Angle resolved scattering of strong-field electromagnetic radiation

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Abstract

We simulate X-ray scattering beyond perturbation theory, relevant for X-ray free electron laser (XFEL) pulses. Previous work by Mattia Mantovani implemented a numerical solution of the exact Schrödinger equation involving the full coupling of an electron dynamics with the vector potential of an ultrashort electromagnetic pulse.

Our thesis reaches a further step in this Maxwell-Schrödinger model, providing a theoretical discussion and a numerical implementation of the calculation of the far-field scattering angular pattern, given the current density as obtained from Mantovani’s code. Our predictions are in good accord with the perturbative results for small to intermediate pulse average intensities, whereas we observe non-linear effects beyond $10^{27} \text{W m}^{-2}$. We relate our results to the Keldysh parameter $\gamma$, which estimates inversely the prevalence of field-induced tunneling ionization: a large value of the parameter compared to 1 is often taken as a justification for perturbative methods. Our results confirm that non linear effects are observed when $\gamma < 1$.

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# Contents

1 Introduction .................................................. 5

2 State of the art .................................................. 9
   2.1 The Schrödinger approach .................................... 9
       2.1.1 Minimal coupling Hamiltonian ............................ 9
       2.1.2 Gauge choice ............................................. 10
       2.1.3 Charge and current density ............................. 11
   2.2 X-ray scattering in the perturbative limit ................. 12
   2.3 The Keldysh parameter ...................................... 13

3 Radiation from an assigned current density ................. 15
   3.1 Radiated electric and magnetic fields ....................... 16
   3.2 The Poynting vector and the radiated power ............... 18
   3.3 Cross section ............................................... 20

4 The numerical implementation .................................. 21
   4.1 The Discrete Fourier Transform ............................. 21
   4.2 Discretization of space and spatial integration .......... 23
   4.3 The incoming pulse ......................................... 24
   4.4 Convergence ................................................ 26

5 Results ................................................................... 30
   5.1 The perturbative limit ....................................... 30
   5.2 High intensities .............................................. 31

6 Conclusions and outlooks ....................................... 36

A Atomic units .................................................... 38

Ringraziamenti ..................................................... 40

Bibliography ......................................................... 41
Al professor Giacinto Biasco,  
che mi guarda dal cielo.
Chapter 1

Introduction

Since their discovery in 1895, X-rays evolved into an ever-growing field with multiple applications in many areas of science and technology. X-rays have proved to be extremely useful in the investigation of structural properties of matter, thanks both to their wavelengths (0.01 to 10 nm) which yields the adequate spatial resolution for imaging nanoscale objects (single atoms, molecules, polymers), and to their energies (100 eV to 10 keV) which matches inner-shell binding energies, enabling core absorption, photo-emission and other spectroscopies.

During the past century, special efforts have been made to develop novel X-ray sources. Techniques have been invented to increase brilliance, monochromaticity and coherence of the pulses [1]. In 1947 synchrotron radiation was first observed, and so the first generation of synchrotron-radiation facilities started, where X-rays were produced as a parasitic effect in synchrotrones. Soon dedicated storage rings were built with insertions of devices such as undulators and wigglers (second and third generations). Such devices are basically periodic magnetic structures, that produce a sinusoidal magnetic field. Depending on the strength and the period of the magnetic field, the radiation produced at every cycle can sum coherently or incoherently: in the first case the structure is referred to as an undulator, in the second as a wiggler (Fig. 1.1). These tools allowed to produce spectrally narrow and collimated pulses: that is, pulses with high spectral brightness.

In recent years, a fourth generation of X-ray sources has started, thanks to the invention of free-electron lasers (FELs), which usually are based on very long undulators inserted in high-energy linear electron accelerators. Such devices can generate a peak brightness up to $10^{20}$ W m$^{-2}$, many orders of magnitude beyond that of the previous-generation sources, concentrated in pulses of duration 100 fs or shorter. FEL pulses are much better spatially coherent than those from synchrotron sources. X-ray free electron lasers (XFELs) in particular have begun
to attract great interest in physicists, due to their unprecedented brightness that could be exploited to image small, non-periodic objects, such as single atoms and molecules (see Fig. 1.2, Ref. [2]). For such nanoscale objects, which are not packed in a periodic structure, standard diffraction techniques that exploit the amplification coming from the coherent superposition of scattered waves cannot be used. The difficulties in determining the structure of proteins that cannot crystallize is one of the leading challenges of structural biology: the extremely bright, coherent pulses of the XFELs have the potential to get around this problem.

Several facilities for the production and study of X-ray FEL pulses are al-

Table 1.1: Characteristics of the light pulses produced in the two projects FEL-1 and FEL-2 at FERMI (https://www.elettra.trieste.it) and at FLASH (https://flash.desy.de); predicted characteristic of the XFEL pulses that will be produced at European-XFEL (http://xfel.desy.de).

* Measured in photons s\(^{-1}\) mrad\(^{-2}\) mm\(^{-2}\)/0.1%bw.
** Estimated from the previous parameters.

<table>
<thead>
<tr>
<th></th>
<th>FEL-1</th>
<th>FEL-2</th>
<th>FLASH</th>
<th>E-XFEL</th>
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<tr>
<td>Photon energy (eV)</td>
<td>12-62</td>
<td>62-310</td>
<td>25-300</td>
<td>260-25000</td>
</tr>
<tr>
<td>Pulse length (fs)</td>
<td>30-100</td>
<td>&lt; 100</td>
<td>&lt; 30-200</td>
<td>100</td>
</tr>
<tr>
<td>Bandwidth (%)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.5-2</td>
<td>100</td>
</tr>
<tr>
<td>Energy/pulse (µJ)</td>
<td>20-100</td>
<td>20-100</td>
<td>1-500</td>
<td>-</td>
</tr>
<tr>
<td>Peak power (GW)</td>
<td>0.2-1</td>
<td>1</td>
<td>1-5</td>
<td>24</td>
</tr>
<tr>
<td>Photons/pulse</td>
<td>10(^{14})</td>
<td>10(^{13})</td>
<td>10(^{11})-10(^{13})</td>
<td>-</td>
</tr>
<tr>
<td>Spot size (µm)</td>
<td>290</td>
<td>140</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Beam divergence (µrad)</td>
<td>50</td>
<td>15</td>
<td>-</td>
<td>0.8</td>
</tr>
<tr>
<td>Peak brillance (*)</td>
<td>-</td>
<td>-</td>
<td>10(^{28})-10(^{31})</td>
<td>5.4 × 10(^{33})</td>
</tr>
<tr>
<td>Average intensity**</td>
<td>10(^{16})</td>
<td>1-5 × 10(^{16})</td>
<td>10(^{17})</td>
<td>6 × 10(^{18})</td>
</tr>
</tbody>
</table>

Figure 1.1: A schematic representation of an undulator.
1: Periodic magnetic structure with alternating poles (red = north, green = south); 2: Incoming electron beam; 3: Radiated light; \(\lambda_u\): spatial period of the magnetic field.
Figure 1.2: From top left: the diffraction pattern produced by a microscale test object investigated by a single FEL pulse; the pattern of the following FEL pulse showing the damage to the object caused by the first pulse; the test object and its image reconstructed from the first diffraction pattern using a phase retrieval algorithm which does not make use of the original image.

ready in operation, and other are currently under construction. The FLASH laboratory (2005) in Hamburg and the FERMI laboratory (2010) in Trieste operate in the soft X-ray and UV range. In the hard X-ray regime, facilities like LCLS (USA, 2009), SACLA (Japan, 2012) and PAL-XFEL (South Korea, 2016) are already in operation, whereas the European-XFEL in Germany and the SwissFEL in Switzerland are expected to start in 2017 (See Tab. 1.1).

The possibility of single-molecule imaging, however, presents several difficulties. The high intensities of the XFELs pulses is quite likely damage the sample, that often can undergo a Coulomb explosion, possibly resulting in a deteriorated or even useless scattering signal. In order to understand these phenomena, several theoretical approaches have been used in past years to model the interaction and predict the scattered radiation pattern, mostly based on perturbation theory [3]. These methods are usually justified by the small scattering cross section (of order $10^{-2}$ b) and/or by the value of the Keldysh parameter, which estimates the prevalence of field induced ionization [4]. However, due to the extremely high intensities of the fields in XFEL pulses, there is no guarantee that the perturbative limit is fulfilled [5]. Non-linear effects may arise, as predicted by theoretical calculations based on plasma models [6].

The present work fits in this theoretical research, and it is conceived as a continuation of the previous work by Mattia Mantovani [7], who implemented and studied a Maxwell-Schrödinger approach to the scattering of ultra-intense, ultra-fast X-ray pulses from a nano-object. Mantovani set up a numerical solution of the time-dependent Schrödinger equation for a one-electron atom, subject to a radiation pulse. The peculiarity of this approach is that the coupling of the electron dynamics and the radiation does not rely to any weak-coupling or long-wavelength approximations (specifically, not to the dipole approximation, as was
done in previous works). The electromagnetic fields are treated classically, which is expected to be accurate for the incoming radiation due to extremely high intensities (and thus great number of photons), but does not take quantum effects (e.g. the Compton effect) into account.

