Matter

3.5.1. Interaction Hamiltonian

Quantum theory informs us that for a one-particle system the interaction Hamiltonian is given by

$$\hat{H}' = \frac{q}{m}(\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}) + \frac{q^2 \hat{\mathbf{A}}^2}{2m} \quad (3.35)$$

in which q and m are the charge and the mass of the particle on which the EM-field is operating [14]. $\hat{\mathbf{A}}$ and $\hat{\mathbf{p}}$ are operators that correspond with the vector potential of the field and the momentum of the particle respectively. They are given by

$$\hat{\mathbf{p}} \equiv \frac{\hbar}{i} \nabla \quad (3.36)$$

$$\hat{\mathbf{A}}(\mathbf{r}) \equiv (\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \left[\hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} + \hat{a}_{k, \mu}^+ e^{-i\mathbf{k} \cdot \mathbf{r}} \right] \mathbf{e}_{\mathbf{k}, \mu} \quad (3.37)$$

in which V is the volume of a cube that includes the diffraction system and detector, ω_k is the frequency and $\mathbf{e}_{\mathbf{k}, \mu}$ is the unit vector in the direction of polarization μ of wave \mathbf{k} . $\hat{a}_{k, \mu}^+$ and $\hat{a}_{k, \mu}$ are the creation and the annihilation operators defined in (3.6) and (3.7). The cube allows periodic boundary conditions to be applied. As was stated before the Coulomb gauge, $\nabla \cdot \mathbf{A} = 0$, allows the vector potential to have only two independent directions, both perpendicular to \mathbf{k} . Thus μ is either 1 or 2.

Substitution of (3.37) in (3.35) yields three interaction terms:

$$H' = H^- + H^+ + H^{(2)} \quad (3.38)$$

in which

$$H^- = \frac{q}{m} (\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \frac{\hbar}{i} \nabla \quad (3.39)$$

$$H^+ = \frac{q}{m}(\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \hat{a}_{k, \mu}^+ e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \frac{\hbar}{i} \nabla \quad (3.40)$$

$$\begin{aligned} H^{(2)} &= \frac{q^2}{2m}(\varepsilon_0 V)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mu, \mu'} \left(\frac{\hbar^2}{4\omega_k \omega_{k'}} \right)^{1/2} \left[\hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} + \hat{a}_{k, \mu}^+ e^{-i\mathbf{k} \cdot \mathbf{r}} \right] \\ &\times \left[\hat{a}_{k', \mu'} e^{i\mathbf{k}' \cdot \mathbf{r}} + \hat{a}_{k', \mu'}^+ e^{-i\mathbf{k}' \cdot \mathbf{r}} \right] \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{e}_{\mathbf{k}', \mu'} \end{aligned} \quad (3.41)$$

The product of creation and annihilation terms in turn yields 4 terms:

$$\begin{aligned} &\hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} \hat{a}_{k', \mu'} e^{i\mathbf{k}' \cdot \mathbf{r}}, \quad \hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} \hat{a}_{k', \mu'}^+ e^{-i\mathbf{k}' \cdot \mathbf{r}}, \\ &\hat{a}_{k, \mu}^+ e^{-i\mathbf{k} \cdot \mathbf{r}} \hat{a}_{k', \mu'} e^{i\mathbf{k}' \cdot \mathbf{r}}, \quad \hat{a}_{k, \mu}^+ e^{-i\mathbf{k} \cdot \mathbf{r}} \hat{a}_{k', \mu'}^+ e^{-i\mathbf{k}' \cdot \mathbf{r}} \end{aligned} \quad (3.42)$$

leading to the interaction Hamiltonians

$$H^{--} = \frac{q^2}{2m}(\varepsilon_0 V)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mu, \mu'} \left(\frac{\hbar^2}{4\omega_k \omega_{k'}} \right)^{1/2} \hat{a}_{k, \mu} \hat{a}_{k', \mu'} e^{i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{e}_{\mathbf{k}', \mu'} \quad (3.43)$$

and corresponding terms for H^{-+}, H^{+-}, H^{++} . When $k, \mu \neq k', \mu'$ the operators $\hat{a}_{k, \mu} \hat{a}_{k', \mu'}^+$ can be commuted. Hence the first two Hamiltonians are the same and (3.38) becomes

$$H' = H^- + H^+ + H^{--} + 2H^{+-} + H^{++} \quad (3.44)$$

3.5.2. Elementary Processes

Each of the five interaction Hamiltonians of (3.44) gives rise to an elementary process. We discuss

$$H^- |i\rangle$$

Substituting (3.39) in H^- and (3.16) in $|i\rangle$ we get

$$H^- |i\rangle = \frac{q\hbar}{im}(\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \nabla |\psi_0^{el}\rangle |1_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots\rangle \quad (3.45)$$

It is clear that only $\hat{a}_{\mathbf{k}_0\mu}$ of the many annihilation operators has to be retained, since the others are ineffective. Hence we can rewrite the RHS of (3.45), omitting all constants:

$$\begin{aligned} & |e^{i\mathbf{k}_0 \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \nabla | \varphi_0^{\text{el}} \rangle \hat{a} | 1_{\mathbf{k}_0}, 0_{\mathbf{k}_1} \rangle \\ &= | 0_{\mathbf{k}_0}, 0_{\mathbf{k}_1} \rangle | e^{i\mathbf{k}_0 \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \nabla | \varphi_0^{\text{el}} \rangle \end{aligned} \quad (3.46)$$

The radiation-field has changed to $| 0_{\mathbf{k}_0}, 0_{\mathbf{k}_1} \rangle$, the vacuum state, and the electronic wave function to

$$e^{i\mathbf{k}_0 \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \nabla | \varphi_0^{\text{el}} \rangle \quad (3.47)$$

This term can be expressed as a linear combination of eigen functions of \hat{H}_{el} , the electronic Hamiltonian:

$$e^{i\mathbf{k}_0 \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \nabla | \varphi_0^{\text{el}} \rangle = \sum_m | \varphi_m^{\text{el}} \rangle c_m \quad (3.48)$$

The coefficients of the excited states are no longer zero, reflecting the fact that excited states got partially occupied during the process. Since at the same time a photon has disappeared, absorption has taken place.

In a similar way H^+ represents creation of a photon. When it operates on the initial state i the electronic part of the wave function changes into

$$e^{-i\mathbf{k}_0 \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \nabla | \varphi_0^{\text{el}} \rangle \quad (3.49)$$

and the radiation part into one of the following states

$$| 2_{\mathbf{k}_0}, 0_{\mathbf{k}_n} \rangle, | 1_{\mathbf{k}_0}, 1_{\mathbf{k}_n} \rangle, \dots \quad (3.50)$$

i.e. the photon ends up in any of many modes: *emission*. Since (3.49) represents a combination of electronic states, the average energy will certainly be higher than the ground state energy. The radiation field will contain one extra photon and will have a higher energy than the radiation part of the initial state. Hence the final energy will be

considerably higher than the energy of the initial state, which makes the transition highly improbable, as we shall discuss in 3.6.2. With an excited electronic state, the transition to an electronic state with lower energy is quite possible.

It is clear that H^{--} and H^{++} lead to two-photon absorption and emission respectively. They do not play a role in the present treatment and will not be discussed any further.

The remaining perturbation Hamiltonian is H^{-+} . Its operation on $|i\rangle$ yields:

$$H^{-+}|i\rangle = \frac{q}{2m}(\varepsilon_0 V)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mu, \mu'} \left(\frac{\hbar^2}{4\omega_k \omega_{k'}} \right)^{1/2} \times \hat{a}_{k, \mu} \hat{a}_{k', \mu'}^+ e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{e}_{\mathbf{k}', \mu'} |\varphi_0^{el}\rangle |1_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots\rangle \quad (3.51)$$

Since only mode \mathbf{k}_0 contains a photon, all annihilation operators with $\mathbf{k} \neq \mathbf{k}_0$ can be omitted. For arbitrary reasons we retain only the creation operator with $\mathbf{k}' = \mathbf{k}_1$. The result is, omitting all constants:

$$|\varphi_0^{el}\rangle |0_{\mathbf{k}_0, \mu}, 1_{\mathbf{k}_1, \mu}\rangle e^{-i(\mathbf{k}_1 - \mathbf{k}_0) \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \mathbf{e}_{\mathbf{k}_1, \mu} \quad (3.52)$$

A photon is transferred from the incident beam to the scattered beam. Notice the phase factor. In Appendix 4.4 we list all elementary processes. Here we represent them with Feynman type diagrams.

3.5.3. Feynman Diagrams

The various elementary interaction processes that find their origin in the interaction Hamiltonians of (3.44) are represented by Feynman-type diagrams shown in Figure 25. All interaction processes between matter and radiation (omitting spin processes) can be represented by these diagrams or combinations of them: at each interaction point we can substitute one of the basic interaction processes of Figure 25.

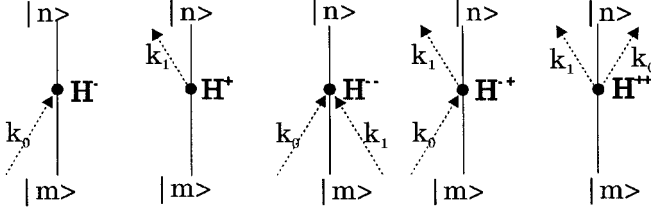


FIGURE 25 Feynman diagrams representing first order perturbation processes: one-photon absorption and emission, two-photon absorption, first-order scattering and two-photon emission. The solid lines represent the target, the dashed ones the photon beams.

3.5.4. Matrix Elements

With each of the heavy dots in Figure 25 corresponds a matrix element. As example we take the matrix element that occurs in the first elementary process:

$$H_{nm}^- \equiv \langle n | H^- | m \rangle \quad (3.53)$$

Using f and i , defined in (3.16) and (3.17) respectively for the states n and m , we get with (3.45)

$$\begin{aligned} \langle f | H^- | i \rangle &= \frac{q}{m} (\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \\ &\times \langle \psi_0^{el} | \langle 0_{\mathbf{k}_0}, 1_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \cdot | \hat{a}_{\mathbf{k}, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \nabla | \psi_0^{el} \rangle | 1_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots \rangle \end{aligned} \quad (3.54)$$

The set of annihilation operators $\hat{a}_{\mathbf{k}, \mu}$ find only one mode to operate on, the mode \mathbf{k}_0 . Hence the sum over \mathbf{k} reduces to one term only. After separating the variables we get

$$\begin{aligned} H_{fi}^- &= \frac{q}{m} (\varepsilon_0 V)^{-1/2} \left(\frac{\hbar}{2\omega_{k_0}} \right)^{1/2} \\ &\times \langle \psi_0^{el} | e^{i\mathbf{k}_0 \cdot \mathbf{r}} \nabla | \psi_0^{el} \rangle \mathbf{e}_{\mathbf{k}_0, \mu} \langle 0_{\mathbf{k}_0}, 1_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \cdot | \cdot 0_{\mathbf{k}_0}, 0_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \cdot \rangle \end{aligned} \quad (3.55)$$

Integration over the spatial coordinates requires some effort. In the present situation it is not necessary to do so, since the orthogonality of photon states with different occupation numbers causes the integral over the radiation variables to vanish. Other matrix elements are found in Appendix 4.4.

Selection rules Not all matrix elements yield nonvanishing results. Perpendicular directions of polarization and unequal number of photons in the resulting radiation states are obvious reasons for vanishing. Symmetry of the electronic states play an important role as well. We start the discussion with considering (3.55).

To simplify the discussion we assume the incident beam to move in the z -direction and to be polarized in the x -direction: $(\mathbf{k}_0)/(|\mathbf{k}_0|) = \mathbf{1}_z$, $\mathbf{e}_{\mathbf{k}_0, x} = \mathbf{1}_x$. The integral over the electronic functions becomes:

$$\langle \varphi_0^{\text{el}} | e^{i\mathbf{k}_0 \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}_0, x} \cdot \nabla | \varphi_0^{\text{el}} \rangle = \left\langle \varphi_0^{\text{el}} \left| e^{i\mathbf{k}_0 \cdot \mathbf{r}} \frac{\partial}{\partial x} \right| \varphi_0^{\text{el}} \right\rangle \quad (3.56)$$

In our case φ_0^{el} has the dimension of an atom. Calculation of the matrix term involves integration over this volume. When the incident beam consists of visible light, the term $e^{i\mathbf{k}_0 \cdot \mathbf{r}}$ can be assumed to remain constant over the volume of the atom and can be taken out of the integration. Hence we can write:

$$\left\langle \varphi_0^{\text{el}} \left| e^{i\mathbf{k}_0 \cdot \mathbf{r}} \frac{\partial}{\partial x} \right| \varphi_0^{\text{el}} \right\rangle = e^{i\mathbf{k}_0 \cdot \mathbf{R}} \left\langle \varphi_0^{\text{el}} \left| \frac{\partial}{\partial x} \right| \varphi_0^{\text{el}} \right\rangle \quad (3.57)$$

where \mathbf{R} is the position of the atom. This assumption is called the dipole approximation for reasons that will become apparent in a moment.

