# ULTRAFAST SCIENCE: A MULTISCALE MODELING APPROACH TO FEMTOSECOND ELECTRON DIFFRACTION AND ITS APPLICATIONS

By

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#### ABSTRACT

#### ULTRAFAST SCIENCE: A MULTISCALE MODELING APPROACH TO FEMTOSECOND ELECTRON DIFFRACTION AND ITS APPLICATIONS

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The focus of this work is the study of processes at the edge of the current space and time resolutions. This includes both efforts in the development of an ultrafast electron microscope (UEM) and in the study of correlated electron systems that reflect measurements taken with this instrument.

The development of a reliable ultrafast electron diffraction and imaging system requires a low emittance source of photoemitted electrons and an understanding of how the properties of the generated bunch depend on the photocathode properties. In order to gain more understanding of this process, we combine the so-called three-step photoemission model with N-particle electron simulations. By using the Fast Multipole Method to treat space charge effects, we are able to follow the time evolution of pulses containing over 10<sup>6</sup> electrons and investigate the role of laser fluence and extraction field on the total number of electrons that escape the surface as well as virtual cathode physics and the limits to spatio-temporal and spectroscopic resolution originating from the image charge on the surface and from the profile of the exciting laser pulse. The results of these simulations are compared to experimental images of the photoemission process collected using the shadow imaging technique. By contrasting the effect of varying surface properties (leading to expanding or pinned image charge) and laser profiles (Gaussian, uniform and elliptical) under different extraction field strengths and numbers of generated electrons, we quantify the effect of these experimental parameters on macroscopic pulse properties such as emittance, brightness (4D and 6D), coherence length and energy spread. Based on our results, we outline optimal conditions of pulse generation for UEM systems.

With our knowledge of the photoemitted pulse properties, we also present our development of a design for the whole UEM column using the Analytic Gaussian model. We summarize the derivation of the equations governing this mean field model and show how the contributions due to the photoemission gun and the relativistic motion of the electrons can be added to this formalism to make it applicable for our system. We then explain the procedure used for optimizing the lens and RF cavity strengths and analyze both the effect of each separate optical element and their role in the column. We discuss the limits of this model and calculate the achievable temporal and spatial resolutions under different photoemission conditions.

We conclude the present work with an investigation of Tantalum Disulphide (TaS<sub>2</sub>), a material that presents interesting ultrafast phenomena that can be probed using the UEM. TaS<sub>2</sub> is a transition-metal layered compound that for T < 190 K displays a commensurate charge density wave (C-CDW) phase characterized by insulating behavior with the opening of a gap at the Fermi energy. To better understand the C-CDW phase and explain its quantum mechanical origin, we perform density functional theory calculations of the electronic band structure of 1T-TaS<sub>2</sub> and quantify the effect that spin orbit coupling and Hubbard repulsion have on the ground state. Our results show that neither of these interactions is sufficient to reproduce the insulating gap seen in experiment, an observation which is confirmed by our calculation of the phonon band structure and absorption spectrum. We also consider the effect of different stacking configurations of the TaS<sub>2</sub> layers and find evidence of gap opening for bilayers in the presence of disordered stacking. Yet all experience is an arch where thro' Gleams that untravell'd world whose margin fades For ever and for ever when I move.

— Tennyson, Ulysses

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## Chapter 1

## Introduction

### 1.1 Why study ultrafast science

Phenomena in the natural world take place on a variety of time scales, ranging from the millions of years one deals with in cosmology, to the infinitesimally small fractions of seconds involved with chemical, atomic and nuclear reactions. As the title of this thesis suggests, in the present work we are interested in ultrafast science, that is we seek to understand the transient non-equilibrium processes that happen in materials on timescales of less than  $10^{-9}$  seconds. Very broadly speaking, there is also often a correlation between timescale and size in physical systems, meaning that as the time scales of the phenomena we are interested in get smaller, so do the length scales over which these take place. For this reason when speaking of ultrafast science, we are also implicitly talking about length scales roughly between  $10^{-6}$  and  $10^{-10}$  meters.

With these considerations in mind, we have a very broad field that includes a number of interesting time dependent processes ranging from biology [2-5] to material science (from ultrafast phase transitions [6-11] to charge transport at nanointerfaces [12, 13] and dynamics in correlated electron materials [14–16]), from chemistry [17–20] to plasma physics [21–24]. As seen in the examples of Fig. 1.1 these phenomena take place across several different orders of magnitude of spatial and temporal resolution, but in each case further understanding of the fundamental interactions that determine the system's properties requires gaining more insight into atomic motion on a timescale corresponding to the period of the atomic vibrations. In addition to this, further understanding in this field would open the doors for numerous technological applications [30].



Figure 1.1: Spatial and temporal timescales of the various processes of interest in Ultrafast Science. The plot was compiled with the data reported in [2–25]

### 1.2 Pump probe microscopy

In practice these systems are best explored by using pump-probe measurements: we excite the system under consideration by perturbing it with a pump and measure its response at various delay times with a probe. By recording the response of the system as a function of delay time, we can obtain a description of the time evolution of the sample. In order to resolve these ultrafast phenomena, both the pump and the probe pulse need to be sufficiently short in time, which is the reason why the vast majority of this type of measurement use a femtosecond laser [31–33] to excite the system in virtue of its short duration, high peak power, broad bandwidth and commercial availability.

As far as probes are concerned, the main candidates are x-rays and electrons [25, 34, 35]. The advantage of using x-rays is that they offer Angstrom size wavelength, high spatial coherence and short pulse length, but their generation with a high enough brightness requires large scale facilities (such as SLAC's Linac). In addition to this, the interaction of x-rays with matter has a very small cross section, meaning that a high intensity and sensitive detection are required to achieve a good signal to noise ratio.

Electron probes, on the other hand, are easily generated using tabletop scale equipment, deal less damage to the sample compared to x-rays and have a high scattering cross section. As a consequence of this high cross section, the mean free path of the probe electrons inside the material is shorter than for x-rays and typically better matches the optical penetration depth, allowing to only probe the pumped volume. The drawback presented by this probe is that one has to deal with the space charge broadening due to the Coulomb repulsion between electrons, which leads to a decreased coherence length and increased pulse size. In addition, due to the short penetration length, there is a limited thickness that can be measured making experiments in liquid phases very challenging.

Given these considerations, one should view electrons and x-rays as complementary probes to use in ultrafast studies of materials. For the present work, though, we will only discuss systems using electrons as a probe.

#### **1.3** Ultrafast Electron Microscope at MSU

In the Ultrafast Research group at Michigan State University, we are working on the development of an Ultrafast Electron Microscope (UEM) that would allow measurements of some of the processes described in the previous sections. More specifically, we want to perform single-shot diffraction to observe irreversible processes in materials, such as photo-induced non equilibrium dynamics of lattice and charge transfer. Single-shot means that enough electrons for good signal to noise ratio are contained in a single probe pulse, in contrast to the stroboscopic mode in which the measurement for a given time delay between pump and probe is repeated over many shots to collect enough signal. The Rose criterion tells us that approximately 100 electrons per pixel are needed to resolve a pattern, which translates to roughly  $10^5$  to  $10^7$  electrons needed in a single pulse for diffraction and  $10^7$  to  $10^9$  electrons if one is interested in imaging.

The requirement of such a high number of electrons means that the expansion of the pulse due to space charge effects must be carefully considered and reversed in order to focus the pulse at the sample. In the transverse direction this can be easily done by using magnetic lenses but focusing in the longitudinal direction is harder to achieve. The solution we adopted is to use a radio frequency (RF) cavity phase locked with the photoexciting laser that generates the electron pulse. A schematic of the UEM system is shown in Fig. 1.2 and further details can be found in recent dissertations by Zhensheng Tao and Kiseok Chang. which cover the experimental development. This thesis covers some of the theoretical components of the project.



Figure 1.2: Schematic diagram of the Ultrafast Electron Microscope system. (Image courtesy of the Ruan Group, unpublished)

### 1.4 Overview

The central focus of this dissertation is to gain more insight into the development of the UEM system and on its applications. To do so, in the first part of this work, we give an overview of the simulations relative to the UEM system. In **Chapter 2**, we look at the details of the

photoemission process under different experimental conditions and discuss how to generate optimal electron pulses for our application. The code used for the simulations was developed by He Zhang [36]; using it to understand the photoemission process and extending it to different laser and surface image charge configurations was my own contribution.

In **Chapter 3** we proceed to simulations of the whole microscope column using a mean field model and provide estimates of the achievable resolution in the system, given different initial conditions. This so-called Analytic Gaussian model was originally derived by Michalik and Sipe [37, 38] and refined by Berger and Schroeder [39]; my contribution was extending it to treat the photoemission gun and the relativistic motion of the electrons and writing a program to apply it to the study of the UEM system and combine it with an optimization routine.

Chapter 4 moves away from microscope design and presents an example of a system, TaS<sub>2</sub>, displaying interesting ultrafast phenomena that can be probed using the microscope. By performing ab-initio calculations of the band structure, phonon modes and optical properties of this material, we shine light on the microscopic mechanisms underlying the insulating gap seen in experiments. All the simulations in this chapter were performed by myself using the well established Vienna Ab-initio Simulation Package (VASP).

Chapter 5 presents the conclusions of this thesis and an outlook on future research directions.

## Chapter 2

## Generation of the electron pulse

#### 2.1 Importance of the initial stages of pulse generation

Once an electron pulse has been generated in the initial stage of the UEM microscope introduced in the previous chapter, it can be shaped as it travels through the column using a variety of technologies such as magnetic lenses and radio frequency cavities [5,25,40–45]. What sets limits on the achievable temporal and spatial resolutions, though, is the phase space volume the pulse occupies, which in turn is defined by the photoemission conditions and the initial Coulomb expansion.

In the transverse direction our ability to resolve spatial features can be quantified with the coherence length  $L_c$ , which at the beam waist can be expressed as [46]

$$L_c = \frac{h}{2m_0 c} \frac{\sigma_x}{\epsilon_{n,x}},\tag{2.1}$$

where we have assumed that the transverse and longitudinal directions are decoupled, h is Plank's constant,  $m_0$  is the rest mass of the electron, c is the speed of light,  $\sigma_x$  is the beam radius and  $\epsilon_{n,x}$  is the normalized transverse emittance defined as [47–53]

$$\epsilon_{n,x} = \frac{1}{mc} \sqrt{\langle x^2 \rangle \langle p_x^2 \rangle - \langle x p_x \rangle^2}.$$
(2.2)

In the longitudinal direction, using the uncertainty principle and assuming a Gaussian pulse shape, we have that

$$\Delta E = \frac{\epsilon_z}{\Delta t} \gamma m_0 c. \tag{2.3}$$

where  $\epsilon_{n,z}$  is the normalized longitudinal emittance,  $\Delta t$  and  $\Delta E$  are, respectively, the temporal and energy resolutions and  $\gamma$  is the relativistic Lorentz factor.

One last figure of merit for electron sources is the normalized beam degeneracy, defined as [40,43]

$$\eta = B_{6D}\epsilon_0^3 = \frac{N_e}{\epsilon_x \epsilon_y \epsilon_z} \epsilon_0^3, \tag{2.4}$$

where  $B_{6D}$  is the 6D beam brightness and  $\epsilon_0 = h/(m_0c)$  is the emittance quantum. Considering that a single electron can have two possible spin orientations, the upper limit calculated using the Pauli exclusion principle is  $\eta = 2$ , with typical values ranging from  $\simeq 10^{-4}$  for a cold field emission gun to  $\simeq 10^{-12}$  if using a thermionic gun [40]. An ideal source of electron pulses would maximize the coherence length  $L_c$  and the degeneracy  $\eta$ , while maintaining a low energy spread  $\Delta E$  which, in turn, requires minimizing the longitudinal emittance  $\epsilon_{n,z}$ .

It is worth noting here that the emittance defined in Eq. 2.2 is a statistical approximation of the true 6D emittance, where correlations between the x, y and z directions have been neglected. We calculate this quantity and parameters derived from it as traditionally the emittance has been used as a key figure of merit for UEM systems, being an estimate of the phase space occupied by the pulse and therefore setting limits on the achievable resolution [26].

For all these reasons it is very important for the design of high brightness, high resolution electron beams to control the initial stages of pulse formation, so that the increase in beam emittance due to space charge effects can be minimized while maintaining a high number of electrons. To better understand the nonlinear interplay between the space charge driven expansion and laser and photocathode material properties on the generated electron bunch, we have conducted explicit N-particle simulations of the electron photoemission process using COSY Infinity, a code designed for high performance scientific computing and beam dynamics simulations [54]. In the following sections we will first introduce the model used to describe this process, followed by a description of the key elements of the simulation and then proceed to a discussion of the results and their comparison with experimental data.

#### 2.2 Modeling the photoemission process

In the UEM system, the electron bunch is generated through photoemission from a gold photocathode irradiated with a 50fs laser pulse. This process can be described using the socalled three-step photoemission model [48,55] in which each electron is emitted independently as a result of (1) absorbing a photon of energy  $\hbar\omega$ , (2) diffusing to the surface and (3) escaping to the vacuum [Fig. 2.1(a)]. As the thickness of the photocathode used in the experiment is smaller than the electron mean free path, electron-electron scattering does not contribute and step (2) can be neglected by simply treating all of the electrons as generated on the surface. We will now look at the remaining steps in the photoemission process in more detail.

The photocathode is irradiated with a laser pulse with energy  $\hbar\omega$ =4.66 eV. As the photon

energy is higher than the gold work function, W=4.0 eV to 4.6 eV [41, 56–58], a fraction of the electrons inside the metal can absorb enough energy to overcome the potential barrier and escape to the vacuum. The energy difference,  $\Delta E = \hbar \omega - W$ , allows only electrons with energies in the range  $[E_F - \Delta E, E_F]$  to be emitted, and since  $\Delta E$  is small, the generated bunch has a narrow energy spread. The lower limit for this range is set by the condition that the energy of the electron after the collision with the photon must satisfy  $E = E_i + \hbar \omega > E_F + W$ , while the upper limit reflects the fact that only states up to the Fermi energy are initially occupied. We assume an uniform distribution of states within this energy band.

In order to escape the photocathode, the electrons need to cross the metal-vacuum boundary with sufficient velocity in the direction perpendicular to the surface:

$$v_z \ge v_{z\,min} = \sqrt{\frac{2(E_F + W)}{m}},\tag{2.5}$$

where  $v_{z \min}$  is the velocity corresponding to the minimum kinetic energy required to overcome the potential barrier  $E_F + W$  and the z axis is assigned to the direction perpendicular to the metal surface [Fig. 2.1(b)].

Given an electron with initial energy  $E_i \in [E_F - \Delta E, E_F]$ , we have that

$$v_i = \sqrt{\frac{2(E_i + \hbar\omega)}{m}},\tag{2.6}$$

which, together with the equation for  $v_{z \min}$  (Eq. 2.5), determines a maximum internal angle for which the electron can escape:

$$\cos \theta_{i,max} = \frac{v_{z\,min}}{v_i} = \sqrt{\frac{E_F + W}{E_i + \hbar\omega}}.$$
(2.7)



Figure 2.1: (a) Schematic of the three-step photoemission model: (1) the electron absorbs a photon of energy  $\hbar \omega$ , (2) migrates to the surface and (3) escapes to the vacuum. (b) Definition of the coordinate system used in the simulation. Also shown is the Gaussian profile of the laser pulse on the photocathode surface. The electron is emitted with velocities given by equations (2.11)-(2.13). (c) Diagram showing the velocity of the electron inside the metal and in vacuum. Notice the conservation of transverse velocity across the interface and the decrease of the velocity in the perpendicular direction,  $v_z$ , due to the potential barrier at the surface.

Therefore inside the cathode:

$$v_{x\,in} = v_i \sin \theta_i \cos \phi_i,\tag{2.8}$$

$$v_{y\,in} = v_i \sin \theta_i \sin \phi_i,\tag{2.9}$$

$$v_{z\,in} = v_i \cos \theta_i,\tag{2.10}$$

where  $\theta_i \in [0, \theta_{max}]$  and  $\phi_i \in [0, 2\pi]$ . Outside the cathode the velocities in the directions parallel to the surface are conserved, while the velocity in the z direction is reduced due to the potential barrier [see Fig. 2.1(c)]:

$$v_{x out} = v_{x in} = v_i \sin \theta_i \cos \phi_i, \tag{2.11}$$

$$v_{y out} = v_{y in} = v_i \sin \theta_i \sin \phi_i, \qquad (2.12)$$

$$v_{z out} = \sqrt{v_{z in}^2 - 2(E_F + W)/m} = \sqrt{(v_i \cos \theta_i)^2 - 2(E_F + W)/m}.$$
 (2.13)

In addition to defining the initial velocities of the electrons with the above equations, the initial positions must also be calculated. The coordinates in directions parallel to the surface (x, y in our notation) are randomly generated from the spatial profile of the laser pulse. More details on how this is done in practice for the pulse profiles considered are given in Appendix 5. The initial z coordinate is set equal to zero since, as previously mentioned, we treat all of the electrons as generated on the surface. The physical parameters used to describe the system in the simulation are summarized in Table 2.1.

Fermi energy, $E_F$	$5\mathrm{eV}$
Work function, $W$	$4.45\mathrm{eV}$
Photon energy, $\hbar\omega$	$4.66\mathrm{eV}$
Laser pulse duration, $\Delta t$	$50\mathrm{fs}$
Laser pulse width, $\sigma_r$	$91\mu{ m m}$

Table 2.1: Physical parameters used in the simulation of the photoemission process.

In each simulation run, given the total number of electrons to generate,  $N_e^0$ , the number of electrons emitted during each infinitesimal time interval can be calculated assuming that the laser pulse has a Gaussian distribution in time with a standard deviation  $\sigma = \Delta t/(2\sqrt{2 \ln 2})$ , where  $\Delta t$  is the laser duration (FWHM). Considering then the range of times  $[-3\sigma, +3\sigma]$  and dividing it into N parts (typically N = 100), it is possible to calculate the number of

electrons generated in each  $i^{th}$  interval as

$$N_{i} = N_{e}^{0} \frac{\operatorname{erf}(t_{i}/\sqrt{2\sigma^{2}}) - \operatorname{erf}(t_{i-1}/\sqrt{2\sigma^{2}})}{2C}, \qquad (2.14)$$

where erf is the error function and

$$C = \frac{1}{\sigma\sqrt{2\pi}} \int_{-3\sigma}^{+3\sigma} dx e^{-\frac{x^2}{2\sigma^2}} \simeq 0.997.$$
 (2.15)

Note that the quantity  $N_e^0$  indicates the number of electrons that are emitted due to the laser illumination and is therefore directly proportional to the laser fluence F. The proportionality constant depends on the quantum efficiency as:

$$F = \frac{\hbar\omega N_e^0}{A} QE \cdot (1-R), \qquad (2.16)$$

where  $A = \pi \sigma_x \sigma_y$  is the area of the laser spot on the cathode surface, QE is the quantum efficiency, typically on the order of  $\simeq 10^{-4}$  [48], and R is the reflectivity of the sample surface.

To conclude the discussion on the model used, it is necessary to point out that each emitted electron contributes to the formation of an image charge on the surface of the photocathode model. This positive field plays an important role in shaping the electron pulse dynamics and will be discussed in more detail in section 2.4. Taking this into account, each electron in the system is treated as subject to both the space charge field between the particles in the bunch and the positive field generated by the image charge on the surface. In addition to the Coulomb electron-electron forces and the field due to the image charge, a constant electric field is applied in the direction perpendicular to the photocathode surface. Typical values for extraction fields are between 0.1-1MV/m for the thermionic gun geometry [40], between 1-10MV/m for the DC electron gun [59] and 10-100MV/m for the RF gun [60]. To provide relevant data over the whole range, we vary the extraction field between 0.1MV/m and 10MV/m which corresponds to generation of electrons with energies ranging from  $5 \cdot 10^{-3}$ keV to 100 keV at t=120ps.

#### 2.3 Details of the simulations

As we wish to simulate the time evolution of the electron bunch after the photoemission process has taken place, it is necessary to find a good scheme to treat the Coulomb interaction that would be both accurate and computationally advantageous. In the present work we have used COSY INFINITY [54], which treats the space charge effects with a Multiple Level Fast Multipole Method (MLFMM). In short, the MLFMM uses a tree algorithm to partition the simulated space into boxes until the number of charges in each one is lower than a certain threshold (typically  $N_{BOX} < 100$ ), after which the near and far region of each box are determined. The near region includes the adjacent boxes, for which the electromagnetic field is calculated directly. For the far region, a multipole expansion is used to calculate the field in the box of interest. This approach gives an algorithm that scales almost linearly with the number of particles with a prefactor that depends on the multipole order used. Further detail on the MLFMM are given elsewhere [36, 61].

In order to further reduce the computational time and allow simulations with higher numbers of electrons, we use macroparticles so that typically one simulated particle corresponds to 100 electrons. The effect of using macroparticles made of different numbers of electrons  $(N_{MP} = 1, 10, 100)$  was checked and the results for a typical set of parameters are shown in Fig. 2.2. The use of macroparticles does not affect the simulation results significantly, with the biggest effect being a constant shift of about 6% of the transverse momentum standard deviation,  $\sigma_{px}$  for the  $N_{MP} = 100$  case. This shift is propagated to the calculated emittance  $\epsilon_{n,x}$  but, since it is only fractions of  $\mu$ m and since our main interest is comparing values obtained with the same  $N_{MP}$  varying the other emission conditions, it does not have a significant impact on the discussion that follows.

To treat the time evolution of the emitted electrons, their equations of motion are solved at each time step using a fourth order Runge Kutta algorithm. The particles that fall back on the surface (z < 0) are removed from the simulation. Collisions between electrons are avoided by imposing a maximum force cutoff, which is translated into a constraint on the minimum allowed distance between two particles:  $r_{min} = \gamma r_a$ , where  $\gamma = 0.001$  and  $r_a$  is the average distance of electrons in the selected box. For an analysis of the effect of imposing this cutoff, see Chapter 5 in [36].

The value of the time step,  $\Delta t$ , is adjusted throughout the simulation in order to achieve a good compromise between numerical accuracy and simulation length. In particular during the initial stages when the electrons are photoemitted and are very close to each other and to the surface, a shorter time-step is needed to keep the forces finite and avoid excessive errors due to the force cutoff. As the electron pulse expands, progressively longer time-steps can be used. For this reason, while the electrons are being inserted into the simulation box,  $\Delta t = 3\sigma_t/50 = 1.26$  fs. After this phase concludes (at  $N_{step} = 100$ ),  $\Delta t$  is increased every 100 time steps to, respectively,  $\Delta t = 4.5$ , 14, 80fs until reaching the final value of  $\Delta t = 0.55$  ps, which is kept constant for the remainder of the simulation.