The Schrödinger equation is solved numerically through finite-element analysis (FEA) employing backward differentiation formulas (BDFs) within a spherical region which is discretized by a tetrahedral mesh. The solution of the Schrödinger equation provides both the wave function $\psi(x,t)$ and, as a derived value, the probability current density $j(x,t)$ (See Fig. 1.3). Both $\psi$ and $j$ are available at discrete points $x_i$ (the vertexes of the tetrahedra) and at discrete, equally spaced times ($t_n = n\Delta t$, $n = 0, 1, ..., N$). The computation of the scattered radiation is based on the assumption that we can treat the probability current, multiplied by the electron charge $e$, as an electric current: the scattered radiation is computed as the radiation emitted by such current.

In the present work we address the problem of computing the far-field radiation pattern generated by the motion of the electron, given its electric current density function $J(x_i, t_n) = e j(x_i, t_n)$. In Chapter 2 we collect summarize the Schrödinger problem as it is portrayed by Mantovani. In Chapter 3 we describe the formalism for the main problem of this thesis, obtaining a general expression for the radiated energy and the differential cross section in the far-field approximation. In Chapter 4 we describe the numerical implementation and discuss its convergence. In Chapter 5 we report the results of the application of our method, comparing them with the formulas of perturbation theory.
Chapter 2

State of the art

We summarize the basis for a Maxwell-Schrödinger approach to ultrafast X-ray scattering [7]. We recall the minimal coupling Hamiltonian for a particle subject to an electromagnetic field, and we derive the expression for the probability current density for such particle. We give the analytical expressions for the scattering cross section in the perturbative limit and we define the Keldysh parameter, whose value is sometimes taken as a gauge of the validity of perturbative method.

2.1 The Schrödinger approach

2.1.1 Minimal coupling Hamiltonian

The electric and magnetic fields, $E$ and $B$, are expressed in term of the scalar potential $\Phi$ and the vector potential $A$ as

$$ E = -\nabla \Phi - \frac{\partial A}{\partial t}, \quad B = \nabla \times A, \quad (2.1) $$

where $c$ is the speed of light in the vacuum. The Coulomb force on a particle at position $x$ and velocity $\dot{x}$ in terms of the potentials is:

$$ F = q(E + \dot{x} \times B) = q \left[ -\nabla \Phi - \frac{\partial A}{\partial t} + \dot{x} \times (\nabla \times A) \right]. \quad (2.2) $$

It is easy to check that the $i$-th component of the force (2.2) can be rewritten as

$$ F_i = -\frac{\partial U}{\partial x_i} + \frac{d}{dt} \frac{\partial U}{\partial \dot{x}_i}, \quad (2.3) $$

with $U = q\Phi - q\dot{x} \cdot A$. Thus, the coupling of a particle with an electromagnetic field is described by the Lagrangian

$$ \mathcal{L} = T - U = \frac{1}{2} m\dot{x}^2 - q\Phi + q\dot{x} \cdot A. \quad (2.4) $$
To switch to the Hamiltonian formalism, we introduce the momentum $p$, whose components are

$$p_j = \frac{\partial \mathcal{L}}{\partial \dot{x}_j} = m \dot{x}_j + q A_j .$$

(2.5)

The Hamiltonian of the system is obtained using the standard definition:

$$H = p \cdot \dot{x} - \mathcal{L} = \frac{(p - q A)^2}{2m} + q \Phi$$

(2.6)

This relation is known as *minimal coupling* Hamiltonian of a classical charged particle with the electromagnetic fields.

Following [7], we choose the sample for our simulations to be an atom of hydrogen, for simplicity. We also neglect the dynamics of the nucleus as it moves much slower than the electron and produces a negligible current density. Moreover we treat the nucleus-electron potential as if it was a non-electromagnetic force ...

The quantum Hamiltonian is obtained by substituting the classical coordinates $x$ and $p$ with the operators $\hat{x}$ and $\hat{p}$. In coordinate representation, the resulting time-dependent Schrödinger equation is

$$i \hbar \frac{\partial \psi}{\partial t} = \left[ \frac{1}{2m_e} (-i \hbar \nabla + e A)^2 - e \Phi - \frac{e^2}{4\pi \varepsilon_0 |x|} \right] \psi .$$

(2.7)

### 2.1.2 Gauge choice

Exploiting the gauge freedom of electromagnetism, we chose to describe the incident radiation in the Coulomb gauge, imposing

$$\nabla \cdot A = 0 .$$

(2.8)

In this gauge the scalar and vector potentials satisfy the following equations, with the charge density $\rho$ and the current density $J$ as sources (See Ref. [8], Sec 6.3):

$$\nabla^2 \Phi = - \frac{\rho}{\varepsilon_0}$$

(2.9)

$$\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = - \mu_0 J + \frac{1}{c^2} \nabla \frac{\partial \Phi}{\partial t} .$$

(2.10)

Specifically, Eq. (2.9) is the Poisson equation, which has solution

$$\Phi(x, t) = \frac{1}{4\pi \varepsilon_0} \int d^3 x' \frac{\rho(x', t)}{|x - x'|} .$$

(2.11)

In the present work, as in [7], we neglect the effects on its wave function of the electromagnetic field produced by the electron. This assumption is based
on the principle that an electromagnetic interaction of the electron with itself is not physical: if it was, the electron would tend to repel itself. Moreover, we deal with strong-field radiation, with incoming fields that are surely much larger than the ones produced by the electron, which can be then neglected. With this assumption, \( \rho \) and \( J \) in Eq. (2.9) are vanishing, and in particular \( \Phi = 0 \).

With this gauge choice, Eq. (2.6) is rewritten as

\[
\frac{\hbar}{i} \frac{\partial \psi}{\partial t} = \left[ -\frac{\hbar^2}{2m_e} \nabla^2 - \hbar \frac{e}{m_e} A \cdot \nabla + \frac{e^2}{2m_e} A^2 - \frac{e^2}{4\pi\epsilon_0 |x|} \right] \psi .
\]

(2.12)

### 2.1.3 Charge and current density

Here we report the relations between the wave function \( \psi \), obtained numerically from the solution of Eq. (2.12) and the charge and current density functions: especially the current density is the basis of our method for calculating the scattering cross section, as we will show in Section 3. For a field-free particle, the number and number current density operators are defined as

\[
\hat{\rho}(x) := \delta(x - \hat{x})
\]

(2.13)

\[
\hat{j}(x) := \frac{1}{2} \{\hat{x}, \hat{\rho}(x)\} = \frac{1}{2m} \{\hat{p}, \hat{\rho}(x)\}
\]

(2.14)

where \( \{\cdot, \cdot\} \) indicates the anticommutator. For one electron, the mean values of such operators in a normalized state \( |\psi\rangle \) are

\[
\rho(x) = \langle \psi | \hat{\rho}(x) | \psi \rangle = |\psi(x)|^2
\]

(2.15)

\[
\hat{j}(x) = \langle \psi | \hat{j}(x) | \psi \rangle = -\frac{i\hbar}{2m} [\psi^*(x) \nabla \psi(x) - \psi(x) \nabla \psi^*(x)]
\]

(2.16)

and they satisfy the continuity equation (conservation of probability)

\[
\frac{\partial \rho}{\partial t}(x, t) + \nabla \cdot j(x, t) = 0 .
\]

(2.17)

Considering now a particle in an electromagnetic field, the definitions Eq. (2.13) and Eq (2.14) hold the same, and so does Eq. (2.17), but, as one can see from Eq. (2.5), the current density operator in terms of the canonical momentum \( \hat{p} \) is different:

\[
\hat{j}(x) = \frac{1}{2m} \{\hat{p} - qA(x), \hat{\rho}(x)\}
\]

(2.18)

The electric current density for an electron is simply obtained by multiplying by the charge \( q = -e \) the mean value of operator \( \hat{j}(x) \):

\[
J(x, t) = -e \langle \psi, t | \hat{j}(x) | \psi, t \rangle
\]

(2.19)

\[
= \frac{ie\hbar}{2m} [\psi^*(x, t) \nabla \psi(x, t) - \psi(x, t) \nabla \psi^*(x, t)] - \frac{e^2}{m} A(x, t) |\psi(x, t)|^2 .
\]


The coordinate system chosen to express the differential cross section, with the incident radiation described by the wave vector $k_i$, oriented along the $z$-axis, and the scattered radiation described by the wave vector $k_f$.