In the case of X-rays this is not true in general. In anomalous scattering, as used in X-ray diffraction, the initial state is usually the state of an inner electron in a transition element or a heavier one. The orbitals of these electrons are much smaller than the dimensions of the atom and we can still invoke the dipole approximation.

When we take as inner orbital the (1s)-orbital, $Ne^{-c|\mathbf{r}|}$, we get

$$\begin{aligned}\frac{\partial}{\partial x} \left| \varphi_0^{\text{el}} \right\rangle &= \frac{\partial}{\partial x} |Ne^{-c|\mathbf{r}|}\rangle \\ &= \frac{c|xNe^{-c|\mathbf{r}|}}{|\mathbf{r}|} = xg(|\mathbf{r}|)\end{aligned}\quad (3.58)$$

The resulting function has the symmetry of a p_x function. This means that it can be written as a linear combination of hydrogen-type p_x functions. Since hydrogen-type orbitals with different values for the quantum numbers l and m are orthogonal, i.e. $\langle \varphi_{l=p,m} | \varphi_{l=q,m} \rangle = \delta_{pq}$, only final electronic states φ_f^{el} with p_x symmetry will yield nonvanishing values. This is the physical basis of the selection rules of spectroscopy. From the point of symmetry, the operator in (3.58) is equivalent to $e\hat{\mathbf{x}}$, the operator of the electronic dipole moment. Hence the name of dipole approximation. More on the matrix term (3.57) can be found in Appendix 4.4.

When the dimension of the orbital of the initial state becomes larger, one has to take the changes of the exponential $e^{i\mathbf{k}_0 \cdot \mathbf{r}}$ explicitly into account. This is usually done by writing it as a series of which only the first few terms are kept. Of course other selection rules apply in this case. In Appendix 4.4 more can be found on matrix elements.

3.6. Scattering

Scattering corresponds to annihilation of a photon \mathbf{k}_0 and the creation of a new photon \mathbf{k}_1 . Hence it requires the operators $\hat{a}_{\mathbf{k}_0}\hat{a}_{\mathbf{k}_1}^+$ or $\hat{a}_{\mathbf{k}_1}^+\hat{a}_{\mathbf{k}_0}$. When \mathbf{k}_0 and \mathbf{k}_1 refer to different plane waves, the order of the operators does not matter, i.e. they commute. These products can be obtained by a double operation of $\hat{\mathbf{A}}$, i.e. from the term $\hat{\mathbf{A}} \cdot \hat{\mathbf{A}} = \hat{\mathbf{A}}^2$, or by applying the operator $\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}$ twice. The latter occurs in the second Born approximation and will be discussed below. We thus get the following Feynman diagrams representing scattering (Figure 26).

3.6.1. First Order Transition: Thomson Scattering

The first order scattering represented by Figure 26(a) is known as Thomson scattering. It is based on the operation of the interaction term H^{+-} of (3.51), which in turn is based on the operator $\hat{\mathbf{A}}^2$. In the

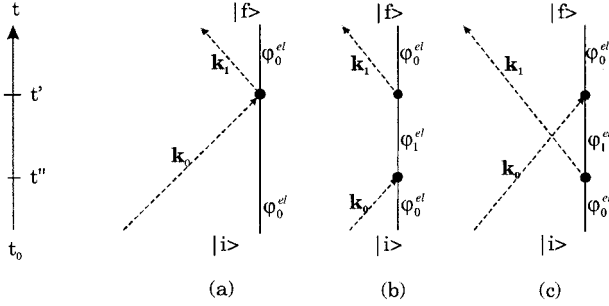


FIGURE 26 Feynman diagrams of scattering: (a) Thomson scattering, (b) and (c) Rayleigh scattering. The arrows represent photon beams. At left we see the time axis with the times at which the interaction processes take place. Of course we have to integrate over these times, adding all partial results.

initial state at t_0 we find the electron of the target in the ground state, while it is immersed in plane wave of EM-radiation with one photon. In the short time interval dt' at t' the EM-field interacts with the electron. The most likely result is that nothing changes because the interaction is weak. Nevertheless a finite chance exists that the state of the system, consisting of field and electron, does change. The resulting state will, in general, not be an eigenstate of $\hat{H}^{(0)}$. It can be expanded in eigenstates of this operator as was done in (3.14), state f being one of these. In first order transitions the coefficient of the final state is given by (3.33). Because H'_{fi} is time-independent we get, with $c_i(t_0) = 1$,

$$\begin{aligned}
 c_{fi}^{(1)}(t) &= \frac{H_{fi}^{+-}}{i\hbar} \int_{t_0}^t dt' e^{i\omega_{fi}t'} \\
 &= \frac{H_{fi}^{+-}}{i\hbar} \frac{e^{i\omega_{fi}t} - e^{i\omega_{fi}t_0}}{i\omega_{fi}} = -\frac{H_{fi}^{+-}}{\hbar\omega_{fi}} e^{i\omega_{fi}(t_0+T/2)} (e^{i\omega_{fi}T/2} - e^{-i\omega_{fi}T/2}) \\
 &= -\frac{H_{fi}^{+-}}{\hbar\omega_{fi}} e^{i\omega_{fi}(t_0+T/2)} 2i \sin(\omega_{fi}T/2)
 \end{aligned} \tag{3.59}$$

in which $T = t - t_0$, the length of time of interaction.

Using the delta-type function $\delta^{(T)}$, defined and shown in Appendix 4.4.1. we rewrite:

$$c_{fi}^{(1)}(T) = -2i \frac{H_{fi}^{+-}}{\hbar} e^{i\omega_{fi}(t_0+T/2)} \pi \delta^{(T)}(\omega_{fi})$$

Removing the phase factor, $e^{i(t_0+T/2)}$, by choosing $t_0 = -T/2$, multiplying by 2 according to (3.44) yields:

$$c_{fi}^{(1)}(T) = -2\pi i \frac{2H_{fi}^{+-}}{\hbar} \delta^{(T)}(\omega_{fi}) \quad (3.60)$$

The $\delta^{(T)}$ function ensures that with large T $c_f^{(1)}$ assumes nonvanishing values only when $\omega_{fi} \approx 0$. Hence in the case of long interaction times we only find transitions from the initial state i to states f that do not differ in energy: *conservation of energy*. This condition follows from the derivation and is not introduced independently.

Adiabatic growth of the perturbation Often one finds in the literature that use is made of the method of adiabatic growth. The basic idea is that we assume a perturbation that slowly grows to the full value. In this way we avoid ripples that are the result of a sudden turning on of the perturbation. In practice these ripples do not occur, because the perturbation is due to a wave packet. Owing to interference between the modes of slightly different frequency contributions to the field at the target before a certain time in the past and beyond a certain time in the future vanish. Hence it makes no difference when we multiply the interaction Hamiltonian with $\exp(\eta t)$ with η a very small quantity. The resulting matrix terms are

$$H_{fi} e^{\eta t} \quad (3.61)$$

At the beginning of the perturbation, at $t_0 = -\infty$, the matrix terms vanish, while at t -values around the present, $t \approx 0$, they take on their original value.

We now turn to the expression for Thomson scattering, (3.59) and get with the help of (4.15):

$$\begin{aligned} c_{fi}^{(1)}(t) &= \frac{2H_{fi}^{+-}}{i\hbar} \lim_{\eta \rightarrow 0} \int_{-\infty}^t dt' e^{i\omega_{fi}t' + \eta t'} = \frac{2H_{fi}^{+-}}{i\hbar} \left[\lim_{\eta \rightarrow 0} \frac{e^{i\omega_{fi}t + \eta t}}{i\omega_{fi} + \eta} \right] \\ &= \frac{2H_{fi}^{+-}}{i\hbar} \left[\lim_{\eta \rightarrow 0} \frac{1}{i} \frac{e^{i\omega_{fi}t}}{\omega_{fi} - i\eta} \right] = -2\pi i \frac{2H_{fi}^{+-}}{\hbar} \delta(\omega_{fi}) \end{aligned} \quad (3.62)$$

the same value as found in (3.60).

3.6.2. Second Order Transitions: Rayleigh Scattering

Figure 26(b) shows the transition from the initial to the final state as a two-step process in which first at t'' a virtual transition occurs to the intermediate state m , consisting of the electron in the excited state φ_1^{el} and no photon in the EM-field. Of course state m is only one of the many states that result from the interaction. Then at t' another virtual transition takes place: a photon is created in the plane wave \mathbf{k}_1 and the electron returns from the excited state to the ground state. Again, many transitions occur, with creation of photons in all different plane waves, but only one is considered, the one that takes the photon to the detector. Thus many paths exist to go from state i to state f .

Figure 26(c) represents an unexpected process. Already before a photon is absorbed, the electron in the ground state emits a photon and goes into an excited state. It is clear that in this transition, energy is not conserved: between t'' and t' we have two photons and the electron in the excited state vs one photon and the electron in the ground state before t' . We appreciate, however, that the interaction time for the first transition is limited: from Figure 24 we get $t_0 < t < t'$ and conservation of energy is not mandatory, but only very unlikely. Hence these terms are usually much smaller and we omit them for simplicity.

The contribution to the coefficient c_f by the second order transitions is given by

$$c_{fi}^{(2)}(t) = \lim_{\eta \rightarrow 0} \sum_m \frac{H_{fm} H_{mi}}{(i\hbar)^2} \int_{t_0}^t dt' e^{i\omega_{fm}t'} \int_{t_0}^{t'} dt'' e^{i\omega_{mi}t''} \quad (3.63)$$

In the method of adiabatic growth this becomes with $\omega_{fm} + \omega_{mi} = \omega_{fi}$,

$$\begin{aligned} c_{fi}^{(2)}(t) &= \lim_{\eta \rightarrow 0} \sum_m \frac{H_{fm}^+ H_{mi}^-}{(i\hbar)^2} \int_{t_0}^t dt' e^{i\omega_{fm}t' + \eta t'} \int_{t_0}^{t'} dt'' e^{i\omega_{mi}t'' + \eta t''} \\ &= \lim_{\eta \rightarrow 0} \sum_m \frac{H_{fm}^+ H_{mi}^-}{(i\hbar)^2} \frac{1}{(i\omega_{mi} + \eta)} \int_{-\infty}^t dt' e^{i\omega_{fi}t' + 2\eta t'} \\ &= \lim_{\eta \rightarrow 0} \sum_m \frac{H_{fm}^+ H_{mi}^-}{(i\hbar)^2} \frac{1}{(i\omega_{mi} + \eta)} \frac{1}{i} \frac{e^{i\omega_{fi}t + 2\eta t}}{\omega_{fi} - 2i\eta} \end{aligned} \quad (3.64)$$

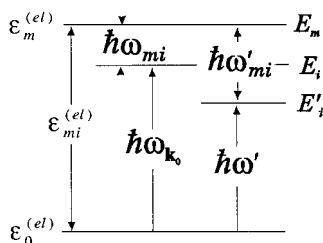


FIGURE 27 The bonded intermediate state m . Shown are the various quantities used in the text.

See Figure 27 for the meaning of the energy terms. When we are not very close to resonance ($\omega_{mi} \neq 0$) η can be omitted in the second denominator. Substituting (4.20) we get

$$c_{fi}^{(2)}(t) = 2\pi i \sum_m \frac{H_{fm}^+ H_{mi}^-}{\hbar^2 \omega_{mi}} \delta(\omega_{fi}) \quad (3.65)$$

Owing to ω_{mi} in the denominator, contributions to the total process by states m far from resonance, vanish.

In general, the second order contributions are much smaller than the first order one. Only when we are close to resonance, $\omega_{mi} \approx 0$, they become important. Anomalous scattering finds its origin in this term and we shall turn to it in the coming sections. The expression contains the delta function because we still have to integrate the intensities over the frequencies of the final states f .

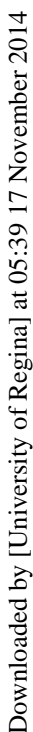
3.6.3. Resonant Scattering

Introduction Expression (3.65) suggests that we run into problems when the energy of the initial state of the full system equals the energy of the intermediate one and $\omega_{mi} = 0$, a singularity in the relation between $c_{fi}^{(2)}$ and ω . It seems that the second-order approach fails to describe the situation in a satisfactory way. We therefore have a closer look into the process. First we have to realize that in most X-ray scattering the energy of the incident photons exceeds the energy to set the electron free. This means that the virtual transitions

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photon states empty, and the states m_2, m_3 , etc. with the electron in the ground state and a photon state with one of the modes singly occupied. It is simple to see that only state m_1 can be reached by H^+ and H^- in one step from the initial state. In second order perturbation theory we assume that the coefficient of the intermediate state $|\varphi_n^{\text{el}}\rangle$ does not change between t'' and t' . This holds when $t' - t''$ is small, which is the case when the difference in energy between the initial state and the intermediate one is not negligible, i.e. when we are far from resonance.