Typical simulations run for  $N_{step} = 620$ , which corresponds to a final time of t = 120 ps and take about 1.5hrs on 8 cores, for  $N_e^0 = 1 \cdot 10^7$  electrons and extraction field  $F_a = 1 \text{ MV/m}$ . The standard parallel MPI routines implemented in COSY INFINITY and its



Figure 2.2: Effect of varying the number of electrons in each macroparticle for  $N_e^0 = 10^6$ , extraction field  $F_a=0.32 \text{ MV/m}$  and  $N_{macr} = 1, 10, 100$ . The pulse center of mass position  $(\bar{x}, \bar{z})$ , width  $(\sigma_x, \sigma_z)$ , momentum standard deviation  $(\sigma_{px}, \sigma_{pz})$  and emittance  $(\epsilon_{n,x}, \epsilon_{n,z})$ are plotted as a function of time in both the transverse (x) and longitudinal (z) directions. Because of the radial symmetry, the x and y directions are equal so only the parameters in the x direction are plotted.

MLFMM extension, were used and the parallel simulations were run on the cluster of the High Performance Computer Center (HPCC) at Michigan State University.

At each step the pulse parameters (position and momentum averages and standard de-

viations) are saved to a text file and every 10 steps the positions and momenta of all of the electrons are saved to a separate file for post processing purposes, such as the calculation of the normalized rms emittance (Eq. 2.2).

#### 2.4 Treatment of the positive surface field

As briefly mentioned, the image charge generated on the surface by the emitted electrons plays an important role in determining the final properties of the electron bunch. In order to model this effect, the charge on the surface is approximated with a continuous distribution and its field is calculated by dividing the surface into circular strips with a width  $\Delta r \ll \sigma_r$ , where  $\sigma_r$  is the laser pulse width. Each strip is approximated as having a uniform charge density and, thanks to the circular symmetry of our problem, the field due to each one can be calculated using the well known equation for the field of a uniformly charged ring [62]. The total radial and longitudinal electric fields are then simply given by a sum of the fields generated by each ring. Note that the value of the positive charge on the surface depends on the number of electrons in the pulse and is therefore reduced by electron recombination. The equations describing the details of this positive field depend on the shape of the exciting laser pulse and will be presented in the next section.

## 2.4.1 Equations for the surface field: Gaussian, Uniform and Elliptical cases

Since the laser pulse used for the photoemission is radially symmetric in the photocathode plane, we take a circular area with radius  $R_0$  around the center of the laser spot and divide it into  $N_r = 1000$  concentric rings where each has width  $R_0/N_r$  and radii  $r_{i,int} = (i-1)R_0/N_r$ ,  $r_{i,ext} = iR_0/N_r$  with  $i \in [1, N_r]$ . The charge in each ring can now be calculated as

$$Q_i = Q \int_0^{2\pi} d\theta \int_{r_{i,int}}^{r_{i,ext}} dr \ r \cdot f(r), \qquad (2.17)$$

where  $Q = N_e e$  is the total charge in the system and f(r) is the normalized charge distribution on the surface.

Since  $R_0/N_r \ll \sigma_r$ , we now approximate each ring as being infinitesimally thin and located at  $r_{i,0} = (r_{i,int} + r_{i,ext})/2$  with charge  $Q_i$ . Given this, the radial and longitudinal electric fields are simply given by the textbook equations [62] for a ring of charge as:

$$E_r(r,z) = \frac{2Q_i}{\pi} \frac{1}{rR^2} \left[ \frac{E(k)}{1-k^2} \frac{r^2 + rr_0}{R} - \frac{R}{2} \left( \frac{E(k)}{1-k^2} - K(k) \right) \right],$$
(2.18)

$$E_z(r,z) = \frac{2Q_i}{\pi} \frac{1}{R^3} \frac{E(k)}{1-k^2} (z-z_0), \qquad (2.19)$$

where K(k) and E(k) are the complete elliptic integrals of first and second kind respectively:

$$K(k) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \theta}},$$
(2.20)

$$E(k) = \int_0^{\pi/2} d\theta \sqrt{1 - k^2 \sin^2 \theta},$$
 (2.21)

and

$$k^2 = \frac{4rr_0}{R^2},\tag{2.22}$$

$$R^{2} = (r + r_{0})^{2} + (z - z_{0})^{2}, \qquad (2.23)$$

where  $r_0$  is the radius of the ring and  $z_0$  is the coordinate of its center, with  $z_0 = 0$  in our

system.

The sum of the fields generated by each ring i with  $i \in [1, N_r]$  is then calculated on a mesh and saved to a file for use in the simulation. The mesh is typically a square 201 x 201 grid from 0 mm to 1.16 mm in both the longitudinal and transverse directions and the COSY-MLFMM code linearly interpolates the electric field between the mesh points.

Details on the laser pulse shape enter in the calculation through the function f(r) that specifies the charge distribution on the surface and is used in the calculation of the charge of each ring  $Q_i$ . For a Gaussian distribution

$$f(r) = \frac{1}{2\pi\sigma_r^2} \exp\left(-\frac{r^2}{2\sigma_r^2}\right),\tag{2.24}$$

and

$$Q_i = Q \int_0^{2\pi} d\theta \int_{r_{i,int}}^{r_{i,ext}} dr \ r \cdot f(r) = Q \left[ \exp\left(-\frac{r_{i,int}^2}{2\sigma_r^2}\right) - \exp\left(-\frac{r_{i,ext}^2}{2\sigma_r^2}\right) \right].$$
(2.25)

We choose  $R_0 = 4\sigma_r$  so that  $r_{i,int} = (i-1)4\sigma_r/N_r$ ,  $r_{i,ext} = i4\sigma_r/N_r$  and  $r_{i,0} = 4\sigma_r/N_r(i-1/2)$ .

In the case of a Uniform (top-hat) distribution

$$f(r) = \begin{cases} C = \frac{1}{\pi R_0^2} & r \le R_0 \\ 0 & r > R_0 \end{cases}$$
(2.26)

where  $R_0$  is the radius of the laser pulse on the surface and the constant is chosen so that  $\int f(r)rdrd\theta = 1$ . In this case the charge contained in each ring is given by

$$Q_{i} = Q \int_{0}^{2\pi} d\theta \int_{r_{i,int}}^{r_{i,ext}} dr \ r \cdot f(r) = Q \left[ \left( \frac{r_{i,ext}}{R_{0}} \right)^{2} - \left( \frac{r_{i,int}}{R_{0}} \right)^{2} \right].$$
 (2.27)
Since  $r_{i,int} = (i-1)R_0/N_r$ ,  $r_{i,ext} = iR_0/N_r$  and  $r_{i,0} = R_0/N_r(i-1/2)$ , we can rewrite this as

$$Q_i = Q \frac{2i - 1}{N_r^2}.$$
 (2.28)

We choose  $R_0 = 2\sigma_r$ , so that the standard deviation of the Gaussian and Uniform distributions in the transverse direction is the same.

In the elliptical case, the laser pulse has a distribution on the surface given by

$$f(r) = \frac{3}{2\pi R_0^2} \sqrt{1 - \left(\frac{r}{R_0}\right)^2},$$
(2.29)

where  $R_0$  is again the radius of the laser pulse on the surface and  $0 < r < R_0$ . Each ring on the surface contains a fraction of the total charge equal to

$$Q_i = Q \int_0^{2\pi} d\theta \int_{r_{i,int}}^{r_{i,ext}} dr \ r \cdot f(r) = Q \left[ \left( 1 - \frac{r_{i,int}^2}{R_0^2} \right)^{3/2} - \left( 1 - \frac{r_{i,ext}^2}{R_0^2} \right)^{3/2} \right].$$
(2.30)

Again we wish to compare distributions of equal width and therefore choose  $R_0 = \sqrt{5}\sigma_r$  so that the standard deviation of the transverse distribution is the same as in the Gaussian case.

### 2.4.2 Time evolution of the positive field

In the treatment presented so far we implicitly assumed that the positive field on the surface had no time dependence. In the initial stages of the simulation the shape of the electron pulse mirrors the profile of the exciting laser pulse, so it is natural to assume that this would be also true for the positive charge on the surface. Given  $R_0$ , the spatial width of the image charge distribution on the surface, we can safely assume that  $R_0(t = 0)$  corresponds to the width of the laser profile in the direction parallel to the surface. In general  $R_0$  does depend on time and its temporal evolution has a complex dependence on the instantaneous shape of the emitted pulse and on the cathode properties, as both surface characteristics and film thickness play a role in determining the image charge created by the electrons.

To simplify this complex dependence into something treatable, the experimental systems can be divided into roughly two categories. If the positive charges are pinned on the surface, as would be the case for example in a patterned photocathode [63], the expansion of  $R_0$  will be hindered or even blocked. We approximate these cases by taking  $R_0(t) = R_0(t = 0)$ , so that the image charge is pinned to a small constant area on the surface corresponding to its initial value.

On the other hand if the positive charges on the surface are able to expand and mirror the dynamics of the electron pulse, such as for a flat metal surface, the radius of the positive charge  $R_0(t)$  will increase as the electron pulse spreads. This can be treated in a simple way by taking the standard deviation of the surface charge distribution equal to the instantaneous transverse width (standard deviation) of the electron pulse. This means that each uniform ring of charge  $Q_i$  has a radius  $r_{i,0}$  that increases with time.

In the simulation code the positive field is calculated on a mesh, so we note that if, for example, we double the radius of each ring,  $r'_0 = 2r_0$ , and also double the coordinates of each mesh point r' = 2r, z' = 2z, then we get

$$R^{\prime 2} = (r^{\prime} + r_0^{\prime})^2 + z^{\prime 2} = 4\left[(r + r_0)^2 + z^2\right] = 4R^2, \qquad (2.31)$$

$$k'^{2} = \frac{4r'r'_{0}}{R'^{2}} = \frac{4(2r)(2r_{0})}{4R^{2}} = \frac{4rr_{0}}{R^{2}} = k^{2}.$$
(2.32)

This means that in our expression for the electric field, the terms depending on k are not

affected by this transformation, while the ones depending on R would be doubled. This translates to a transformation of the electric field where E' = E/4, as can be seen by taking, for example, the field in the z direction:

$$E'_{z}(r',z') = \frac{2Q_{i}}{\pi} \frac{z'}{R'^{3}} \frac{E(k)}{1-k^{2}} = \frac{1}{4} \frac{2Q_{i}}{\pi} \frac{z}{R^{3}} \frac{E(k)}{1-k^{2}} = \frac{1}{4} E_{z}(r,z), \qquad (2.33)$$

where we have performed the substitutions  $z' \to 2z$ ,  $R' \to 2R$ . A similar calculation can be done for the field in the radial direction. This result can be explained intuitively by noting that the units of the electric field are [charge]/[length]<sup>2</sup>. If the length is doubled, the electric field scales as one fourth of the original value.

In practice for the simulations presented here, this means that if the radius of the surface charge increases as  $r'_0 = \alpha r_0$ , it is sufficient to increase the coordinates corresponding to the mesh points as  $r' = \alpha r$ ,  $z' = \alpha z$  and scale the electric field at each point as  $E'_{r,z} = E_{r,z}/\alpha^2$ , where  $E_{r,z}$  is a value calculated and tabulated before each simulation run. This method has the effect of increasing the mesh spacing as the pulse expands, with the advantage that the values for the positive field at a point need to be calculated only once, saving computational time and resources.

### 2.5 Pulse time evolution

We now turn our attention to the results of these N-particle simulations, starting from an analysis of the time dependent evolution of a single pulse followed by a comparison of the properties of the emitted pulses for varying extraction conditions.

We begin by presenting, in Fig. 2.3, the temporal dependence of various key pulse

parameters for  $N_e^0 = 7 \cdot 10^6$  generated electrons with extraction fields of  $F_a$ =0.32 MV/m and  $F_a$ =10 MV/m. In panel (a) of the figure, the number of electrons  $N_e$  is plotted as a function of time on a log-log scale, showing the increase in  $N_e$  during the initial photoemission phase lasting up to 0.1 ps. During the time evolution of the pulse, the electrons can recombine with the photocathode surface, leading to a decrease in  $N_e$  at later times. This effect plays a significant role for low extraction fields since the pulse remains closer to the surface, and is absent in the high field case (dashed line in the figure). Figure 2.3(b) shows the pulse center of mass distance from the surface for the two extraction fields considered compared to a free particle moving in the corresponding electric field [ $z = 1/2(eF_a/m)t^2$ ]. The center of mass evolution for  $F_a$ =10 MV/m is free particle like, while at lower values of  $F_a$ , the positive surface field hinders the pulse propagation.

Next, we look at the pulse size and normalized emittance [panels (c) and (d)], two parameters that are relevant for our imaging and diffraction applications. Looking at the transverse components of these quantities [black lines in panels (c), (d)], we note that they remain close to the initial values for both data sets presented, with a weak dependence on extraction field, seen mostly in the increase of the pulse width  $\sigma_x$  for t > 50 ps and  $F_a=10$  MV/m due to the weaker effect of the positive surface charge, which for  $F_a=0.32$  MV/m keeps the electrons focused towards the central region of the pulse. On the other hand, the longitudinal components of both pulse size and emittance [red lines in panels (c), (d)] show a very rapid increase during the first 20 ps of the simulation, due to the strong Coulomb repulsion between the electrons extracted from the photocathode surface and even after this initial expansion stage, both longitudinal components keep increasing for the duration of the simulation.

To better understand these features we look at the time evolution of the pulse in the x - z plane, shown in Fig. 2.4 with a color map of the charge distribution in the rest



Figure 2.3: Time evolution of key pulse parameters, for  $N_e^0 = 7 \cdot 10^6$ , extraction fields of  $F_a=0.32 \,\text{MV/m}$  (continuous lines) and  $F_a=10 \,\text{MV/m}$  (dashed lines): (a) number of electrons  $N_e$  (note the logarithmic scale of both axes). (b) Pulse center of mass distance from the surface and corresponding free particle time evolution  $[z = 1/2(eF_a/m)t^2, \text{ dotted lines}]$ . (c) Transverse (black) and longitudinal (red) pulse size. (d) Transverse (black) and longitudinal (red) pulse size.

frame of the bunch overlaid with arrows representing the average electron velocity. For short timescales we observe that the spatial profile of the pulse retains the Gaussian distribution of the generating laser pulse [Fig. 2.4(a)] and the velocities show a turbulent flow related to the initial thermal distribution from which they were generated and independent of extraction field, since the repulsion due to the space charge has not had time to play a big role. At later times the pulse begins to move away from the surface, with a significant residual charge left behind for low extraction fields [Fig. 2.4(b)]. The final profile of the pulse as t=120 ps, depends strongly on the extraction field. Comparing panels 2.4(c) and 2.4(d), corresponding respectively to  $F_a=0.32$  MV/m and  $F_a=10$  MV/m, we see that in the latter picture the flow has become fully laminar and the pulse has evolved into the typical pancake shape, while for the lower extraction field the pulse retains some turbulent flow and does not fully detach from the surface.

Figure 2.4(e) presents the radial pulse profile at t=120 ps for three different extraction fields fitted to a combination of Gaussian  $[G = a \exp(r^2/2\sigma^2)]$  and Ellipsoidal  $[E = a\sqrt{1-(r/R)^2}]$  functions. The laminar flow observed in the charge distribution plots [panel (d)] can be seen to correspond to the formation of an Ellipsoidal profile, which is advantageous due to its linear internal force field that leads to a non increasing emittance [53, 64]. As a consequence even though the pulse will expand and change its dimensionality ratio, this expansion can be fully corrected with appropriate beam optics such as compression [65] and aberration corrections [40]. On the other hand at  $F_a=0.32$  and 1 MV/m, the flow is not fully laminar; this component can be described by a Gaussian with extended tails representative of the thermal-like population (accounting for, respectively 35% and 27% of the total number of electrons), which coexists with the elliptical component.

Overall the emergence of a 2D ellipsoidal profile from the complex interplay of image- and



Figure 2.4: (a)-(d) Color map of the charge distribution in the rest frame of the bunch projected onto the x-z plane, overlaid with arrows representing the average electron velocity. Panel (a) shows the initial stage of photoemission, which is independent of extraction field. Panel (b), (c) show the intermediate and final stages for weak ( $F_a=0.32 \text{ MV/m}$ ) extraction field at times t=60 ps and t=120 ps. Panel (d) corresponds to the final stage for the strong field case ( $F_a=10 \text{ MV/m}$ ). Note that the number of emitted electrons is the same in all cases,  $N_e^0 = 7 \cdot 10^6$ , while the final number of emitted electrons depends on the extraction field. (e) Transverse charge density profiles under different extraction fields ( $F_a=0.32, 1$  and 10 MV/m) fitted with a combination of Gaussian (G) and Ellipsoidal (E) functions [26].

space charge effects, is somewhat surprising since formation of an ellipsoidal beam driven by self fields is expected only at zero surface charge limit, i.e.  $\sigma_0/\epsilon_0 \ll F_a$ , where  $\epsilon_0$  is vacuum permittivity and  $\sigma_0 = 3N_e e/(2\pi r^2)$  is the surface charge density. Inserting the parameters used for the simulations in Fig. 2.4 into the equation gives  $\sigma_0=5.35 \times 10^{-5} \text{ C/m}^2$  and  $\sigma_0/\epsilon_0 =$ 6.04 MV/m, showing that the extraction fields used ( $F_a$ ) are comparable to this value. With the highest number of particles considered,  $N_e^0 = 2 \cdot 10^8$ ,  $\sigma_0/\epsilon_0 = 172.55 \text{ MV/m}$ , and this condition is definitely not satisfied. This is in contrast with the situation described elsewhere in the literature such as in the work by Luiten et al. [53,64] where the extraction field  $F_a =$ 100 MV/m and  $\sigma_0/\epsilon_0 = 5 \text{ MV/m}$ , in which case the bunch evolution is solely dependent on its self fields as image- and space-charge effects are negligible.

We conclude this section with a comparison of the simulated data to the values measured in the shadow imaging experiments [66] (Fig. 2.5). Panel (a) shows the raw experimental images, while panels (b)-(d) compare the longitudinal pulse profile in experiment (red circles) and simulation (black line) at various times. The shaded box indicates the region in the proximity of the surface, which cannot be accurately imaged with the shadow imaging technique. The experimental data is shifted horizontally to fix the position of the surface and scaled vertically to match the units used in the simulation. This fitting is done for the data set at t=50 ps (not shown) and fixed for the remainder of the plots. Given the few parameters used in the simulation, we see a remarkable agreement with the measured pulse profile over a time period of  $t \simeq 50$  ps. This provides a validation that the simulation method used correctly describes the experimental system.



Figure 2.5: Comparison to experimental data. Panel (a) shows the raw experimental images, while panels (b)-(d) show a comparison of the longitudinal pulse profile at various times in experiment (red circles) and simulation (black line), corresponding to an extraction field of  $F_a = 0.32 \text{ MV/m}$  and  $N_e^0 = 10^8$  [26].

## 2.6 Optimal pulse generation

In this section we investigate the optimal conditions for pulse generation in terms of laser fluence (or, equivalently, initial number of electrons,  $N_e^0$ ) and extraction field  $F_a$  for different experimental realizations. We start the discussion by presenting our results for photoemission using a Gaussian laser pulse from a flat surface (modeled with a radially expanding positive surface charge), followed by a comparison with the pinned case (stationary positive charge on the surface). To understand the effect of the spatial profile of the laser, we also discuss our results for the radially Uniform (top-hat) and Elliptical profiles.

### 2.6.1 Gaussian pulse

In order to use the generated electron bunch for single-shot imaging, a high enough number of electrons is necessary, so one of the first quantities of interest is the final number of electrons at time t=120 ps. This is shown in Fig. 2.6 as a function of the initial number of electrons,  $N_e^0$  for extraction fields  $F_a = 0.1$  MV/m to 40 MV/m. For a low number of generated electrons  $(N_e < 10^6)$ , all of the particles escape the surface, creating the linear relationship seen in the first part of the figure. As the initial number of electrons is increased, the space charge effect also increases due to both the electrons and the image charge on the surface. This creates the so-called virtual cathode (VC) limit in which the negative charge of the electrons emitted at earlier times, combined with the attractive surface field, hinders further emission of particles and effectively limits the final number of electrons extracted, a feature that can be seen in the flattening of the curves shown. Increasing the extraction field shifts the onset of this phenomenon enabling the emission of a higher number of particles from the photocathode.

The dependence of the onset of the virtual cathode effect on extraction field is investigated by calculating the critical number of electrons from a linear fit of the two regimes described. The resulting data is plotted in the inset of Fig. 2.6 as a function of extraction field  $F_a$ . If we approximate the electron pulse as a sheet of charge and define the onset of the virtual cathode regime to be when the electric field generated by the sheet of emitted electrons is equal to the extraction field  $F_a$  [67], we can express the critical current required as:

$$J_{crit} = \epsilon_0 F_a / \tau_p, \tag{2.34}$$

where  $\tau_p$  is the pulse duration. Having assumed a thin sheet of charge, we can write  $\sigma = J\tau_p$ ,

where  $\sigma = N_e^{crit}/(\pi r^2)$  is the electron charge density in the xy plane so that

$$\sigma = \epsilon_0 F_a. \tag{2.35}$$

The fit of our data to this equation is also shown in the inset of Fig. 2.6, with a numerical prefactor of  $\alpha = 1.65$  so that  $\sigma = \alpha \epsilon_0 F_a$  ( $\alpha = 1$  in the ideal case).



Figure 2.6: Number of electrons emitted at t=120 ps as a function of number of generated electrons for various extraction fields. The lines serve as a guide to the eye for the scaling  $N_e^{emit} \propto N_e^0$  and  $N_e^{emit} \propto (N_e^0)^{1/3}$ . The data shows evidence of virtual cathode formation. Inset: Critical number of electrons for virtual cathode formation as a function of extraction field  $F_a$ . The dashed line shows the critical number of electrons as a function of  $F_a$  obtained by using Eq. 2.35 [26].

The onset of the VC limit also acts on the longitudinal pulse width,  $\sigma_z$  (Fig. 2.7). For pulses in the sub-VC regime,  $\sigma_z$  increases linearly with the number of particles, while in the VC regime the width of the pulse does not show a strong dependence on the number of electrons emitted. Our simulations show that the trend of  $\sigma_z \propto (N_e^{emit})^{1/2}$  seen in the experimental data (right panel of Fig. 2.7), is a result of the linear growth of  $\sigma_z$  in the sub-VC regime combined with its reduced increase as the VC regime sets in.



Figure 2.7: Longitudinal pulse width,  $\sigma_z$ , as a function of number of electrons at time t=120 ps, for various extraction fields  $F_a$  from the simulation (left panel) and compared to experimental data (right panel). The lines serve as a guide to the eye for the cases  $\sigma_z \propto N_e^{emit}$  and  $\sigma_z \propto (N_e^{emit})^{1/2}$  [26].