2.2 X-ray scattering in the perturbative limit

We recall here the formula for the scattering cross section calculated with the perturbative method. We give the formula for the elastic (coherent) scattering. Consider a photon with initial wave vector $k_i$, that after the elastic scattering has a wave vector $k_f$ (with $|k_f| = |k_i|$), the scattering cross section as a function of the momentum transfer $q = k_f - k_i$ is given by

$$
\frac{d\sigma}{d\Omega} = \left( \frac{d\sigma}{d\Omega} \right)_T |f^0(q)|^2.
$$

The first factor in Eq. (2.20) is the cross section for Thomson scattering, which describes the scattering from one electron with negligible momentum transfer ($q \simeq 0$). It can be written as the sum of two contributions, corresponding to the two possible polarizations of the incoming X-ray: assuming that $k_i = k_i \hat{z}$ and expressing the cross section in terms of the polar angles $\theta_f$ and $\phi_f$ for $k_f$, as in Fig. 2.1 we have

$$
\left( \frac{d\sigma}{d\Omega} \right)_T^{\text{pol-x}} = r_e^2 (1 - \cos^2 \phi_f \sin^2 \theta_f)
$$

and

$$
\left( \frac{d\sigma}{d\Omega} \right)_T^{\text{pol-y}} = r_e^2 (1 - \sin^2 \phi_f \sin^2 \theta_f)
$$

where $r_e = e^2/(4\pi \epsilon_0 m_e c^2)$ is the classical radius of the electron. The integrated cross section for Thomson scattering (whether polarized or un-polarized) is

$$
\sigma_T = \int_{4\pi} d\Omega \left( \frac{d\sigma}{d\Omega} \right)_T = \frac{8\pi}{3} r_e^2 \simeq 0.665 \text{ b} = 6.65 \times 10^{-29} \text{ m}^2
$$

The second factor in Eq. (2.20) in the case of an atom is called atomic form factor, defined as

$$
f^0(q) = \int d^3 x \rho(x)e^{-iq \cdot x},
$$
where $\rho(x)$ is the ground state electron number density. The form factor for hydrogen in his ground state is:

$$f^0(q) = \frac{16}{(4 + q^2 a_0^2)^2}. \quad (2.25)$$

As the module of the momentum transfer $q$ is related to the photon energy and to $\theta_f$ by the relation $q = 2k_i \sin \frac{\theta_f}{2}$, the atomic form factor gives an increasingly important contribution with increasing photon energy: its overall effect is null in the forward direction, while it tends to suppress the backward scattering ($\theta_f = \pi$). For a photon energy of 10 keV the total cross section, obtained by integrating Eq. (2.20) over the entire solid angle, is significantly smaller than $\sigma_T$ [9]:

$$\sigma_H(\hbar \omega_0 = 10 \text{ keV}) \simeq 41.21 \text{ mb} \simeq 0.06 \sigma_T. \quad (2.26)$$

### 2.3 The Keldysh parameter

In a publication dated 1965 [4], L. V. Keldysh proposed a model for ionization in the presence of monochromatic electromagnetic radiation, and introduced a parameter that characterizes the dominant ionization process, the Keldysh adiabaticity parameter:

$$\gamma = \frac{\omega_0 \sqrt{2m_e I_p}}{eE_0}. \quad (2.27)$$

Here $E_0$ and $\omega_0$ are respectively the amplitude and the angular frequency of the electric field, and $I_p$ is the electron ionization potential for the considered material.

The physical meaning of this parameter can be understood as follows. By considering the combining potential energy for the electron in the nuclear attraction and the external electric field at a fixed time (see Fig. 2.2), it is possible to

![Figure 2.2: The resulting potential on a bounded electron in an electric field at a fixed time.](image-url)
estimate the thickness of the barrier that the electron must overcome to leave the nucleus as

$$l = \frac{I_p}{eE_0}. \quad (2.28)$$

The mean speed of the electron sitting at a boundstate at energy $-I_p$ is of order

$$\langle v \rangle = \sqrt{\frac{2I_p}{m_e}}. \quad (2.29)$$

We can estimate the characteristic time of tunneling as the time that it takes the electron to pass through the barrier:

$$\tau = \frac{l}{\langle v \rangle} = \frac{1}{eE_0} \sqrt{\frac{m_eI_p}{2}}. \quad (2.30)$$

Given the period of the electromagnetic oscillation $T_0 = 2\pi/\omega_0$, the Keldysh parameter (2.27) is proportional to the ratio of the tunneling time $\tau$ to the half-period of the radiation:

$$\gamma = \frac{2\pi \tau}{T_0/2}. \quad (2.31)$$

Tunnel ionization is dominant if $\tau < T/2$, i.e. $\gamma \ll 1$, while for $\tau > T/2$ the electron does not have time enough to tunnel through the barrier.

Keldysh showed that for $\gamma \ll 1$ tunnel ionization is dominant, while for $\gamma \gg 1$ ionization can be caused by linear or non-linear processes as single- or multi-photon ionization, but the tunneling ionization is negligible. When strong radiation is considered, as in our work, it is useful to evaluate the Keldysh parameter as a rough estimator of the validity of perturbation theory. It can be fair to assume that the perturbative limit is fulfilled for $\gamma \gg 1$ (negligible tunneling): as indicated by the definition (2.27), this condition is satisfied for high radiation frequencies and/or small field amplitude.
Chapter 3

Radiation from an assigned current density

In the present chapter we evaluate the expression for the radiation fields emitted by a given current density as a function of the observation direction. In this calculation we assume the hypothesis of far-field radiation: this means that we assume the current density to vanish outside a restricted region of space, of linear size $d$, and that we observe the radiation at a distance $r \gg d$. This hypothesis is totally justified in the experimental framework for which the present work is relevant, where the current density is represented by the motion of the electrons of a single atom or molecule: such electrons are constrained in a region of at most a few nanometers (the size of the molecule), whereas the detector cannot be placed nearer than few centimeters from the sample.

We assume the current density to be localized not only in space, but also in time, in a time interval $0$ to $T$. Specifically, as previously discussed, we imagine to deal with an electromagnetic pulse produced by an XFEL, whose durations is of the order of tens to hundreds of femtoseconds: after the end of the pulse the molecular system relaxes rapidly, so that the current vanishes again shortly after the end of the pulse, and before time $T$ it is completely negligible. This is the only hypothesis that we make: we want to build a theory that makes no further requirement on the form, amplitude and polarization of the radiation pulse.
3.1 Radiated electric and magnetic fields

We start our calculation from the general expression of the vector potential in the Lorenz gauge (see Ref. [8], Sect.s 6.4 and 6.5):

\[
A(x, t) = \frac{\mu_0}{4\pi} \int d^3x' \int dt' \frac{J(x', t')}{|x - x'|} \delta(t' - t + \frac{|x - x'|}{c})
\]

\[= \frac{\mu_0}{4\pi} \int d^3x' \frac{J(x', t - \frac{|x - x'|}{c})}{|x - x'|}, \quad (3.1)
\]

where \(\mu_0\) is the magnetic permeability of vacuum, related to the electric permeability \(\epsilon_0\) and the velocity of light \(c\) by the relation \(c^2 = 1/\epsilon_0 \mu_0\); \(J\) is the current density function; the apostrophized coordinates \(t'\) and \(x'\) refer to the time and position of emission, while the non-apostrophized \(t\) and \(x\) refer to the time and position of observation. The spatial integral in Eq. (3.1) extends in principle over all space, but since \(J\) vanishes outside a compact region of linear size \(d\) around the origin of \(x\) space, it can be restricted to that region.

It is convenient to analyze separately the different frequencies of which \(J\) is composed by means of the Fourier theorem. We recall the definition of the continuous Fourier transform \(\mathcal{F}\) and of the inverse Fourier transform \(\mathcal{F}^{-1}\), which we use in the present theoretic discussion. (Later on, in the numerical implementation, we will use the discrete Fourier transform, and we will give the precise definition also for that.)

\[
\tilde{f}(\omega) = \mathcal{F}[f](\omega) := \int_{-\infty}^{\infty} dt f(t) e^{-i\omega t} \quad (3.2)
\]

\[
f(t) = \mathcal{F}^{-1}[\tilde{f}](t) := \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{f}(\omega) e^{i\omega t} \quad (3.3)
\]

Here \(\tilde{f}(\omega)\) indicates the Fourier transform of \(f(t)\) from the time-domain to the frequency-domain, calculated at frequency \(\omega\).