Close to resonance, the situation changes considerably. In addition to unperturbed propagation of the excited electronic state, the long interaction time allows many other processes, such as the one in which the electron in the excited state $|\varphi_n^{\text{el}}\rangle$ emits a photon \mathbf{k}_n , while it returns to the ground state $|\varphi_0^{\text{el}}\rangle$. The electron may still be in the ground state at time t' when the system is supposed to emit the photon \mathbf{k}_1 . It is clear that in this case the emission of another photon \mathbf{k}_1 is ruled out. Another possibility is that before time t' the photon is absorbed again and the electron is back in state $|\varphi_n^{\text{el}}\rangle$. Since in this case the lifetime of photon \mathbf{k}_n is limited, energy does not have to be conserved. This means that the photon \mathbf{k}_n can have a range of energies. In fact the electron does not have to go back to the ground state either; in principle any state with the proper symmetry suffices. The various processes that can take place are represented by the diagrams of Figure 29.

In Appendix 4.3.3 it is shown that the interaction of the excited state m_1 with the electromagnetic field has a twofold effect: the energy is slightly reduced and c_m , the population amplitude of the state m , decays exponentially with time. This decay is shown to be due to processes in which energy is conserved. This is consistent with the idea that the decay is due to emission of radiation and a permanent return to the ground state of the electronic system. The effect of the two processes is collected in the replacement of $c_m(t')$ by

$$c_m(t') = c_m(t'')e^{-\gamma_m(t' - t'')} \quad (3.66)$$

This modification requires us to rewrite the last term of (3.63) as follows:

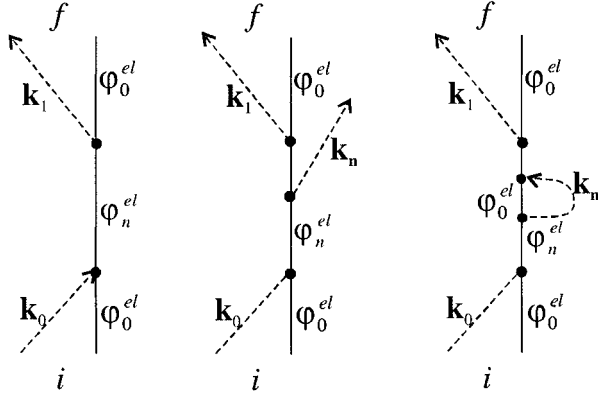


FIGURE 29 Time evolution of the intermediate state. Unperturbed evolution is represented at the left hand. The middle diagram shows emission of a photon. Emission and subsequent absorption is shown at the right hand.

$$\begin{aligned}
 & (i\hbar)^{-2} \lim_{\eta \rightarrow 0} \sum_m \int_{-\infty}^t dt' H_{fm}^+ e^{i\omega_{fm}t'} e^{\eta t'} \int_{-\infty}^{t'} dt'' e^{-\gamma(t'-t'')} H_{mi}^- e^{i\omega_{mi}t''} e^{\eta t} \\
 &= (i\hbar)^{-2} \lim_{\eta \rightarrow 0} \sum_m \int_{-\infty}^t dt' H_{fm}^+ e^{i\omega_{fm}t'} e^{-\gamma_m t'} e^{\eta t'} \int_{-\infty}^{t'} dt'' e^{\gamma_m t''} H_{mi}^- e^{i\omega_{mi}t''} e^{\eta t} \\
 &= \frac{-1}{\hbar^2} \lim_{\eta \rightarrow 0} \sum_n \frac{H_{fm}^+ H_{mi}^-}{i\omega_{mi} + \gamma_m + \eta} \int_{-\infty}^t dt' e^{i\omega_{fi}t'} e^{2\eta t'} \\
 &= \frac{1}{\hbar^2} \lim_{\eta \rightarrow 0} \sum_n \frac{H_{fm}^+ H_{mi}^-}{\omega_{mi} - i\gamma_m - i\eta} \frac{e^{i\omega_{fi}t}}{\omega_{fi} - 2i\eta} \\
 &= 2\pi i \delta(\omega_{fi}) \sum_n \frac{H_{fm}^+ H_{mi}^-}{\hbar^2} \frac{1}{\omega_{mi} - i\gamma_m}
 \end{aligned} \tag{3.67}$$

It should be noted that even when γ_m becomes infinitely small, the summation still contains an imaginary term according to (4.15):

$$\lim_{\gamma \rightarrow 0} \frac{1}{\omega - i\gamma} = \mathbf{P} \frac{1}{\omega} + i\pi \delta(\omega)$$

To understand the physical significance of this result we return to Figure 24 and take the simple case of a hydrogen atom as target. At t_0 the electron is in the ground state ($c_i = 1$) while the second order

term has caused a transition to the $2p$ state. At t'' the perturbation operates and the state of the electron is described by

$$|1s\rangle c_i(t) + |2p\rangle c_{fi}^{(2)}(t)$$

corresponding with a oscillating dipolar charge distribution (see Figure 20). The decaying character of this state causes this distribution to return slowly to the spherical distribution corresponding with the $1s$ state. The decay is due to interaction of the excited state with the radiation field and Figure 29 shows that the description of this interaction requires at least 4th order perturbation theory. See Appendix 4.3.3 for further discussion.

Free intermediate states The transition from the initial state i to the final state f goes via virtual transitions to and from the states m . In Figure 28 we showed the various energy levels that play a role. Since all these paths have a slightly different phase due to their energy differences, we get interference. The result is calculated with the help of (3.67). The states m form a continuum of free electron states and we can replace the summation by integration over the variable ω_m .

The number of energy levels in an interval $d\omega_m$ is given by $\rho_m(\omega_m)d(\omega_m)$. The lower level of integration is, according to Figure 28, given by $E_{\text{ion}}/\hbar \equiv \omega_K$. We then get

$$c_{fi}^{(2)} = 2\pi i \delta(\omega_{fi}) \int_{\omega_K}^{\infty} d\omega_m \rho(\omega_m) \frac{H_{fm}^+ H_{mi}^-}{\hbar^2} \frac{1}{\omega_{mi} - i\gamma(\omega_m)} \quad (3.68)$$

In both cases of resonant scattering the final state contains other states than radiation state \mathbf{k}_1 only. Normalization of the wave function requires that

$$|c_{k_0}|^2 + |c_{k_1}|^2 + \sum_{n \neq k_0, k_1} |c_n|^2 = 1 \quad (3.69)$$

both before and after the interaction. When scattering in the direction \mathbf{k}_1 is the only result of the interaction of the incident beam \mathbf{k}_0 , the sum of the intensities of beams \mathbf{k}_0 and \mathbf{k}_1 after the interaction equals the

intensity of the incident beam before interaction. When other processes occur as well, both the incident and the scattered beam will weaken due to nonvanishing values c_n .

To keep the notation as transparent as possible, we kept the matrix elements in the various expressions in the formal notation. In Appendix 4.4 of the appendix they have been worked out.

3.7. Scattering Factor

3.7.1. Intensity

In the previous sections we obtained the following contributions to the final state: from Thomson scattering: (3.60)

$$c_{fi}^{(1)}(T) = -2\pi i \delta^{(T)}(\omega_{fi}) \frac{2H_{fi}^{+-}}{\hbar}$$

from nonresonant Rayleigh scattering, substituting (4.87): $H_{fm}^+ H_{mi}^- = |H_{mi}^-|^2 \equiv |H_{mi}|^2$ in (3.65).

$$c_{fi}^{(2)}(T) = 2\pi i \delta^{(T)}(\omega_{fi}) \sum_m \frac{|H_{mi}|^2}{\hbar^2 \omega_{mi}}$$

from resonant Rayleigh scattering with discrete, bonded intermediate states (3.67)

$$c_{fi}^{(2)}(T) = 2\pi i \delta^{(T)}(\omega_{fi}) \sum_n \frac{|H_{mi}|^2}{\hbar^2} \frac{1}{\omega_{mi} - i\gamma_m}$$

from resonant Rayleigh scattering with free intermediate states: (3.68):

$$c_{fi}^{(2)}(T) = 2\pi i \delta^{(T)}(\omega_{fi}) \int_{\omega_K}^{\infty} d\omega_m \rho_m(\omega_m) \frac{|H_{mi}|^2}{\hbar^2} \frac{1}{\omega_{mi} - i\gamma(\omega)}$$

in which T is the interaction time. There is some discussion whether bound-bound transitions should be included since their contribution turns out to be small and of the same magnitude as the experimental error [19].

Adding these contributions yields

$$\begin{aligned}
 c_{fi}(T) = & -2\pi i \delta^{(T)}(\omega_{fi}) \left[\frac{2H_{fi}^{-+}}{\hbar} - \sum_m \frac{|H_{mi}|^2}{\hbar^2 \omega_{mi}} - 2\pi i \delta(\omega_{fi}^{(T)}) \right. \\
 & \times \sum_n \frac{|H_{mi}|^2}{\hbar^2} \frac{1}{\omega_{mi} - i\gamma_m} \\
 & \left. - \int_{\omega_K}^{\infty} d\omega \rho(\omega) \frac{|H_{mi}|^2}{\hbar^2} \left[\mathbf{P}\left(\frac{1}{\omega}\right) + i\pi \delta(\omega) \right] \right] \\
 \equiv & -2\pi i \delta^{(T)}(\omega_{fi}) C_{\mathbf{k}_1}
 \end{aligned} \tag{3.70}$$

The intensity of the diffracted beam is proportional to the rate at which photons \mathbf{k}_1 are created. This is equal to the increase with time of the probability $|c_f(t)|^2$ to find the system in the state $|f\rangle \equiv |\psi_0^{el}\rangle |0_{\mathbf{k}_0}, 1_{\mathbf{k}_1}, 0_{\mathbf{k}_2}, \dots\rangle$. With N photons in the primary beam the intensity will be N times as large.

From (3.70) we get:

$$\begin{aligned}
 |c_{fi}(T)|^2 &= 4\pi^2 |C_{\mathbf{k}_1}|^2 (\delta^{(T)}(\omega_{fi}))^2 \\
 &= 4\pi^2 |C_{\mathbf{k}_1}|^2 \delta^{(T)}(\omega_{fi}) \times \frac{\sin(\omega_{fi}T/2)}{\pi\omega_{fi}}
 \end{aligned} \tag{3.71}$$

The wave packet is many wavelengths long, so we can safely assume that T , the length of time of interaction, is long. Hence we can replace $\delta^{(T)}(\omega_{fi})$ by the Dirac delta function $\delta(\omega_{fi})$. Consequently, the right hand side vanishes for all values $\omega_{fi} \neq 0$ and the quotient can be replaced by

$$\lim_{\omega_{fi} \rightarrow 0} \frac{\sin \omega_{fi} T/2}{\omega_{fi}} = T/2$$

Substituting in (3.71)

$$|c_{fi}(T)|^2 = 4\pi |C_{\mathbf{k}_1}|^2 \delta(\omega_{fi}) \times T/2 \tag{3.72}$$

The probability is seen to increase linearly with the time of interaction. Hence we can get the intensity simply by dividing by T :

$$I_{\mathbf{k}_1} = 2\pi |C_{\mathbf{k}_1}|^2 \delta(\omega_{fi}) \tag{3.73}$$

Up to now we tacitly assumed that only one mode \mathbf{k}_1 enters the detector. To get the measured intensity we have to sum over all of modes with the right direction and frequency. Owing to the small range in energy, all these modes interact in the same way with the target. The frequency differences between these modes is so small that we can replace the sum by an integral and use $\omega_{fi} \equiv \omega_f - \omega_i$:

$$\begin{aligned} I &= \int_{\Delta\omega_{\mathbf{k}_1}} 2\pi |C_{\mathbf{k}_1}|^2 \delta(\omega_f - \omega_i) \rho_{\mathbf{k}_1}(\omega_f) d\omega_f \\ &= 2\pi |C_{\mathbf{k}_1}|^2 \rho_{\mathbf{k}_1}(\omega_i) \end{aligned} \quad (3.74)$$

in which $\rho_{\mathbf{k}_1}(\omega_i)$ is the density of modes \mathbf{k}_1 at the frequency of the incident beam. Expression (3.74) is the well-known *Fermi's Golden Rule*. Up to now we considered a one-electron atomic system. In the notation of X-ray diffraction theory, the observed intensity is proportional to $|f(\mathbf{K})|^2$, in which $f(\mathbf{K})$ is the scattering factor of reflection \mathbf{K} , with $\mathbf{K} \equiv \mathbf{k}_1 - \mathbf{k}_0$. Comparison with (2.13) shows that $f(\mathbf{K}) \sim C_{\mathbf{k}_1}$. Omitting all constants we get

$$\begin{aligned} f(\mathbf{K}) &= \frac{2H_{fi}^{+-}}{\hbar} - \sum_m \frac{|H_{mi}|^2}{\hbar^2 \omega_{mi}} - \sum_n \frac{|H_{mi}|^2}{\hbar^2} \frac{1}{\omega_{mi} - i\gamma_m} \\ &\quad - \int_{\omega_K}^{\infty} d\omega_m \rho_m(\omega_m) \frac{|H_{mi}|^2}{\hbar^2} \left[P\left(\frac{1}{\omega_{mi}}\right) + i\pi\delta(\omega_m) \right] \end{aligned} \quad (3.75)$$

where we have written the form factor as the sum of f_0 , the Thomson term, f_1 , the real part of the resonant and non resonant Rayleigh scattering, and if'' , the imaginary term from resonant scattering. For the definition of the variables see Figures 27 and 28.