### 2.6.2 Effect of image charge pinning

We now focus on the effect that pinning of the image charge on the surface has on the onset of the VC limit and on the final pulse parameters, as this will provide information on the optimal photocathode geometry one should employ. By looking at the charge distribution and transverse profiles of individual pulses (Fig. 2.8), we observe that in the pinned case the positive image charge field provides a focusing effect, increasing the fraction of electrons at the center of the pulse and consequently reducing the fraction of electrons in the lateral region. The particles in the central region are also pulled back towards the surface by the strong electric field, creating a channel of electrons that prevents the pulse from becoming fully pancake-like even at t=120 ps.



Figure 2.8: (a),(b) Color map of the charge distribution in the rest frame of the bunch projected onto the x-z plane, overlaid with arrows representing the average electron velocity. Panel (a) shows the distribution at t=120 ps for extraction field  $F_a = 10$  MV/m and number of emitted electrons  $N_e^0 = 7 \cdot 10^6$ . Panel (b) shows the charge distribution under the same conditions but with the image charge pinned to a small area on the photocathode surface. (c) Transverse charge density profiles under different extraction fields ( $F_a=0.32$ , 1 and 10 MV/m) showing the central focusing peak caused by the pinned image charge.

Image charge pinning has very little effect on the longitudinal pulse width  $\sigma_z$  or on the number of electrons emitted from the surface before the onset of the VC (Fig. 2.9). Upon reaching the VC limit, though, the number of electrons in the pinned case is reduced by  $\approx 5\%$  compared to the non-pinned case, while maintaining the same linear dependence on  $N_e^0$  seen in Fig. 2.6.



Figure 2.9: (a) Number of electrons emitted at t=120 ps as a function of number of generated electrons for various extraction fields in the presence of a pinned image charge. The red lines show the data corresponding to the expanding image charge. (b) Longitudinal pulse width,  $\sigma_z$ , as a function of number of electrons at time t=120 ps, for various extraction fields  $F_a$  with a pinned image charge. The red lines, again, show the data corresponding to the expanding image charge.

### 2.6.3 Effect of transverse laser profile

We now turn our attention to the effect of the laser pulse shape on the properties of the photoemitted electron pulse and start by observing the temporal evolution of an electron bunch generated from a radially uniform laser pulse (Fig. 2.10), where the laser intensity  $I(r) \propto const$ . Also shown for comparison is the time evolution of a similarly generated pulse in the absence of the surface image charge. Similarly to the pinned case, the positive field on the surface attracts the electrons and causes a focusing of the electron density towards the center of the pulse where the field is strongest [Fig. 2.10(e)]. This effect is seen to be more pronounced for low extraction fields  $F_a$ , as the pulse remains close to the surface throughout the simulation.

In the case of an elliptical laser pulse we have that the intensity  $I(r) \propto \sqrt{1 - (r/R)^2}$ ,



Figure 2.10: (a)-(d) Color map of the charge distribution in the rest frame of the bunch projected onto the x-z plane, overlaid with arrows representing the average electron velocity for the top-hat (uniform) pulse. Panels (a) and (b) show the initial and final stages of photoemission in the presence of an image charge on the surface. Panels (c), (d) correspond to the case without image charge. Note that the number of emitted electrons is the same in all cases,  $N_e^0 = 1 \cdot 10^7$ , with an extraction field  $F_a = 1 \text{ MV/m}$ . (e) Transverse charge density profiles under different extraction fields ( $F_a=0.32$ , 1 and 10 MV/m), showing the effect of the image charge.

where R corresponds to the spatial width of the laser. Figure 2.11 shows the phase space plots and radial distributions corresponding to this case both with and without the image charge. Again we observe a dramatic change in the overall pulse shape that is a consequence of the drastic disruption of the linear self fields otherwise present in the elliptical pulse [53]. Projecting the charge distribution onto the x-axis [Fig.2.11(e)], show that this effect results in the formation of a pronounced central peak. A fit of the data to Gaussian and elliptical distributions shows an increasing weight of the Gaussian pulse component at low extraction fields (67% at  $F_a = 0.32MV/m$  and 37% at  $F_a = 10MV/m$ ) for which the perturbation to the pulse profile is more pronounced as the electrons remain closer to the surface throughout the simulation.

# 2.7 Guidelines for generation of high brightness electron beams

Next we wish to compare the pulse properties obtained under these different conditions of pulse generation. As our goal is to be able to do time resolved imaging, both the transverse and longitudinal emittances are of importance since they determine, respectively, the spatial and temporal resolutions. We also compare the emittance, coherence length and energy spread obtained in each case.

Figure 2.12 shows the emittances corresponding to the Gaussian laser pulse both with expanding and pinned surface charges. Our data shows a strong increase of the transverse emittance  $\epsilon_x$  [panel (a)] upon reaching  $N_e^{crit}$ , due to the onset of the VC regime. From the inset, which shows the temporal evolution of  $\epsilon_x$  at  $F_a = 0.32$ , 1 MV/m, we see that a steady state value of  $\epsilon_x$  is reached after approximately 40 ps and is correlated with the region where



Figure 2.11: (a)-(d) Color map of the charge distribution in the rest frame of the bunch projected onto the x-z plane, overlaid with arrows representing the average electron velocity for the elliptically shaped pulse. Panels (a) and (b) show the initial and final stages of photoemission in the presence of an image charge on the surface. Panels (c), (d) correspond to the case without image charge. Note that the number of emitted electrons is the same in all cases,  $N_e^0 = 1 \cdot 10^7$ , with an extraction field  $F_a = 1 \text{ MV/m}$ . (e) Transverse charge density profiles under different extraction fields ( $F_a=0.32$ , 1 and 10 MV/m), showing the effect of the image charge.

the previously discussed 2D elliptical pulse structure dominates. In contrast,  $\epsilon_z$  [Fig. 2.12(b)] shows no change in behavior as the VC regime is reached and is also rather insensitive to the extraction field. This is an indicator that in our pancake-like regime, the transverse emittance is driven by the strong nonlinear fields while the longitudinal component has a universal dependence on  $N_e^{emit}$ . This is particularly evident in the inset, showing  $\epsilon_z(t)$  for three very different external field values and  $N_e^{emit} = 10^7$ . Pinning of the surface charge has the effect of increasing the transverse emittance significantly once the virtual cathode limit is reached; the longitudinal emittance is also similarly affected.

Changing the shape of the laser profile used to emit the electrons also has a significant impact on the normalized emittance (Fig. 2.13). For  $F_a = 1 \text{ MV/m}$  (black symbols and lines), the elliptical shape (circles) is favorable below the VC limit as it has a smaller transverse emittance [panel (a)] compared to the Gaussian and uniform (top-hat) profiles. Previous literature [53, 64], showed this to be the case for negligible image charge fields due to the internal linear self-forces that limit the increase of the emittance. It is non-trivial that this would still be the case even in the presence of the positive field on the surface, which disrupts the linearity of the electron-electron forces and drastically changes the resulting pulse profile, as we saw in Fig. 2.11. The results in Fig. 2.13 show that once the VC limit is reached, at about  $N_e^{emit} \simeq 1 \cdot 10^7$  for  $F_a = 1 \,\mathrm{MV/m}$ , both the elliptical and uniform profiles present a sharp scaling with the number of electrons, while the Gaussian profile retains a more favorable scaling, with a slope for the emittance increase that is 1/3 that of the elliptical case. The origin of this scaling can be understood by looking at the inset in Fig. 2.13, which presents the number of emitted electrons  $N_e^{emit}$  as a function of  $N_e^0$ , the initial number of electrons. In the elliptical and uniform case, the VC effect completely blocks the increase in  $N_e^{emit}$ , such that for  $N_e^0 > 10^7$ , the curves shown in the inset are flat. With a Gaussian



Figure 2.12: (a) Transverse normalized emittance  $\epsilon_x$  and (b) longitudinal normalized emittance  $\epsilon_z$  as a function of number of emitted electrons  $N_e^{emit}$  and extraction field  $F_a$  at 120 ps for a Gaussian pulse. Insets: time dependence of  $\epsilon_x$  and  $\epsilon_z$  for three selected cases at  $N_e^{emit} = 10^7$  [26].

laser profile the emission of electrons is, instead, only hindered allowing an extraction of a higher number of particles under the same conditions. An increase in the extraction field  $F_a$  has the effect of shifting the onset of the VC regime to higher  $N_e^{emit}$ , thus increasing the regime before the VC is reached in which the elliptical pulse is optimal. The longitudinal emittance  $\epsilon_z$  [Fig. 2.13(b)] scales linearly with the number of electrons for all laser profiles considered, with a weak dependence on the extraction field. The signature of the onset of the VC regime is also seen here in the sudden increase of  $\epsilon_z$  by about one order of magnitude for  $N_e^{emit} \simeq 1 \cdot 10^7$ .

The influence of the image charge on the emittance can be understood by comparing the time evolution of the 6D normalized emittance  $(\epsilon_x \cdot \epsilon_y \cdot \epsilon_z)$  as a function of laser pulse profile and presence of image charge, shown in Fig. 2.14 both below and above the VC limit. Below the virtual cathode limit [Fig. 2.14(a)], the image charge acts as a weak perturbation on the pulse dynamics with some effect only during the initial stages (t < 60 ps) of pulse formation. In contrast for extraction conditions above the virtual cathode limit [panel (b)], the strong positive field on the surface has a small effect on the emittance of the Gaussian pulse profile (black continuous and dashed lines) but is a significant perturbation in the case of both the elliptical (red) and uniform (green) cases.

From this we can conclude that the optimal extraction conditions depend on a delicate balance between the image charge, which disrupts the favorable internal self-fields of both the elliptical and uniform cases, the number of electrons emitted and the extraction field, which controls the onset of the virtual cathode limit. Below this limit the image charge has a weak effect with the pulse properties primarily controlled by the laser parameters (laser profile and fluence), while above the VC limit the image charge strongly perturbs the expansion of the pulse with a nonuniform dependence on the pulse profile.

A further check of these considerations is shown in Fig. 2.15 where the 6D emittance is plotted as a function of time for the Gaussian and elliptical cases using different models for the image charge: expanding radially, pinned, and placed behind the surface at a distance



Figure 2.13: (a) Transverse normalized rms emittance  $\epsilon_x$  and (b) longitudinal normalized rms emittance  $\epsilon_z$  dependence on number of emitted electrons  $N_e^{emit}$  and extraction field  $F_a$  for varying shapes of the exciting laser pulse at t = 120ps. Inset: number of emitted electrons  $N_e^{emit}$  at t=120 ps as a function of  $N_e^0$ , the initial number of electrons for  $F_a = 1$  MV/m and varying laser profile.

 $z = -z_{CM}$ , where  $z_{CM}$  is the distance of the center of mass of the electron pulse. Below the virtual cathode limit, the emittance values are robust with respect to the different choices



Figure 2.14: Time dependence of the 6D normalized emittance for  $F_a = 1 \text{ MV/m}$  both (a) below and (b) above the virtual cathode limit. The data shown corresponds to the Gaussian (G), Elliptical (E) and Uniform (U) cases, with the subscript 0 indicating the absence of the image charge (G0, E0, U0 respectively).

in treating the image charge. On the other hand in the nonlinear regime shown by the pulse above the VC limit, the choice of the model for the image charge can have the effect of varying the final value of emittance by about 2 orders of magnitude for the elliptical case, and by about one for the Gaussian profile. Conventionally UEM systems always operate below the VC regime where the image charge field does not have a critical effect, but this raises an important issue that needs to be addressed in pushing to higher brightness electron pulses.

To conclude our discussion and extract useful guidelines for electron beam generation, we compare the brightness (Fig. 2.16), coherence length and energy spread (Fig. 2.17) for pulses generated under the different conditions described in the previous sections. Since pinning of the image charge on the surface has a negligible effect below the VC and an unfavorable scaling after the VC, it has been omitted for clarity from the discussion that follows.

The first parameters we wish to look at are the 4D and 6D brightness defined as  $B_{4D} = N_e/(\epsilon_x \cdot \epsilon_y)$  and  $B_{6D} = N_e/(\epsilon_x \cdot \epsilon_y \cdot \epsilon_z)$ , reported in Fig. 2.16. If temporal resolution is not required, the appropriate figure of merit is the 4D brightness [panel (a)], where we observe three distinct regimes for a given extraction field  $F_a$ . At low pulse currents ( $N_e < 10^4$  for  $F_a = 1 \,\mathrm{MV/m}$ ), it is independent on the transverse pulse shape. For intermediate values of  $N_e$  ( $10^4 < N_e < 3 \cdot 10^7$  for  $F_a = 1 \,\mathrm{MV/m}$ ), an elliptical spatial profile offers the best solution. At high numbers of electrons ( $N_e > 3 \cdot 10^7$  for  $F_a = 1 \,\mathrm{MV/m}$ ), the Gaussian pulse offers a better scaling than the Elliptical or Uniform but is associated with a very low peak brightness. Increasing the extraction field solves this issue by shifting the boundaries between the regimes discussed to higher values of  $N_e$ . On the contrary, if temporal resolution is a concern, it is necessary to include the longitudinal pulse properties in the discussion and therefore the 6D brightness is the relevant figure. From our results in Fig. 2.16(b), we conclude that in this case an elliptical transverse profile offers the optimal choice for the whole parameter range considered.

Other key quantities for electron source design are the coherence length (Eq. 2.1) and



Figure 2.15: Time dependence of the 6D normalized emittance for  $F_a = 1 \text{ MV/m}$  both (a) below and (b) above the virtual cathode limit. The data shown corresponds to the Gaussian (G) and Elliptical (E) cases, for different ways of considering the image charge field: expanding, pinned to the surface or mirroring the electron pulse distance from the surface.

the energy spread (Eq. 2.3), These two quantities are plotted in Fig. 2.17 as a function of emitted electron number and photoemitting laser pulse shape. The Elliptical profile presents



Figure 2.16: (a) 4D brightness and (b) 6D brightness as a function of number of electrons emitted,  $N_e^{emit}$  for the Gaussian, Uniform and Elliptical cases. The data shown corresponds to  $F_a = 1 \,\mathrm{MV/m}$  (closed circles) and  $F_a = 10 \,\mathrm{MV/m}$  (open circles).

the highest coherence length compared to the other two data sets even after reaching the VC limit. Increasing the extraction field offers the advantage of pushing the onset of the VC limit to higher  $N_e$ , increasing the range over which the coherence length is constant. In terms

of the energy spread, the Elliptical and Uniform profiles are both equally favorable, having a lower  $\Delta E$  than the Gaussian case and, overall, this parameter is relatively insensitive to the extraction field.



Figure 2.17: Coherence length (a) and energy spread (b) as a function of number of electrons emitted,  $N_e^{emit}$  for the Gaussian, Uniform and Elliptical profiles. The data shown corresponds to  $F_a = 1 \,\mathrm{MV/m}$  (closed circles) and  $F_a = 10 \,\mathrm{MV/m}$  (open circles).

# Chapter 3

# Analytic Gaussian Model

The photoemission process previously described is only the first step in the operation of an Ultrafast Electron Microscope (UEM) system. We now use the knowledge acquired from the simulations of pulse formation as an input for calculations involving the whole microscope column, which was introduced in Chapter 1. To do so, we use the so-called Analytic Gaussian model introduced by Michalik and Sipe [37,38] and refined by Berger and Schroeder [39]. We begin the discussion with an overview of the derivation of the equations for this mean-field model and the proceed to show how we added the contributions due to the photoemission gun and the relativistic motion of the electrons to this formalism to make it applicable for our system. We then explain the procedure used for optimizing the lens and RF cavity strengths and analyze the results obtained, taking into account the limits inherent in this model.

## 3.1 Derivation of the Analytic Gaussian equations

This section elucidates the derivation of the mean field Analytic Gaussian differential equations, following the work in [37]. We start with the propagation of an N-electron pulse in free space, and then add in the effects of lenses, radio frequency (RF) cavities, photoemission gun and relativistic motion.

### 3.1.1 N-electron pulse in the absence of external forces

The equations of motion for a classical system of N electrons are given by

$$\frac{d\mathbf{r}_i(t)}{dt} = \frac{\mathbf{p}_i(t)}{m},\tag{3.1}$$

$$\frac{dt}{dt} = -\frac{1}{m}, \qquad (0.1)$$

$$\frac{d\mathbf{p}_i(t)}{dt} = -\sum_{j \neq i} \frac{\partial V[\mathbf{r}_i(t) - \mathbf{r}_j(t)]}{\partial \mathbf{r}_i(t)}, \qquad (3.2)$$

where  $\mathbf{r}_i$  are the positions of particles i = 1, ..., N,  $\mathbf{p}_i$  are the momenta, m is the electron mass and  $V(\mathbf{r})$  is the Coulomb potential

$$V(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}|},\tag{3.3}$$

with e the electron charge and  $\epsilon_0$  the vacuum permittivity. We now introduce a discrete distribution to describe the particles in the system, which we formally write as

$$f_D(\mathbf{r}, \mathbf{p}; t) = \sum_{i=1}^N \delta\left[\mathbf{r}_i(t) - \mathbf{r}\right] \delta\left[\mathbf{p}_i(t) - \mathbf{p}\right], \qquad (3.4)$$

where  $f_D$  is normalized so that

$$\int d\mathbf{r} d\mathbf{p} f_D(\mathbf{r}, \mathbf{p}; t) = N.$$
(3.5)

The Boltzmann equation for this distribution can then be written as

$$\frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial t} = -\frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{r}} \cdot \frac{\partial \mathbf{r}}{\partial \mathbf{t}} - \frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{p}} \cdot \frac{\partial \mathbf{p}}{\partial \mathbf{t}},\tag{3.6}$$

$$= -\frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{r}} \cdot \frac{\mathbf{p}}{m} - \frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{p}} \cdot \mathbf{F}, \qquad (3.7)$$

where Eqs. 3.1 and 3.2 have been used. We rewrite the force term

$$F = -\sum_{j \neq i} \frac{\partial V[\mathbf{r}_i(t) - \mathbf{r}_j(t)]}{\partial \mathbf{r}_i(t)},$$
(3.8)

$$= -\frac{\partial}{\partial \mathbf{r}} \int d\mathbf{r}' \rho(\mathbf{r}') V(\mathbf{r} - \mathbf{r}'), \qquad (3.9)$$

$$= -\frac{\partial}{\partial \mathbf{r}} \int d\mathbf{r}' d\mathbf{p}' f_D(\mathbf{r}', \mathbf{p}'; t) V(\mathbf{r} - \mathbf{r}'), \qquad (3.10)$$

where  $\rho(\mathbf{r}')$  is the local density equal to

$$\rho(\mathbf{r}') = \int d\mathbf{p}' f_D(\mathbf{r}', \mathbf{p}'; t), \qquad (3.11)$$

and then substitute Eq. 3.10 into Eq. 3.7 to obtain

$$\frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial t} = -\frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{r}} \cdot \frac{\mathbf{p}}{m} + \frac{\partial f_D(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{r}} \int d\mathbf{r}' d\mathbf{p}' f_D(\mathbf{r}', \mathbf{p}'; t) V(\mathbf{r} - \mathbf{r}'). \quad (3.12)$$

The discrete distribution  $f_D$  depends on the specific initial positions and momenta of

the particles, so next we take an ensemble average over a set of initial conditions, which we indicate as  $f(\mathbf{r}, \mathbf{p}; t) = \langle f_D(\mathbf{r}, \mathbf{p}; t) \rangle$ . Performing this average, Eq. 3.12 becomes

$$\frac{\partial f(\mathbf{r},\mathbf{p};t)}{\partial t} = -\frac{\partial f(\mathbf{r},\mathbf{p};t)}{\partial \mathbf{r}} \cdot \frac{\mathbf{p}}{m} + \left\langle \frac{\partial f_D(\mathbf{r},\mathbf{p};t)}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{r}} \int d\mathbf{r}' d\mathbf{p}' f_D(\mathbf{r}',\mathbf{p}';t) V(\mathbf{r}-\mathbf{r}') \right\rangle.$$
(3.13)

As is typical in this kind of problem, it is impossible to derive a closed form expression without solving for higher order moments such as  $\langle f_D(\mathbf{r}, \mathbf{p}; t) f_D(\mathbf{r}', \mathbf{p}'; t) \rangle$ . By using a mean field approach, we approximate  $\langle f_D(\mathbf{r}, \mathbf{p}; t) f_D(\mathbf{r}', \mathbf{p}'; t) \rangle \simeq \langle f_D(\mathbf{r}, \mathbf{p}; t) \rangle \langle f_D(\mathbf{r}', \mathbf{p}'; t) \rangle$ , so that Eq. 3.13 becomes

$$\frac{\partial f(\mathbf{r}, \mathbf{p}; t)}{\partial t} = -\frac{\partial f(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{r}} \cdot \frac{\mathbf{p}}{m} + \frac{\partial f(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{r}} \int d\mathbf{r}' d\mathbf{p}' f(\mathbf{r}', \mathbf{p}'; t) V(\mathbf{r} - \mathbf{r}').$$
(3.14)

Even with this approximation, it is not possible to solve Eq. 3.14 analytically, so we choose to parameterize the distribution  $f(\mathbf{r}, \mathbf{p}; t)$  with some time-dependent parameters for which we can derive ordinary differential equations. Using the cylindrical symmetry present in the UEM system and assuming for simplicity a Gaussian distribution for both the transverse and longitudinal components, we write

$$f(\mathbf{r}, \mathbf{p}; t) = C \exp\left[-\frac{x^2 + y^2}{2\sigma_T} - \frac{z^2}{2\sigma_z} - \frac{\left[p_x - (\gamma_T/\sigma_T)x\right]^2 + \left[p_y - (\gamma_T/\sigma_T)y\right]^2}{2\eta_T} - \frac{\left[p_z - (\gamma_z/\sigma_z)z\right]^2}{2\eta_z}\right]$$
(3.15)

where  $\sigma_{T,z}$ ,  $\eta_{T,z}$  and  $\gamma_{T,z}$  are time dependent parameters that describe, respectively, the spatial width, kinetic energy spread and chirp of the electron pulse (see Fig. 3.1). Note that the units for the parameters are  $\sigma_{T,z}$  units of length squared,  $\eta_{T,z}$  units of momentum squared and  $\gamma_{T,z}$  units of action (length x momentum). *C* is a time dependent normalization  $\operatorname{constant}$ 

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Figure 3.1: Schematic representation of the pulse parameters used in the Analytic Gaussian model in phase space.