According to Eq. (3.3), the general form of \(J(x, t)\) is the integral over all possible frequencies of \(e^{-i\omega t}/2\pi\), weighted by the function \(\tilde{J}(x, \omega)\):

\[
J(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{J}(x, \omega) e^{i\omega t} = \mathcal{F}^{-1}[\tilde{J}](x, t), \quad (3.4)
\]

With the decomposition (3.4), Eq. (3.1) can be rewritten as

\[
A(x, t) = \frac{\mu_0}{4\pi} \int d^3x' \frac{\int_{-\infty}^{\infty} d\omega \tilde{J}(x', \omega) e^{-ik|x - x'|} e^{i\omega t}/2\pi}{|x - x'|}
\]

\[= \frac{\mu_0}{4\pi} \int_{-\infty}^{\infty} d\omega \frac{1}{2\pi} \int d^3x' \frac{\tilde{J}(x', \omega) e^{-ik|x - x'|}}{|x - x'|} e^{i\omega t}, \quad (3.5)
\]
with \( k = \omega/c \). The retardation effect expressed by the \( \delta \)-function in Eq. (3.1) has been wrapped to a frequency-dependent phase factor \( e^{-ik|x-x'|} \). Comparing Eq. (3.5) with the definition of the inverse FT, Eq. (3.3), we get

\[
\tilde{A}(x, \omega) = \frac{\mu_0}{4\pi} \int d^3x' \tilde{J}(x', \omega) e^{-ik|x-x'|}/|x-x'|.
\] (3.6)

In Eq. (3.5) we have changed the order of integration: this is possible thanks to the fact that our current density function \( J(x, t) \) is supposed to be localized in space and time, and thus every integral, both in time and in space, is granted to converge (Ref. [10], Ch. 48). This hypothesis also allow us to move the limit operators from inside to outside the integration symbol and vice versa (Lebesgue’s dominated convergence theorem [11]), and in particular to change the order of integrals and derivatives (Ref. [10], Ch. 53). These facts, alongside with the linearity of the relations between \( J, A \) and the fields \( E \) and \( B \), Eq. (3.1), (3.10) and (3.11), are fundamental to ensure us the possibility of making a Fourier analysis, as we are going to do: we can solve the equations for the fields in the Fourier space and than go back to the time-domain by an inverse transform, and that is equivalent to solving the entire problem in the time-domain.

Now we apply the far-field approximation (Ref. [8], Ch. 9), and thus assume \( r := |x| \gg |x'| \). A first-order Taylor expansions leads to

\[
\frac{|x-x'|}{r} = 1 - \hat{n} \cdot \frac{x'}{r} + o\left(\frac{|x'|^2}{r^2}\right),
\]

where \( \hat{n} = x/r \) is the versor pointing to the direction of observation.

We rewrite Eq. (3.5) in this approximation: in the expansion of \( 1/|x-x'| \) we neglect all terms that decay faster than \( 1/r \), as they do not contribute to far-field radiation, as we will see in Sect. 3.2; in the factor \( e^{-ik|x-x'|} \) we expand \( |x-x'| \) neglecting all terms that vanish for \( r \to \infty \). The equation that we obtain is:

\[
\tilde{A}(x, \omega) \simeq \frac{\mu_0}{4\pi} e^{-ikr} \int d^3x' \tilde{J}(x', \omega) e^{ik\hat{n} \cdot x'}. \] (3.7)

Notice that in Eq. (3.7) we do not expand the exponential \( e^{ik\hat{n} \cdot x'} \), as we have not made any assumption on the relation between the typical size \( d \) and the wavelength of the current, which is similar to the typical wave lengths of the pulse, related to \( k \) by the formula \( k = 2\pi/\lambda \). If, for some reason, we could assume \( \lambda \gg d \) (thus \( kd \ll 1 \)), we might further expand the factor \( e^{ik\hat{n} \cdot x'} \): that is known as the multi-polar expansion. Unfortunately, the wave-length of photons with energy \( h\nu \simeq 10 \text{ keV} \), like the ones that are produced at European-XFEL (see Tab. 1.1), is \( \simeq 1.2 \text{ Å} \), comparable to the typical size of the electronic motion.
The magnetic field \( \mathbf{B} \) can be obtained by the formula

\[
\mathbf{B}(x,t) = \nabla \times \mathbf{A}(x,t),
\]  
(3.8)

which holds also in the frequency domain, with \( \tilde{\mathbf{B}}(x,\omega) \) and \( \tilde{\mathbf{A}}(x,\omega) \). We evaluate the rotor in spherical coordinates \((r, \theta, \phi)\) and we take the asymptotic form for \( r \to \infty \), neglecting all terms that decay faster than \( 1/r \) because they do not contribute to far-field radiation. We obtain:

\[
\begin{aligned}
\tilde{B}_r(x,\omega) &\approx \hat{n} \times k \tilde{A}(x,\omega), \\
\tilde{B}_\theta(x,\omega) &\approx -ik \tilde{\phi}(x,\omega), \\
\tilde{B}_\phi(x,\omega) &\approx ik \tilde{\theta}(x,\omega).
\end{aligned}
\]  
(3.9)

The fact that the \( r \)-component decays faster than the others reflects the well-known fact that electromagnetic radiation waves in vacuum are transverse. It is easy to show that the far-field equations (3.9) can be reduced to the following:

\[
\tilde{\mathbf{B}}(x,\omega) = i\hat{n} \times k \tilde{\mathbf{A}}(x,\omega).
\]  
(3.10)

The electric field \( \mathbf{E}(x,t) \) can be derived from the fourth Maxwell equation,

\[
\nabla \times \mathbf{B}(x,t) = \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t}(x,t),
\]

that in the Fourier representation becomes

\[
\tilde{\mathbf{E}}(x,\omega) = i\frac{c^2}{\omega} \nabla \times \tilde{\mathbf{B}}(x,\omega),
\]  
(3.11)

By calculating the rotor of expression (3.10) and making the same approximations as those made for the magnetic field, we obtain:

\[
\tilde{\mathbf{E}}(x,\omega) = -c\hat{n} \times \tilde{\mathbf{B}}(x,\omega) = ic\left[\hat{n} \times k \tilde{\mathbf{A}}(x,\omega)\right] \times \hat{n}.
\]  
(3.12)

### 3.2 The Poynting vector and the radiated power

Having derived the far-field expressions for the electric (3.12) and magnetic (3.10) fields, we can now calculate the Poynting vector \( \mathbf{S} \): as we are dealing with complex fields, we need to define the complex Poynting vector, whose real part represents the power flux out of an infinitesimal surface orthogonal to its direction (see Ref. [8], Sect. 6.9).

\[
\mathbf{S}(x,t) := \frac{1}{2\mu_0} \mathbf{E}(x,t) \times \mathbf{B}^*(x,t) = \frac{1}{2\mu_0} \mathcal{F}^{-1}[\tilde{\mathbf{E}}](x,t) \times (\mathcal{F}^{-1}[\tilde{\mathbf{B}}](x,t))^* \\
= \frac{c}{2\mu_0} \left((\hat{n} \times \mathcal{F}^{-1}[k \tilde{\mathbf{A}}](x,\omega)) \times \hat{n}\right) \times \left((\hat{n} \times \mathcal{F}^{-1}[k \tilde{\mathbf{A}}](x,\omega))^*\right),
\]  
(3.13)
After a few simplifications, making use of the Levi-Civita symbol $\epsilon_{ijk}$, it can be shown that Eq. (3.13) can be reduced to the following:

$$S(x, t) = \frac{c}{2\mu_0} \left( \hat{n} \times \mathcal{F}^{-1}[k\tilde{A}](x, t) \right) \cdot \left( \hat{n} \times \mathcal{F}^{-1}[k\tilde{A}](x, t) \right)^* \hat{n}$$

$$= \frac{c}{2\mu_0} |\hat{n} \times \mathcal{F}^{-1}[k\tilde{A}](x, t)|^2 \hat{n}.$$  \hspace{1cm} (3.14)

It is not surprising that in the far-field approximation the only relevant component of $S$ is that in the $\hat{n}$ direction. Notice, further, that in the far-field approximation the Poynting vector is fully real. By substituting the expression for $\tilde{A}$, Eq. (3.5), we obtain

$$S(x, t) = \frac{Z_0 \hat{n}}{32\pi^2 r^2} \left| \hat{n} \times \mathcal{F}^{-1}[ke^{-ikr} \int d^3 x' \tilde{J}(x', \omega)e^{ik\hat{n} \cdot x'}](x, t) \right|^2$$

$$= \frac{Z_0 \hat{n}}{32\pi^2 r^2} |\hat{n} \times f(x, t)|^2,$$  \hspace{1cm} (3.15)

where $Z_0 = \sqrt{\mu_0 / \epsilon_0}$ is called *impedance of free space*, and where we define

$$f(x, t) := \mathcal{F}^{-1} \left[ ke^{-ikr} \int d^3 x' \tilde{J}(x', \omega)e^{ik\hat{n} \cdot x'} \right](x, t),$$  \hspace{1cm} (3.16)

a vector field with the dimensions of electric current, namely $[\text{electric charge} \times \text{time}]$.