3.7.2. Thomson Scattering Factor

The first term, coming from Thomson scattering, contains

$$\begin{aligned} H_{fi}^{+-} &= \frac{q^2}{2m} (\varepsilon_0 V)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mu, \mu'} \left(\frac{\hbar^2}{4\omega_k \omega_{k'}} \right)^{1/2} \\ &\quad \times \langle 0_{\mathbf{k}_0}, 1_{\mathbf{k}_1} | \hat{a}_{k, \mu} \hat{a}_{k', \mu'}^+ | 1_{\mathbf{k}_0}, 0_{\mathbf{k}_1} \rangle \langle \varphi_0^{el} | e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} | \varphi_0^{el} \rangle \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{e}_{\mathbf{k}', \mu'} \end{aligned} \quad (3.76)$$

Most of the annihilation operators do not apply, since the corresponding modes are not present in the initial state, while most creation operators create states that do not satisfy the requirements. Thus we get

$$\begin{aligned} H_{fi}^{+-} &= \frac{q^2}{2m} (\varepsilon_0 V)^{-1} \left(\frac{\hbar^2}{4\omega_{k_0}\omega_{k_1}} \right)^{1/2} \langle \varphi_0^{\text{el}} | e^{i(\mathbf{k}_0 - \mathbf{k}_1) \cdot \mathbf{r}} | \varphi_0^{\text{el}} \rangle \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \mathbf{e}_{\mathbf{k}_1, \mu'} \\ &= \frac{q^2}{2m} (\varepsilon_0 V)^{-1} \frac{\hbar}{2\omega_{k_0}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \mathbf{e}_{\mathbf{k}_1, \mu'} \int_V |\varphi_0^{\text{el}}|^2 e^{-i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r} \end{aligned} \quad (3.77)$$

where we used the fact that in elastic scattering the incident beam has the same frequency as the scattered one. The integral, known as the *structure factor* F can also be written as:

$$F(\mathbf{K}) = \int_V |\varphi_0^{\text{el}}|^2 e^{-i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r} = \int_V \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r} \quad (3.78)$$

in which $\rho(\mathbf{r})$ is the electron density distribution of the target. Appendix 4.4 shows that the same expression holds for a many electron system.

3.7.3. The Real Part of Rayleigh Scattering: f'

From (3.75):

$$f'(\mathbf{K}) = \left[- \sum_m \frac{|H_{mi}|^2}{\hbar^2 \omega_{mi}} - \text{P} \int_{\omega_K}^{\infty} d\omega_m \rho_m(\omega) \frac{|H_{mi}|^2}{\hbar^2 \omega_{mi}} \right] \quad (3.79)$$

The terms of the RHS of (3.79) accounts for non-resonant and resonant Rayleigh scattering respectively. We first consider the matrix terms H_{mi}^- and H_{fm}^+ , involving annihilation and creation of a photon respectively.

From Appendix (4.86), after integration over the photon states: (see Figure 27 for meaning of the symbols)

$$H_{nm}^- = i \frac{q}{\hbar} (\varepsilon_0 V)^{-1/2} \left(\frac{\hbar}{2\omega_{\mathbf{k}_0}} \right)^{1/2} e^{i\mathbf{k} \cdot \mathbf{R}} \varepsilon_{nm}^{\text{el}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{r}_{nm} \quad (3.80)$$

Omitting all constants we get

$$-\sum_m \frac{|H_{mi}|^2}{\hbar\omega_{mi}} = -\sum_m \frac{(\varepsilon_{mi}^{\text{el}})^2 |\mathbf{e}_{\mathbf{k},\mu} \cdot \mathbf{r}_{mi}|^2}{(\varepsilon_{mi}^{\text{el}}) - \hbar\omega_{\mathbf{k}_0}}$$

The transitions we consider are those in which an electron from a core orbital is promoted. All of the lower and many of the higher states are occupied and no transitions between them are allowed. This makes ω_{mi} positive. The core region extends over a small volume about the nucleus and the electronic wave function of the core electrons has necessarily a very small wavelength. The wavelengths of the bonded excited states differ considerably with the result that the overlap almost vanishes. The presence of the perturbation Hamiltonian does not change these basic characteristics and hence the discrete terms are often neglected.

The second part of f' involves the continuum of free electron states and the summation over m has been replaced by integration. The lower free states have a better transition dipole moment with the core state and hence a larger $|H_{mi}|$. When the photon energy of the incident beam is high, the major contributions to f' come from states with a lower energy level than E_i . Hence ω_{mi} is negative and f' positive. With decreasing frequency, the balance turns and f' becomes negative, (see Figure 30).

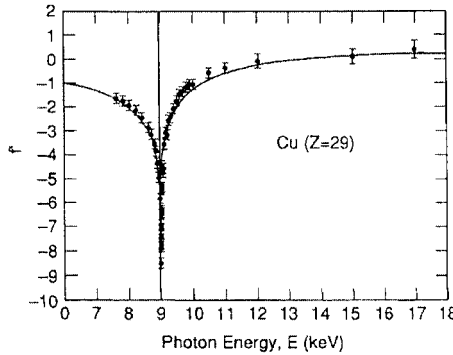


FIGURE 30 The real part f' of the Rayleigh scattering factor as function of the photon energy. The solid line represents calculations from Kissel *et al.* [20] the measurements are from Stanglmeier *et al.* [21] Source: Roy *et al.* [16].

3.7.4. The Imaginary Part of Resonant Scattering

From (3.75) we get

$$f''(\omega_{\mathbf{k}_0}) = -\frac{\pi}{\hbar^2} \sum_m |H_{mi}|^2 \delta(\omega_{mi}) - \frac{\pi}{\hbar^2} \int_{\omega_K}^{\infty} d\omega_m \rho_m(\omega_m) |H(\omega_m)|^2 \delta(\omega_{mi}) \quad (3.81)$$

The contribution from the free intermediate states is given by

$$f''(\omega) = -\pi \rho_m(\omega_{\mathbf{k}_0}) |H(\omega_{\mathbf{k}_0})|^2 \hbar^2 \quad (3.82)$$

a negative quantity.

In the previous section we discussed that calculation of the matrix elements of (3.82) involves integration over the volume of the products of the orbitals on the initial and the intermediate state. Owing to the small size of the core orbital we can neglect change of the phase of the incident and the diffracted beam over this volume. In addition the core orbital is spherical and the plane waves of the intermediate states with the same energy are equivalent. Hence we can consider the imaginary part of Rayleigh scattering as coming from a polarizable point charge. This makes the scattering independent of \mathbf{K} , which is confirmed by experiment [22].

In standard X-ray Crystallography the relation between charge density and scattering factor is given by [23]:

$$f(\mathbf{K}) = \int \rho(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r} \quad (3.83)$$

We notice that this convention yields a scattering factor with a phase angle that is opposite to the present treatment, see (3.78).

Far from the absorption edge, where f'' is vanishing small, this does not matter. *When, however, f'' is used to establish the absolute configuration, the standard convention requires $f''_{\text{classical}} = -f''_{\text{quantum}}$.*

We now derive a most interesting and important relation between the two components of Rayleigh scattering. For practical purposes we limit ourselves to the discrete terms. Consider the integral

$$\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{f''(\omega')}{\omega' - \omega} d\omega'$$

Substituting the first term of the RHS of (3.81) we get

$$\begin{aligned}
& \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\pi \sum_m |H_{mi}|^2 \delta((\varepsilon_{mi}^{\text{el}}/\hbar) - \omega')}{\omega' - \omega} d\omega_{\mathbf{k}} \\
&= \sum_m \frac{|H_{mi}|^2}{((\varepsilon_{mi}^{\text{el}}/\hbar) - \omega)} = \sum_m \frac{|H_{mi}|^2}{\omega_{mi}} \\
&= f'(\omega_{\mathbf{k}_0})
\end{aligned} \tag{3.84}$$

Nothing changes when we replace the summation by integration and apply Cauchy's Principal Value:

$$f'(\omega) = \frac{1}{\pi} \text{P} \int_{-\infty}^{\infty} \frac{f''(\omega')}{\omega' - \omega} d\omega' \tag{3.85}$$

Here we meet again one of the Kramers–Kronig relations. The other one is:

$$f''(\omega) = \frac{-1}{\pi} \text{P} \int_{-\infty}^{\infty} \frac{f'(\omega')}{\omega' - \omega} d\omega' \tag{3.86}$$

Since according to (2.53) the imaginary part of the scattering factor is closely linked to the absorption coefficient, it is the one that is most accessible by experiment. By measuring absorption over the whole relevant frequency range, one can derive the real part of Rayleigh scattering from it.

4.7.5. Conclusion

Both in the classical and in the quantum theory, the origin of anomalous scattering is found in the loss of energy in the scattering process. This requires decay of the scattering dipole moment. It is the requirement of decay that determines the sign of the imaginary component of the scattering factor. In both cases, it was shown that this loss is a most natural part of the interaction between the target and the radiation field. Hence the adjective anomalous is ill chosen.

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4. APPENDICES

4.1. The Dirac Delta Function and Related Mathematical Identities

4.1.1. Dirac Delta Function [7,24]

In scattering theory, we often encounter the function

$$f = \frac{\sin nx}{x} \quad (4.1)$$

where n is a positive number. In Figure 31 we plot this function for

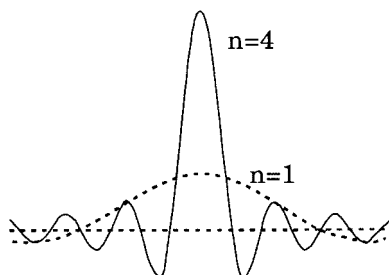


FIGURE 31 The function $\pi\delta^{(n)}(x) = \sin(nx)/x$ for different values of n . The values of the peak are seen to increase with n , while the width decreases.

some values of n and see that its value at $x \approx 0$ steeply increases with n . For infinitely large values of n f is seen to be an infinitely high, infinitely thin spike. Integration of f yields:

$$\int_{-\infty}^{\infty} \frac{\sin(nx)}{x} dx = \pi$$

independent of n . When we define

$$\delta^{(n)} = \frac{\sin nx}{\pi x} \quad (4.2)$$

the Dirac delta function is given by

$$\delta(x) = \lim_{n \rightarrow \infty} \delta^{(n)}(x). \quad (4.3)$$

Strictly speaking the limits do not exist, but we can take n very large in which case $\delta^{(n)}(x) = 0$ for all values of x that differ measurably from zero. Hence the delta function is usually defined by

$$\delta(x) = 0 \quad \text{for } x \neq 0 \quad (4.4)$$

and

$$\int_{-\infty}^{\infty} f(x)\delta(x)dx = f(0) \quad (4.5)$$

where $f(x)$ is a function that is smooth at $x = 0$.

Other functions have the same limiting properties as the function $\sin(nx)/(\pi x)$:

$$\begin{aligned}\delta^{(n)}(x) &= \frac{n}{\sqrt{\pi}} e^{-n^2 x^2} \\ \delta^{(n)}(x) &= \frac{n}{\pi} \frac{1}{1 + n^2 x^2} \\ \delta^{(n)}(x) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ixt} dt\end{aligned}\quad (4.6)$$

Instead of taking the limit at $n = \infty$, we can also take the $\lim_{\varepsilon \rightarrow 0}$ when we use the functions:

$$\frac{1}{2\varepsilon} e^{-|x|/\varepsilon}, \quad \frac{1}{\pi} \frac{\varepsilon}{x^2 + \varepsilon^2}, \quad \frac{1}{\varepsilon\sqrt{\pi}} e^{-x^2\varepsilon^2}, \quad \frac{\sin(x/\varepsilon)}{\pi x} \quad (4.7)$$

4.1.2. Cauchy Principal Value

The Cauchy principal value, denoted by \mathbf{P} , is defined by:

$$\int_{-A}^B dx \mathbf{P} \frac{f(x)}{x} \equiv \mathbf{P} \int_{-A}^B dx \frac{f(x)}{x} \equiv \lim_{\delta \rightarrow 0} \left[\int_{-A}^{-\delta} dx \frac{f(x)}{x} + \int_{\delta}^B dx \frac{f(x)}{x} \right]; \quad A, B > \delta \quad (4.8)$$

where δ is positive and $f(x)$ is smooth at $x=0$.

It excludes the singularity at $x=0$.

With this we can write

$$\int_{-\infty}^{\infty} dx \frac{f(x)}{x} = \mathbf{P} \int_{-\infty}^{\infty} dx \frac{f(x)}{x} + \int_{-\delta}^{\delta} dx \frac{f(x)}{x} \quad (4.9)$$

To calculate the last term, we turn to the complex plane in which the real part of a point z is given on the horizontal axis and the imaginary part along the vertical one. We consider the integral

$$\int_A^D \frac{f(z)}{z} dz \quad (4.10)$$

along a path given in Figure 32.