We can rewrite Eq. 3.15 in a more general form as a multivariate normal distribution

$$f(\mathbf{u};t) = \frac{N}{\sqrt{(2\pi)^k |\chi|}} \exp\left(-\frac{1}{2}\mathbf{u}^T \chi^{-1}\mathbf{u}\right), \qquad (3.17)$$

where  $\mathbf{u} = (x, p_x, y, p_y, z, p_z)$ , k is the dimension of  $\mathbf{u}$  (k = 6 in our case),  $\chi$  is the covariance matrix and  $|\chi|$  is its determinant. The distribution is multiplied by N to obey the normalization constraint in Eq. 3.5. Comparing Eqs. 3.15 and 3.17, we see that

$$\chi^{-1} = \begin{pmatrix} a_T & 0 & 0 \\ 0 & a_T & 0 \\ 0 & 0 & a_z \end{pmatrix},$$
(3.18)

with

$$a_{i} = \begin{pmatrix} \frac{1}{\sigma_{i}} + \frac{\gamma_{i}^{2}}{\eta_{i}\sigma_{i}^{2}} & \frac{\gamma_{i}}{\eta_{i}\sigma_{i}} \\ \frac{\gamma_{i}}{\eta_{i}\sigma_{i}} & \frac{1}{\eta_{i}} \end{pmatrix}, \qquad (3.19)$$

where i = T or z. Calculating the covariance matrix  $\chi$  is trivially done by inverting the matrix in Eq. 3.18 giving

$$\chi = \begin{pmatrix} a_T^{-1} & 0 & 0 \\ 0 & a_T^{-1} & 0 \\ 0 & 0 & a_z^{-1} \end{pmatrix},$$
(3.20)

where  $a_i^{-1}$  represents the inverse of matrix  $a_i$ :

$$a_i^{-1} = \begin{pmatrix} \sigma_i & \gamma_i \\ & \\ \gamma_i & \eta_i + \frac{\gamma_i^2}{\sigma_i} \end{pmatrix},$$
(3.21)

where, again, i = T or z.

Using the definition of the covariance matrix [68], we know that

$$\chi_{i,j} = \langle u_i u_j \rangle = \frac{1}{N} \int d\mathbf{u} \ u_i \ u_j f(\mathbf{u}; t), \tag{3.22}$$

where we use  $\langle ... \rangle$  to represent an expectation value over the  $u_i$ ,  $u_j$  components of the vector  $\mathbf{u} = (x, p_x, y, p_y, z, p_z)$ . We now take a time derivative of Eq. 3.22:

$$\frac{\partial}{\partial t}\chi_{i,j} = \frac{1}{N} \int d\mathbf{u} \ u_i \ u_j \frac{\partial f(\mathbf{u};t)}{\partial t},\tag{3.23}$$

and substitute  $\partial f(\mathbf{u}; t) / \partial t$  with the mean-field equation 3.14 to obtain differential equations

for each matrix component  $\chi_{i,j}$ 

$$\frac{\partial}{\partial t}\chi_{i,j} = K_{ij}^{flow} + K_{ij}^{force},\tag{3.24}$$

where

$$K_{ij}^{flow} = -\frac{1}{N} \int d\mathbf{u} \ u_i \ u_j \frac{\mathbf{p}}{m} \cdot \frac{\partial f(\mathbf{u}; t)}{\partial \mathbf{r}}, \tag{3.25}$$

$$K_{ij}^{force} = \frac{1}{N} \int d\mathbf{u} \ u_i \ u_j \frac{\partial f(\mathbf{u}; t)}{\partial \mathbf{p}} \cdot \frac{\partial \Phi}{\partial \mathbf{r}}, \tag{3.26}$$

with the notation  $\mathbf{u} = (x, p_x, y, p_y, z, p_z)$ ,  $\mathbf{r} = (x, y, z)$ ,  $\mathbf{p} = (p_x, p_y, p_z)$  and

$$\Phi = \int d\mathbf{u}' f(\mathbf{u}'; t) V(\mathbf{r} - \mathbf{r}').$$
(3.27)

Note that due to the symmetry of the problem, the terms corresponding to the x and y coordinates are equal, meaning that  $\chi_{11} = \chi_{33}$ ,  $\chi_{22} = \chi_{44}$  and  $\chi_{12} = \chi_{21} = \chi_{34} = \chi_{43}$ . Similar relations hold for the  $K_{ij}$  terms. For this reason in the following discussion we will only consider components in the x direction.

The  $K^{flow}$  terms describe the geometric motion of the electrons and are easily evaluated by substituting the explicit form of  $f(\mathbf{u}; t)$  (Eq. 3.15) and solving the resulting Gaussian integrals. It is easy to see that the  $K_{22}^{flow}$ ,  $K_{44}^{flow}$ ,  $K_{66}^{flow}$  elements vanish and that the remaining terms are

$$K_{11}^{flow} = \frac{2}{m} \gamma_T, \tag{3.28}$$

$$K_{12}^{flow} = \frac{1}{m} \left( \eta_T + \frac{\gamma_T^2}{\sigma_T} \right), \qquad (3.29)$$

$$K_{55}^{flow} = \frac{2}{m}\gamma_z,\tag{3.30}$$

$$K_{56}^{flow} = \frac{1}{m} \left( \eta_z + \frac{\gamma_z^2}{\sigma_z} \right). \tag{3.31}$$

The  $K^{force}$  terms (Eq. 3.26), which incorporate the internal Coulomb repulsion felt by the electrons, are harder to solve due to the interaction potential  $\Phi$  but, nevertheless, substituting Eq. 3.15 and manipulating the resulting integrals allows them to be expressed in terms of the pulse parameters. We will skip the details of this calculation as it is somewhat cumbersome and tedious and limit ourselves to reporting the relevant results (for details see [37]):

$$K_{11}^{force} = K_{55}^{force} = 0, (3.32)$$

$$K_{22}^{force} = \frac{2\gamma_T}{\sigma_T} K_{12}^{force}, \qquad (3.33)$$

$$K_{66}^{force} = \frac{2\gamma_z}{\sigma_z} K_{56}^{force}, \qquad (3.34)$$

$$K_{12}^{force} = \frac{1}{4\pi\epsilon_0} \frac{Ne^2}{6\sqrt{\sigma_T\pi}} L_T(\xi), \qquad (3.35)$$

$$K_{56}^{force} = \frac{1}{4\pi\epsilon_0} \frac{Ne^2}{6\sqrt{\sigma_z \pi}} L_z(\xi), \qquad (3.36)$$

where  $\epsilon_0$  is the vacuum permittivity, N is the number of electrons in the pulse, e and m are

the electron charge and rest mass, respectively, and

$$L_T(\xi) = \frac{3}{2} \left[ L(\xi) + \frac{\xi^2 L(\xi) - \xi}{1 - \xi^2} \right], \qquad (3.37)$$

$$L_z(\xi) = \frac{3\xi^2}{\xi^2 - 1} \left[\xi L(\xi) - 1\right], \qquad (3.38)$$

with  $\xi = \sqrt{\sigma_z/\sigma_T} > 0$  and

$$L(\xi) = \frac{1}{2} \int_0^{\pi} \frac{d\theta}{1+\xi\sin\theta} = \begin{cases} \frac{\arcsin\sqrt{1-\xi^2}}{\sqrt{1-\xi^2}} & \text{for } 0 \le \xi \le 1\\ \frac{\ln(\xi+\sqrt{\xi^2-1})}{\sqrt{\xi^2-1}} & \text{for } \xi > 1. \end{cases}$$
(3.39)

Note that for  $\xi = 1$ ,  $L(1) = L_T(1) = L_z(1) = 1$ . The functions  $L(\xi)$ ,  $L_T(\xi)$  and  $L_z(\xi)$  (Fig. 3.2) describe the effect of the Coulomb interactions on the pulse's time evolution and are the only coupling in our model between the transverse and longitudinal degrees of freedom.



Figure 3.2: Functions  $L(\xi)$  (Eq. 3.39),  $L_T(\xi)$  (Eq. 3.37) and  $L_z(\xi)$  (Eq. 3.38) as a function of  $\xi = \sqrt{\sigma_z/\sigma_T}$ .

Once the  $K_{ij}^{flow}$  and  $K_{ij}^{force}$  terms are known, we can use Eqs. 3.20 and 3.21 to derive differential equations for the parameters describing the pulse,  $\sigma_{T,z}$ ,  $\eta_{T,z}$  and  $\gamma_{T,z}$  as

$$\frac{d\sigma_{T(z)}}{dt} = \frac{\partial}{\partial t}\chi_{11(55)} = K_{11(55)}^{flow},\tag{3.40}$$

$$\frac{d\gamma_{T(z)}}{dt} = \frac{\partial}{\partial t}\chi_{12(56)} = K_{12(56)}^{flow} + K_{12(56)}^{force}, \tag{3.41}$$

$$\frac{d\eta_{T(z)}}{dt} = \frac{\partial}{\partial t}\chi_{22(66)} - \frac{2}{\sigma_{T(z)}}\frac{\partial}{\partial t}\chi_{12(56)} + \frac{\gamma_{T(z)}^2}{\sigma_{T(z)}^2}\frac{\partial}{\partial t}\chi_{11(55)} = -\frac{2}{\sigma_{T(z)}}K_{12(56)}^{flow} + \frac{\gamma_{T(z)}^2}{\sigma_{T(z)}^2}K_{11(55)}^{flow}.$$
(3.42)

Substituting the previously calculated terms gives the final result:

$$\frac{d\sigma_i}{dt} = \frac{2}{m}\gamma_i,\tag{3.43}$$

$$\frac{d\gamma_i}{dt} = \frac{1}{m} \left( \eta_i + \frac{\gamma_i^2}{\sigma_i} \right) + \frac{1}{4\pi\epsilon_0} \frac{Ne^2}{6\sqrt{\sigma_i\pi}} L_i(\xi), \qquad (3.44)$$

$$\frac{d\eta_i}{dt} = -\frac{2\gamma_i\eta_i}{m\sigma_i},\tag{3.45}$$

where i = T or z. Note that the quantity  $\sqrt{\sigma_i \eta_i}$ , corresponding to the pulse emittance, is conserved in this formulation.

To check our calculation we consider the limit of zero Coulomb force, in which Eqs. 3.43-3.45 reduce to

$$\frac{d\sigma_i}{dt} = \frac{2}{m}\gamma_i,\tag{3.46}$$

$$\frac{d\gamma_i}{dt} = \frac{1}{m} \left( \eta_i + \frac{\gamma_i^2}{\sigma_i} \right), \tag{3.47}$$

$$\frac{d\eta_i}{dt} = -\frac{2\gamma_i\eta_i}{m\sigma_i}.$$
(3.48)

This system of equations can be easily solved by noting that  $d^2\gamma/dt^2 = 0$  and by integrating,
with the result

$$\sigma_i(t) = \frac{\eta_i(0)}{m} t^2 + \sigma_i(0), \qquad (3.49)$$

$$\gamma_i(t) = \frac{\eta_i(0)}{m}t,\tag{3.50}$$

$$\eta_i(t) = \frac{\sigma_i(0)}{t^2/m^2 + \sigma_i(0)/\eta_i(0)}.$$
(3.51)

These equations, together with Eq. 3.15, are an exact solution of Eq. 3.14, which in the absence of the Coulomb force reads

$$\frac{\partial f(\mathbf{r}, \mathbf{p}; t)}{\partial t} = -\frac{\partial f(\mathbf{r}, \mathbf{p}; t)}{\partial \mathbf{r}} \cdot \frac{\mathbf{p}}{m}.$$
(3.52)

In the general case which includes the Coulomb force, no analytic solution of Eqs. 3.43-3.45 exists and one must numerically integrate the equations.

#### 3.1.2 Lenses and RF cavities

So far we have described the time evolution of an electron pulse with no applied forces, but for the Analytic Gaussian model to be useful in describing the UEM column, we need to incorporate the effect of the optical elements (lenses and RF cavities) and we do so following the work by Berger and Schroeder [39].

Rewriting the differential equation for the covariance matrix (Eq. 3.24) with an additional external position dependent force term gives

$$\frac{\partial}{\partial t}\chi_{i,j} = K_{ij}^{flow} + K_{ij}^{force} + K_{ij}^{ext}, \qquad (3.53)$$

where  $K_{ij}^{flow}$  and  $K_{ij}^{force}$  are defined in Eqs. 3.25 and 3.26 and

$$K_{ij}^{ext} = \frac{1}{N} \int d\mathbf{u} \ u_i \ u_j \overrightarrow{F}_{ext}(\mathbf{r}) \cdot \frac{\partial f(\mathbf{u};t)}{\partial \mathbf{p}}, \tag{3.54}$$

where  $\mathbf{u} = (x, p_x, y, p_y, z, p_z)$ ,  $\mathbf{r} = (x, y, z)$ ,  $\mathbf{p} = (p_x, p_y, p_z)$  and  $\overrightarrow{F}_{ext}(\mathbf{r})$  is the external force. In this case Eqs. 3.43-3.45 become

$$\frac{d\sigma_{T(z)}}{dt} = \frac{2}{m}\gamma_{T(z)} + K_{11(55)}^{ext},$$
(3.55)

$$\frac{d\gamma_{T(z)}}{dt} = \frac{1}{m} \left( \eta_{T(z)} + \frac{\gamma_{T(z)}^2}{\sigma_{T(z)}} \right) + \frac{1}{4\pi\epsilon_0} \frac{Ne^2}{6\sqrt{\sigma_{T(z)}\pi}} L_{T(z)}(\xi) + K_{12(56)}^{ext},$$
(3.56)

$$\frac{d\eta_{T(z)}}{dt} = -\frac{2\gamma_{T(z)}\eta_{T(z)}}{m\sigma_{T(z)}} + \frac{\gamma_{T(z)}^2}{\sigma_{T(z)}^2}K_{11(55)}^{ext},$$
(3.57)

where we have made use of the fact that

$$K_{12(56)}^{ext} = K_{21(56)}^{ext} = \frac{\sigma_{T(z)}}{2\gamma_{T(z)}} K_{22(66)}^{ext}.$$
(3.58)

Using these equations, any optical element can be added into our system by specifying its force on the electron pulse,  $\overrightarrow{F}_{ext}(\mathbf{r})$ , and by calculating  $K_{11(55)}^{ext}$  and  $K_{12(56)}^{ext}$ .

In the transverse direction the electron pulse can be focused by using magnetic lenses. Taking a perfect parabolic lens, the external force is linear with distance

$$\overrightarrow{F}_{lens}(\mathbf{r}) = -M_T x \hat{x} - M_T y \hat{y}, \qquad (3.59)$$

where  $M_T$  characterizes the strength of the lens and is positive for pulse focusing. Performing the integrals it is easy to see that  $K_{11(55)}^{ext} = 0$ ,  $K_{56}^{ext} = 0$  and  $K_{12}^{ext} = M_T \sigma_T$ , so that the equations describing the system read

$$\frac{d\sigma_i}{dt} = \frac{2}{m}\gamma_i,\tag{3.60}$$

$$\frac{d\gamma_i}{dt} = \frac{1}{m} \left( \eta_i + \frac{\gamma_i^2}{\sigma_i} \right) + \frac{1}{4\pi\epsilon_0} \frac{Ne^2}{6\sqrt{\sigma_i\pi}} L_i(\xi) + M_i \sigma_i, \qquad (3.61)$$

$$\frac{d\eta_i}{dt} = -\frac{2\gamma_i\eta_i}{m\sigma_i},\tag{3.62}$$

with i = T or z and  $M_z = 0$ . To specify the physical region in which the lenses act, we take

$$M_i \to M_i \exp\left[-\left(\frac{z'-z'_{lens}}{L_{lens}/2}\right)^{2n}\right],$$
(3.63)

where z' is the position of the pulse center of mass in the lab frame,  $z'_{lens}$  is the position of the center of the lens,  $L_{lens}$  is the length of the lens and n is a super-Gaussian order parameter that sets the sharpness of the lens edge, where n = 1 corresponds to a Gaussian profile and  $n \to \infty$  is a top-hat.

To incorporate RF cavities into our treatment, we follow a similar procedure considering, for simplicity, a cylindrical (pillbox) cavity operating in the  $TM_{010}$  mode. In this case the electric and magnetic fields inside the cavity may be written in cylindrical coordinates and to first order in r as [69]

$$E_z(r, z, z') = E_0(z') \sin\left[\frac{\Omega(z'-z)}{v_0} + \phi\right],$$
(3.64)

$$E_r(r, z, z') = -\frac{r}{2} \frac{\partial E_0(z')}{\partial z} \sin\left(\frac{\Omega z'}{v_0} + \phi\right), \qquad (3.65)$$

$$B_{\phi}(r, z, z') = -\frac{r}{2} E_0(z') \frac{\Omega}{c^2} \cos\left(\frac{\Omega z'}{v_0} + \phi\right), \qquad (3.66)$$

where  $\Omega$  and  $\phi$  are the RF field frequency and phase, so that the cavity will act as a pulse

compressor if  $\phi \simeq 0$ , while for  $\phi \simeq \pm \pi/2$  it will accelerate the pulse. z' and  $v_0$  are the position and velocity of the pulse center of mass in the cavity, which extends between z' = -d/2 and z' = d/2, and r and z correspond to the position of an electron in the pulse with respect to the center of mass.  $E_0(z')$  is the field amplitude which we write in a form similar to that of the lens strength as

$$E_0(z') = E_0 \exp\left[-\left(\frac{z' - z'_{rf}}{d/2}\right)^{2n}\right],$$
(3.67)

where  $z'_{rf}$  is the position of the center of the cavity and n is the super-Gaussian order parameter that sets the sharpness of the edge of the RF cavity field.

In the longitudinal direction, if the spatial dimension of the pulse is small compared to the cavity size,  $\Omega z \ll v_0$ , we can expand Eqs. 3.64 as

$$E_z(r, z, z') = E_0(z') \left[ \sin\left(\frac{\Omega z'}{v_0} + \phi\right) - \frac{\Omega z}{v_0} \cos\left(\frac{\Omega z'}{v_0} + \phi\right) \right], \qquad (3.68)$$

which shows that the RF cavity both accelerates the center of mass of the pulse (first term on the RHS) and compresses (or expands) it (second term on the RHS). Since the accelerating component is constant with respect to the pulse coordinates (r,z), it will not contribute to the force but it must be included in the calculation of the center of mass velocity. The resulting force on the pulse is therefore

$$F_z = -\frac{eE_0(z')\Omega}{v_0}\cos\left(\frac{\Omega z'}{v_0} + \phi\right)z\hat{z}.$$
(3.69)

In the transverse direction we substitute Eq. 3.67 into Eq. 3.65 and take the derivative,

with the result that

$$E_r(r, z, z') = E_0(z') r \frac{2n}{d} \left(\frac{z' - z'_{rf}}{d/2}\right)^{2n-1} \sin\left(\frac{\Omega z'}{v_0} + \phi\right).$$
(3.70)

The force in the radial direction can then be written as

$$F_r = eE_r(r, z, z') - ev_0 B_\phi(r, z, z')$$
(3.71)

$$= eE_0(z') \left[ \frac{2n}{d} \left( \frac{z' - z'_{rf}}{d/2} \right)^{2n-1} \sin\left( \frac{\Omega z'}{v_0} + \phi \right) + \frac{\Omega v_0}{2c^2} \cos\left( \frac{\Omega z'}{v_0} + \phi \right) \right] r\hat{r}.$$
(3.72)

From Eqs. 3.69 and 3.72, we can calculate the terms entering our equations as  $K_{11(55)}^{ext} = 0$ , and  $K_{12(56)}^{ext} = M_{T(z)}^{rf} \sigma_{T(z)}$ , with

$$M_T^{rf} = eE_0(z') \left[ \frac{2n}{d} \left( \frac{z' - z'_{rf}}{d/2} \right)^{2n-1} \sin\left( \frac{\Omega z'}{v_0} + \phi \right) + \frac{\Omega v_0}{2c^2} \cos\left( \frac{\Omega z'}{v_0} + \phi \right) \right],$$
(3.73)

$$M_z^{rf} = -\frac{eE_0(z')\Omega}{v_0}\cos\left(\frac{\Omega z'}{v_0} + \phi\right).$$
(3.74)

#### 3.1.3 Photoemission gun

The last element we need to incorporate into our UEM column is the photoemission gun. In the initial part of the microscope, inside the gun, the electrons are accelerated under a constant electric field. Therefore particles in the tail of the pulse spend more time in the gun region and are accelerated to a higher velocity. Overall this has the effect of decreasing the chirp of the pulse as it exits the gun, and we need to incorporate this effect into our model.

We represent the field in the gun region with a step function,  $E_{gun} = \Theta(z - d)$  where d is the spacing between cathode and anode and  $\Theta$  is the Heaviside theta function. In the pulse center of mass frame of reference, in which our Analytic Gaussian equations are formulated, we have two cases: if the pulse center of mass is still inside the region with the electric field, z' < d, the portion of the pulse extending outside the anode (z > d - z') will feel a force  $F = -eE_{gun}$ . On the other hand if z' > d, the portion of the pulse before the anode, z < d - z' will be subject to a force  $F = eE_{gun}$ . This is summarized in Fig. 3.3 and Eq. 3.75.



Figure 3.3: Effect of stepwise electric field of photoemission gun: (a) z' < d, (b) z' > d

$$\begin{cases}
F_{z} = -eE_{gun}\hat{z} & \text{for } z' < d, \quad z > d - z' \\
F_{z} = eE_{gun}\hat{z} & \text{for } z' > d, \quad z < z' - d.
\end{cases}$$
(3.75)

Following the procedure used to incorporate the lenses and RF cavity, we write Eq. 3.54 as

$$K_{ij}^{gun} = \frac{1}{N} \int d\mathbf{u} \ u_i \ u_j F_z \frac{\partial f(\mathbf{u}; t)}{\partial p_z}.$$
(3.76)

Inserting the expression for  $f(\mathbf{u};t)$  (Eq. 3.15) and performing the derivative, gives

$$K_{ij}^{gun} = \frac{1}{N} \int d\mathbf{u} \ u_i \ u_j F_z \frac{1}{\eta_z} \left( p_z - \frac{\gamma_z}{\sigma_z} z \right) f(\mathbf{u}; t), \tag{3.77}$$

with  $\mathbf{u} = (x, p_x, y, p_y, z, p_z)$ . In the previous section we showed how any external force could be added by simply calculating the elements  $K_{11}^{ext}$ ,  $K_{12}^{ext}$ ,  $K_{55}^{ext}$  and  $K_{56}^{ext}$ . In this case it is clear that the terms  $K_{11}^{gun}$ ,  $K_{55}^{gun}$  and  $K_{12}^{gun}$  vanish, so the only term of interest is

$$K_{56}^{gun} = \frac{1}{N} \int d\mathbf{u} \ z \ p_z F_z \frac{1}{\eta_z} \left( p_z - \frac{\gamma_z}{\sigma_z} z \right) f(\mathbf{u}; t)$$
(3.78)

$$= \frac{1}{2\pi\sqrt{\sigma_z\eta_z^3}} \int dz dp_z \ z \ p_z F_z \left(p_z - \frac{\gamma_z}{\sigma_z}z\right) \exp\left[-\frac{z^2}{2\sigma_z} - \frac{\left[p_z - (\gamma_z/\sigma_z)z\right]^2}{2\eta_z}\right]$$
(3.79)

$$= \frac{1}{\sqrt{2\pi\sigma_z}} \int dz \ F_z \ z \exp\left(-\frac{z^2}{2\sigma_z}\right),\tag{3.80}$$

where the second line was obtained after integration over  $x, y, p_x, p_y$  and in the third line we integrated over  $p_z$  as well. Now we have two possibilities, if z' < d, then the force is nonzero only for z > d - z' and

$$K_{56}^{gun} = -eE_{gun} \frac{1}{\sqrt{2\pi\sigma_z}} \int_{d-z'}^{\infty} dz \ z \exp\left(-\frac{z^2}{2\sigma_z}\right)$$
(3.81)

$$= -eE_{gun}\sqrt{\frac{\sigma_z}{2\pi}}\exp\left(-\frac{(d-z')^2}{2\sigma_z}\right).$$
(3.82)

A calculation for z' > d and z < z' - d gives the same final result. We conclude that exiting the gun region has the effect of a reduction in the chirp  $\gamma_z$  of the pulse proportional to  $\sqrt{\sigma_z}$ multiplied by a spatial profile that decays as  $\exp[-(d-z')^2/(2\sigma_z)]$ .