The total radiated power $P$ is the integral over the surface of a sphere with radius $r \gg x'$ of $S \cdot \hat{n} = |S|$, namely

$$P(t) = \int r^2 d\Omega |S(r, \theta, \phi, t)| = \frac{Z_0 \hat{n}}{32\pi^2} \int d\Omega |\hat{n} \times f(x, t)|^2,$$

where $d\Omega = \sin \theta d\theta d\phi$. Now it is clear why, in Eq. (3.7) we kept only the terms to $\sim 1/r$: if we had kept terms $O(1/r^2)$, they would appear in the Poynting vector as terms $O(1/r^3)$, whose integral over the surface would vanish for $r \to \infty$. We can define the *instantaneous differential radiated power*, depending on the position of observation, as

$$\frac{dP}{d\Omega}(x, t) = \frac{Z_0 \hat{n}}{32\pi^2} |\hat{n} \times f(x, t)|^2.$$  \hspace{1cm} (3.17)

The actual quantity we are interested in, however, is not this time-dependent emitted power, but rather the total emitted energy $\frac{d\mathcal{E}}{d\Omega}(x)$, namely the integral of expression (3.17) over all times. We recall that the laser pulse of an XFEL has a time duration of some femtoseconds, and thus the radiation we detect is contained in a time interval of the same order, which is smaller than the time-resolution of any available detector. Thus, we define the total emitted energy per unit solid angle as follows:

$$\frac{d\mathcal{E}}{d\Omega}(x) := \int_0^{T'} \frac{dP}{d\Omega} dt,$$  \hspace{1cm} (3.18)
where \( T' \simeq T + r/c \) is a time after which we can assume that the radiated power vanishes at distance \( r \) from the scatterer. As we assume that the fields at \( \mathbf{x} \) vanish outside the interval \([0, T']\), we can as well extend the integration to all times, and by substituting Eq. (3.17) we obtain:

\[
d\dot{E}/d\Omega(\mathbf{x}) = \frac{Z_0}{32\pi^2} \int_{-\infty}^{\infty} |\hat{n} \times f(\mathbf{x}, t)|^2 dt = \frac{Z_0}{32\pi^2} \int_{-\infty}^{\infty} |\hat{n} \times \tilde{f}(\mathbf{x}, \omega)|^2 \frac{2\pi}{d\omega}.
\] (3.19)

In the second equivalence we have exploited the fact that the Fourier transform is a unitary operator and thus conserves the \( L^2 \)-norm of the function, except for a factor \( 2\pi \) depending on normalization chosen in the definition: this result is also known as Parseval’s theorem (see Ref. [12], Sect. 8.5-8.6).

Notice that, due to the fact that Eq. (3.19) depends the Fourier transform of \( f \), the radiated energy \( d\dot{E}/d\Omega \) does not depend on the radius \( r \), and thus \( d\dot{E}/d\Omega = d\dot{E}/d\Omega(\hat{n}) \).

Actually, the \( r \)-dependence of Eq. (3.18) comes about only in the factor \( e^{-ikr} \) that is present in the definition of \( f \), Eq. (3.16): in the frequency-domain it is only an irrelevant phase factor, whose norm is 1:

\[
|\hat{n} \times \tilde{f}(\mathbf{x}, \omega)|^2 = |\hat{n} \times ke^{-ikr} \int d^3x' \tilde{J}(\mathbf{x}', \omega)e^{ik\hat{n} \cdot \mathbf{x}'}|^2 = k^2|\hat{n} \times \int d^3x' \tilde{J}(\mathbf{x}', \omega)e^{ik\hat{n} \cdot \mathbf{x}'}|^2.
\] (3.20)

### 3.3 Cross section

To obtain the differential cross section we evaluate the ratio of the emitted energy in the direction \( \hat{n} \) to the integrated intensity (energy per unit time and surface) of the incident beam:

\[
\frac{d\sigma}{d\Omega} = \frac{\int_{0}^{T'} \frac{dP}{d\Omega}(t)dt}{\int_{0}^{T} I(t)dt} = \frac{d\dot{E}}{d\Omega} \int_{0}^{T} I(t)dt.
\] (3.21)

Notice that with this definition the cross section has the correct dimensions of a surface per unit solid angle: precisely, the numerator has the dimensions of energy over solid angle, and the denominator of energy over surface. The total cross section \( \sigma \) is obtained by integrating expression (3.21) over the entire solid angle:

\[
\sigma = \int_{4\pi} \frac{d\sigma}{d\Omega} d\Omega.
\] (3.22)
Chapter 4

The numerical implementation

4.1 The Discrete Fourier Transform

In Section 3 we showed that the first step for calculating the radiation cross section, given the current density, is to calculate its time-frequency Fourier transform. However, since the current density is known as a numerical solution of the Schrödinger problem, it is available in discrete points (those defined by the spatial mesh), and at discrete, equally spaced times. For this kind of data, we need to use the discrete Fourier transform (DFT) [13].

Suppose we are given the value of a function \( f(t) \) at \( N \) equally spaced times \( t_m = m\Delta t \), with \( m = 0, 1, 2, ..., N - 1 \), and we want to calculate its Fourier transform: with \( N \) numbers of input we can produce no more than \( N \) independent numbers of output, and thus we can calculate \( \tilde{f}(\omega) \) only at discrete angular frequencies \( \omega_n \), with \( n = 0, 1, 2, ..., N - 1 \). To chose these frequencies among all possible frequencies, we rely to an important theorem, known as the sampling theorem (see Ref. [13], Sect. 12.1). For any sampling interval \( \Delta t \) we define a special frequency \( \nu_c \), called Nyquist critical frequency, given by

\[
\nu_c := \frac{1}{2\Delta t}. \tag{4.1}
\]

If a continuous function \( h(t) \), sampled at an interval \( \Delta t \) (i.e. \( h_k = h(k\Delta t) \), \( k = ..., -3, -2, -1, 0, 1, 2, 3, ... \)), happens to be bandwidth limited to frequencies smaller than \( \nu_c \) (i.e. \( \tilde{h}(\omega) = 0 \) for all \( |\omega| \geq 2\pi\nu_c \)), then the function \( h(t) \) is completely determined at all times by its samples \( h_k \): precisely, it is given by the following formula:

\[
h(t) = \Delta t \sum_{k=-\infty}^{\infty} h_k \frac{\sin[2\pi\nu_c(t - k\Delta t)]}{\pi(t - k\Delta t)}. \]
When, on the other hand, the function is not bandwidth limited to less than the Nyquist critical frequency, it happens that the frequencies that lie outside the interval \([-ν_c, ν_c]\) are spuriously moved into that range, due to the act of discrete sampling: this phenomenon is called aliasing.

For this reason, we must make sure that the frequencies for calculating the Fourier transform are inside the range \([-ν_c, ν_c]\). Accordingly, we define

$$\omega_n := n Δω, \quad (4.2)$$

where \(Δω = \frac{2π}{NΔt}\) and \(n = -\frac{N}{2} + 1, -\frac{N}{2} + 2, ..., \frac{N}{2}\), resulting in \(-2πν_c < ω_n ≤ 2πν_c\).

To avoid aliasing we have to be aware (approximately) of the bandwidth of the actual function and to sample it at a rate sufficiently rapid to let the maximum involved frequency be smaller in module than \(ν_c\): for example, for a sinusoidal function, we must take at least two samples per cycle.

Now we can define the DFT, by approximating the formula of the continuous Fourier transform computed at the frequencies \(ω_n\). The integral in Eq. (3.2) is approximated by the sum of the integral at times \(t_m\) multiplied by the width of the interval \(Δt\):

$$\tilde{f}_n := \tilde{f}(ω_n) = \int_{-∞}^{∞} dt f(t)e^{-iω_n t} ≈ \Delta t \sum_{m=0}^{N-1} f_m e^{-iω_n t_m} = Δt \sum_{m=0}^{N-1} f_m e^{-\frac{2πnm}{N}} \quad (4.3)$$

Let us define \(F_n := \sum_{m=0}^{N-1} f_m e^{-\frac{2πnm}{N}}\). Thus

$$\tilde{f}_n = Δt F_n \quad (4.4)$$

The inverse transform is defined in analogy with Eq. (3.3):

$$f_m = f(t_m) ≈ \frac{Δω}{2π} \sum_{n=-N/2}^{N/2-1} \tilde{f}_n e^{\frac{2πnm}{N}} = \frac{1}{N} \sum_{n=-N/2}^{N/2-1} F_n e^{\frac{2πnm}{N}}. \quad (4.5)$$

The discrete form of Parseval’s theorem is

$$\sum_{m=0}^{N-1} |f_m|^2 = \frac{1}{N} \sum_{n=-N/2}^{N/2-1} |F_n|^2. \quad (4.6)$$

From Eq. (4.3) it is evident that computing the DFT is essentially a multiplication of a vector with \(N\) components by a \(N \times N\) matrix. The computational cost of such operation is \(O(N^2)\). Fortunately, this cost can be reduced drastically by exploiting the periodicity of the matrix elements \(e^{-\frac{2πnm}{N}}\): the algorithm that implements this optimized calculation is called Fast Fourier Transform (FFT). It reduces the number of operations to \(O(N \log_2 N)\). The implementation that we use is that provided by the FFTW library [13].
4.2 Discretization of space and spatial integration