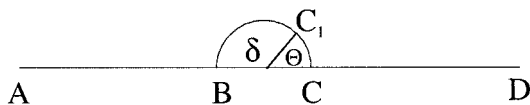


FIGURE 32 The path in the complex plane. The points A, B, C, D are on the real axis at $-\infty, -\delta, \delta$ and ∞ respectively.

The integral (4.10) consists of three parts. By taking the limit in which δ , the radius of semicircle C_1 , goes to zero, we can write the contributions of the parts $(A-B) + (C-D)$ as

$$\mathbf{P} \int_{-\infty}^{\infty} dx \frac{f(x)}{x} \quad (4.11)$$

To calculate the contribution of the integral along C_1 we write z in polar coordinates:

$$z = \delta e^{i\theta}$$

Since δ is very small, we can write

$$f(z) = f(0)$$

The integral along C_1 becomes

$$\lim_{\delta \rightarrow 0} f(0) \int_{\pi}^0 \frac{1}{\delta e^{i\theta}} i \delta e^{i\theta} d\theta = f(0) i(-\pi) \quad (4.12)$$

The integrand is seen to be independent of δ .

The integral (4.9) thus becomes:

$$\begin{aligned} \int_{-\infty}^{\infty} dx \frac{f(x)}{x} &= \mathbf{P} \int_{-\infty}^{\infty} dx \frac{f(x)}{x} - i\pi f(0) \\ &\equiv \int_{-\infty}^{\infty} dx f(x) \left(\mathbf{P} \left(\frac{1}{x} \right) - i\pi \delta(x) \right) \end{aligned} \quad (4.13)$$

Accordingly under the integral sign we can make the following replacement:

$$\frac{1}{x} \Rightarrow \mathbf{P} \left(\frac{1}{x} \right) - i\pi \delta(x) \quad (4.14)$$

N.B. We have drawn the semicircle in the upper part of the complex plane, assuming that in this semiplane $f(x)$ will behave well, i.e. will vanish when we move far from the origin and remain finite elsewhere. If $f(x)$ will only vanish in the lower semi plane, we have to draw the semicircle there and the sign of the last term of (4.14) will change. To remind us of the direction, we can include it in the expression explicitly and write [24]

$$\lim_{\eta \rightarrow 0} \frac{1}{x \pm i\eta} = \mathcal{P} \frac{1}{x} \mp i\pi\delta(x) \quad (4.15)$$

4.1.3. Other Integrals

$$\lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{e^{i\omega t}}{\omega} \quad (4.16)$$

We write

$$\begin{aligned} \lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{e^{i\omega t}}{\omega} &= \lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\cos(\omega t)}{\omega} \\ &\quad + i \lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\sin(\omega t)}{\omega} \end{aligned} \quad (4.17)$$

The singularity is found in the first right hand term. Hence we use (4.13) and write

$$\lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} f(\omega) \frac{\cos(\omega t)}{\omega} d\omega = \mathcal{P} \lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} f(\omega) \frac{\cos(\omega t)}{\omega} d\omega + i\pi f(0) \cos(0) \quad (4.18)$$

For large t the exponential oscillates rapidly for all nonvanishing values of ω . Since $f(\omega)$ changes slowly with ω the integral vanishes.

The second integral of the right hand side of (4.17) can, for large t , be written as

$$\begin{aligned} i \lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\sin(\omega t)}{\omega} &= i\pi \int_{-\infty}^{\infty} d\omega f(\omega) \delta(\omega) \\ &= i\pi f(0) \end{aligned} \quad (4.19)$$

Substituting (4.18) and (4.19) in (4.17) we get

$$\lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega f(\omega) \frac{e^{i\omega t}}{\omega} = 2\pi i f(0) \quad (4.20)$$

4.2. Fields from Charges and Currents

The whole field of electricity and magnetism is contained in the Maxwell equations:

$$\begin{aligned} \text{(a) } \nabla \cdot \mathbf{E} &= \rho/\varepsilon_0 & \text{(b) } \nabla \cdot \mathbf{B} &= 0 \\ \text{(c) } \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t} & \text{(d) } c^2 \nabla \times \mathbf{B} &= \mathbf{j}/\varepsilon_0 + \frac{\partial \mathbf{E}}{\partial t} \end{aligned} \quad (4.21)$$

In electrostatics the field \mathbf{E} can be written as the gradient of a potential ϕ : $\mathbf{E} = \nabla\phi$. When in addition to charges currents are also present, we need four potentials to describe the six fields: $\mathbf{E}_x, \dots, \mathbf{B}_z$. We introduce the vector potential \mathbf{A} with its three components satisfying the following relations:

$$\mathbf{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t} \quad (4.22)$$

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (4.23)$$

Since $\nabla \cdot (\nabla \times \mathbf{V}) \equiv 0$, we automatically satisfy (4.21(b)). We realize that if we add the gradient of some function, $\nabla\psi$, to \mathbf{A} the resulting \mathbf{B} is the same because $\nabla \times \nabla\psi \equiv 0$.

\mathbf{E} will change however, unless we change ϕ to $\phi - \partial\psi/\partial t$. The change in \mathbf{E} becomes:

$$-\nabla \frac{\partial\psi}{\partial t} + \frac{\partial}{\partial t} \nabla\psi = 0.$$

This leaves us the freedom to fix \mathbf{A} in such a way that our equations become simpler.

We now want to relate \mathbf{A} and ϕ to the sources of the fields. From (4.21) we get

$$-\nabla^2 \phi - \frac{\partial}{\partial t} \nabla \cdot \mathbf{A} = \rho/\varepsilon_0 \quad (4.24)$$

Equation (4.21(c)) can be rewritten as

$$c^2 \nabla \times (\nabla \times \mathbf{A}) - \frac{\partial}{\partial t} \left(-\nabla\phi - \frac{\partial \mathbf{A}}{\partial t} \right) = \mathbf{j}/\varepsilon_0$$

This relates the potentials to the source \mathbf{j} .

Since $\nabla \times (\nabla \times \mathbf{A}) \equiv \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$, we get

$$-c^2 \nabla^2 \mathbf{A} + \nabla(\nabla \cdot \mathbf{A}) + \frac{\partial}{\partial t} \nabla \phi + \frac{\partial^2 \mathbf{A}}{\partial t^2} = \mathbf{j}/\epsilon_0 \quad (4.25)$$

We now use the freedom promised above and choose $\nabla \cdot \mathbf{A} = (-1/c^2)(\partial \phi / \partial t)$. This choice changes the second term into $c^2 \nabla((-1/c^2)(\partial \phi / \partial t))$ which just cancels the third term. The result is

$$-c^2 \nabla^2 \mathbf{A} + \frac{\partial^2 \mathbf{A}}{\partial t^2} = \mathbf{j}/\epsilon_0 \quad (4.26)$$

Integration yields:

$$\mathbf{A}(\mathbf{r}, t) = \int_0^\infty \frac{\mathbf{j}(\mathbf{r}', t - r_{12}/c)}{4\pi\epsilon_0 r_{12}} d^3\mathbf{r}' \quad (4.27)$$

with $r_{12} \equiv |\mathbf{r} - \mathbf{r}'|$

Along the same line we obtain the relation between the potential ϕ and the charge density ρ :

$$\nabla^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = -\rho/\epsilon_0 \quad (4.28)$$

4.2.1. The Field of an Oscillating Dipole

A point charge $+q$ oscillates with a frequency ω , resulting in a displacement from the origin:

$$\mathbf{r}_q = \mathbf{r}_q^0 e^{i\omega t} \quad (4.29)$$

The charge and current density are given by

$$\begin{aligned} \rho(\mathbf{r}', t) &= q\delta(\mathbf{r}' - \mathbf{r}_q(t)) \\ \mathbf{j}(\mathbf{r}', t) &= q\mathbf{v}_q\delta(\mathbf{r}' - \mathbf{r}_q(t)) \end{aligned} \quad (4.30)$$

We turn to (4.27) to calculate the vector potential at a point $P(\mathbf{r})$. When the distance r to P , the point of observation, is much larger than the amplitude of the oscillation we get $r \simeq |\mathbf{r} - \mathbf{r}'|$.

We then have

$$\mathbf{A}(\mathbf{r}, t) = \int_V \frac{q\mathbf{v}_q(t - r/c)\delta(\mathbf{r}' - \mathbf{r}_q)}{r} d^3\mathbf{r}' = \frac{q\mathbf{v}_q(t - r/c)}{r} \quad (4.31)$$

To derive the electric and magnetic fields at $P(\mathbf{r})$ we choose a Cartesian coordinate system with the z -axis pointing from the origin to the observer at P , the x -axis in the plane through \mathbf{A} and z , perpendicular to the latter. The y -axis follows in the usual way (Figure 33).

The vector potential \mathbf{A} does not, to first order, change when we move P in the x - or y -direction. So

$$\frac{\partial \mathbf{A}_i}{\partial x} = \frac{\partial \mathbf{A}_i}{\partial y} = 0, \quad i = x, z \quad \text{and} \quad A_y = 0 \quad (4.32)$$

We now calculate the magnetic field $\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t)$ with the help of (4.32):

$$\mathbf{B} = \begin{vmatrix} \mathbf{1}_x & \mathbf{1}_y & \mathbf{1}_z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ A_x & A_y & A_z \end{vmatrix} = \mathbf{1}_y \frac{\partial A_x(\mathbf{r}, t)}{\partial z}$$

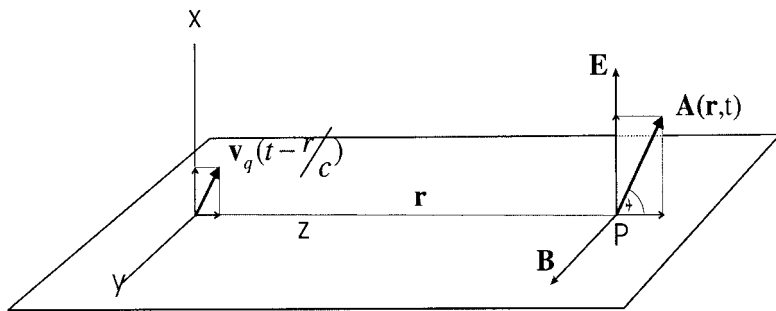


FIGURE 33 The relation between the velocity of a point charge and the vector potential at a later time and a different position.

This means that only the oscillation of the charged particle in the plane perpendicular to \mathbf{r} contributes to the magnetic field. With (4.31) we get:

$$\begin{aligned} B_y(\mathbf{r}, t) &= \frac{\partial A_x(\mathbf{r}, t)}{\partial z} = \frac{q}{4\pi\epsilon_0 c^2} \left[\frac{\partial}{\partial z} \frac{(\mathbf{v}_q(t - (z/c)))_x}{z} \right] \\ &= \frac{q}{4\pi\epsilon_0 c^2} \left[\frac{1}{z} \frac{\partial}{\partial z} \mathbf{v}_q(t - z/c) + \mathbf{v}_q(t - z/c) \frac{\partial}{\partial z} \frac{1}{z} \right]_x \end{aligned} \quad (4.33)$$

To understand the importance of the terms we plot the function $[(\mathbf{v}_q(t - (z/c)))_x/z]$ as function of z . According to (4.29) the numerator equals $(\mathbf{v}_q(t - z/c))_x = i\omega x_q^0 e^{i\omega(t - (z/c))}$. At $t=0$, the real part of the function becomes $=(\omega x_q^0/z) \sin 2\pi(z/\lambda)$; the result, on arbitrary scale, is given in Figure 34.

We notice that at larger distances the z -dependence of A_x is mainly due to the oscillatory function. Consequently, we neglect the second right hand term of (4.33) and get

$$\begin{aligned} B_y &= \frac{1}{4\pi\epsilon_0 c^2} \frac{\omega x_q^0}{z} \frac{2\pi}{\lambda} \cos 2\pi z/\lambda \\ &= \frac{1}{4\pi\epsilon_0 c^3} \frac{\omega^2 x_q^0}{z} \cos 2\pi z/\lambda \end{aligned} \quad (4.34)$$

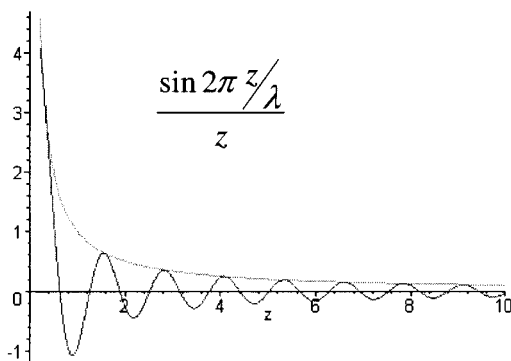


FIGURE 34 Dependence of A_x on the distance between oscillator and observer in arbitrary units.

