Numerical Simulation of Fermionic Wave Functions in Potential Wells: Bound State Transitions induced by Multi-Photon Excitation from Laser Sources operating within the Non-Perturbative Regime

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To Cai, Marti and Dale Karasek.
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List of Acronyms

MPI Multi-Photon Ionization.
ATI Above-Threshold Ionization.
MPI Multi-Photon Ionization.
MPE Multi-Photon Excitation.
MFT Mean Field Theory.
DFT Density Functional Theory.
SAE Single-Active Electron.
NLO Nonlinear Optics.
SHG Second Harmonic Generation.
THG Third Harmonic Generation.
MHG Multiple Harmonic Generation.
LOHG Low-Order Harmonic Generation.
HOHG High-Order Harmonic Generation.
QFT Quantum Field Theory.
QED Quantum Electrodynamics.
QCD Quantum Chromodynamics.
GPGPU General Purpose Graphics Processing Unit.
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Finally, my wife, family and parents, for their love and support despite never wanting to listen long enough to hear what exactly it was I was working on.
“If you cannot explain it simply, you don’t understand it well enough”

Albert Einstein

“What we observe as material bodies and forces are nothing but shapes and variations in the structure of space.”

Erwin Schrödinger

“God used beautiful mathematics in creating the world.”

Paul Dirac

“Young man, in mathematics you don’t understand things. You just get used to them.”

John von Neumann

“... and as we learned from Deepak Chopra, Quantum Mechanics means that anything can happen at any time for no reason at all!”

Professor Hubert J. Farnsworth
Abstract of the Thesis

Numerical Simulation of Fermionic Wave Functions in Potential Wells: Bound State Transitions induced by Multi-Photon Excitation from Laser Sources operating within the Non-Perturbative Regime

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Energy state transitions leading to linear and nonlinear optical effects have had a major impact on many fields in optics since their discovery. We developed a numerical simulation to investigate how Time-Dependent Schrodinger Equations (TDSE) of electrons traveling within atomic and molecular potential wells, propagated with Finite Difference Methods, and excited with different types of laser sources, can show photonic output and the possibility of output which is nonlinear with respect to the excitation from the source.

In particular, here we are interested in resonance conditions of these systems. The parameters of a laser source, as well as the source type, have a substantial impact on the wave equations of the particles within a system. With the right conditions, and knowledge of the systems current energy state, we can effectively choose what energy state to move the system to. We can likewise reduce the energy state by choosing conditions matching transitions to lower states, reducing the energy state of the system and stimulating photonic output.

In this thesis we will show the effects of laser source conditions both in and out of resonance, in several different atomic systems with potential wells, and resulting photonic output from state transitions for each combination of parameters. The source will be strong enough to have a substantial impact on the system, thus leaving the perturbative range of intensity, yet not so strong as to completely overpower the system’s coulomb potential, staying out of reach of the strong field range of intensity where system potential wells are next to irrelevant.
Chapter 1

Introduction

1.1 Description of Problem

Electronic structure shifts in atomic, molecular and nanoscale unit cell structures, while of great and still growing importance to many fields in optics, are difficult to simulate with precision in anything more complex than the first few elements. Both the complexity of interactions and exponentially increasing memory requirements contribute to this problem. While on a classical scale the effects from such methods may be estimated statistically from the correspondence principle [1], this is more inaccurate with smaller sample sizes, and completely ignores the cumulative pieces which contribute to certain phenomena.

The ability to predict which effects will be seen from a situation where an atomic or molecular source is struck by photon packets from a laser source would be an extremely useful tool. One could determine in advance what should be seen, and verify. Or, one could even find new combinations that were not thought of before.

Absorption and emission of photons from electrons within atomic systems are simulated in our model. Absorption occurs between the incident laser field and the electron, while emission from the electron is limited to stimulated emission [I]. A fully accurate treatment of spontaneous emission requires a full quantum electrodynamics approach [2]. We will include this in a future version of our model.

A quantum treatment of the systems under study is required to provide full understanding of these processes. Our technique utilizes the Quantum Finite-Difference Time-Domain (FDTD-Q) method, an iterative scheme similar to Yee's cube for electromagnetic finite difference methods. Nonrelativistic Schrödinger equations are used for a quantum treatment of electron wave functions.
As the models simulated include the infinite square well and the hydrogen atom, radial symmetry allows for a 1-dimensional model.

Because we operated in the non-perturbative regime of laser intensity, the correspondence principle worked in our favor, allowing a classical description of laser field, rather than requiring a full quantum description \[1\] \[2\]. Future versions of our model are planned to have a full quantum treatment.

We test our model on several linear systems, including an infinite square well. Resonant and non-resonant laser fields were applied to both models with varying intensities, and energy output corresponding to photon emission was calculated from each combination of laser field parameters.

1.1.1 Goals of Study

We developed a model simulation of various atomic potential wells, excited by incident laser sources with adjustable wavelength, intensity, pulse shape, and direction. They were able to show, with the notable exception of spontaneous emission, what happens and when it happens. This simulation should be very useful for our experiments utilizing nonlinear phenomena, and help us understand better what is occurring at a fundamental level.