The other important ingredient in our formula for the radiated energy, Eq. (3.19), is the spatial integration, involved in the definition of $f$, Eq. (3.16). The result from the numerical solution of the Schrödinger equation is a set of values of the the current density (3 complex components) evaluated at discretized times and points of space. The computational region is a sphere of radius $R = 30a_0$, discretized by a tetrahedral mesh with two different fineness levels: an inner sphere of radius $R_0 = 3a_0$ with a finer mesh and an outer shell of thickness $R - R_0$ with a coarser mesh ([7], see Fig. 4.1). The output current density is evaluated at the vertices of the tetrahedra, plus at some extra points needed for the derivation of the electron wave function. We have neglected these extra points for simplicity. The integration method consists in assigning each tetrahedron the average of the values of the function at its vertexes, and summing this average value multiplied by the volume of the tetrahedron, over all tetrahedra: thus, for a given function
\[ f(x) \]
\[ \int d^3x f(x) \simeq \sum_{h=1}^{N_{\text{tetr}}} V_h \left( \frac{1}{4} \sum_{l=1}^{4} f_{hl} \right), \quad (4.7) \]
where \( N_{\text{tetr}} \) is the total number of tetrahedra, \( V_h \) is the volume of the \( h \)-th tetrahedron, and \( f_{hl} \) indicates the value of function \( f \) at the \( l \)-th vertex of the \( h \)-th tetrahedron.

As the corners are in common to several tetrahedra, the term \( f_{hl} \) appears in the sum as many times as many tetrahedra share that corner, and each time it is multiplied by \( 1/4 \) and by the volume of the tetrahedron: thus, we can rewrite expression (4.7) summing not on all tetrahedra, but rather on all corners, and assigning each corner a weight depending on the number of tetrahedra that share that corner and the corresponding volumes:

\[ \int d^3x f(x) \approx \sum_{j=1}^{N_{\text{vert}}} f_j \left( \frac{1}{4} \sum_{k=1}^{n_{\text{tetr}}^{(j)}} V_{jk} \right) = \sum_{j=1}^{N_{\text{vert}}} f_j w_j, \quad (4.8) \]

where \( N_{\text{vert}} \) is the total number of the vertexes, \( n_{\text{tetr}}^{(j)} \) is the number of tetrahedra that share the \( j \)-th vertex, \( V_{jk} \) is the volume of the \( k \)-th tetrahedron that shares the corner \( j \). Equation (4.8) implies the definition of the weight of the \( j \)-th point as

\[ w_j := \frac{1}{4} \sum_{k=1}^{n_{\text{tetr}}^{(j)}} V_{jk}. \]

We can evaluate these weights once for all at the beginning. Once we have assigned each mesh-point its weight, the computational cost of Eq. (4.8) is \( O(N_{\text{vert}}) \).

### 4.3 The incoming pulse

We solve the time-dependent Schrödinger equation (2.12) with the excitation radiation described by a vector potential producing a \( z \)-linearly polarized pulse propagating along the \( z \)-axis (see Fig. 4.2):

\[ A(z, t) = \begin{cases} \frac{E_0}{\omega_0} \sin^2 \left( \frac{x}{\omega_0 \tau} (k_0 z - \omega_0 t) \right) \sin(k_0 z - \omega_0 t) \hat{x} & \text{for } 0 \leq k_0 z - \omega_0 t \leq \omega_0 \tau \\ 0 & \text{elsewhere} \end{cases} \quad (4.9) \]

Here \( \tau = N_{\text{osc}} \times 2\pi/\omega_0 \) is the duration of the pulse, that corresponds to one period of the squared-sine modulating wave, and to \( N_{\text{osc}} \) complete oscillations of the leading sinusoidal wave at frequency \( \omega_0 \). In our simulations, following Ref. [7],
Figure 4.2: The vector potential from Eq. (4.9) with mean frequency \( \omega_0 = 365 \text{ a.u.} \simeq 1.5 \times 10^{19} \text{s}^{-1} \), evaluated at the origin \( x = 0 \).

we use \( N_{\text{osc}} = 10 \), and thus, for a pulse with \( \omega_0 = 10 \text{ keV/}\hbar \), the total duration of the pulse is \( \simeq 0.172 \text{ a.u.} \simeq 4.2 \text{ as} \). This is an extremely short impulse, and it is not experimentally reproducible with today’s technology: we choose such a short pulses to ensure the convergence of the numerical solution of the Schrödinger equation within a practical simulation time. To simulate more realistic pulses the numerical solution should be improved, and powerful parallel computers should be used.

The electric field amplitude \( E_0 \) is related to the intensity \( I_0 \), which parametrizes the intensity of the pulse:

\[
E_0 = \sqrt{\frac{2I_0}{\epsilon_0 c}} .
\]

Equation (4.10) is the relation between the amplitude of the electric field and the average intensity of a plane wave of the form

\[
\mathbf{E}(z, t) = E_0 e^{i(kz - \omega t)} \hat{x}
\]

Clearly Eq. (4.10) does not hold strictly for our polychromatic pulse. We use \( I_0 \) as a handy parameter for our studies. We evaluate the integral over time of the radiation intensity of the pulse of Eq. (4.9), which is proportional to \( I_0 \):

\[
\int_0^\tau S dt = \frac{\epsilon_0 c E_0^2}{2} \frac{2\pi N_{\text{osc}}}{\omega_0} \left( \frac{3}{16} + \frac{1}{16N_{\text{osc}}^2} \right) = \frac{I_0 \tau}{16} \left( 3 + \frac{1}{N_{\text{osc}}^2} \right) .
\]
Eq. (4.12), valid for \( N_{osc} > 1 \), was obtained empirically. It fits perfectly the analytical integral obtained for \( N_{osc} = 2 \) and \( N_{osc} = 3 \). Moreover, for \( N_{osc} \to \infty \) the average intensity on one oscillation is \( 3I_0/16 \), namely \( I_0 \) multiplied by \( 3/8 \) (the average value of \( \sin^4 \)) and by \( 1/2 \) (the average value of \( \cos^2 \)). This is coherent with what we might expect thinking that, for large \( N_{osc} \), the electric field obtained from (4.9) is \( \approx E_0 \sin^{\left[ \frac{\pi}{\omega_0 \tau} (k_0 z - \omega_0 t) \right]} \cos(k_0 z - \omega_0 t) \), and that the intensity is proportional to \( |E|^2 \).

Fixed \( N_{osc} \), the two parameters on which one can act to modify the pulse and study the dependence of the cross section are its intensity \( I_0 \) and the photon mean energy \( \mathcal{E}_0 = \hbar \omega_0 \). For convenience, in the numerical implementation we adopt the atomic units \( (e = \hbar = m_e = 4\pi\epsilon_0 = 1, \text{see Appendix A}) \). We can rewrite Eq. (4.10) in these units:

\[
E_0 = \sqrt{8\pi\alpha I_0},
\]

(4.13)

where \( \alpha \) is the fine-structure constant. From now on we will refer to \( I_0 \) in atomic units: to convert it to the SI one can multiply it by the atomic intensity unit \( E_{Ha} \approx 6.436 \times 10^{19} \text{ W/m}^2 \).

### 4.4 Convergence

We first compute the DFT of the function \( J(x'_j, t_m) \), obtaining the set of values \( \tilde{J}_{jn} := \tilde{J}(x'_j, \omega_n) \). This calculation has a cost \( N_{vert} \times N \log_2 N \). The main computational effort comes now when we compute the emitted radiation. Chosen a direction \( \hat{n} \), the discrete version of Eq. (3.19), including the explicit expression for \( \tilde{f} \) in Eq. (3.20), is

\[
\frac{d\mathcal{E}}{d\Omega}(\hat{n}) = \frac{Z_0}{32\pi^2 N} \Delta t \sum_{n=-N/2}^{N/2-1} \left( \frac{\omega_n}{c} \right)^2 \left| \hat{n} \times \sum_{j=1}^{N_{vert}} w_j \tilde{J}_{jn} e^{ik\hat{n} \cdot x'_j} \right|^2.
\]

(4.14)

It is clear that this formula has a computational cost of order \( O(N \times N_{vert}) \): if we want to calculate the radiated energy in \( N_{dir} \) different directions, the total cost becomes \( O(N \times N_{vert} \times N_{dir}) \).