The general expression is:

$$\mathbf{B}(\mathbf{r}, t) = \frac{-1}{4\pi\epsilon_0 c^3} \frac{1}{r} \ddot{\mathbf{p}}(t - r/c) \times \mathbf{1}_r \quad (4.35)$$

in which the dipole moment \mathbf{p} is given by $\mathbf{p} = q\mathbf{r}_q$

The calculation of the E-field is somewhat more involved. We can use, however, the fact that far from the oscillating charge we have

$$|\mathbf{E}| = c|\mathbf{B}| \quad (4.36)$$

with the field \mathbf{E} perpendicular to both \mathbf{B} and \mathbf{r} . The final result is:

$$|\mathbf{E}| = \frac{1}{4\pi\epsilon_0 c^2} \frac{1}{r} |\ddot{\mathbf{p}}(t - r/c) \times \mathbf{1}_r| \quad (4.37)$$

The direction of \mathbf{E} is perpendicular to \mathbf{r} and \mathbf{B} .

4.2.2. Radiation of Energy: Damping

When a charge is oscillating, energy is carried away with the emitted wave. The amount of energy, that passes per second through a square meter of a surface normal to the direction in which the wave is going, is given by:

$$S = \epsilon_0 c \langle E^2 \rangle \quad (4.38)$$

in which $\langle E^2 \rangle$ is the time average of the square of the electric field.

With (4.37) we find for S :

$$S = \frac{\ddot{\mathbf{p}}^2 \sin^2 \theta}{16\pi^2 \epsilon_0 r^2 c^3} \quad (4.39)$$

in which θ is the angle between the directions of oscillation and observation.

When we draw a sphere with the oscillator as center and assume the oscillation to be in the vertical direction, all points in a thin horizontal annular segment of the sphere receive the same amount of radiation.

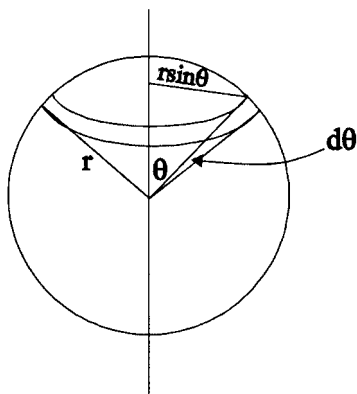


FIGURE 35 Segment of a sphere around an oscillating charge.

The area of the segment is according to Figure 35:

$$dA = 2\pi r^2 \sin \theta d\theta \quad (4.40)$$

The amount of energy flowing through the segment per second is SdA . Integration over the sphere yields the total amount of energy emitted per second.

$$\begin{aligned} P &= \int_{\text{sphere}} SdA = \frac{q^2 \langle \ddot{r}_q^2 \rangle}{8\pi\epsilon_0 c^3} \int_0^\pi \sin^3 \theta d\theta \\ &= \frac{q^2 \langle \ddot{r}_q^2 \rangle}{6\pi\epsilon_0 c^3} \end{aligned} \quad (4.41)$$

Considerations, based on conservation of energy, state that this radiated energy equals in magnitude the loss of energy of the system contained by the sphere, i.e. a decrease of energy W of the oscillator:

$$P = -dW/dt$$

When the decrease is slow, we can assume that over a short time (4.29) still holds. Taking the real part we get:

$$\ddot{\mathbf{r}} = -\omega^2 \mathbf{r}_q^0 \cos \omega t$$

and

$$\langle \ddot{\mathbf{r}}_q^2 \rangle = \omega^4 (\mathbf{r}_q^0)^2 \cos^2 \omega t = \frac{1}{2} \omega^4 (r_q^0)^2$$

and the energy emitted by the oscillator per second:

$$P = \frac{q^2 \omega^4 |\mathbf{r}_q^0|^2}{12\pi\epsilon_0 c^3} \quad (4.42)$$

The energy of the oscillator is the sum of the kinetic and potential energy:

$$W = T + U \quad (4.43)$$

With

$$T = \frac{1}{2} m \dot{x}^2 = \frac{1}{2} m \omega^2 |\mathbf{r}_q^0|^2 \sin^2 \omega t \quad (4.44)$$

and

$$U = \frac{1}{2} k x^2 = \frac{1}{2} m \omega^2 |\mathbf{r}_q^0|^2 \cos^2 \omega t \quad (4.45)$$

we get for the energy

$$W = \frac{1}{2} m \omega^2 |\mathbf{r}_q^0|^2 \quad (4.46)$$

The fractional decrease of energy per second, $\alpha = (-dW/dt)/W = P/W$, can be calculated with (4.42):

$$\alpha = \frac{(q^2 \omega^4 |\mathbf{r}_q^0|^2)/(12\pi\epsilon_0 c^3)}{(1/2)m\omega^2 |\mathbf{r}_q^0|^2} = \frac{q^2 \omega^2}{6\pi\epsilon_0 c^3} \quad (4.47)$$

Since the fractional decrease per second is independent of W we can write:

$$W = W_0 e^{-\alpha t} \quad (4.48)$$

This fractional decay of the oscillation suggest damping. The mechanism of the damping can be found in the action of the electromagnetic

field on the oscillator. The detailed calculation of this action is rather complex and will not be reproduced here.

The present theory allows to calculate the lifetime of the oscillation that brings about the atomic emission spectra, such as the well known yellow line of sodium. Its wavelength is about 6000 \AA , corresponding with a frequency of $\omega = 2\pi c/\lambda \sim 0.31 \times 10^{16}$. The corresponding α is 0.62×10^8 . This means that in $1/\alpha = 0.16 \times 10^{-7} \text{ s}$, the energy of the oscillator reduces to $1/e$ of its original value. Note however that this short time is enough for about 10 million oscillations.

4.3. Energy Levels of Interacting Systems

4.3.1. Introduction

To gain some understanding of the effect of interaction, we consider a simple system, the molecular ion H_2^+ , consisting of two protons and one electron. When the protons are far apart, it consists of a hydrogen atom at site A and proton on B and a good approximation to the wave function is

$$\psi_1 = \phi_a^A \otimes \phi_p^B \quad (4.49)$$

Equally good is the wave function

$$\psi_2 = \phi_p^A \otimes \phi_a^B \quad (4.50)$$

with the atom on B and a proton on A . The product form of these two wave functions suggests that no interaction exists. The interaction, however, makes it possible that the electron jumps from A to B when the protons are not too far apart. In other words, the wave function can change from ψ_1 to ψ_2 , indicating that they do not represent stationary states. We now construct

$$\psi = \psi_1 c_1 + \psi_2 c_2 \quad (4.51)$$

Symmetry dictates that the electron is equally often found on either proton and, consequently, $|c_1| = |c_2|$. Two new, stationary states arise:

$$\Psi_+ = C_+(\psi_1 + \psi_2) \quad (4.52)$$

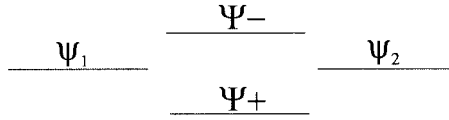


FIGURE 36 Energy levels emerging from the interaction of two interacting states.

and

$$\Psi_- = C_-(\psi_1 - \psi_2) \quad (4.53)$$

in which C_+ and C_- are normalization constants.

One of the new energies is higher, the other one lower than the energies we started from. This remains true when we start with states that differ in energy.

4.3.2. Eigenstates of Electrons Interacting with Radiation

Again we have two systems that interact: an atom and an electromagnetic field. This time there is no symmetry to help us find the coefficients c_i of (4.51) and we have to resort to other methods. We shall show with a simple numerical case the main features of the result of the interaction.

We consider a one-electron atom with two electronic states, φ_0 and φ_1 , with energies ε_0^{el} and ε_1^{el} respectively. Embedded in a radiation field with modes k_{-1} , k_0 , k_1 . The states of the noninteracting system, our basis states, are:

$$\begin{array}{l} |0\rangle = |\varphi_0\rangle|0_{k_{-1}}, 0_{k_0}, 0_{k_1}\rangle, \\ |1\rangle = |\varphi_1\rangle|0_{k_{-1}}, 0_{k_0}, 0_{k_1}\rangle, \quad |2\rangle = |\varphi_0\rangle|1_{k_{-1}}, 0_{k_0}, 0_{k_1}\rangle, \\ |3\rangle = |\varphi_0\rangle|0_{k_{-1}}, 1_{k_0}, 0_{k_1}\rangle, \quad |4\rangle = |\varphi_0\rangle|0_{k_{-1}}, 0_{k_0}, 1_{k_1}\rangle \end{array} \quad \left| \right.$$

with energies $E_0 = \varepsilon_0^{el}$, $E_1 = \varepsilon_1^{el}$, $E_2 = \varepsilon_0^{el} + \hbar\omega_{k_{-1}}$, $E_3 = \varepsilon_0^{el} + \hbar\omega_{k_0}$ and $E_4 = \varepsilon_0^{el} + \hbar\omega_{k_1}$ respectively. The frequencies of the three modes are very similar. Since only states with comparable energy interact appreciably, state $|0\rangle$ can be left out, as well as states with more than one photon.



FIGURE 37 The energy levels of the basis states in the absence of interaction.

We notice that these functions are orthogonal: $\langle m | n \rangle = 0$, owing to the orthogonality of the electronic states, $\langle \varphi_0 | \varphi_1 \rangle = 0$, and/or of the radiation states: $\langle 1_{k_1}, 0, 0 | 0, 1_{k_0}, 0 \rangle = 0$. We can calculate the state functions of the interacting system as follows:

$$\hat{H}|\psi_i\rangle = |\psi_i\rangle E_i \quad (4.54)$$

Substituting

$$\psi_i = \sum_{n=1}^4 |n\rangle c_{ni} \quad (4.55)$$

We get:

$$\sum_{n=1}^4 \hat{H}|n\rangle c_{ni} = \sum_{n=1}^4 |n\rangle c_{ni} E_i \quad (4.56)$$

Multiplying from the left with $\langle m |$ and integrating yields:

$$\sum_{n=1}^4 H_{mn} c_{ni} = \sum_{n=1}^4 \langle m | n \rangle c_{ni} E_i \quad (4.57)$$

Orthogonality reduces the right hand sum to one term, $c_{mi} E_i$. For the terms of the left hand sum we used the abbreviations

$$H_{mn} \equiv \langle m | \hat{H} | n \rangle$$

In matrix notation:

$$(H_{m1} \ H_{m2} \ H_{m3} \ H_{m4}) \begin{pmatrix} c_{1i} \\ c_{2i} \\ c_{3i} \\ c_{4i} \end{pmatrix} = c_{mi} E_i \quad (4.58)$$

The expression can be extended so as to include the equations for the other energy values

$$\begin{pmatrix} H_{11} & \cdot & \cdot & H_{14} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ H_{41} & \cdot & \cdot & H_{44} \end{pmatrix} \begin{pmatrix} c_I & \cdot & \cdot & c_{IV} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ c_I & \cdot & \cdot & c_{IV} \end{pmatrix} = \begin{pmatrix} c_I & \cdot & \cdot & c_{IV} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ c_I & \cdot & \cdot & c_{IV} \end{pmatrix} \times \begin{pmatrix} E_I & 0 & 0 & 0 \\ 0 & E_{II} & 0 & 0 \\ 0 & 0 & E_{III} & 0 \\ 0 & 0 & 0 & E_{IV} \end{pmatrix} \quad (4.59)$$

This equation can be written as

$$\mathbf{HC} = \mathbf{CE} \quad (4.60)$$

in which \mathbf{E} is a diagonal matrix.

When we multiply both sides with \mathbf{C}^{-1} we get

$$\mathbf{C}^{-1}\mathbf{HC} = \mathbf{E} \quad (4.61)$$

We thus have to find a matrix \mathbf{C} that transforms \mathbf{H} into a diagonal matrix by what is called a similarity transformation. The values on this diagonal are the desired energy values, while the matrix that performs this diagonalisation is the coefficient matrix.

We now turn to the matrix elements of the Hamiltonian. The Hamiltonian can be written as

$$H = H^{(0)} + H' \quad (4.62)$$

The unperturbed Hamiltonian $H^{(0)}$, of which the basis states are eigenstates, can be written as the sum of a term that operates on the

electronic part of the state and a term that operates on the radiation part:

$$\begin{aligned}
 H^{(0)} &= H_{el}^{(0)} + H_{rad}^{(0)} \\
 H_{11} &= \langle 1 | \hat{H} | 1 \rangle = \langle \varphi_1 | \langle 0, 0, 0 | H_{el}^{(0)} + H_{rad}^{(0)} + H' | \varphi_1 \rangle | 0, 0, 0 \rangle \\
 &= \langle \varphi_1 | H_{el}^{(0)} | \varphi_1 \rangle \langle 0, 0, 0 | 0, 0, 0 \rangle + \langle \varphi_1 | | \varphi_1 \rangle \langle 0, 0, 0 | H_{rad}^{(0)} | 0, 0, 0 \rangle \\
 &\quad + \langle \varphi_1 | \langle 0, 0, 0 | H' | \varphi_1 \rangle | 0, 0, 0 \rangle
 \end{aligned} \tag{4.63}$$

The first term of the second line is ε_1^{el} , the energy of the excited state of the atom. The second term is the zero-point energy of the radiation field. Since it has the same value in all cases, we take it to be zero.