#### **3.1.4** Relativistic transformations

The equations we have written so far describe the electron pulse in its center of mass frame of reference, while our observations are performed in the laboratory frame of reference. If the center of mass of the pulse is moving at non-relativistic speeds ( $v_0/c \ll 1$ , where  $v_0$  is the magnitude of the COM velocity and c is the speed of light), a simple classical transformation can be used:

$$f_{lab}(\mathbf{r}, \mathbf{p}; t) = f(\mathbf{r} - \mathbf{r}_0 - \mathbf{v}_0 t, \mathbf{p} - m\mathbf{v}_0; t), \qquad (3.83)$$

where  $\mathbf{r}_0$  and  $\mathbf{v}_0$  are, respectively, the initial center of mass position and velocity.

The addition of an external constant electric field  $\mathbf{E}$  can also be handled in a simple way, since the transformation to the lab frame of the distribution  $f(\mathbf{r}, \mathbf{p}; t)$  simply becomes

$$f_{lab}(\mathbf{r}, \mathbf{p}; t) = f(\mathbf{r} - \mathbf{r}_0 - \mathbf{v}_0 t, \mathbf{p} - m\mathbf{v}_0 - e\mathbf{E}t; t).$$
(3.84)

In the context of typical UEM systems, where the pulse is initially accelerated with extraction fields ranging from 0.1 MV/m to 100 MV/m, resulting in velocities of the center of mass in the z-direction (taken parallel to the column axis) that are some fraction of the speed of light, these transformations are not applicable as it is necessary to take relativistic effects into account. In the center of mass frame the electrons are not moving relativistically with respect to each other, so the only modification to the Analytic Gaussian model comes from the transformations that connect the COM frame to the lab frame of reference.

In general, the transformations from a coordinate frame at rest (F) to a frame moving at a velocity v (F') can be easily written if one first defines the rapidity  $\beta$  [70,71] as a function of the velocity v:

$$\frac{v}{c} = \tanh\beta,\tag{3.85}$$

where we assume v to be parallel to the z-axis. In this case the Lorentz transformations are

simply written as

$$z = z' \cosh\beta + ct' \sinh\beta, \tag{3.86}$$

$$ct = ct' \cosh\beta + z' \sinh\beta, \qquad (3.87)$$

where z, t are coordinates in the rest frame (F), while the primed quantities denote variables in the moving frame (F'). Note that in this notation the Lorentz factor  $\gamma_L = \cosh \beta$ . For a generic particle moving at a speed  $u = c \tanh \alpha$  with respect to the rest frame F, both energy E and momentum p can be expressed as

$$E = mc^2 \cosh \alpha, \tag{3.88}$$

$$p = mc \sinh \alpha, \tag{3.89}$$

and the transformation of these quantities to the frame F' moving at a speed v is conveniently handled due to the additivity of the rapidity, resulting in

$$v' = c \tanh(\alpha + \beta), \tag{3.90}$$

$$E' = mc^2 \cosh(\alpha + \beta), \qquad (3.91)$$

$$p' = mc\sinh(\alpha + \beta). \tag{3.92}$$

Now, assuming the electron pulse in our model has been accelerated to a velocity  $\mathbf{v}_0 = (0, 0, v_0)$ , where  $v_0/c > 0$ , and that no external fields are acting on it, the transformation from the distribution in the COM frame to the lab frame of reference is conveniently given

by [70]

$$f_{lab}(x, y, z, p_x, p_y, p_z; t) = f(x', y', z', p'_x, p'_y, p'_z; t'),$$
(3.93)

with

$$\frac{v_0}{c} = \tanh \beta,$$
  

$$x' = x,$$
  

$$y' = y,$$
  

$$z' = z \cosh \beta - ct \sinh \beta,$$
  

$$p'_x = p_x,$$
  

$$p'_y = p_y,$$
  

$$p'_z = mc \sinh(\alpha - \beta),$$
  

$$ct' = ct \cosh \beta - z \sinh \beta,$$

where  $\alpha$  is defined by  $p_z = mc \sinh \alpha$ .

On the other hand for a constant electric field,  $\mathbf{E}_0 = (0, 0, E_z)$ , the COM frame accelerates with respect to the lab frame with an acceleration in the z-direction equal to  $a = eE_z/m$ and the transformation between the two coordinate systems now reads

$$z + z_0 = (z' + z_0) \cosh\left[\beta(t')\right], \qquad (3.94)$$

$$ct = (z' + z_0) \sinh[\beta(t')],$$
 (3.95)

where, again, z, t are coordinates in the lab frame while the primed quantities denote vari-

ables in the pulse COM frame and we have defined

$$z_0 = \frac{c^2}{a},$$
 (3.96)

$$\beta(t') = \frac{at'}{c}.\tag{3.97}$$

In the limit of zero acceleration, these equations reduce to the transformation previously written.

Using these equations, it is possible to compute the time evolution of the pulse in its COM frame of reference using the Analytic Gaussian equations and then transform the resulting distribution into the lab frame of reference. More importantly, as we are interested in the pulse parameters  $\sigma_i$ ,  $\gamma_i$ , and  $\eta_i$ , with i = T or z, we know that they are simply transformed as

$$\sigma_T^{lab} = \sigma_T, \tag{3.98}$$

$$\sigma_z^{lab} = \sigma_z / \cosh\beta = \sigma_z / \gamma_L^2, \tag{3.99}$$

$$\gamma_T^{lab} = \gamma_T, \tag{3.100}$$

$$\gamma_z^{lab} = \gamma_z, \tag{3.101}$$

$$\eta_T^{lab} = \eta_T, \tag{3.102}$$

$$\eta_z^{lab} = \eta_z \cosh\beta = \eta_z \gamma_L^2, \tag{3.103}$$

where  $\beta$  is the rapidity of the COM with respect to the lab frame,  $\gamma_L$  is the Lorentz factor and the equations we wrote simply represent the well known length contraction and time dilation phenomena in relativistic mechanics (note that in our notation  $\sigma_i$  has units of length squared and, similarly,  $\eta_i$  is in units of momentum squared). In addition to this, it is also necessary to consider the relativistic transformations of the applied electric and magnetic fields. Taking the fields in the lab frame to be known, **E** and **B**, their transformation to the pulse frame is given by

$$\mathbf{E}_{\perp}' = \gamma_L (\mathbf{E}_{\perp} + \mathbf{v}_0 \times \mathbf{B}), \qquad (3.104)$$

$$\mathbf{E}_{z}^{\prime} = \mathbf{E}_{z},\tag{3.105}$$

$$\mathbf{B}_{\perp}' = \gamma_L (\mathbf{B}_{\perp} - \frac{1}{c^2} \mathbf{v}_0 \times \mathbf{E}), \qquad (3.106)$$

$$\mathbf{B}_{z}^{\prime} = \mathbf{B}_{z},\tag{3.107}$$

where  $\gamma_L$  is the Lorentz factor,  $\mathbf{v}_0 = (0, 0, v_0)$  is the velocity of the pulse center of mass, **E** and **B** are the electric and magnetic fields in the lab frame, and the primed quantities denote variables in the pulse frame.

In the COM frame the average velocity is equal to zero, so the force acting on the pulse center of mass is given by F' = eE'. The longitudinal electric field is not modified so we have that  $F'_z = eE'_z = eE_z = F_z$ . To consider the effect in the transverse direction, it is convenient to think in terms of cylindrical coordinates. For a magnetic lens,  $B_{\phi} \neq 0$ ,  $\mathbf{E} = 0$ , so that  $E'_r = -\gamma_L v_0 B_{\phi}$  and  $F'_r = -q\gamma_L v_0 B_{\phi} = \gamma_L F_r$ , where  $F_r = -qv_0 B_{\phi}$  is the force in the lab frame. In our formalism this corresponds to an increase of the lens strength equal to  $\gamma_L$ . For an RF cavity,  $E_r \neq 0$ ,  $B_{\phi} \neq 0$  and  $E'_r = \gamma_L (E_r - v_0 B_{\phi})$ , resulting in a similar effect. These contributions can be incorporated in our formulation by renormalizing the transverse lens and RF cavity strengths in the following way:

$$M_T^{lens} \to \gamma_L M_T^{lens},$$
 (3.108)

$$M_z^{lens} = 0, (3.109)$$

$$M_T^{rf} \to \gamma_L M_T^{rf}, \tag{3.110}$$

$$M_z^{rf} = M_z^{rf}.$$
 (3.111)

The field in the photoemission gun, which is entirely in the z direction, is not affected as fields parallel to the relativistic motion are not transformed. However, our derivation of the effect of the gun region resulted in a term  $\propto \exp\left[-(d_{gun} - z')^2/(2\sigma_i)\right]$ , where  $d_{gun}$  and z' are the length of the photoemission gun and the position of the pulse center of mass in the lab frame. It becomes clear that the width of the pulse appearing in this expression should also be taken in the lab frame, meaning that we perform the substitution  $\sigma_i \rightarrow \sigma_i/\gamma_L^2$ .

For reference we now report the equations governing the Analytic Gaussian model with the inclusion of the optical elements discussed in the text and the effects of relativistic motion. Note that the units for the parameters are:  $\sigma_i$  units of length squared,  $\eta_i$  units of momentum squared and  $\gamma_i$  units of action (length x momentum).

$$\frac{d\sigma_i}{dt} = \frac{2}{m}\gamma_i,$$

$$\frac{d\gamma_i}{dt} = \frac{1}{m}\left(\eta_i + \frac{\gamma_i^2}{\sigma_i}\right) + \frac{1}{4\pi\epsilon_0}\frac{Ne^2}{6\sqrt{\sigma_i\pi}}L_i(\xi) + (M_i^{lens} + M_i^{rf})\sigma_i - M_i^{gun}\sqrt{\sigma_i}\exp\left[-\frac{(d_{gun} - z')^2}{2\sigma_i/\gamma_L}\right],$$

$$(3.112)$$

$$(3.113)$$

$$\frac{d\eta_i}{dt} = -\frac{2\gamma_i\eta_i}{m\sigma_i},\tag{3.114}$$

with i = T or z and

$$\xi = \sqrt{\sigma_z / \sigma_T},\tag{3.115}$$

$$L_T(\xi) = \frac{3}{2} \left[ L(\xi) + \frac{\xi^2 L(\xi) - \xi}{1 - \xi^2} \right], \qquad (3.116)$$

$$L_z(\xi) = \frac{3\xi^2}{\xi^2 - 1} \left[\xi L(\xi) - 1\right], \qquad (3.117)$$

$$L(\xi) = \begin{cases} \frac{\arcsin\sqrt{1-\xi^2}}{\sqrt{1-\xi^2}} & \text{for } 0 \le \xi \le 1\\ \frac{\ln(\xi+\sqrt{\xi^2-1})}{\sqrt{\xi^2-1}} & \text{for } \xi > 1, \end{cases}$$
(3.118)

$$M_T^{lens} = \gamma_L M_T \exp\left[-\left(\frac{z'-z'_{lens}}{L_{lens}/2}\right)^{2n}\right],\tag{3.119}$$

$$M_z^{lens} = 0, (3.120)$$

$$M_T^{rf} = \gamma_L e E_0(z') \left[ \frac{2n}{d} \left( \frac{z' - z'_{rf}}{d/2} \right)^{2n-1} \sin\left( \frac{\Omega z'}{v_0} + \phi \right) + \frac{\Omega v_0}{2c^2} \cos\left( \frac{\Omega z'}{v_0} + \phi \right) \right], \quad (3.121)$$

$$M_z^{rf} = -\frac{eE_0(z')\Omega}{v_0} \cos\left(\frac{\Omega z'}{v_0} + \phi\right),\tag{3.122}$$

$$E_0(z') = E_0 \exp\left[-\left(\frac{z' - z'_{rf}}{d/2}\right)^{2n}\right],$$
(3.123)

$$M_T^{gun} = 0, (3.124)$$

$$M_z^{gun} = eE_{gun} \frac{1}{\sqrt{2\pi}}.$$
(3.125)

See previous text for further details of the notation used.

# 3.2 Methods

The set of equations we have derived (Eqs. 3.112-3.125) describing all the optical elements in our column, have to be numerically integrated to give the time evolution of the electron pulse inside the microscope. To do so we developed a program written in Fortran 90 that performs this numerical integration using a fourth order Runge Kutta method with adaptive step size control, implemented following the procedure outlined in [72]. Given the positions and properties of the elements one wishes to use, it is then possible to calculate the beam size, chirp and momentum spread at the target position.

In order to provide information to guide the development of the electron microscope, an optimization routine was also implemented to adjust the strengths of the magnetic lenses and RF cavity in order to focus both the longitudinal and transverse pulse components at the target and minimize the pulse size at the focal point. This was done using the Levenberg–Marquardt algorithm [72], a quasi-Newton optimization method which allows to minimize a given objective function F that depends on a set of parameters  $\mathbf{p}$ . In our case the components of  $\mathbf{p}$  correspond to the RF cavity and magnetic lens strengths and what we want to achieve is a focal spot in which both the transverse and longitudinal widths have a minimum value. To do this we choose to use the following objective function

$$F = c_1 \left(\frac{z_{min,z} - z_{min,T}}{z_{min,z}}\right)^2 + c_2 \left(\frac{\sigma_{min,z}}{\sigma_{0,z}}\right) + c_3 \left(\frac{\sigma_{min,T}}{\sigma_{0,T}}\right), \qquad (3.126)$$

where  $c_1$ ,  $c_2$ ,  $c_3$  are the relative weights of each term,  $\sigma_{min,z(T)}$  is the minimum pulse width squared (following the notation used in our model) and  $z_{min,z(T)}$  is the corresponding position in the longitudinal (transverse) direction.  $\sigma_{0,z}$ , and  $\sigma_{0,T}$  are the initial pulse widths.

Given our function  $F(\mathbf{p})$  and a set of parameters  $\mathbf{p}_i$ , the Levenberg–Marquardt algorithm

updates these parameters to minimize  $F(\mathbf{p})$  in the following way

$$\mathbf{p}_{i+1} = \mathbf{p}_i - \left(\mathbf{H} + \lambda \mathbf{H}_{diag}\right)^{-1} \mathbf{d}, \qquad (3.127)$$

where

$$H_{i,j} = \frac{\partial F(\mathbf{p})}{\partial p_i} \frac{\partial F(\mathbf{p})}{\partial p_j},\tag{3.128}$$

$$\mathbf{d} = F(\mathbf{p}) \frac{\partial F(\mathbf{p})}{\partial \mathbf{p}}.$$
(3.129)

**H** is an approximation of the true Hessian matrix obtained by multiplying the first order derivatives and  $\mathbf{H}_{diag}$  is a matrix formed with the diagonal elements of **H**. The parameter  $\lambda$ , which is adjusted throughout the optimization procedure, determines the behavior of the algorithm: for large  $\lambda$  the above equation approaches the steepest descent method, while for small  $\lambda$  it approaches the Gauss-Newton algorithm. In practice we adjust  $\lambda$  so that far from the minimum we use the former, while as we get closer to a minimum of  $F(\mathbf{p})$ , we incorporate more of the latter. We stop the minimization routine after performing a certain number of steps (typically we choose N=3) where the fractional change in  $F(\mathbf{p})$  is less than  $10^{-3}$ . Once convergence has been reached, an evaluation of the matrix **H** gives information on the covariance of the optimization parameters.

### 3.3 Results

In this section we present the results obtained using the Analytic Gaussian model and the code we developed. We start by looking at the time evolution of an electron pulse in a drift region and compare the Analytic Gaussian results to N particle simulations done using the COSY-MLFMM code described in chapter 2. We then proceed to analyze the effect of each optical element on the electron pulse and then combine them to simulate the whole microscope column.

#### 3.3.1 Drift

It is clear that our simple mean field Analytic Gaussian model cannot capture the details of the dynamics of an electron pulse, since it assumes a Gaussian pulse shape at all times and neglects any nonlinear contributions of the optical elements. Nevertheless, we expect it to be reasonably accurate in those sections of the column where the higher order electron– electron correlations and aberrations can be ignored. In particular, since there are long drift segments between the optical components of the microscope, we want to understand how well our model performs in describing them. Having observed in our photoemission simulations that there are two regimes of interest, below and above the virtual cathode (VC) limit, we compare the predictions of the Analytic Gaussian model in both of these cases by fitting the pulse profile at the end of the photoemission process (t = 120 ps) with the Gaussian profile in Eq. 3.15 and then calculating the time evolution over a period of 50 ps using both codes.

Below the VC and for a Gaussian laser profile, even though the photoemitted pulse displays some nonlinear distortions both in the transverse and longitudinal directions, the Analytic Gaussian model is able to describe the evolution of the pulse phase space (Fig. 3.4) and capture the time evolution of the pulse parameters remarkably well (Fig. 3.5), with fractional errors less than 1.5 %. The pulse momentum spread is calculated from the Analytic Gaussian parameters as

$$\sigma_{p_i} = \eta_i + \frac{\gamma_i^2}{\sigma_i},\tag{3.130}$$

where i = T or z and  $\eta_i$ .



Figure 3.4: Color map of the charge distribution of an electron bunch below the virtual cathode limit ( $F_a=1$ MV/m,  $N_e=10^6$ , Gaussian laser profile) in the rest frame of the bunch projected onto the  $p_x$ -x plane [(a), (b)] and  $p_z$ -z plane [(c),(d)]. Also shown is the time evolution of the Analytic Gaussian model for the pulse, with the black line indicating the contour where the intensity drops to 0.5 times its peak value.

Since our photoemission simulations showed that it is advantageous to use an Elliptical transverse laser profile, in Figs. 3.6 and 3.7 we compare the N particle and Analytic Gaussian simulations with the electron pulse generated using an elliptical laser profile  $[I(r) \propto \sqrt{1 - (r/R)^2}]$ . Our Analytic Gaussian model is able to accurately simulate the time evolution in this case as well, and in fact, due to the more linear nature of the phase



Figure 3.5: Time evolution of pulse parameters below the virtual cathode limit ( $F_a=1$ MV/m,  $N_e=10^6$ , Gaussian laser profile) comparing N-particle simulations and the Analytic Gaussian model. Panel (a) shows the pulse center of mass position, panels (b)-(d) show the transverse (T) and longitudinal (z) pulse width  $\sqrt{\sigma_i}$  [panel (b)], chirp  $\gamma_i$  [panel (c)] and momentum spread  $\sqrt{\sigma_{p_i}}$  [panel (d)].

space, the fractional errors in the parameters are smaller than for the previous case, with all parameters presenting a difference of less than 1.0 %.

On the other hand, above the virtual cathode limit, the pulse is very strongly nonlinear (Fig. 3.8) and it is clear that a Gaussian fit of this pulse shape does not reflect its complex dynamics. The time evolution of the pulse parameters, using a Gaussian laser profile, is shown in Fig. 3.9. While the spatial width of the pulse is still reasonably captured, with a fractional error that after 50ps is less than 1%, the momentum distribution is not accurately described. In the transverse direction the fractional errors for  $\gamma_T$  and  $\sqrt{\sigma_{p_T}}$  are between 3-4%, while in the longitudinal direction the error is 5-6% at t=50ps. As a result of these, for longer time simulations, we expect that also the spatial width  $\sigma_i$  would deviate from the N-particle prediction. Similar results hold for the Elliptical laser profile.



Figure 3.6: Color map of the charge distribution of an electron bunch below the virtual cathode limit ( $F_a=1$ MV/m,  $N_e=10^6$ , Elliptical laser profile) in the rest frame of the bunch projected onto the  $p_x$ -x plane [(a), (b)] and  $p_z$ -z plane [(c),(d)]. Also shown is the time evolution of the Analytic Gaussian model for the pulse, with the black line indicating the contour where the intensity drops to 0.5 times its peak value.

From these results we conclude that below the virtual cathode limit, the Analytic Gaussian is indeed able to describe the evolution of the pulse with a high degree of fidelity even though the N-particle distribution is not truly Gaussian. Above the VC limit, on the other hand, this approximation breaks down and major differences start showing already after 50ps.



Figure 3.7: Time evolution of pulse parameters below the virtual cathode limit ( $F_a=1$ MV/m,  $N_e=10^6$ , Elliptical laser profile) comparing N-particle simulations and the Analytic Gaussian model. Panel (a) shows the pulse center of mass position, panels (b)-(d) show the transverse (T) and longitudinal (z) pulse width  $\sqrt{\sigma_i}$  [panel (b)], chirp  $\gamma_i$  [panel (c)] and momentum spread  $\sqrt{\sigma_{p_i}}$  [panel (d)].

#### 3.3.2 Photoemission gun

Next we turn our attention to the various elements that compose the microscope, starting from the effect that crossing the anode plane of the photoemission gun, corresponding to the end of the extraction field, has on the pulse properties. We consider varying numbers of electrons below the virtual cathode limit, which from our previous photoemission simulations we estimate to be about  $N_e = 1.5 \cdot 10^7$  for  $F_a=1$ MV/m. As the transverse components are not directly affected by this so-called acceleration gap, we focus on the longitudinal pulse parameters in Fig. 3.10. The slower electrons in the tail of the pulse spend more time in the acceleration region and are accelerated more, resulting in a reduction of the pulse chirp, as seen in the Figure. This effect is seen to be more step-like for lower number of electrons  $(N_e = 10^5)$  due to the smaller pulse size  $\sigma_z$  compared to the  $N_e = 10^7$  case.



Figure 3.8: Color map of the charge distribution of an electron bunch above the virtual cathode limit ( $F_a=1$ MV/m,  $N_e=10^8$ , Gaussian laser profile) in the rest frame of the bunch projected onto the  $p_x$ -x plane [(a), (b)] and  $p_z$ -z plane [(c),(d)]. Also shown is the time evolution of the Analytic Gaussian model for the pulse, with the black line indicating the contour where the intensity drops to 0.5 times its peak value.