We now analyse the sources of error of our study. As we make no approximation in the theory (apart from the far-filed approximation, which however is completely realized experimentally and thus introduces a negligible error, and the classical treatment of electromagnetic fields), the only approximation of this method arises when passing from the continuous formula (3.19) to the discretized formula (4.14). Thus, when calculating the differential cross section we have two sources of error: the finite discrete time sampling and the spatial discretization. Moreover, when we want to calculate the total cross section we need to
approximate the integral in Eq. (3.22) with a finite sum over finite elements \( \Delta \Omega = \sin \theta \Delta \theta \Delta \phi \). This fact introduces a third source of error that we will refer to as finite angular resolution. Note that this third source of error can be easily reduced at will, as Eq. (4.14) poses no limit to the number of directions at which one computes the radiation: it is just a question on how much computer time one is willing spend. As the calculations for different directions are totally independent from one another, the computation can be completely parallelized.

In the present study of convergence we set up a simulation for an incoming pulse of intensity \( I_0 = 10^6 \text{ a.u.} \simeq 6.4 \times 10^{25} \text{ W m}^{-2} \) and mean energy 365 a.u. \( \simeq 10 \text{ keV} \) (see Sect. 4.3). Figures 4.3, 4.4 and 4.5 report the analysis of convergence of our method as a function of several parameters. The time-stepping is reported in units of the period of the leading wave \( \tau_0 = 2\pi/\omega_0 \): we adapt the choice of the sampling time to the frequency of the pulse in order to keep the ratio \( \Delta t/\tau_0 \) constant. For the studies in the following sections we adopted the following default parameters, indicated by the arrows in the figures:

- time-step \( \Delta t/\tau_0 = 0.365/\pi \simeq 0.116 \),
- maximal mesh spacing in the finest region \( 0.4a_0 \),
- angular resolution (for the total cross section) \( \Delta \theta = \Delta \phi = 3^\circ \).

With this choice of the parameters, our main sources of error are expected to be the spatial mesh and the angular resolution, and we estimate our numerical error on the total cross section to be of the order \( \Delta \sigma = 0.2 \text{ mb} \).
Figure 4.3: The total cross section as a function of the ratio of sampling time $\Delta t$ to the period of the leading wave $\tau_0 = 2\pi/\omega_0$, with all other parameters fixed: larger spacing of the mesh $0.4a_0$, angular resolution $\Delta \theta = \Delta \phi = 9^\circ$.

Figure 4.4: The total cross section as a function of the mesh maximal spacing in the region $|x| < 3a_0$, with all other parameters fixed: time-step $\Delta t/\tau_0 = 0.365/\pi \simeq 0.116$, angular resolution $\Delta \theta = \Delta \phi = 9^\circ$. 
Figure 4.5: The total cross section as a function of the angular resolution $\Delta \theta = \Delta \phi$, with all other parameters fixed: time-step $\Delta t/\tau_0 = 0.365/\pi \simeq 0.116$, maximal spacing of the mesh $0.4a_0$. 
Chapter 5

Results

5.1 The perturbative limit

We first test our code with a relatively moderate-intensity pulse, \( I_0 = 10^4 \) a.u., for which we expect, following Ref. \[7\], the perturbative result to hold. The cross section (2.20) does not consider the incoherent (Compton) scattering: we compare our results to this formula, as, due to our classical treatment of the electromagnetic fields, we can not predict quantum effects such as the Compton scattering. Inelastic scattering plays a dominant role in low-Z atoms: in particular for the hydrogen atom the total inelastic cross section at 10 keV is \( \sigma_C \simeq 0.64 \) b \( \gg \) \( \sigma_T \) (see Sec. 2.2) and thus Compton is the dominant effect. However, for large atoms or molecules, which are the main target of experimental interest, inelastic scattering is comparably smaller, and thus for those objects our method will be more accurate.

The fact that our method does not count for incoherent scattering is shown also by a Fourier analysis of the scattered radiation (See Fig. 5.1): for increasing \( \theta \) some non-elastic components of the scattered radiation are observed, but they are significantly smaller than the elastic peaks.

To illustrate how the photon energy affects the angular dependence of the cross section, we set up two simulations with a different mean energy \( \hbar \omega_1 = 365 \) a.u. \( \simeq 10 \) keV and \( \hbar \omega_2 = 36.5 \) a.u. \( \simeq 1 \) keV. Figure 5.2 reports the results of our calculations compared with the perturbative result (2.20) for \( x \)-linearly polarized monochromatic radiation, as our vector potential of Eq. (4.9) is: we plot the angular dependence of the differential cross section as a function of \( \theta \), for \( \phi = 0^\circ \) (polarization plane) and \( \phi = 90^\circ \) (perpendicular to the polarization).
Figure 5.1: a: Spectral distribution of incoming beam ($\propto \omega |\tilde{A}(\omega)|^2$) in arbitrary unit, for a pulse with photon energy 365 a.u. $\simeq 10$ keV and $I_0 = 10^4$, see Fig. 4.2. b-d: The corresponding scattered photon spectral distribution (radiated energy/$\hbar \omega$) in arbitrary unit, evaluated in different directions.

5.2 High intensities

Now we study the behaviour of the cross section in presence of high-intensity radiation, in search of non linear effects. With intensities greater that $I_0 = 10^7$, at the incident photon energy of 10 keV, our simulations have problems of convergence. We try different methods of integration of the Schrödinger equation, and we monitor the conservation of the wave function, namely the integral of $|\psi(x,t)|^2$ over the entire computational region, which in absence of ionization should remain 1 at all times: deviations signal convergence problems. We test two different integration methods: the generalized-$\alpha$ and the method based on backward differentiation formulas (BDF), with different settings on the time-stepping, see Fig. 5.3. Based on this comparison, eventually we adopt, for all calculations described in the following, the BDF integration method, with conservative time-stepping, initial and maximum step 0.01 a.u. and relative acceptance 0.001, solid curve in
Figure 5.2: Angular dependence of the differential cross section for the scattering of a laser pulse with $I_0 = 10^4$, composed of photons of central peak energy $\hbar \omega_1 \simeq 10$ keV (a) and $\hbar \omega_2 \simeq 1$ keV (b). The points report the numerical results, the lines track the perturbation-theory formula Eq. (2.20).

Fig. 5.3: this method is stable also beyond $I_0 = 10^7$, keeping the norm of the wave function within the 10% up to $I_0 = 10^9$.

Variations in the norm of the wave function also determine variations in the amplitude of the current density, and thus in the computed cross section. To avoid such unphysical variations, determined by convergence problems in the numerical solution of the Schrödinger equation, we export the function $J(x, t)$ obtained starting from the normalized wave function, i.e. divided by the squared $L^2$-norm of the wave function

$$||\psi||(t) = \sqrt{\int d^3x |\psi(x, t)|^2}$$

at each time.

Figure 5.4 reports the total cross section as a function of intensity, with average photon energy $\hbar \omega_0 = 365$ a.u. $\simeq 10$ keV, compared to the perturbative result, which is of course independent of the incident intensity. The perturbative
Figure 5.3: **a**: The time evolution of the wave function norm with different integration methods. The simulations are performed with an incident radiation with intensity $I_0 = 10^7$ a.u., and photon energy 10 keV. The BDF method is tested with different settings: conservative time-stepping with initial and maximum step $0.05$ and relative acceptance $0.005$ (1); adaptive time-stepping with initial and maximum step $0.05$ and relative acceptance $0.005$ (2); conservative time-stepping with initial and maximum step $0.01$ and relative acceptance $0.001$ (3). **b**: The vector potential Eq. (4.9), evaluated at the origin.

value in Fig. 5.4 is obtained by numerically integrating the differential cross section Eq. (2.20), with $\omega_0 = 365$ a.u. The computed cross section is compatible with the perturbative value up to intensity $\simeq 10^{27}$ W m$^{-2}$: beyond that value non-linear effects are observed, with increasing of the cross section of 8.5% for intensity $10^{28}$ W m$^{-2}$. Non-linear effects at these intensities were already observed in the previous work by Mantovani [7].

Figure 5.5 shows the angle-resolved cross section for scattering of a high intensity pulse, $I_0 = 10^9$. For such high frequencies we observe an increased cross section in the forward scattering ($\theta \simeq 0^\circ$) compared to the perturbative result.

We can calculate the Keldysh parameter for the pulses produced in a few FEL facilities from the data in Tables 1.1. Expressing the quantities in atomic units, the ionization potential $I_p$ for valence electrons is of order $\simeq 1/2$, and $E_0$ can be estimated from the intensity by relation (4.13). Thus Eq. (2.27) for $\gamma$
The Keldysh parameter was introduced for studying the tunnel ionization induced by \textit{quasi-static} electric fields, and thus it has a clear meaning only for radiation with lower frequency than the ionization potential. When coming to high frequency, the quasi-static assumption does not hold, and thus also the Keldysh parameter may not have a particular meaning \cite{15}. However, our results show that also for X-ray frequencies the perturbative limit is fulfilled as long as $\gamma \gg 1$.