The interaction term H' will be dealt with in Appendix 4.4. Here we use the result that the interaction term consists of terms that are a product of the following type

$$H' = H'_{el} * H'_{rad} \tag{4.64}$$

H'_{el} has only nonvanishing values between electronic states that differ by ± 1 in angular momentum l_z , while H'_{rad} has only nonvanishing values between radiation states that differ ± 1 in the occupation number of one of the modes. Hence H' does not contribute to the diagonal elements. Since the basis states are eigenstates of $H^{(0)}$, it is clear that this operator only couples a state with itself: all non-diagonal matrix elements of $H^{(0)}$ vanish.

$$\begin{aligned}
 H_{11} &= \varepsilon_1^{el} \\
 H_{22} &= \langle \varphi_0 | H_{el}^{(0)} | \varphi_0 \rangle + \langle 1, 0, 0 | H_{rad}^{(0)} | 1, 0, 0 \rangle = \varepsilon_0^{el} + \hbar\omega_{-1} \\
 H_{33} &= \langle \varphi_0 | H_{el}^{(0)} | \varphi_0 \rangle + \langle 0, 1, 0 | H_{rad}^{(0)} | 0, 1, 0 \rangle = \varepsilon_0^{el} + \hbar\omega_0 \\
 H_{44} &= \langle \varphi_0 | H_{el}^{(0)} | \varphi_0 \rangle + \langle 0, 1, 0 | H_{rad}^{(0)} | 0, 0, 1 \rangle = \varepsilon_0^{el} + \hbar\omega_1
 \end{aligned}$$

The energy of state $|3\rangle$ is chosen to be the same as that of state $|1\rangle$. We choose then as reference level:

$$E_1 = E_3 = 0$$

higher and δ lower respectively. The nondiagonal states can be divided into two groups: those that involve both ϕ_0 and ϕ_1 , and all others.

For simplicity all terms of the first group are assumed to be equal.

$$\begin{aligned} H_{12} &= \langle 1 | \hat{H} | 2 \rangle = \langle \varphi_1 | H'_{el} | \varphi_0 \rangle \langle 0, 0, 0 | H'_{rad} | 1, 0, 0 \rangle \\ &= H_{13} = H_{14} = H_{21} = H_{31} = H_{41} \equiv \nu \end{aligned}$$

All other terms are zero since the same electronic state is involved.

To illustrate the procedure, we assume $\nu = 0.3$ and the energy spacing between the modes to be 1. The resulting Hamilton matrix \mathbf{H} is seen below. A similarity transformation of \mathbf{H} yields \mathbf{E} .

$$H := \begin{bmatrix} 0 & -0.3 & -0.3 & -0.3 \\ -0.3 & -1 & 0 & 0 \\ -0.3 & 0 & 0 & 0 \\ -0.3 & 0 & 0 & 1 \end{bmatrix} \quad \mathbf{E} = \begin{bmatrix} -1.1 & 0 & 0 & 0 \\ 0 & -0.1 & 0 & 0 \\ 0 & 0 & 0.1 & 0 \\ 0 & 0 & 0 & 1.1 \end{bmatrix}$$

and the coefficient matrix:

$$\mathbf{C} = \begin{bmatrix} -0.29 & -0.64 & 0.64 & -0.29 \\ -0.95 & 0.27 & -0.15 & 0.042 \\ -0.81 & -0.70 & -0.70 & 0.081 \\ -0.42 & -1.5 & 0.27 & 0.95 \end{bmatrix}$$

We represent these results in an energy diagram.

The energy levels $\mathbf{E}_I \dots \mathbf{E}_{IV}$ correspond to an eigenstate of the ‘coupled’ system with eigenfunctions $\Psi_I \dots \Psi_{IV}$ respectively. The degree to which a particular basis state $|n\rangle$ occurs in the different eigenfunctions is shown in Figures 39 and 40.

The corresponding distribution for the basis photon state $|3\rangle (= |k_0\rangle)$ is very similar to this one, whereas the distributions for $|2\rangle$ and $|4\rangle$ differ widely.

Conclusion When an atom is placed in space, its energy levels turn into bands, even when no radiation is coming in: the radiation states do not have to be occupied to have interaction with an atomic system.

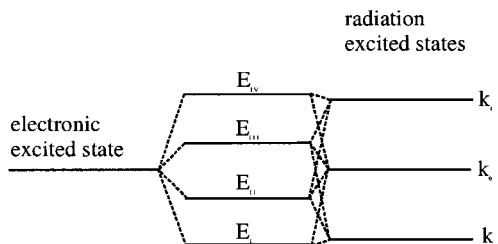


FIGURE 38 The energy levels resulting from the interaction between the excited electronic state and the three photon states.

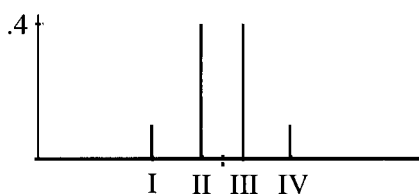


FIGURE 39 The participation of the original excited state ($=|1\rangle$) in each of the new eigenstates.

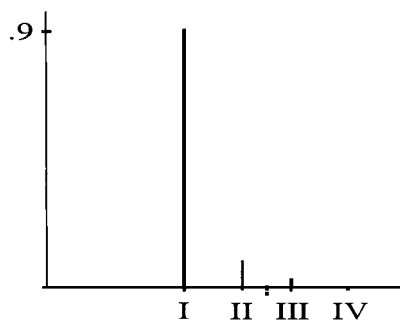


FIGURE 40 The participation of state $|2\rangle$ ($=$ photon state $|k_{-1}\rangle$) in the new eigenstates.

4.3.3. Decay of the Excited State in Second Order

In the previous section we saw how out of the interaction between the original noninteracting states new eigenstates arise. This does not happen instantaneously. When the interaction is switched on, the basis states are no longer eigenstates and transitions to other states

start to occur. Hence the probability of finding the system in the initial state will decrease with time. Here we consider the initial state $|1\rangle$ with an excited electron and no photon:

$$|\psi(t=0)\rangle = |1\rangle \equiv |\varphi_1\rangle |0_{k_{-1}}, 0_{k_0}, 0_{k_1}\rangle$$

and ask how much of it will be left after a time t . Or, stated differently, how often will we find the atom in the excited state after some time t . This amounts to calculating $c_1(t)$ with $c_1(0) = 1$. The main basic processes that take place are transitions from $|1\rangle$ to $|2\rangle$, $|3\rangle$ and $|4\rangle$ and back. Direct transitions between the three photon states are not possible by a simple creation or annihilation process. Such a two-step process with a return to the initial state is represented in Figure 41. For obvious reasons it is called a bubble process. The decrease of $c_1(t)$ is called the decay of the original state. When we limit the calculation to two-step processes, we speak of second order decay.

We now leave the four state system and turn to a more general situation. We start with state $|m\rangle$ and calculate how much of it remains after appropriate two-step processes will take us back to it. From (3.63) we derive:

$$c_{mm}^{(2)}(t) = \sum_n \frac{|H_{mn}|^2}{(i\hbar)^2} \int_0^t dt' e^{i\omega_{mn}t'} \int_0^{t'} dt'' e^{i\omega_{mn}t''} \quad (4.65)$$

The states n , differing by the direction and magnitude of \mathbf{k}_n , form a continuum and we replace the sum by an integral. We neglect degeneration. As variable we choose $\omega \equiv \omega_{nm} = (E_n - E_m)/\hbar = -\omega_{mn}$. The number of states n in interval $d\omega$ is given by $\rho(\omega)d\omega$.

$$c_{mm}^{(2)} = \int_{-\infty}^{\infty} d\omega \rho(\omega) \frac{|H(\omega)|^2}{(i\hbar)^2} \int_0^t dt' e^{-i\omega t'} \int_0^{t'} dt'' e^{i\omega t''} \quad (4.66)$$

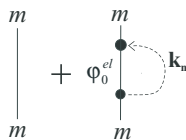


FIGURE 41 Bubble diagram, representing second order decay of an excited electronic state.

We now change the order of integration:

$$\begin{aligned}
 c_{mm}^{(2)} &= \int_0^t dt' \int_{-\infty}^{\infty} d\omega \rho(\omega) \frac{|H(\omega)|^2}{(i\hbar)^2} e^{-i\omega t'} \int_0^{t'} dt'' e^{i\omega t''} \\
 &= \frac{-1}{\hbar^2} \int_0^t dt' \int_{-\infty}^{\infty} d\omega \rho(\omega) |H(\omega)|^2 i \frac{e^{-i\omega t'} - 1}{\omega} \\
 &= \frac{1}{\hbar^2} \int_0^t dt' \int_{-\infty}^{\infty} d\omega \rho(\omega) |H(\omega)|^2 \left[i \frac{(1 - \cos \omega t')}{\omega} - \frac{\sin \omega t'}{\omega} \right] \quad (4.67)
 \end{aligned}$$

The real part of the term between brackets we met before in 4.1.1: $\sin \omega t' / \omega = \pi \delta^{(t')}(\omega)$. We then substitute (4.14) in the imaginary term. The result is:

$$c_{mm}^{(2)}(t) = \frac{1}{\hbar^2} \int_0^t dt' \int_{-\infty}^{\infty} d\omega \rho(\omega) |H(\omega)|^2 \left[iP \frac{1 - \cos \omega t'}{\omega} - \pi \delta^{(t')}(\omega) \right] \quad (4.68)$$

Although not justified for small t' we approximate the last term by $\pi \delta^{(t')}(\omega) = \pi \delta(\omega)$. Since for most of the integration range $\cos \omega t'$ fluctuates much more rapidly than the other terms of the integrand, we can drop it. Changing the order of integration then yields:

$$c_{mm}^{(2)}(t) = t \int_{-\infty}^{\infty} d\omega \rho(\omega) \frac{|H(\omega)|^2}{\hbar^2} \left[-\pi \delta(\omega) + iP \frac{1}{\omega} \right] \quad (4.69)$$

Hence to second order

$$c_{mm}(t) = c_{mm}(0)(1 + c_{mm}^{(2)}(t)) \quad (4.70)$$

The real part of $c_{mm}^{(2)}(t)$ is negative, indicating decay.

For real large values of t , second order perturbation does not suffice and we have to add more bubbles and other perturbations, which will change the time dependence. We can take some of the effect of consecutive bubbles into account by making the *ansatz* that the decay proceeds according to

$$c_{mm}(t) = c_{mm}(0)e^{-\gamma t} \quad (4.71)$$

which for small t can be written as:

$$c_{mm}(t) = c_{mm}(0)(1 - \gamma t) \quad (4.72)$$

Comparison of (4.70) and (4.72) shows that the *ansatz* is consistent with the results obtained above. We now return to the notation of (4.65) and get:

$$\begin{aligned} \gamma &= \int_{-\infty}^{\infty} d\omega_{mn} \rho(\omega_{mn}) \frac{|H(\omega_{mn})|^2}{\hbar^2} \left[\pi \delta(\omega_{mn}) - iP \frac{1}{\omega_{mn}} \right] \\ &= \pi \rho(\omega_{mn}) \frac{|H_{mn}|^2}{\hbar^2} - iP \int_{-\infty}^{\infty} d\omega_{mn} \rho(\omega_{mn}) \frac{|H(\omega_{mn})|^2}{\hbar^2} \frac{1}{\omega_{mn}} \\ &\equiv \text{Re}(\gamma) + \text{Im}(\gamma) \end{aligned} \quad (4.73)$$

where the first and the second term are positive and negative respectively.

To understand the physical meaning of these terms we write the time dependence of the intermediary state m as follows:

$$c_{mm}(t)|m\rangle e^{-iE_m t} = c_{mm}(0)|m\rangle e^{-i(E_m + \text{Im}(\gamma))t} e^{-\text{Re}(\gamma)t} \quad (4.74)$$

The energy is seen to decrease by $\Delta E = |\text{Im}(\gamma)|$ while the magnitude of the coefficient decays by $e^{-\text{Re}(\gamma)t}$. A qualitative discussion of this energy change was given in Section 4.3.2. For our purpose, the decay of the intermediate state is more important since it causes the anomalous scattering.