#### 3.3.3 Lens

We now analyze the treatment of magnetic lenses with the Analytic Gaussian model. Each lens is described by three parameters: the strength  $M_0$ , the spatial width  $L_{lens}$ , and an order parameter n (n = 1 corresponds to a Gaussian profile). Given the magnetic field data for the lenses used in the microscope, we use Eq. 3.119 with  $\gamma_L = 1$  to perform a fit and obtain the following values: n = 1 and  $L_{lens} = 2.157$ mm.  $M_0$ , proportional to the current in the



Figure 3.9: Time evolution of pulse parameters above the virtual cathode limit ( $F_a=1$ MV/m,  $N_e=10^8$ , Gaussian laser profile) comparing N-particle simulations and the Analytic Gaussian model. Panel (a) shows the pulse center of mass position, panels (b)-(d) show the transverse (T) and longitudinal (z) pulse width  $\sqrt{\sigma_i}$  [panel (b)], chirp  $\gamma_i$  [panel (c)] and momentum spread  $\sqrt{\sigma_{p_i}}$  [panel (d)].

magnetic lens, is left as a variable to adjust the focal length, as shown in Fig. 3.11 where we plot the variation of the transverse pulse parameters due to a lens at z=45mm. In our derivation, the lens affects  $d\gamma_T/dt$  directly with a term proportional to  $M_0\sigma_T$ , which is seen in the change of  $\gamma_T$  in Fig. 3.11(c). The reduction in  $\gamma_T$  results in a focusing of  $\sigma_T$  due to the coupling between the parameters and, since the emittance  $\epsilon = \sqrt{\sigma_i \eta_i}$ , is conserved in our model, this results in a defocusing of  $\eta_T$ . As the strength of the lens is decreased, the focal distance increases and so does the pulse size at the focal point.

For a given lens, for which we take  $M_0 = 5$ , the focusing power depends on the number of electrons and the emittance of the pulse. Given the same initial conditions [Fig. 3.12(a)], the higher the number of electrons, the harder it is to focus the pulse. In our data this is seen in the increased focal length and spot size at the focal point in the case of the  $N_e = 10^7$  pulse.



Figure 3.10: Longitudinal pulse parameters as a function of distance along the microscope column for  $F_a=1$ MV/m, as the pulse crosses the anode plane (at z=45mm, indicated with dashed line). Panel (a) shows the center of mass velocity as a fraction of the speed of light c, while panels (b)-(d) show the variation of the longitudinal (z) pulse width  $\sqrt{\sigma_z}$  [panel (b)], chirp  $\gamma_z/\gamma_0$ , where  $\gamma_0$  is the initial chirp [panel (c)] and local momentum variance  $\sqrt{\eta_z}$  [panel (d)].

On the other hand, from our study of the photoemission process, we know that increasing the number of electrons emitted results also in an increase in the pulse emittance. Therefore, using the data from our photoemission simulations as the initial condition corresponds to different initial values of the pulse emittance as  $N_e$  is varied. In our model pulses with a higher emittance are focused more easily and to a smaller spot size than those with a lower emittance, since focusing can be achieved at the expense of increasing the momentum spread  $\eta_i$ . This results in pulses with a higher  $N_e$ , which have a higher emittance, being focused better that those with lower  $N_e$ , as seen in Fig. 3.12(b), which shows that the focal length of the lens is approximately the same for all the pulses considered with the  $N_e = 10^7$  pulse



Figure 3.11: (a) Fractional lens strength  $M(z)/M_0$  as a function of position. (b)-(d) Transverse pulse parameters as a function of distance along the microscope column for  $N_e=10^6$ , with a magnetic lens of varying strength  $M_0$  at z=45mm (indicated with a dashed line). Shown are the transverse (T) pulse width  $\sqrt{\sigma_T}$  [panel (b)], chirp  $\gamma_z/\gamma_0$  [panel (c)] and local momentum variance  $\sqrt{\eta_z}$  [panel (d)].

displaying a smaller size at the focal spot than the other two.

These results lead to two observations: first they highlight the importance of correctly simulating the photoemission process. The previous works using the Analytic Gaussian model [37–39] did not consider the details of how the electrons are emitted and assumed that the initial conditions would be the same regardless of the number of electrons in the pulse. We have shown here how this is not the case and that varying the initial emittance changes the focusing obtained in this model.

Our second consideration is about the limits of the Analytic Gaussian model, since so far we have assumed that the lenses used are linear regardless of focusing strength and pulse



Figure 3.12: Transverse (T) pulse width  $\sqrt{\sigma_T}$  as a function of distance along the microscope column with a magnetic lens ( $M_0 = 5$ ) at z=45mm (indicated with a dashed line) for varying numbers of electrons in the pulse. (a) Effect of lens given the same initial conditions. (b) Effect of lens using the initial conditions from the photoemission simulations.

size. This approximation is only valid in the limit where the pulse size is much smaller than the lens diameter. Checking the magnetic field calculated for the actual lens in the microscope, we see that it retains a mostly Gaussian shape for  $r \leq 0.8$ mm, meaning that for values of  $\sqrt{2\sigma_T}$  greater than this, or  $\sqrt{\sigma_T} > 0.57$ mm, this approximation is not correct. Comparing this value to the data shown in Fig. 3.12 shows that the width of the  $N_e = 10^7$ pulse is well above this value before the lens, so that in a real system it would not be focused to such a tight spot as our model predicts. To improve this, in principle, one could include spherical aberrations in the Analytic Gaussian model by adding nonlinear external forces, but it would disregard the mean field approach inherent in its derivation and cause pulse breakup. In practice this means that while the AG model can give an estimate of the properties of the column, these should be seen as best-case estimates and one should use other simulation tools to capture the details of the dynamics, specially as the number of electrons in each pulse is increased.

#### 3.3.4 RF cavity

The last element to analyze in our column is the RF cavity, which is used to focus the pulse in the longitudinal direction at the expense of a defocusing of the transverse components, as seen in Figure 3.13. The parameters used for the RF cavity in our simulations are n = 2,  $L_{rf} = 22.5$ mm,  $\Omega = 2\pi \cdot 1.013$ GHz and  $E_r f = 1.0-2.4$ MV/m, matching the parameters of the cavity used in the actual microscope. In order to focus the pulse, the time dependent field in the RF cavity needs to be zero when the center of mass of the pulse is at the center of the cavity, so that the tail of the pulse is accelerated and the front is decelerated, with no net change of the COM velocity [see Fig. 3.13(a)]. To do this it is necessary to match the phase of the RF cavity with the time it takes the electron pulse to reach the center of the cavity, which is not trivial to do in practice in a real microscope. Also, in addition to this, the time of flight of the pulse through the cavity should be at most half of the oscillation period, to prevent unwanted defocusing due to the oscillating field in the cavity. This sets a limit on the maximum longitudinal pulse size that a cavity at a given frequency can compress, which for our cavity and 100keV electrons can be estimated to be  $\sqrt{\sigma_z} \lesssim 20$ mm.

As seen in the discussion on the magnetic lenses, the increased Coulomb repulsion present in pulses with higher numbers of electrons, makes them harder to focus and this is true also in the longitudinal direction (Fig. 3.14), resulting in a larger spot size at the focal point for increasing  $N_e$ .

#### 3.3.5 Column

So far we have discussed the optical elements individually, now we combine them to model the proposed design for the Ultrafast Electron Microscope under development in our group.



Figure 3.13: Pulse parameters as a function of distance along the microscope column for  $N_e=10^6$  with an RF cavity centered at z=45mm (indicated by the vertical dashed line) for different RF field strengths. (a) Center of mass velocity as a fraction of speed of light c and electric field as a fraction of the peak value  $E_0$ . (b)-(d) Transverse (T) and longitudinal (z) pulse width  $\sqrt{\sigma_i}$  [panel (b)], chirp  $\gamma_i/\gamma_0$  [panel (c)] and local momentum variance  $\sqrt{\eta_i}$  [panel (d)]. The continuous (dashed) lines indicate the longitudinal (transverse) components and the colors correspond, respectively, to  $E_{rf} = 2.4MV/m$  (black) and  $E_{rf} = 1.0MV/m$  (red).

The positions and properties of the photoemission gun, magnetic lenses and RF cavity used in the microscope are summarized in Table 3.1. The strengths of the lenses and of the electric field in the RF cavity were used as variables in the optimization routine to control the focal point position and spot size. The initial pulse parameters (number of electrons, center of mass velocity and Analytic Gaussian parameters) were extracted from our simulations of the photoemission process discussed in the previous chapter.

Results for the column optimized for  $N_e = 10^6$  electrons generated with a Gaussian laser pulse are shown in Fig. 3.15, where we plot the longitudinal and transverse pulse width  $\sqrt{\sigma_i}$ ,



Figure 3.14: (a) Transverse pulse width  $\sqrt{\sigma_T}$  and (b) longitudinal pulse width  $\sqrt{\sigma_z}$  as a function of distance along the microscope column for varying  $N_e$ , with an RF cavity centered at z=45mm (indicated by the vertical dashed line) with  $E_{rf}=2.4$ MV/m.

Photoemission gun	
Extraction field	$2.2 \mathrm{MV/m}$
Cathode position	z=0mm
Anode position	z=45mm
Magnetic lenses	$n=1, L_{lens}=2.157mm$
Lens 1	z=70.2mm
Lens 2	z=360.0mm
Lens 3	z=1066.0mm
RF cavity	$n=2, L_{rf}=22.5mm$
$\Omega/2\pi = 1.013 \mathrm{GHz}$	z=640.8mm
Sample	z=1080.5 $\pm$ 25.4 mm

Table 3.1: Parameters used in the simulation of the UEM system using the Analytic Gaussian model.

chirp  $\gamma_i$  and local momentum variance  $\sqrt{\eta_i}$  as a function of position along the microscope. The focal point is at 1088.62mm, with pulse size  $\sqrt{\sigma_T} = 0.92 \mu m$  and  $\sqrt{\sigma_z} = 2.27 \mu m$ . Due to the strength of the lens used to focus the pulse, for positions close to the focal point, the transverse width diverges rapidly so accurate positioning of the sample at the focal spot is crucial for good spatial resolution. The divergence of the longitudinal component is much less severe.

We perform a similar optimization varying the number of electrons in the pulse and the



Figure 3.15: Longitudinal (black) and transverse (dashed red) pulse parameters as a function of distance along the microscope column for  $N_e=10^6$ . Shown are the (a) pulse width  $\sqrt{\sigma_i}$ , (b) chirp  $\gamma_i$  and (c) local momentum variance  $\sqrt{\eta_i}$ . The region corresponding to the photoemission gun is shown in blue, while that corresponding to the RF cavity is in green. The dashed lines correspond to the magnetic lenses.

transverse profile of the photoemitting laser and summarize our results in Fig. 3.16 and Table 3.2. We see that in our model the position of the focal spot is relatively insensitive to the charge in the pulse. The longitudinal width  $\sqrt{\sigma_z}$  and the corresponding time resolution, defined as  $\delta t = 2\sqrt{2\sigma_z}/v_0$ , are increased from 0.76 $\mu$ m ( $\delta t$ =13fs) for the 10<sup>5</sup> Gaussian electron pulse to 17 $\mu$ m ( $\delta t$ =288fs) for the Gaussian pulse with 10<sup>7</sup> electrons. The transverse pulse sizes are comparable for all the simulations reported using a Gaussian laser profile but, as discussed in section 3.3.3, this is a result of neglecting aberrations which would certainly play a role as the width of the pulse is increased. Using an elliptical laser profile to generate the electron pulse offers some advantages in terms of a decreased transverse emittance, which leads to a focal spot size that is half of what is predicted for the Gaussian case. In the longitudinal direction the laser profile plays a less significant role, and the temporal resolution is comparable to that obtained with a Gaussian laser.



Figure 3.16: Detail of the transverse and longitudinal pulse widths in the optimized column around the focal spot for a Gaussian laser pulse with (a)  $N_e = 10^5$ , (b)  $N_e = 10^6$  and (c)  $N_e = 10^7$  electrons and (d) for an elliptical laser pulse with  $N_e = 10^6$  electrons.

In conclusion, we have derived a mean field formalism to simulate the propagation of

	$z_{focus}$	$\sqrt{\sigma_T}$	$\sqrt{\sigma_z}$	$\delta t$
	(mm)	$(\mu m)$	$(\mu m)$	(fs)
Gaussian - $N_e = 10^5$	1088.54	0.98	0.76	13.1
Gaussian - $N_e = 10^6$	1088.62	0.92	2.27	39.2
Gaussian - $N_e = 10^7$	1088.57	0.95	16.6	288
Elliptical - $N_e = 10^6$	1088.61	0.46	2.37	41.1

Table 3.2: Focal spot position and corresponding pulse width for varying number of electrons  $N_e$  and transverse photoexciting laser profile.

an electron pulse through a microscope column with different optical elements. By comparing the time evolution of the pulse described with the Analytic Gaussian model to our N-particle simulations, we have shown good agreement for extraction conditions under the virtual cathode limit. Following a discussion of the effects of the different optical elements composing the microscope column, we have built a model to describe our UEM system and given quantitative predictions of the achievable spatial and temporal resolutions. Given the limitations of the Analytic Gaussian model, these predictions should be viewed as best case results, since aberrations and deviations of the pulse from the assumed self similar Gaussian profile were neglected. Nevertheless, due to the simplicity of the model and the resulting ease of computation, we believe these results can offer a valuable tool in understanding the achievable resolution in UEM systems and allow one to search optimal configurations over a vast range of parameters. Other simulation tools (such as the COSY-MLFMM code) could then be used to analyze the most promising configurations in more detail.

# Chapter 4

# Microscopic origin of the properties of $TaS_2$

The final part of this work will focus on an example of a material, Tantalum Disulphide  $(TaS_2)$ , that can be studied with the Ultrafast Electron Microscope described in the previous chapters. To do this, we first give a brief introduction to correlated electron systems with an emphasis on Charge Density Wave (CDW) insulators, followed by a survey of the existing experimental and theoretical results on  $TaS_2$ . We then proceed to illustrate the simulation methods used and conclude with a discussion of the results.

# 4.1 Physics of correlated electron systems

Materials with partially filled d- and f-orbitals have received considerable interest over the last decades due to the challenges they present. The localized nature of these orbitals can lead to the opening of a gap in the ground state in systems that would otherwise be metallic. Moreover, varying the temperature (or other macroscopic parameters such as pressure or doping), can lead to a transition from the insulating to the metallic state with a change in resistivity of several orders of magnitude. Over the last 30 years explaining these interesting features has been a major challenge to theory and experiment alike and has led to the development of many novel techniques (for an introduction to the subject see [73] and [27] and references therein).

The unusual behaviors seen in these so-called correlated electron systems represent a many-body problem that arises from the interaction of electronic and structural degrees of freedom. Based on the driving mechanism of gap opening, it is possible to define three categories of insulators (Fig. 4.1). The first category is the so-called **Mott insulator**, in which the electron-electron Coulomb repulsion drives a gap opening at the Fermi energy  $E_F$ and leads to localization of the valence electrons on the atomic sites. The second type of insulator is the **excitonic insulator**, resulting from unscreened electron-hole interactions. In these materials a Charge Density Wave (CDW) is formed together with a small distortion of the lattice that is caused by a finite electron-phonon coupling. Due to an avoided crossing of valence and conduction bands, a gap opens at  $E_F$  that stabilizes this distortion. The third type of insulating behavior is the result of electron-phonon interactions and is called the **Peierls insulator**. In this case a gap opens as a result of the simultaneous formation of a CDW and a periodic lattice distortion with a wavelength that is determined by the periodicity of the Fermi surface. The energy of the occupied levels is lowered by an amount that is greater than the Coulomb repulsion resulting from the distortion.

The term Charge Density Wave introduced here indicates a periodic modulation of the ground state electron density. This phenomenon was first described by Peierls in 1955 [74] when he noted that a one dimensional metal is not stable at low temperature. A periodic modulation of the charge density, accompanied by a periodic lattice distortion due



Figure 4.1: Three classes of insulators and their respective characteristic response times. (a) Mott insulator (b) Excitonic insulator (c) Peierls insulator. In each case the gray shading and dashed lines indicate the metallic state and the solid lines and colored shading show the resulting insulating state both in real and momentum space. (d) Timescales corresponding to probing these processes with a pump-probe experiment. [27]

to electron-phonon interactions, leads to an insulating ground state with an energy that is lower than that of the metallic state. The size of the insulating gap depends on the amplitude of the lattice distortion, while the filling of the levels in the system determines the periodicity. For more details on CDW formation, we refer the reader to the classic text by Gruner [75].

Of course real materials present competing electron-electron and electron-phonon interactions and thus rarely fit in a single one of the categories described above. However, as shown in the cartoon of Fig. 4.1(d), these interactions can be separated based on the temporal response of the system to perturbation with a pump pulse. Electron hopping processes are typically very fast and act on timescales of  $\tau < 10$  fs. The buildup of charge screening that results in the formation of excitonic behavior is a slower process characterized by time constants  $\tau = 10-100$  fs. The excitation of phonon modes leading to charge oscillations requires a transfer of energy from the excited electrons to the lattice and therefore takes place at later times, with  $\tau > 100$  fs. Based on this separation of time scales, pump-probe measurements have become a key technique to investigate these systems, as measuring the relaxation of the system to equilibrium after perturbation with the pump pulse allows decoupling of these degrees of freedom.

## 4.2 Structural and electronic properties of $TaS_2$

For the present work we chose to investigate Tantalum Disulphide as this material is thought to be a combined Mott-Peierls insulator exhibiting strong electronic localization, CDW formation and lattice distortion. TaS<sub>2</sub> is a member of the transition metal dichalcogenides group and presents a 2 dimensional layered structure, as seen in Fig. 4.2, with weak Van der Waals interactions between the layers and covalent bonds between atoms in the same layer [76,77]. The stacking of the layers is thought to be disordered [78–80]. The charge density wave distortion leads to the formation of a commensurate superlattice of size  $\sqrt{13}x\sqrt{13}$ and rotated by 13.9° with respect to the original 1x1 unit cell for temperatures T < 180 K [81]. In this "Star of David" arrangement, shown in Fig. 4.3, we can distinguish three types of inequivalent atoms: one central atom which is not shifted with respect to the original lattice (site a), its six nearest (b sites) and next-nearest neighbors (c sites) which undergo a contraction towards the central atom forming the clusters drawn in the figure. This in-plane displacement is accompanied by an out-of-the-plane swelling of the sulfur layers [1].

The CDW distortion alone is not sufficient to fully open a gap in  $TaS_2$ , as only twelve of the thirteen electrons of the reconstructed cell occupy levels below the distortion-generated gap. Since Angle Resolved Photoemission Spectroscopy (ARPES) results [81–85] and resistivity data [83,86] show this material to be an insulator, some further interaction is needed to explain these results. Conventionally it is thought that a gap opens as a consequence of the splitting of the band corresponding to the thirteenth electron, localized on the central atom,
into upper and lower Hubbard bands due to Coulomb repulsion leading to the development of a Mott insulating state [28]. This explanation for the origin of the gap is not entirely convincing as some photoelectron spectroscopy (PES) investigations [87], tight-binding [81] and DFT calculations [1,88,89] show that the system retains a finite density of states at the Fermi energy. An alternative explanation suggests that the existence of a gap could be due to Anderson localization caused by disorder [89]. The origin and nature of this insulating gap is one of the topics that will be investigated in the present work.



Figure 4.2:  $TaS_2$  structure corresponding to the primitive unit cell (undistorted metallic phase): (a) 3D view, (b) Top view and (c) Side view. Ta atoms are drawn in blue, S atoms in red. The black lines delimit the primitive 1x1 unit cell.

Increasing the temperature leads to breaking of the commensurate CDW (C-CDW) and the insulating state, and between T = 190K and T = 350K the system exhibits a nearly commensurate CDW (NC-CDW) corresponding to a temperature dependent rotation of the CDW vector from the commensurate value of  $13.9^{\circ}$  to about  $11^{\circ}$  and a simultaneous formation of domains [77,90,91] with a size inversely dependent on temperature. For 350K < T < 550K, we find an incommensurate CDW (IC-CDW) in which the CDW vector is aligned with the underlying lattice and no domain structure is visible. For T > 550K the system



Figure 4.3: Positions of the Ta atoms corresponding to the reconstructed "Star of David" arrangement in a 2x2 unit cell. The undistorted positions are shown in yellow, while the reconstructed lattice and bonds resulting from the contraction associated with CDW formation are drawn in blue. The labels correspond to the three inequivalent atom types of the distorted cell.

becomes metallic and reverts to a monoclinic undistorted lattice. Figure 4.4 shows resistivity as a function of temperature and permits a clear identification of the phases discussed. Also shown is the trigonal phase obtained upon heating between T = 200K and T = 280K [77].



Figure 4.4: Resistivity as a function of temperature in 1T-TaS<sub>2</sub>. The phases shown are: C-CDW below 190K, NC-CDW below 350K, IC-CDW below 550K and metallic for T>550K. Also shown is the trigonal phase present during the heating cycle between 200-280K. [28]

Both pressure [28,92,93] and doping [94] can be used to modify the boundaries between these phases and even induce the formation of a superconducting state. How this phase is formed and whether it coexists with the CDW in real space or in reciprocal space is still an unanswered question in the field and is outside of the scope of the present work.

As we have seen, experimental techniques that probe out of equilibrium conditions, such as pump-probe measurements, can untangle the different timescales involved in the interactions between electronic and phononic degrees of freedom and offer an excellent tool to better understand the complex phase diagram present in TaS<sub>2</sub>. By performing time resolved ARPES measurements, Perfetti et al. [95,96] showed the ultrafast collapse of the electronic gap after photoexcitation due to the creation of a hot electron distribution, and its successive revival after 680 fs. The nuclear and phononic degrees of freedom, acting on longer time scales due to the coupling to the electronic ones, lead to periodic oscillations of the system at long times (t>1-2ps) due to excited phonon modes. A qualitative explanation of these results using a single band Hubbard model in the context of DFT+DMFT was advanced by Freericks et al. [97], but several discrepancies such as a strongly insulating behavior absent in the experiments, limit the applicability of these results.

More recently, time resolved x-ray photoemission spectroscopy (TR-XPS) has been used to probe the melting of the CDW at specific atomic sites [27,86] and the transition from C-CDW to NC-CDW. The authors find an initial ultrafast subpicosecond reduction of the CDW peak and its successive partial recovery with a time constant of ~900 fs. This seems to suggest that the system relaxes into a state with an inhomogeneous distribution of undistorted (metallic) islands inserted into a CDW background, instead of recovering the superstructure network typical of the equilibrium NC-CDW.

Recent experiments were also conducted by Prof. Ruan's group at Michigan State (cur-

rently unpublished) to understand the laser fluence and wavelength dependence of the transition from NC-CDW to IC-CDW in  $TaS_2$ . By measuring both the CDW peak amplitude and rotation angle, they observe a transition dependent on the incident photon density, rather than on energy density as would be expected. This suggests that the transition is not thermodynamically driven but rather driven by a direct distortion of the CDW.