1.1.2 Experiment Setup

In this study, due to the relative simplicity of structures and symmetry conditions exploited, only one workstation was used. It contained an Intel i7 4790 (4.0GHz, overclocked to 4.8GHz on an ASUS Maximus VII Hero motherboard), and 32GB of system memory (Corsair CMZ32GX3M4X1600C10) \[3\] \[4\] \[5\]. Parallel methods were tested on an NVidia GTX Titan Black (2880 CUDA cores, 890MHz, 6GB memory) \[6\]. Large dataset size was handled with a RAID-5 of four Western Digital RE4’s, providing 6TB of storage with acceptably quick access times. Due to excessive power requirements for a single workstation, a Corsair AX1200i PSU was used, and the exorbitant amount of heat generated from the setup was cooled with a Swiftech H220-X, with an added full cover block for the GTX Titan Black \[7\]. At 100% load, temperature dropped from well over \(~100^\circ C\) to \(~80^\circ C\) on the CPU, and more than \(~100^\circ C\) to \(~65^\circ C\) on the GPU.

As a result of the overclock and cooling, and especially the parallelized algorithms, a single workstation was capable of running the simulations. However unless computer power improves significantly, larger simulations would benefit from a cluster or using core-hours on a supercomputer.
CHAPTER 1. INTRODUCTION

1.2 Summary

1.2.1 Project Origin

This project originally started as a study of second harmonic generation in different types of organic media [8]. A search for more and more accurate descriptions of the origin of frequency multiplied photons led to the atomic and molecular level. The intention was to construct a single unit cell of Collagen type 1- α , and model the effects [9]. From this single unit cell, the response from the rest of the structure could be estimated. One feature of the larger structure which this would assist is the determination of the arrangement of fibrils within the structure [10]. For an overview of unit cells, and the structure of the collagen helix, please refer to Appendix D.

Simple systems may be solved for one electron, or the SAE approximation, so this was the place to begin. Eventually, larger structures could be approximated with DFT or MFT.

After attending CCP2014 (Conference on Computational Physics 2014, at Boston University in Boston, MA) it became clear that the eventual goal would require a system to be built using fully quantized schemes and methods, not to mention relativistic effects such as spin and electron-electron interactions.

A single-electron model implemented using CPU-only methods was presented at Photonics West 2015, where we proved bound-state transitions between energy levels could be achieved with the proper wavelength and intensity formulation of source interacting with our system [11]. From these transitions, harmonic spectra could be predicted.

The latest version as of the time of writing is a parallelized scheme capable of working with arbitrary wells, thanks to higher-order imaginary time methods.

1.2.2 Model Formulation

A one-dimensional model with radial symmetry was chosen for this phase of the study. Incident upon the model was an external source, a laser modeled semi-classically, which supplied a wave of photons with specified wavelength and intensity over time. The external source was coupled to the system’s coulomb potential field via the Coulomb Gauge in the dipole approximation, although other Gauges and multi-pole approximations are given as well. Due to the maximum system size and minimum photon wavelength here, the long-wavelength approximation was also valid.
CHAPTER 1. INTRODUCTION

1.2.3 Example Structures

A Square Well and Hydrogen atom were demonstrated, although any system with one electron may be accurately simulated. Multi-electron systems may be estimated with the SAE model, but its accuracy is limited. Relativistic effects such as spin and electron-electron interactions must be accounted for in order to accurately calculate multi-particle systems.

To ensure effects from nuclear motion and other larger structure concerns do not interfere with the solution, the maximum time is kept below $\sim 25 \cdot 10^{-15}$ (s) . Absorption and stimulated emission are demonstrated, but spontaneous emission cannot be accurately accounted for without a fully quantized method, such as QED.

1.2.4 External Sources

External sources tested are a continuous wave laser, and a chirped-pulse laser. However, the chirped-pulse source was prone to inducing ionization and stronger effects than the continuous wave source, and was dropped from the current study. Chirped-pulse sources are far more useful for studying HOHG than LOHG.

The sources operated in the non-perturbative regime and touched on both the high end of the perturbative regime and touched on the very low end of the strong field regime:

$$\sim 5 \cdot 10^{11} \left( \frac{W}{cm^2} \right) \leq I_0 \leq \sim 5 \cdot 10^{14} \left( \frac{W}{cm^2} \right)$$

Within this range, neither the system’s coulomb field nor the external source field are clearly dominant, and so the non-dominant contribution may not be ignored. Both contributions must be taken into account for an accurate answer. This regime was chosen due to the importance of bound-state transitions, which are the most common source of LOHG such as SHG or THG. Outside of the non-perturbative regime non-harmoinc effects may be seen from from lower, perturbation regime effects, or in higher regimes strong field effects such as total ionization, or even complete electron-stripping from extreme potential warping in the relativistic regime.