4.4. Elementary Processes and Matrix Terms

From Chapter 3 we learned:

$$\hat{H}' = \frac{q}{m} (\hat{\mathbf{A}} \cdot \hat{\mathbf{p}}) + \frac{q^2 \hat{\mathbf{A}}^2}{2m} \quad (4.75)$$

The first RHS term was shown to lead to the Hamiltonians H^- and H^+ and the second term to H^{-+} and H^{+-} , where

$$H^- = \frac{q}{m} (\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \hat{a}_{k, \mu} e^{i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \frac{\hbar}{i} \nabla \quad (4.76)$$

$$H^+ = \frac{q}{m} (\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \hat{a}_{\mathbf{k}, \mu}^+ e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \frac{\hbar}{i} \nabla \quad (4.77)$$

$$H^{+-} = H^{-+} = \frac{q}{2m} (\varepsilon_0 V)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mu, \mu'} \left(\frac{\hbar^2}{4\omega_k \omega_{k'}} \right)^{1/2} \hat{a}_{\mathbf{k}, \mu} \hat{a}_{\mathbf{k}', \mu'}^+ e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{e}_{\mathbf{k}', \mu'} \quad (4.78)$$

Whereas the integration over the radiation parameters in the matrix elements is easily performed, see (3.6) and (3.7), integration over the spatial variables require more effort. The matrix term $\langle n | H^- | m \rangle$ requires the integration

$$\langle \varphi_n^{\text{el}} | e^{i\mathbf{k} \cdot \mathbf{r}} \nabla | \varphi_m^{\text{el}} \rangle \mathbf{e}_{\mathbf{k}, \mu} \quad (4.79)$$

When the target is an atom or molecule, the electronic wave functions φ_n^{el} and φ_m^{el} have molecular dimensions, i.e. they range over a distance of about 10 Å. We then write $\mathbf{r} \equiv \mathbf{R} + \Delta\mathbf{r}$ where \mathbf{R} is the coordinate of the center of the molecule or atom. This turns the exponent into $i\mathbf{k} \cdot \mathbf{r} = i(\mathbf{k} \cdot \mathbf{R} + (2\pi(\Delta r_k / \lambda)))$ with Δr_k the component of \mathbf{r} in the direction of \mathbf{k} . When visible light is used, $|\Delta\mathbf{r}|$ is much less than the wavelength of the radiation and the second right hand term vanishes. When we choose the z-axis of our coordinate system to be parallel to $\mathbf{e}_{\mathbf{k}, \mu}$, (4.79) turns into

$$e^{i\mathbf{k} \cdot \mathbf{R}} \left\langle \varphi_n^{\text{el}} \left| \frac{\partial}{\partial z} \right| \varphi_m^{\text{el}} \right\rangle \quad (4.80)$$

When φ_n^{el} and φ_m^{el} happen to be both symmetric with respect to reflection by the x-y-plane the integral will vanish. This is the basis of the selection rules in spectroscopy.

X-rays, however, have the same dimensions as an atom and it is no longer valid to assume that the exponent $i\mathbf{k} \cdot \mathbf{r}$ remains constant over the atom or molecule. Fortunately, anomalous scattering is mainly based on excitation of an electron from an inner shell and the assumption can still be used [22]. In forward scattering ($\mathbf{K} = \mathbf{k}_1 - \mathbf{k}_0 = \mathbf{0}$), the assumption is valid by definition.

For a further reduction of (4.79) we study the commutator $[H^{\text{el}}, \mathbf{r}]$ of the electronic Hamiltonian and the position operator \mathbf{r} , defined by

$$[H^{\text{el}}, \mathbf{r}]\varphi \equiv H^{\text{el}}\mathbf{r}\varphi - \mathbf{r}H^{\text{el}}\varphi \quad (4.81)$$

We get

$$[H^{\text{el}}, \mathbf{r}] = \left(\frac{-\hbar^2}{2m} \nabla^2 + V \right) \mathbf{r}\varphi - \mathbf{r} \left(\frac{-\hbar^2}{2m} \nabla^2 + V \right) \varphi$$

In multiplication the order does not matter, so the term with the potential V drops out:

$$[H^{\text{el}}, \mathbf{r}] = \frac{-\hbar^2}{2m} (\nabla^2 \mathbf{r}\varphi - \mathbf{r} \nabla^2 \varphi) \quad (4.82)$$

The first term between brackets can be written as:

$$\begin{aligned} \nabla^2 \mathbf{r}\varphi &= \mathbf{i} \nabla^2 x\varphi + \mathbf{j} \nabla^2 y\varphi + \mathbf{k} \nabla^2 z\varphi \\ &= \mathbf{i} \frac{\partial^2}{\partial x^2} x\varphi + \mathbf{j} \frac{\partial^2}{\partial x^2} y\varphi + \mathbf{k} \frac{\partial^2}{\partial x^2} z\varphi + \mathbf{i} \frac{\partial^2}{\partial y^2} x\varphi + \dots \\ &= \mathbf{i} \frac{\partial}{\partial x} \left[\varphi + x \frac{\partial \varphi}{\partial x} \right] + \mathbf{j} y \frac{\partial^2 \varphi}{\partial x^2} + \dots \\ &= \mathbf{i} \left[\frac{\partial \varphi}{\partial x} + \frac{\partial \varphi}{\partial x} + x \frac{\partial^2 \varphi}{\partial x^2} \right] + \mathbf{j} y \frac{\partial^2 \varphi}{\partial x^2} + \dots \\ \nabla^2 \mathbf{r}\varphi &= 2\nabla \varphi + \mathbf{r} \nabla^2 \varphi \end{aligned}$$

Substituting the result in (4.82) we get

$$\nabla \varphi = \frac{-m}{\hbar^2} [H^{\text{el}}, \mathbf{r}] \varphi \quad (4.83)$$

(4.80) now becomes

$$\begin{aligned} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \varphi_n^{\text{el}} | \frac{\partial}{\partial z} | \varphi_m^{\text{el}} \rangle &= e^{i\mathbf{k} \cdot \mathbf{R}} \frac{-m}{\hbar^2} \langle \varphi_n^{\text{el}} | [H^{\text{el}}, \mathbf{r}] | \varphi_m^{\text{el}} \rangle \\ &= e^{i\mathbf{k} \cdot \mathbf{R}} \frac{-m}{\hbar^2} [\varepsilon_n^{\text{el}} \langle \varphi_n^{\text{el}} | \mathbf{r} | \varphi_m^{\text{el}} \rangle - \langle \varphi_n^{\text{el}} | \mathbf{r} | \varphi_m^{\text{el}} \rangle \varepsilon_m^{\text{el}}] \\ &= e^{i\mathbf{k} \cdot \mathbf{R}} \frac{-m}{\hbar^2} \varepsilon_{nm}^{\text{el}} \mathbf{r}_{nm} \end{aligned} \quad (4.84)$$

in which we made use of the fact that H_m is an Hermitic operator, i.e.

$$\langle \varphi | H_m | \psi \rangle = \langle (H_m \varphi) | \psi \rangle = \langle \varphi | (H_m \psi) \rangle$$

Analogously to the definition of dipole moment as $\mathbf{p} = q \langle \varphi | \mathbf{r} | \varphi \rangle$ the integral

$$q \langle \varphi_n^{\text{el}} | \mathbf{r} | \varphi_m^{\text{el}} \rangle \equiv q \mathbf{r}_{nm} \quad (4.85)$$

is called the transition dipole moment.

Collecting all intermediate results, we get

$$H_{nm}^- = i \frac{q}{\hbar} (\varepsilon_0 V)^{-1/2} \sum_{\mathbf{k}, \mu} \left(\frac{\hbar}{2\omega_k} \right)^{1/2} \langle \text{rad}_n | \hat{\mathbf{a}}_{k, \mu} | \text{rad}_m \rangle e^{i\mathbf{k} \cdot \mathbf{R}} \varepsilon_{nm}^{\text{el}} \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{r}_{nm} \quad (4.86)$$

The matrix element H_{fm}^+ is derived along similar lines with the result:

$$H_{fm}^+ = (H_{mi}^-)^* \quad (4.87)$$

Central in Thomson scattering stands H_{nm}^{+-} . We shall derive the case where $m=i$, given in (3.16), and $n=f$, the final state of the scattering process, given in (3.17)

With (4.78) we get:

$$H_{fi}^{+-} = \frac{q}{2m} (\varepsilon_0 V)^{-1} \sum_{\mathbf{k}, \mathbf{k}', \mu, \mu'} \left(\frac{\hbar^2}{4\omega_k \omega_{k'}} \right)^{1/2} \langle 0_{\mathbf{k}_0}, 1_{\mathbf{k}_1} | \hat{\mathbf{a}}_{k, \mu} \hat{\mathbf{a}}_{k', \mu'}^+ | 1_{\mathbf{k}_0}, 0_{\mathbf{k}_1} \rangle \\ \times \langle \varphi_0^{\text{el}} | e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}} | \varphi_0^{\text{el}} \rangle \mathbf{e}_{\mathbf{k}, \mu} \cdot \mathbf{e}_{\mathbf{k}', \mu'} \quad (4.88)$$

Most of the annihilation operators do not apply, since the corresponding modes are not present in the initial state, while most creation operators create states that are orthogonal to the final radiation state.

Thus we get

$$\begin{aligned}
 H_{fi}^{+-} &= \frac{q}{2m} (\varepsilon_0 V)^{-1} \left(\frac{\hbar^2}{4\omega_{k_0}\omega_{k_1}} \right)^{1/2} \langle \varphi_0^{\text{el}} | e^{-i(\mathbf{k}_1 - \mathbf{k}_0)\mathbf{r}} | \varphi_0^{\text{el}} \rangle \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \mathbf{e}_{\mathbf{k}_1, \mu'} \\
 &= \frac{q}{2m} (\varepsilon_0 V)^{-1} \frac{\hbar}{2\omega_{k_0}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \mathbf{e}_{\mathbf{k}_1, \mu'} \int_V |\varphi_0^{\text{el}}|^2 e^{-i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r}
 \end{aligned} \quad (4.89)$$

where we used the fact that in elastic scattering the incident beam has the same frequency as the scattered one. The integral is known as the *structure factor* $F(\mathbf{K})$:

$$F(\mathbf{K}) \equiv \int_V |\varphi_0^{\text{el}}|^2 e^{i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r} = \int_V \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d^3\mathbf{r} \quad (4.90)$$

The same result is obtained by the operator H^{-+} , hence the expression for Thomson scattering contains:

$$H_{fi}^{\text{scat}} \equiv H_{fi}^{+-} + H_{fi}^{-+} = \frac{q}{2m} (\varepsilon_0 V)^{-1} \frac{\hbar}{\omega_{k_0}} \mathbf{e}_{\mathbf{k}_0, \mu} \cdot \mathbf{e}_{\mathbf{k}_1, \mu'} F(\mathbf{K}) \quad (4.91)$$

In the case of a target with N electrons, the interaction Hamiltonian for the first order scattering process is given by

$$H' = \sum_n^N \frac{e^2}{2m} A^2(\mathbf{r}_n) \quad (4.92)$$

where we sum over the electrons.

The electronic part of both the initial and the final state are represented by

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N)\rangle$$

where the position and the spin variables are shown explicitly.

This turns the bracket part of (4.89) into

$$\left\langle \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) \left| \sum_n^N e^{-i\mathbf{K} \cdot \mathbf{r}_n} \right| \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) \right\rangle \quad (4.93)$$

This term becomes a sum of N terms, where in each term another electron of the operator is involved. However, since the electrons are indistinguishable, all these N terms are the same. So we can retain one of them and multiply it with N . Replacing the bracket notation by an integral one, we get

$$\begin{aligned} & N \left\langle \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) \left| \sum_n^N e^{-i\mathbf{K} \cdot \mathbf{r}_1} \right| \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) \right\rangle \\ & \equiv N \int_V \psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) e^{-i\mathbf{K} \cdot \mathbf{r}_1} \\ & \quad \times \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) d^3 r_1 d^3 r_2 \dots d^3 r_N d\sigma_1 \dots d\sigma_N \\ & = N \int_V d^3 r_1 e^{-i\mathbf{K} \cdot \mathbf{r}_1} \int_V \psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) \\ & \quad \times \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) d^3 r_2 \dots d^3 r_N d\sigma_1 \dots d\sigma_N \end{aligned}$$

The right hand integral is known as the *electron density*:

$$\begin{aligned} \rho(\mathbf{r}) & \equiv N \int_V \psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) \\ & \quad \times \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \sigma_1, \sigma_2, \dots, \sigma_N) d^3 r_2 \dots d^3 r_N d\sigma_1 \dots d\sigma_N \end{aligned} \quad (4.94)$$

Hence the bracket term (4.93) becomes

$$\int_V \rho(\mathbf{r}_1) e^{-i\mathbf{K} \cdot \mathbf{r}_1} d^3 r_1 = F(\mathbf{K}) \quad (4.95)$$

as we obtained in (4.90).

SUBJECT INDEX

- absorption 119
anomalous scattering 97, 110, 145
- Born approximation 134
- Compton scattering 146
- damping 166
dipole approximation 140
Dirac delta function 157
dispersion relations 102, 104
- electron density 183
emission 137
energy levels 169
- Fermi's golden rule 152
Feynman diagrams 138
- harmonic forces 121
- intensity 150
interaction Hamiltonian 135
- Maxwell equations 162
- optical theorem 120
oscillating dipole 163
oscillator strength 109
- perturbation theory 133
polar molecules 110
- Rayleigh scattering 144, 153, 155
refractive index 116
resonant scattering 145, 155
response function 99, 100
- scattering 141
scattering factor 107, 150
selection rules 140
structure factor 109, 153
- Thomson scattering 107, 141, 152, 181
- vector potential 126
virtual transitions 134