# 4.3 Methods

To better understand the ground and excited state properties of  $TaS_2$ , we performed ab-initio Density Functional Theory (DFT) calculations of the electronic and phononic structure both in the commensurate CDW phase and in the undistorted metallic phase using the Vienna Abinitio Simulation Package (VASP) [98–101]. A description of the basic equations governing the DFT theory is given in appendix 5. For the calculations presented in the rest of this chapter, the GGA-PBE [102] exchange correlation functional was used and plane waves with the projector augmented wave method [103] were used as the basis set.

The lattice constants and atom positions for the undistorted metallic phase (1 Ta atom and 2 S atoms in the unit cell) were taken from Spijkerman et al. [90]. The  $\sqrt{13}x\sqrt{13}$  C-CDW supercell (13 Ta atoms and 26 S atoms) with a 13.9° rotation was then built from this primitive unit cell using the bond contractions reported by Smith et al. [81]. For each structure, the first step was to determine the appropriate energy cutoff and k-point mesh such that the total (ground state) energy was converged to 1meV/atom. The results of these checks are show in Fig. 4.5 for the undistorted cell and in Fig. 4.6 for the C-CDW supercell. Based on this data, we choose to use an 11x11x6 mesh with an energy cutoff  $E_{cut} = 300$ eV for the metallic system and, for the C-CDW system, a 4x4x8 mesh with  $E_{cut} = 350$ eV.



Figure 4.5: Convergence of the ground state energy for the metallic phase as a function of energy cutoff and k point mesh size. The dashed lines correspond to the acceptable range of values that gives a precision of 1meV/atom. Note that due to the size of the reciprocal unit cell, the Nth k-point mesh corresponds to a mesh of size N in the  $k_x$  and  $k_y$  directions and N/2 in the  $k_z$  direction.



Figure 4.6: Convergence of the ground state energy for the distorted phase as a function of energy cutoff and k point mesh size for varying energy cutoff. The dashed lines correspond to the acceptable range of values that gives a precision of 1 meV/atom. Note that due to the size of the reciprocal unit cell, the Nth k-point mesh corresponds to a mesh of size N in the  $k_x$  and  $k_y$  directions and  $2 \cdot N$  in the  $k_z$  direction.

Next, the positions of the atoms in the C-CDW structure were relaxed by performing self consistent DFT runs with a force calculation. The conjugate gradient algorithm was first used to relax the structure until the force on each atom was less than 0.1 eV/Å and the total and band structure energy changes between steps in the self-consistent electronic

loop were less than  $10^{-2}$ eV. This was followed by a more stringent run in which a residual minimization scheme - direct inversion in the iterative subspace (RMM-DIIS) algorithm [104] was used to relax the forces to less than 0.01eV/Å, with total and band structure energy changes  $\Delta E < 10^{-5}$ eV. The size of the unit cell in all three dimensions was allowed to vary in addition to the atomic positions. To get accurate values for the stress tensor used to calculate the forces on the atoms, it is necessary to increase the energy cutoff when performing structural relaxations, so a cutoff equal to  $1.3 \cdot E_{cut}$  was used, following the recommendation in the VASP documentation. The optimized unit cell with the respective atomic positions was then used in all the following calculations.

To simulate the metallic state originating from pumping with an ultrafast laser, the optimized unit cell for this phase was built using the lattice constants obtained from relaxing the C-CDW structure, with the atoms restored to the initial high symmetry positions. Using the symmetry present in the system, the unit cell of the metallic phase can be reduced to a cell with 1 Ta atom and 2 S atoms.

For both the metallic and the C-CDW phase, we calculated the band structure and the density of states (DOS); for the latter a denser k-point mesh was used equal to, respectively, 21x21x11 (metallic phase) and 8x8x16 (C-CDW phase). The effects of the spin-orbit coupling were also investigated, as previous results from a tight-binding calculation [88] suggest that they play an important role in TaS<sub>2</sub>. To see whether a Mott gap would open in the C-CDW phase, DFT+U [105] was used with varying values of on-site Hubbard interaction, U = 0 - 5eV. Phonon spectra for both the metallic and C-CDW phases were also calculated using density functional perturbation theory [106] in VASP and the results were post processed using the program Phonopy; for the metallic phase a 3x3x3 unit cell was used in this calculation with phonon wave vectors sampled on a 12x12x6 mesh. For the C-CDW phase

we used a 1x1x1 unit cell and an 8x8x16 mesh. Finally, to investigate the optical absorption of these materials, we computed the real and imaginary parts of the dielectric constants in the independent particle approximation [107].

# 4.4 Ground state of $TaS_2$

We begin by presenting our efforts in understanding the ground state of  $TaS_2$  and the origin of the gap that is seen in the experimental data. To do so we calculate the band structure and density of states and investigate whether spin orbit coupling or Hubbard splitting could lead to an insulating state in this material. Following this, we will discuss the role of phonons in thermalizing the hot electron distribution generated by the pump laser used in experiments and conclude with a brief discussion of the optical properties of  $TaS_2$ .

#### 4.4.1 Band structure and DOS

After performing the relaxation of the structural parameters (unit cell vectors and atomic positions) for the unit cell corresponding to the C-CDW phase, as described in the previous section, we find the atomic ground state configuration shown in Fig. 4.7, with lattice parameters indicated in Table 4.1. As expected, we observe a buckling of the S layers both above and below the Ta atomic plane with a variation in height of the S atoms equal to  $\Delta z = 0.2$  Å. The lattice parameters obtained show good agreement with experimental data, with a and b showing a 0.5 % difference from the experimental value. The vertical c axis is elongated by about 13% compared to the experimental result due to the weak Van der Waals interactions between the layers that is underestimated by DFT. The first Brillouin zone corresponding to the C-CDW tetragonal unit cell is shown in Fig. 4.8, with the high symmetry points that

will be discussed in the following text labeled.



Figure 4.7: Top (a) and side (b) views of the relaxed C-CDW structure, with the black line indicating the boundary of the unit cell. Ta atoms are drawn in blue, while S atoms are in red.

	Theory	Exp
a (Å)	12.192	12.129
b (Å)	12.192	12.129
c (Å)	6.677	5.889

Table 4.1: Theoretical and experimental (from [1]) values for the parameters of the C-CDW unit cell



Figure 4.8: First Brillouin zone corresponding to the C-CDW  $TaS_2$  unit cell. The labels represent the conventional high symmetry points. [29]

Our calculated band structure and density of states (DOS) are reported in Fig. 4.9 and agree with similar data previously published in the literature [1]. The uppermost half occupied band shows a weak dispersion in plane ( $\Gamma$ -M-K- $\Gamma$ ), being localized at energies of about -0.1 eV and a strong dispersion in the out of plane direction (A- $\Gamma$ ,  $\Gamma$ -L, H- $\Gamma$ ) that results in a crossing of the Fermi energy at positions close to the  $\Gamma$  point. This band is mostly due to the Ta d<sub>z<sup>2</sup></sub> orbitals. Below this, at energies -0.2 eV to -1.0 eV, we find the six sub-bands corresponding to the remaining d orbitals. These bands are somewhat close at the  $\Gamma$  point (-0.3 eV to -0.5 eV) but elsewhere display a large spread in energies. The DOS plot shows the presence of states at the Fermi energy, mostly due to the d<sub>z<sup>2</sup></sub> band on the central Ta atom, so that the system is not fully gapped.



Figure 4.9: Band structure along high symmetry lines and density of states for the C-CDW phase. The contribution to the DOS due to the Ta d orbitals and that due to only the  $d_{z^2}$  is also plotted.

In contrast the band structure displayed by the metallic case, Fig. 4.10, has an uppermost band which is localized in the vertical A- $\Gamma$  direction and strongly dispersive along the other directions considered. From this we can deduce that the CDW distortion acts in localizing the d<sub>z<sup>2</sup></sub> orbital corresponding to the central Ta atom in plane with the swelling of the S planes caused by the consequent delocalization in the vertical direction. The DOS plot for the metallic phase shows that the density at the Fermi level includes a significant contribution due to the d orbitals which, unlike what seen in the C-CDW phase, is not fully originated by the  $d_{z^2}$  orbital.



Figure 4.10: Band structure along high symmetry lines and density of states for the metallic phase. The contribution to the DOS due to the Ta d orbitals and that due to only the  $d_{z^2}$  is also plotted.

Comparing the ground state energies (Table 4.2), we see that the distorted C-CDW is indeed more stable at low temperatures compared to the metallic phase and that, even though it is not completely gapped, the density of states at the Fermi energy is reduced fivefold.

	C-CDW	Metallic
$E_0 (eV/TaS_2)$	-23.190	-23.145
$n(E_F)$ (states/eV/TaS <sub>2</sub> )	0.290	1.475

Table 4.2: Ground state energy  $E_0$  and density of states at the Fermi energy  $n(E_F)$  in the C-CDW and metallic phases.

#### 4.4.2 Role of spin-orbit coupling

Having investigated the ground states of the metallic and C-CDW phases, we now turn our attention to the effect of the spin orbit coupling on the energy levels of  $TaS_2$ . A previous 2D

tight binding calculation [88] suggested that this coupling could split the band corresponding to the  $d_{xy}$ ,  $d_{x^2-y^2}$  orbitals on the centralized atom, generating a narrow band of states at the Fermi level. DFT calculations on TaS<sub>2</sub> were performed in the presence of spin-orbit coupling [97] but its role on the band structure and density of states was not fully explored.

Figure 4.11 presents our results for the C-CDW phase both with and without spin orbit coupling. Bands below  $E_F$  (doubly occupied) and those above  $E_F$  (unoccupied) are slightly perturbed by introducing this coupling, while the upper half filled band is relatively insensitive to it. The density of states also shows a slight perturbation as a result but no significant changes are observed. To better understand the effect of the spin orbit coupling, we focus on the density of states around  $E_F$  in Fig. 4.12. The atom projected densities [panel (a)] confirm our previous observation that the DOS at the Fermi level is mainly localized on the central Ta atom (a-site - see Fig. 4.3). This remains the case even with the introduction of the SO-coupling, and its main effect is seen in a shift the first peak in the density above  $E_F$  from 0.2 eV to 0.25 eV. The orbital character of the density of states [panel (b)] shows that at  $E_F$  the states are still mostly of  $d_{z^2}$  character. We conclude that the splitting of the antibonding  $d_{x^2-y^2}$  and  $d_{xy}$  bands seen in the 2D tight binding calculations is suppressed in 3 dimensions, where the uppermost band retains its  $d_{z^2}$  character with a strong out of plane dispersion.

We also report the band structure and DOS for the metallic case in the presence of SOcoupling in Fig. 4.13. In this case, in agreement with the previous calculation by Rossnagel et al. [88], the SO-coupling is seen to lift the degeneracy of the  $d_{z^2}$  and  $d_{xy}$ ,  $d_{x^2-y^2}$  at the  $\Gamma$ point and induce an energy splitting of 0.3 eV.



Figure 4.11: Band structure along high symmetry lines and density of states for the C-CDW phase both with (black) and without (red) spin orbit coupling.



Figure 4.12: Detail of the density of states for the C-CDW phase both with (continuous lines) and without (dashed lines) spin orbit coupling. (a) Atom projected densities. (b) Orbital projected densities.

### 4.4.3 Role of Hubbard repulsion

Since spin orbit coupling acts as a perturbation and does not play a significant role in determining the ground state properties of  $TaS_2$ , we now turn our attention to understanding the effect that an on-site Hubbard repulsion has on the ground state of the C-CDW phase



Figure 4.13: Band structure along high symmetry lines and density of states for the metallic phase both with (black) and without (red) spin orbit coupling.

and whether there is evidence of a Mott gap opening. The results for varying values of the electron-electron interaction U are plotted in Fig. 4.14. The first thing we observe is that there is no evidence of a gap opening even at the highest value of U considered (U=5 eV). While this is in agreement with the data presented in a preprint by Darancet et al. [89], previous DFT+DMFT calculations [96, 108, 109] showed a gap opening by using a single band Hubbard model. The origin of the discrepancy it most likely due to the simplified model used in these papers that neglects the effect of the neighboring occupied d orbitals and of the coupling to any unoccupied states.

### 4.4.4 Role of stacking disorder

Since we do not see evidence of the formation of a Mott gap due to Hubbard repulsion, our results suggests that  $TaS_2$  is an in-plane insulator but presents metallic states in the out of plane direction and that the experimentally seen gap is originated in the disordered stacking sequence present in this material. We now proceed to test this hypothesis by using



Figure 4.14: Band structure along high symmetry lines and density of states for the C-CDW phase in the DFT+U approximation with varying values of the on-site electron-electron interaction U

the stacking sequence for  $TaS_2$  proposed in [80], in which the authors find good agreement with the structure factor calculated from the X-ray data in [78, 79] and suggest that the stacking is of type  $AC_iAC_j...$ , where A indicates stacking of layers with the central a-type atoms lying on top of each other, while  $C_i$  indicates configurations where the central a-type atom lies on top of a c-type atom (see Fig. 4.3 for the definition of a and c sites). There are six possible  $C_i$  type stackings due to the six c atoms present in each unit cell and in the discussion that follows we will collectively indicate them simply as C stacking. The order in which these C stacking units repeat is random.

As density functional theory calculations scale approximately as  $O(N^3)$ , where N is the number of atoms in the system, we are limited in how many layers we can consider. Therefore we limit ourselves to the three cases: systems with A stacking (which is what we have used in the calculations presented so far and corresponds to a configuration with no disorder), C stacking and AC stacking; the unit cells used for each system are shown in Fig. 4.15. Note that we use periodic boundary conditions in all three directions, which is the reason for using 4 layers in the unit cell for the AC stacking configuration.



Figure 4.15: Units cells for the stacking sequences considered: (a) A stacking, (b) C stacking and (c) AC stacking.

For each stacking configuration we calculate the band structure and density of states and present our results in Fig. 4.16. In the absence of stacking faults, as we already showed in the previous sections, the system presents a finite density of states at the Fermi energy and no evidence of gap opening. Considering two layers with C stacking, we see that each central a-atom contributes one weakly dispersing band around the Fermi energy. While the broad feature seen in the A stacking for an energy range of -0.25 eV to 0.125 eV is narrowed, the two bands in the C stacking are not fully separated in energy so that no gap opens in this case either. For the AC stacking there are four bands in the energy range -0.25 eV to 0.25 eV, and due to their mutual repulsion, we observe a gap in the density of states.



Figure 4.16: Band structure along high symmetry lines and density of states for the C-CDW phase with different stacking: (a) A stacking, (b) C stacking and (c) AC stacking. The last two panels also show a comparison to the DOS obtained with the A stacking (stacking without disorder).

To check whether the AC stacking is indeed a possible configuration for the system, we consider the ground state energy for each configuration and find values for the A and AC stackings of -301.465 eV/layer and -301.455 eV/layer, respectively, while the C stacking

presents a ground state energy of -301.402 eV/layer. This means that for T > 118K the A and AC stacking sequences differ by less than the thermal energy. For the C stacking to be within kT of the other two, a temperature of T = 730K is required. These results confirm that the ground state of TaS<sub>2</sub> does indeed exhibit random stacking and show that contrary to the conventional wisdom, the presence of a gap in the ground state of this material might be due to stacking disorder rather than Mott physics.

# 4.5 Phonons

Having investigated the ground state of  $TaS_2$  both in the C-CDW and metallic phases, we now want to understand how the system relaxes after being perturbed with a pump laser pulse. tr-ARPES data [95] of the C-CDW phase shows a breakdown and successive recovery of the metal insulator gap 680 fs after photo excitation and a subsequent long lived oscillation of the energy of the system, with a frequency of about 2.5 THz (see Fig. 4 in [95]). We want to explain how the excess energy of the hot electrons is transfered to the lattice and what determines the temporal evolution seen in the experiments.

By using density functional perturbation theory [106], we calculate the phonon band structure of both the C-CDW and the metallic phases and present it in Fig. 4.17. The acoustic mode dispersion curves for the metallic state [panel (a)] show characteristic instabilities expected from a system with CDW formation [75], and the wave vector associated with this instability coincides with the CDW wave vector. The negative values correspond to imaginary frequencies representing unstable modes. The optical branches located above 20 meV are mostly due to vibrations of the lighter S atoms. Overall these results show a mostly in-plane dispersion and localized phonon bands in the vertical direction ( $\Gamma$ -A) and agree with a previous calculation on phonons in the metallic state of  $TaS_2$  reported in the literature [92].



Figure 4.17: Calculated phonon band structure for the metallic (a) and C-CDW (b) phases. Imaginary frequencies, corresponding to unstable modes are represented by negative values. (c) Phonon density of states for the metallic (green) and C-CDW (black) phases. The continuous line represents the total DOS, while the dashed line shows the contribution due to the Tantalum atom vibrations.

On the other hand the phonon band structure for the C-CDW phase [panel (b)] displays a wealth of phonon branches due to the numerous atoms present in the unit cell. Only the lower ones are shown in Fig. 4.17(b); an upper band of modes in the range 20 meV to 50 meV is present but it is not of interest for the current discussion as it is mostly due to motions of the S atoms. Again we observe localized phonon bands in the vertical direction ( $\Gamma$ -A), indicating soft phonon modes. There is also evidence of avoided crossing in the in plane ( $\Gamma$ -M-K- $\Gamma$ ) direction, which points to strong interactions between phonon modes leading to mode mixing. In particular in the  $\Gamma$ -M segment, at about 2/3 of the way to M, we see an avoided crossing of the LA and LO bands, which presents itself again about halfway between M-K and at K. Other avoided crossings are also present in the higher energy optical modes.

The phonon density of states [Fig. 4.17(c)] shows weak mixing between the Ta and S atom vibrations, with a clear separation of the frequency ranges due to each one. Since the distortion of the CDW is due to motions of the Ta atoms, we focus on the low energy range and present in Fig. 4.18, in addition to the total phonon DOS, the projection of the DOS onto the atomic sites in the reconstructed unit cell. In the C-CDW phase, we observe numerous phonon peaks between 8 meV to 16 meV, with the principal one at 13 meV (corresponding to a frequency of 3.1 THz) due to a vibration of the central atom (a-site). In the metallic phase, on the other hand, the main mode is localized at 10 meV (2.3 THz), with a lower energy broad secondary peak at 6 meV (1.5 THz).

As the system is in the metallic state following the pump laser excitation, the phonon DOS for this state will determine what modes are most likely to be excited to dissipate the excess energy. Our data shows the mode at 2.3 THz to be the most likely candidate, in striking agreement with the experimentally measure oscillation frequencies reported by Perfetti (see Fig. 4 in [95]). In the C-CDW phase, this vibrational frequency corresponds to a superposition of modes involving all Ta atoms in the reconstructed cell. These modes then can dissipate their energy through interaction with lower energy modes, seen in the avoided crossings discussed in relation to the band diagram (Fig. 4.17).



Figure 4.18: Detail of the phonon density of states per  $TaS_2$  for the C-CDW phase in the range 0 meV to 18 meV (corresponding to 0 THz to 4 THz). The red lines indicate the site projected DOS.

# 4.6 Optical absorption

We conclude the discussion by presenting the results relative to the optical absorption profile of this system, with the goal of understanding the optimal conditions to excite this material in the experimental setup. The real and imaginary parts of the dielectric function are computed in the independent particle approximation [107] in which classical depolarization effects (local-field effects), electron-hole and electron-electron interactions are not included. The real part  $\epsilon_1(\omega)$  of the dielectric function describes the polarization induced by the field and is therefore related to electron dispersion inside the material, while the complex part  $\epsilon_2(\omega)$  describes the absorption properties. Other optical functions that can be calculated from the dielectric function are: • the complex refractive index  $n(\omega) + ik(\omega)$ :

$$\epsilon_1 = n^2 - k^2, \qquad \epsilon_2 = 2nk, \tag{4.1}$$

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}}, \qquad k = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}},$$
 (4.2)

• the optical absorption coefficient  $\alpha(\omega)$ :

$$\alpha = \frac{4\pi}{hc}\omega k(\omega),\tag{4.3}$$

• the electron energy-loss function:

$$\Im\left(-\frac{1}{\epsilon(\omega)}\right) = \frac{\epsilon_2}{\epsilon_1^2 + \epsilon_2^2},\tag{4.4}$$

• the reflectance  $R(\omega)$ :

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2},\tag{4.5}$$

Note that whenever necessary, we have dropped the frequency dependence from the previous equations for simplicity.

Our results for the in-plane direction are summarized in Fig. 4.19, where the first thing we note is a remarkable agreement between our simulated data and the experimental measurements found in the literature [see Fig. 10(b)-(d) of [76]]. The energies of the two main peaks of the imaginary part of the dielectric function in the C-CDW phase [panel (b)], corresponding to intraband transitions, are well described by our simulations and match with the experimental results. The shoulder present in the peak at 1.5 eV is also captured in our calculations. The main difference present is an overestimation of the value of the imaginary part and an underestimation the value of the real part. This has the effect of introducing additional zero-crossings of  $\epsilon_1$  at energies < 5eV that are not seen in the experimental data and is most likely due to the absence of impurities or defects in our simulated system. The high positive value of  $\epsilon_1(0)$  and the absence of a metallic behavior [ $\epsilon_1(0) < 0$ ], suggests that TaS<sub>2</sub> has a small optical band gap.

The absorption coefficient  $\alpha$  [panel (c)], is also accurately described, as the shapes of the secondary peak at 2.5 eV and of the broad feature between 5 eV and 20 eV are captured. Similar considerations hold for the energy-loss function in panel (d), where the small peak at 2.5 eV due to interband transitions is clearly captured, in addition to the plasmonic peak seen at 20 eV [76]. The strength of this peak is increased by an order of magnitude compared with the experimental data, which again can be explained by the absence of imperfections in the simulated material.

The results for the metallic phase are also reported in Fig. 4.19, but no experimental verification has been found in the literature for this data. Due to the smaller size of the unit cell used, the plots are overall noisier. The absorption coefficient and energy-loss function retain a behavior similar to that seen in the C-CDW phase, even though the details of the dielectric function are modified with the metallic phase displaying a peak in  $\epsilon_2$  at an energy of 0.75 eV, absent in the C-CDW state.

Given the good agreement with experiment, we conclude that the optical transitions in  $TaS_2$  are mostly single particle excitations from occupied valence states to unoccupied conduction states, with electron-electron and electron-hole interactions and polarization effects playing a minor role. Some differences were seen in the magnitude of the optical properties studied, which are due to imperfections in the sample used in the experiments that are not



Figure 4.19: In-plane optical parameters for TaS<sub>2</sub>: real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric constant for the metallic (a) and C-CDW (b) phases. The insets show a detail of the dielectric constant in the energy range relevant for pump-probe experiments. (c) Absorption coefficient (d) Energy-loss function

captured in the simulations. In general we expect the inclusion of local fields to not play a significant role in the in-plane components as the system is mostly homogeneous, while it could have an effect if one is interested in the out of plane optical properties [110]. The peak seen in  $\epsilon_2$  at 1.0 eV suggests that exciting TaS<sub>2</sub> with a wavelength corresponding to this energy, would give the highest absorption and allow probing the material with a lower laser power and higher efficiency. For completeness we also report the predicted out of plane optical parameters for  $TaS_2$ in Fig. 4.20. We note the overall lower value of the imaginary part of the dielectric constant, indicating, as expected, that the material is more absorbing in plane. The absorption coefficient and energy loss function show features very similar to those already discussed for the in-plane direction.