A typical pulse produced at European-XFEL has $\hbar \omega_0 \simeq 370$ a.u. and $I_0 \simeq 1$ a.u.: thus $\gamma \simeq 140 \gg 1$. For standard FEL pulses at FERMI and FLASH, we find again $\gamma > 100$. UV and soft-X rays, however, can be focalized by means of optical techniques, obtaining a great increase of intensity: at FLASH an irradiance of $10^{20}$ W m$^{-2}$ was reached for pulses with photon energy 93 eV, giving $\gamma \simeq 1$.

The Keldysh parameter becomes

$$\gamma = \frac{\omega_0 \text{(a.u.)}}{\sqrt{8\pi\alpha I_0 \text{(a.u.)}}}.$$  \hspace{1cm} (5.1)

\textbf{Figure 5.4:} The total cross section as a function of intensity, for pulses with photon energy 365 a.u.$\simeq 10$ keV. For intensity greater than $10^8$ a.u. non-linear effects arise, determining an increase of the cross section compared to the perturbative value.
Figure 5.5: Angular dependence of the differential cross section for scattering of a laser pulse composed of photon with mean energy $\hbar \omega_0 \simeq 10$ keV and with intensity parameter $I_0 = 10^9$ a.u.: compared to the perturbative result, the numerical computation shows an increase section in the forward direction ($\theta \simeq 0$). We plot only for $\theta \leq 90^\circ$ because beyond this value the cross section is indistinguishable from zero, with our precision.
Chapter 6

Conclusions and outlooks

In the present thesis we have reached a further step in the Maxwell-Schrödinger approach to X-ray radiation started with the work [7]. In particular we offer theoretical basis and numerical implementation to the problem of predicting the far-field scattering cross section, given the time-dependent current density distribution obtained from a solution of the Maxwell-Schrödinger problem. The code we provide has a computational cost which is proportional to the number of points that form the spatial mesh, times the number of steps in which the simulation time is divided, times the number of directions in which the outgoing radiation is computed. An important feature of our code is that the calculations in different directions are completely independent from one another, and thus the computation can in principle be completely parallelized. We tested the code in several pulse conditions, proving that, for low intensities, our predictions are in complete accordance with the analytical result coming from perturbative methods. The code can be applied to any case of scattering, not only from one-electron atoms, provided that we solve the many-body Schrödinger equation and extract the global current density function from it, taking into account the motion of all electrons.

An extension of the model may come from including, in the Schrödinger equation, the electromagnetic field generated by the electronic motion itself, thus solving a system of coupled equations, with the Schrödinger equation solved alongside the equations of the Maxwell potentials, now treated as variables too. This would also implement the energy loss of the electron, which after the excitation falls back into its ground state by emitting energy which is transformed into electromagnetic radiation.

The model may be generalized for heavier atoms and molecules, by implementing a many-body Schrödinger equation. Heavy molecules, which are the main source of interest for experimental applications, may also fit better in this
approach, as the Compton scattering, which we do not take into account due to the classical treatment of electromagnetic fields, may be smaller than in light atoms.

Improvements should be made particularly in the numerical solution of the Schrödinger equation. In particular, the convergence of the algorithm should be enhanced to make it possible to simulate longer pulses, of the order of the fs, which is the typical time scale of FEL pulses.
Appendix A

Atomic units

We report the definition of the system of atomic units which we adopt in the numerical solution of the Schrödinger equation and throughout the code for computing the cross section. Table A.1 collects the fundamental quantities that are taken as units in this system, Table A.2 reports the values of several important constants expressed in atomic units. In Table A.3 we give the SI corresponding values for the atomic units of several physical quantities. We first recall the value of the dimensionless fine structure constant:

\[ \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = 0.00729735257 \simeq 1/137. \]  

(A.1)

which in atomic units is just the inverse of the speed of light.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Name</th>
<th>Symbol</th>
<th>Value (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>electron mass</td>
<td>( m_e )</td>
<td>( 9.109382 \times 10^{-31} \text{ kg} )</td>
</tr>
<tr>
<td>charge</td>
<td>elementary charge</td>
<td>( e )</td>
<td>( 1.602176 \times 10^{-19} \text{ C} )</td>
</tr>
<tr>
<td>action</td>
<td>reduced Planck’s constant</td>
<td>( \hbar )</td>
<td>( 1.054571 \times 10^{-34} \text{ J s} )</td>
</tr>
<tr>
<td></td>
<td>Coulomb force constant</td>
<td>( \frac{1}{4\pi\epsilon_0} )</td>
<td>( 8.987551 \times 10^9 \text{ kg m}^3\text{s}^{-2} \text{ C}^{-2} )</td>
</tr>
</tbody>
</table>

Table A.1: The fundamental physical quantities that are taken as unity in the atomic system of units. The SI value is given for reference.
<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Value (a.u.)</th>
<th>Value (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>speed of light</td>
<td>(c)</td>
<td>(\alpha^{-1} = 137.036)</td>
<td>299 792 458 m s(^{-1})</td>
</tr>
<tr>
<td>vacuum permittivity</td>
<td>(\epsilon_0)</td>
<td>(\frac{1}{4\pi} = 0.079 577)</td>
<td>8.854 188 \times 10^{-12} F m(^{-1})</td>
</tr>
<tr>
<td>vacuum permeability</td>
<td>(\mu_0)</td>
<td>(4\pi\alpha^2 = 6.691 762 \times 10^{-4})</td>
<td>(4\pi \times 10^{-7} V s A^{-1} m^{-1})</td>
</tr>
<tr>
<td>classical electron radius</td>
<td>(r_e)</td>
<td>(5.325 135 \times 10^{-5})</td>
<td>2.817 940 \times 10^{-15} m</td>
</tr>
<tr>
<td>Bohr magneton</td>
<td>(\mu_B)</td>
<td>0.5</td>
<td>9.274 009 \times 10^{-24} J T(^{-1})</td>
</tr>
</tbody>
</table>

**Table A.2:** A few physical constants used in the present thesis, expressed in atomic units, and in the SI.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Name</th>
<th>Symbol</th>
<th>Expression</th>
<th>Value (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>Bohr radius</td>
<td>(a_0)</td>
<td>(\frac{4\pi\epsilon_0\hbar^2}{me^2})</td>
<td>5.291 771 \times 10^{-11} m</td>
</tr>
<tr>
<td>energy</td>
<td>Hartree energy</td>
<td>(E_{Ha})</td>
<td>(\frac{e^2}{4\pi\epsilon_0 a_0})</td>
<td>4.359 744 \times 10^{-18} J</td>
</tr>
<tr>
<td>time</td>
<td>(t_0)</td>
<td>(\frac{\hbar}{E_{Ha}})</td>
<td>2.418 884 \times 10^{-17} s</td>
<td></td>
</tr>
<tr>
<td>frequency</td>
<td>(t_0^{-1})</td>
<td>(\frac{2\pi}{t_0})</td>
<td>4.134 138 \times 10^{16} s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>angular frequency</td>
<td>(\frac{2\pi}{t_0})</td>
<td>2.597 555 \times 10^{17} s(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>power</td>
<td>(\frac{E_{Ha}}{t_0})</td>
<td>0.180 237 8 W</td>
<td></td>
<td></td>
</tr>
<tr>
<td>electric current density</td>
<td>(\frac{e}{\mu_0 a_0})</td>
<td>2.365 337 \times 10^{18} A m(^{-2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>electric field</td>
<td>(\frac{E_{Ha}}{\epsilon_0 a_0})</td>
<td>5.142 207 \times 10^{11} V m(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>electric potential</td>
<td>(\frac{E_{Ha}}{\epsilon})</td>
<td>27.211 385 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>magnetic induction</td>
<td>(\frac{\hbar}{e a_0})</td>
<td>2.350 517 \times 10^{5} T</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vector potential</td>
<td>(\frac{\hbar}{\epsilon_0 a_0})</td>
<td>1.243 840 \times 10^{-5} V s m(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>energy flux (intensity)</td>
<td>(\frac{E_{Ha}}{\mu_0 a_0})</td>
<td>6.436 409 \times 10^{19} W m(^{-2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>magnetic permeability</td>
<td>(\frac{m_e a_0}{e^2})</td>
<td>1.8779 \times 10^{-3} V s A(^{-1}) m(^{-1})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table A.3:** Derived atomic units for the physical quantities appearing in the present work, with their SI value.
Ringraziamenti

Ringrazio di cuore il professor Manini, per la disponibilità che mi ha mostrato ogni volta che avevo bisogno e per i dialoghi costruttivi che ho avuto con lui, in cui ho imparato molte cose, ma soprattutto ho imparato che spesso le cose sono assai più complesse di quello che penso. Ringrazio il professor Onida, al quale devo la possibilità di intraprendere questo lavoro. Voglio ringraziare molto anche Mattia, che pur nel pieno del suo dottorato a Konstanz è sempre stato disponibile a rispondere alle mie domande, con pazienza e chiarezza.

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Bibliography