Figure 4.20: Out of plane optical parameters for TaS<sub>2</sub>: real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric constant for the metallic (a) and C-CDW (b) phases. The insets show a detail of the dielectric constant in the energy range relevant for pump-probe experiments. (c) Absorption coefficient (d) Energy-loss function

# Chapter 5

# Conclusions

The results presented in this thesis show how one can approach Ultrafast Science both from the perspective of instrumentation development, as the achievable spatial and temporal resolutions are fundamental quantities that determine what phenomena one can hope to observe, and from the perspective of materials applications that can be studied with the UEM system.

We started in chapter 2 by simulating the electron pulse photoemission process. By looking at the time dependent evolution of a single pulse and comparing it with experimental results obtained using the shadow imaging technique, we confirmed the validity of our approach and saw that overall, for short timescales, the spatial profile of the pulse is dependent on the transverse laser profile used to generate it, with velocities showing a turbulent flow related to the initial thermal distribution and independent of extraction field. At later times, as the pulse moves away from the surface, the pulse properties display a strong dependence on the extraction field: for high fields the pulse becomes fully laminar, evolving into the typical pancake shape, while for the lower extraction fields it retains some turbulent flow and does not fully detach from the surface. By fitting the resulting transverse profiles with Elliptical and Gaussian functions, we observed the surprising emergence of a 2D ellipsoidal profile from the complex interplay of image- and space charge effects.

Our investigation of the optimal conditions for pulse generation in terms of laser fluence and extraction field  $F_a$  for different experimental realizations showed evidence of virtual cathode (VC) formation as the initial number of electrons was increased due the space charge effect. By approximating the electron pulse as a sheet of charge, we derived a relationship connecting the extraction field to the critical number of electrons required for the onset of the VC.

We also analyzed the role of different photocathode geometries by observing the effect that pinning of the image charge on the surface had on the onset of the VC limit and on the final pulse parameters. In this case the positive image charge field provided a focusing effect, increasing the fraction of electrons at the center of the pulse and preventing the pulse from becoming fully pancake-like. Due to this both the transverse and longitudinal emittances were seen to increase significantly once the virtual cathode limit was reached compared to the case of radially expanding charge.

We showed that changing the shape of the transverse laser profile used to emit the electrons also has a significant impact on the normalized emittance. Using a laser pulse with a transverse elliptical profile gives the optimal pulse properties below the VC limit, while once this limit is reached both the elliptical and uniform (top-hat) profiles present a sharp scaling with the number of electrons, whereas the Gaussian profile retains a slightly less unfavorable scaling. An increase in the extraction field can shift the onset of the VC regime to higher numbers of electrons, thus increasing the favorable regime for the elliptical pulse. The longitudinal emittance was observed to scale linearly with the number of electrons for all laser profiles considered, with a weak dependence on the extraction field.

We conclude that optimal extraction conditions depend on a delicate balance between the image charge, which disrupts the favorable internal self-fields of both the elliptical and uniform cases, the number of electrons emitted and the extraction field, which controls the onset of the virtual cathode limit. Below this limit the image charge has a weak effect with the pulse properties primarily controlled by the laser parameters (transverse profile and fluence), while above the VC limit the image charge strongly perturbs the expansion of the pulse with a nonuniform dependence on the pulse profile. By calculating the brightness, coherence length and energy spread for the pulses considered, we provided quantitative guidelines for pulse generation.

In chapter 3 we built on our knowledge of the initial phases of pulse generation to simulate the UEM system. We derived a mean field formalism to simulate the propagation of the electron pulse through the microscope column, including the effects of the photoemission gun, magnetic lenses, RF cavity and relativistic motion of the electrons. By comparing the time evolution of the pulse described with this Analytic Gaussian model to our previous Nparticle simulations, we showed good agreement for extraction conditions under the virtual cathode limit for both the Elliptical and Gaussian laser profiles. After analyzing the effects of the different optical elements composing the microscope column, we built a model to describe our whole UEM column and gave quantitative predictions of the achievable spatial and temporal resolutions.

Moving forward, the next steps in the development of UEM systems will need to move on two fronts. On the photoemission side, a more detailed model for the positive image charge is needed and, since increasing the extraction field was seen to offer many advantages, strategies to do this should be considered, including the addition of an RF cavity to the photoemission gun, which would allow higher peak values of the electric field at the price of added complexity in the system. On the other hand, to better understand the operation of the whole UEM column, more accurate models and more sophisticated simulation tools (such as the COSY-MLFMM N-particle code) are necessary to analyze in more detail the configurations obtained with our simple Analytic Gaussian model. Given the limitations of this model, the predictions we calculated should be viewed as best case results, since aberrations and deviations of the pulse from the assumed self similar Gaussian profile were neglected. A careful process of modeling the details of the lenses and cavity used in the actual microscope is needed, so that details of their nonlinear effects can also be included in the simulations.

On the applications side, in the last part of this thesis (chapter 4), we showed our work in understanding the properties of  $TaS_2$ , a very promising material that can be studied with the UEM microscope. With our density functional theory calculations of the electronic band structure of  $1T-TaS_2$ , we shone light on the ground state of this material and quantified the effect of spin orbit coupling and Hubbard repulsion both in the metallic and in the commensurate charge density wave (C-CDW) phases. Since our results showed that neither of these interactions is sufficient to reproduce the insulating gap seen in experiment, we also analyzed the effect of different stacking configurations of the  $TaS_2$  layers and found evidence of gap opening for bilayers in the presence of disordered AC stacking. This points to a deviation from the conventional picture of  $TaS_2$  as a Mott insulator, as the measured gap could be due to the repulsion of the levels originating from interactions in the vertical stacking direction. To better understand the processes involved in pump-probe measurements of this material, we also looked at the phonon band structure and absorption spectrum and found a remarkable agreement with the experimental measurements, which allowed us to point out possible mechanisms for dissipation of the pump energy and recovery of the insulating ground state.

Our understanding of stacking disorder in  $TaS_2$  opens the door to the investigation of a variety of other layered materials (such as  $TaSe_2$  or  $TiS_2$ ) whose physics might also be influenced by interlayer coupling, a mechanism that hasn't been considered in the literature so far. In addition to this,  $TaS_2$  itself still presents numerous unanswered questions such as the emergence of superconductivity under pressure or doping, which might be better understood on the basis of our results. On a more general level, the role of disorder as a competing mechanism in addition to Mott and Peierls physics in correlated electron materials is an open question. Simulating disordered systems often requires significant computational resources, but the inclusion of this effect might be necessary to explain some of the experimentally observed material properties.

# APPENDICES

# Appendix A: Generation of electron coordinates

This appendix gives details on how the initial x and y coordinates are generated in the photoemission simulations for the three laser pulse shapes considered: Gaussian, Uniform and Elliptical.

#### A.1 Generation of random numbers with an arbitrary distribution

The standard random number generator available in any programming language will provide numbers with a uniform distribution in the interval (0, 1), but for many problems we wish to use numbers generated at random from an arbitrary distribution. This section will outline the method used to do so.

Starting with the given arbitrary normalized probability distribution, f(x), the first step is to calculate the cumulative probability:

$$g(x) = \int_{-\infty}^{x} dx' f(x'), \qquad (A.1)$$

where the function g(x) represents the sum of probabilities from  $-\infty$  to x and has values between (0,1), while x has values  $(-\infty, \infty)$ . We can now think of g(x) as a one-to-one mapping from the interval of values of  $x (-\infty, \infty)$  to (0,1). For this reason if we invert g(x)by setting g(x) = y and calculating x = h(y), we have a function that maps the y values belonging to the interval (0,1) into x. If we extract random numbers  $(y_1, y_2, ..., y_n)$  from a uniform distribution in the interval (0, 1), then the numbers  $(h(y_1), h(y_2), ..., h(y_n))$  will be random numbers from the original distribution f(x).

The tricky step in this procedure is inverting g(x), since for an arbitrary distribution it might not be possible to find an analytic expression for its inverse. In that case numerical methods would have to be used as an approximation.

### A.2 Gaussian laser profile

In the case of a Gaussian profile, the distribution of coordinates is given by

$$f(x,y) = \frac{1}{2\pi\sigma_r^2} \exp\left(-\frac{x^2 + y^2}{2\sigma_r^2}\right).$$
 (A.2)

We begin by rewriting this distribution in terms of polar coordinates r,  $\theta$ , where  $x = r \cos \theta$ ,  $y = r \sin \theta$ :

$$f(r,\theta) = \frac{1}{2\pi\sigma_r^2} \exp\left(-\frac{r^2}{2\sigma_r^2}\right).$$
 (A.3)

Since this distribution only depends on r, it is clear that we can simply choose  $\theta$  from a uniform distribution  $(0, 2\pi)$ , while for r we will use the procedure presented in the previous section.

We begin by calculating the cumulative probability distribution

$$g(r') = \int_0^{2\pi} d\theta \int_0^{r'} dr r f(r, \theta)$$
(A.4)

$$= \int_{0}^{2\pi} d\theta \int_{0}^{r'} dr r \frac{1}{2\pi\sigma_r^2} \exp\left(-\frac{r^2}{2\sigma_r^2}\right)$$
(A.5)

$$= \int_{0}^{r'} dr r \frac{1}{\sigma_r^2} \exp\left(-\frac{r^2}{2\sigma_r^2}\right)$$
(A.6)

$$= 1 - \exp\left(-\frac{r^{\prime 2}}{2\sigma_r^2}\right). \tag{A.7}$$

Now we set  $g(r') = \alpha$  and solve this for r':

$$\alpha = 1 - \exp\left(-\frac{r^2}{2\sigma_r^2}\right) \tag{A.8}$$

$$1 - \alpha = \exp\left(-\frac{r^2}{2\sigma_r^2}\right) \tag{A.9}$$

$$\log(1-\alpha) = -\frac{r'^2}{2\sigma_r^2} \tag{A.10}$$

$$-2\sigma_r^2 \log(1-\alpha) = r^2 \tag{A.11}$$

$$\sqrt{-2\sigma_r^2 \log(1-\alpha)} = r'. \tag{A.12}$$

Since  $\alpha \in (0,1)$ ,  $1 - \alpha \in (0,1)$  as well and we can substitute  $1 - \alpha$  with  $\alpha$ , giving us

$$r' = \sqrt{-2\sigma_r^2 \log(\alpha)}.\tag{A.13}$$

From this we can go back to our initial x,y coordinates using  $x = r' \cos \theta$ ,  $y = r' \sin \theta$  and

the final result is:

$$x = \sqrt{-2\sigma_r^2 \ln \alpha} \cos(2\pi\phi) \tag{A.14}$$

$$y = \sqrt{-2\sigma_r^2 \ln \alpha} \sin(2\pi\phi), \qquad (A.15)$$

where  $\alpha$  and  $\phi$  are random numbers generated uniformly in the interval (0,1). This is the well known Box-Muller transform.

### A.3 Uniform laser profile

Now we use the same procedure for the distribution consisting of a uniform circle in the xy plane, written in radial coordinates as

$$f(r) = \begin{cases} C = \frac{1}{\pi R_0^2} & r \le R_0 \\ 0 & r > R_0 \end{cases}$$
(A.16)

We note that similarly to the Gaussian case, the probability distribution does not depend on the angle  $\theta$ , which can then simply be taken a from uniform distribution  $(0, 2\pi)$ .

As before, we calculate the cumulative radial probability distribution

$$g(r') = \int_0^{2\pi} d\theta \int_0^{r'} dr r f(r) = \int_0^{r'} dr \frac{2r}{R^2} = \frac{r'^2}{R^2},$$
 (A.17)

and then invert this to get the function that maps the uniform distribution into our desired

one

$$\alpha = g(r') = \frac{r'^2}{R^2}$$
$$r' = R\sqrt{\alpha}.$$

In the end the initial x,y coordinates are given by

$$x = R\sqrt{\alpha}\cos(2\pi\phi) \tag{A.18}$$

$$y = R\sqrt{\alpha}\sin(2\pi\phi),\tag{A.19}$$

where  $\alpha$  and  $\phi$  are random numbers generated uniformly in the interval (0, 1).

### A.4 Elliptical laser profile

The final case we wish to consider is that of a laser with an elliptical profile, given by the distribution

$$f(r) = \frac{3}{2\pi R^2} \sqrt{1 - \left(\frac{r}{R}\right)^2} \qquad 0 \le r \le R.$$
 (A.20)

Since once again this does not depend on  $\theta$ , the angular part is easily treated with a uniform distribution.

For the radial part, we integrate f(r) to obtain the cumulative distribution g(r')

$$g(r') = \int_0^{2\pi} d\theta \int_0^{r'} dr r f(r)$$
  
=  $\frac{3}{R^2} \int_0^{r'} dr r \sqrt{1 - \left(\frac{r}{R}\right)^2}$   
=  $-\frac{(R^2 - r^2)^{3/2}}{R^3} \Big|_0^{r'}$   
=  $1 - \frac{(R^2 - r'^2)^{3/2}}{R^3}.$ 

We now follow the usual procedure to invert g(r')

$$\begin{split} \alpha &= g(r') = 1 - \frac{(R^2 - r'^2)^{3/2}}{R^3} \\ (1 - \alpha) R^3 &= (R^2 - r'^2)^{3/2} \\ (1 - \alpha)^{2/3} R^2 &= R^2 - r'^2 \\ r'^2 &= R^2 \left[ 1 - (1 - \alpha)^{2/3} \right] \\ r' &= R \sqrt{1 - (1 - \alpha)^{2/3}}, \end{split}$$

and by using the same substitution used in the Gaussian case,  $(1 - \alpha) \rightarrow \alpha$ , the equations for the initial coordinates become

$$x = R\sqrt{1 - \alpha^{2/3}}\cos(2\pi\phi) \tag{A.21}$$

$$y = R\sqrt{1 - \alpha^{2/3}}\sin(2\pi\phi),$$
 (A.22)

where  $\alpha$  and  $\phi$  are random numbers generated uniformly in the interval (0, 1).
# Appendix B: Overview of Density Functional Theory

In this appendix we will give a brief overview of the theory and approximations that govern Density Functional Theory. For an in depth discussion of both the fundamentals and the applications of DFT to a variety of systems, the reviews by Gillan [111] and Hafner [112] offer an solid starting point. Also the Nobel prize talks by Kohn [113] and Pople [114] give an excellent discussion of the development of methods to simulate the electronic structure of materials and of the derivation of the DFT equations. More information on the technical aspects of the computation and its implementation in computational codes can be found in the review by Cramer and Truhlar [115] and in the papers by Kresse et al. [98–101, 116], Bloechl [103] and Perdew et al. [102].

#### **B.1** From wavefunctions to a density functional

In principle, if one wishes to study materials using an ab-initio method, all that is required is to write out the Schroedinger equation for the system and solve it. The resulting ground state energy and wavefunctions uniquely determine all the properties of the system under consideration. The term ab-initio here is taken to mean methods in which, in addition to the nuclear mass and coordinates, only the fundamental physical constants enter the calculation and no empirical parameters are included in the solution.

For a system of  $N_{el}$  electrons and  $N_{at}$  nuclei, the non-relativistic and time independent Hamiltonian and Schroedinger equations can be written as

$$\hat{H} = -\frac{1}{2m_{el}}\sum_{i=1}^{N_{el}} \nabla_i^2 - \frac{1}{2}\sum_{i=1}^{N_{at}} \frac{\nabla_i^2}{M_i} + \sum_{i=1}^{N_{el}} \sum_{i\neq j}^{N_{el}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N_{at}} \sum_{j\neq i}^{N_{at}} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_{i=1}^{N_{at}} \sum_{j=1}^{N_{el}} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|}$$
(B.23)

$$\hat{H}\Psi_{\alpha} = E_{\alpha}\Psi_{\alpha},\tag{B.24}$$

where the first two terms are respectively the kinetic energy of the electrons of mass  $m_{el}$ and that of the nuclei of mass  $M_i$ . The following terms include electrostatic interactions between the electrons and nuclei with spatial coordinates  $r_i$  and  $R_i$ .  $\Psi_{\alpha}$  is the wavefunction corresponding to the  $alpha^{th}$  state of the system.

Since we are mostly interested in properties arising from the electronic distribution and nuclei are approximately  $10^4$  times heavier than electrons, with a size that is approximately  $10^{-5}$  times the size of the electronic orbit, we integrate out the nuclear motion and treat them as stationary point particles. This is the so-called Born-Oppenheimer approximation, using which we rewrite the Hamiltonian as

$$\hat{H}_{el} = -\frac{1}{2m_{el}} \sum_{i=1}^{N_{el}} \nabla_i^2 + \sum_{i=1}^{N_{el}} \sum_{i\neq j}^{N_{el}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N_{at}} \sum_{j=1}^{N_{el}} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|}$$
(B.25)

$$= -\frac{1}{2m_{el}}\sum_{i=1}^{N_{el}}\nabla_i^2 + \sum_{i=1}^{N_{el}}\sum_{i\neq j}^{N_{el}}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{N_{el}}V_{ext}(\mathbf{r}_i),$$
(B.26)

and

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}.\tag{B.27}$$

The problem we face now is solving this Schroedinger equation to find the antisymmetric electronic wavefunction  $\psi_{el}$ , which depends on the positions and spins of the  $N_{el}$  electrons for fixed nuclear positions  $\mathbf{R}_i$ . This is a prohibitive task for any system consisting of more than O(10) electrons [113], leading to the idea of describing the system using the density as it only depends on 3 coordinates regardless of the size of the system:

$$n(\mathbf{r}) = N_{el} \int \cdots \int \psi_{el}^* \left( \mathbf{r}, \mathbf{r}_2, \cdots \mathbf{r}_{N_{el}}; \sigma \right) \psi_{el} \left( \mathbf{r}, \mathbf{r}_2, \cdots \mathbf{r}_{N_{el}}; \sigma \right) d\mathbf{r}_2 \cdots d\mathbf{r}_{N_{el}} d\sigma, \qquad (B.28)$$

where the integrals are over the  $N_{el} - 1$  spatial degrees of freedom and the spins (indicated collectively by  $\sigma$ ).

Hohenberg and Kohn [117] showed that the ground state density uniquely determines the Hamiltonian of the system and its ground state energy  $E_0$  and that therefore we can rewrite the problem posed by equations B.26 and B.27 as:

$$E_0 = \min_{n(\mathbf{r})} E[n(\mathbf{r})] \tag{B.29}$$

$$E[n(\mathbf{r})] = E_{kin}[n] + E_{ee}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r},$$
(B.30)

where the unknown is now represented by the density  $n(\mathbf{r})$ .

#### **B.2** The Kohn-Sham equations

Up to this point, the equations written are exact and no approximations have been made. They are also impossible to solve, as the kinetic and electron-electron contributions to the total energy in Eq. B.30 can't be written in an exact form as functionals of the density. To get around this it is necessary to find approximate expressions for  $E_{kin}[n]$  and  $E_{ee}[n]$ . Following the work done by Kohn and Sham [118], we start by rewriting the electron-electron interaction as a sum of the Coulomb interaction term and two non-classical terms that include the electron exchange and correlation effects:

$$E_{ee}[n] = E_{Coul}[n] + E_X[n] + E_C[n]$$
(B.31)

$$= \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_X[n] + E_C[n].$$
(B.32)

We can now rewrite the kinetic energy term as the kinetic energy of independent particles,  $E_{kin,KS}[n]$ , plus the difference of this from the original kinetic energy:

$$E_{kin}[n] = E_{kin,KS}[n] + (E_{kin}[n] - E_{kin,KS}[n]).$$
(B.33)

Putting all of this together gives:

$$\begin{split} E[n] &= E_{kin}[n] + E_{ee}[n] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\ &= E_{kin,KS}[n] + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \\ &+ E_X[n] + E_C[n] + E_{kin}[n] - E_{kin,KS}[n] \\ &= E_{kin,KS}[n] + \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{XC}[n] \\ &= E_{kin,KS}[n] + \int \left[\frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{ext}(\mathbf{r}) + V_{XC}(\mathbf{r})\right] n(\mathbf{r})d\mathbf{r}, \end{split}$$

where the last three terms in the second row have been grouped into the unknown functional

$$E_{XC} = E_X[n] + E_C[n] + E_{kin}[n] - E_{kin,KS}[n] = \int V_{XC}(\mathbf{r})n(\mathbf{r})d\mathbf{r}.$$
 (B.34)

Using the fact that  $E_{kin,KS}[n]$  corresponds to the kinetic energy of independent particles, we can now treat the system as being composed of  $N_{el}$  independent particles such that:

$$\hat{H}_{eff} = \sum_{i=1}^{N_{el}} \hat{h}_{KS}(\mathbf{r}_i) \tag{B.35}$$

$$\hat{h}_{KS}\psi_j(\mathbf{r}) = \left(-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right)\psi_j(\mathbf{r}) = \epsilon_j\psi_j(\mathbf{r})$$
(B.36)

$$V_{KS} = \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{ext}(\mathbf{r}) + V_{XC}(\mathbf{r}).$$
(B.37)

This form of  $V_{KS}$  is chosen so that the density obtained from this system of non-interacting fictitious particles is the same as the ground state density in the true system of interacting electrons. Approximations now enter our calculations in the choice of the expression for  $V_{XC}(\mathbf{r})$ .

A couple of notes to conclude the discussion:

- The Kohn-Sham single particle orbitals,  $\psi_j$ , should not be considered representative of real electron orbitals in the system. Rather they are a mathematical construction used to give the correct ground state density. Also the independent particles used in this description are Kohn-Sham fictitious particles, not real electrons.
- Since  $V_{KS}$  depends on the density, it is necessary to do a self-consistent calculation in which one starts from a guess for the orbitals  $\psi_j$ , then solves the Schroedinger equation (Eq. B.36) to calculate the new orbitals  $\psi_j^{new}$  and iterates this procedure

until convergence is reached.

- In the work presented in chapter 4, the exchange-correlation functional,  $E_{XC}$ , was described using the generalized gradient approximation (GGA) as implemented by Perdew, Burke and Ernzerhof (PBE) [102]. A discussion of the various choices that can be made in terms of exchange-correlation functionals is beyond the scope of this overview, but can be found in numerous reviews (see for example [115]).
- In addition to the approximation resulting from the choice of  $E_{XC}$  or, equivalently,  $V_{XC}$ , the single particle wavefunction is also expanded on a set of basis functions that must be chosen appropriately. In the work presented here, we used plane waves with the projector augmented wave method [103] as the basis set.

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