1.2.5 Algorithms, Schemes and Methods

Finite Difference Methods were used to calculate the distribution of wave functions in the model, since a field theory solution was the goal, and a time-domain approach was used for ease of interpretation.
CHAPTER 1. INTRODUCTION

The FDTD-Q scheme was deemed the most appropriate scheme, as a $2^{nd}$ Order Space, $1^{st}$ Order Time method. Higher order methods are available, but may be difficult to implement, especially for transient problems with time-dependent potentials.

1.2.6 Computational Speedup

Though the simulation was able to run in decent time without parallelization, the substantial reduction in time offered was extremely attractive. A comparison is given of CPU-only serial methods, pre-built GPU methods already present in MATLAB, and custom-built MEX C-libraries & CUDA kernels.

The algorithm to be parallelized is as important as the hardware or strategy to parallelize with. It is always advised to develop using a CPU-only version of code first, before attempting parallelization.

Afterwards, pre-built functionality already within MATLAB (2012b and up) is very useful, offering noticable speedups of several to a dozen times if done properly. Care must be taken, as memory leakage can become a huge problem very easily. Custom-built solutions are extremely time-consuming, often taking as much time as the math and science portions of a project in their own right. However, the speedups offered by such techniques are unparalleled in their efficiency and power, literally several dozen to as much as thousands of times faster for certain operations.
Chapter 2

Nonlinear Optics

2.1 Quantum Optics

2.1.1 Overview of Quantum Theory

Nonlinear optics may be approximated using classical models \[12\] \[13\]. However, for a complete understanding of the underlying principles, we need a quantum treatment of a system’s components. The system hamiltonian \((\hat{H})\) is related to the energy within the system \((E)\) \[14\],

\[ E\Psi = \Psi \hat{H} \quad . \]  \hspace{1cm} (2.1)

A Hamiltonian of a system is the sum of its kinetic and potential energy,

\[ \hat{H} = T + V \quad . \]  \hspace{1cm} (2.2)

From this basic concept, wave and field equations \(\Psi\) may be defined at every point in space, the variety of which depending on the effects to be incorporated and accounted for in the system. For systems investigated in this study, relatively lower energy fermions (nonrelativistic electrons) interacting with bosons (photons) were used. Therefore the nonrelativistic time-dependent Schrodinger equation will accurately predict the behavior of these systems \[15\]. This is appropriate for single fermions in lower energy conditions, where relativistic effects, self-interaction and spin may be safely ignored; other wave functions such as the Dirac or Bethe-Salpeter equations may be used for relativistic electrons or where spin may not be ignored \[16\].
CHAPTER 2. NONLINEAR OPTICS

\[ i\hbar \frac{\partial}{\partial t} \psi(r, t) = \left[ -\frac{\hbar^2}{m_e} \nabla^2 + V_{\text{eff}}(r, t) \right] \psi(r, t) \]  

(2.3)

This is a classic hyperbolic partial differential equation, multiplied by several constants including Planck’s constant \((\hbar)\), and the particle’s mass \((m_e)\) (in this case an electron). On the left the function’s derivative with respect to time is taken, while on the right the laplacian results in the derivative with respect to all spatial dimensions.

Since equation [2.1] is functionally equivalent to equation [2.3], then the nonrelativistic Schrodinger must contain both the kinetic and potential energy terms found in equation [2.2]. The kinetic energy of the particle under study may be determined from its mass and change in position [17],

\[ \langle T \rangle = \left\langle \Psi \left| -\frac{\hbar^2}{2m_e} \nabla^2 \right| \Psi \right\rangle = -\frac{\hbar^2}{2m_e} \nabla^2 \int_{0}^{\infty} \Psi^* \nabla^2 \Psi \cdot \delta r \]  

(2.4)

The other energy component in the Hamiltonian is the potential operator \((V_{\text{eff}})\). It is the combination of the coulomb and external field potentials,

\[ V_{\text{eff}}(r, t) = V_{\text{system}}(r, t) + V_{\text{laser}}(t) \]  

(2.5)

where \((V_{\text{system}})\) and \((V_{\text{laser}})\) are the coulomb potential and potential resulting from the external source, in this case a laser. Nuclei within the system define the coulomb potential contribution to the potential operator. The coulomb potential is modified here, since classically it would have a singularity at the origin. Turning it into a "soft core" potential involves adding a small correction factor \((\kappa = 0.1 \cdot a_0)\), fixing the singularity and allowing us to model the nucleus in a more reasonable fashion [18].

\[ V_{\text{coulomb}}(r) = \frac{Z(Z_{\text{protons}})e^2}{\hat{r}} = \frac{Z(Z_{\text{protons}})e^2}{\sqrt{\hat{r}^2 + \kappa^2}} \]  

(2.6)

The number of protons \((Z)\) define how strong this potential will be, as the only baryons in the system with an electric charge. External fields define the remaining contribution to the potential operator, defined in the next section. We used a laser source, which projects photon packets at
CHAPTER 2. NONLINEAR OPTICS

our target. Photons are bosons and normally relativistic conditions cannot be ignored, requiring a quantum field theory approach such as quantum electrodynamics \[2\]. However, if a large enough number of photons are sent at a time, they may be modeled as a classical field \[1\]. This will remain accurate provided a sufficient number of photons are said to exist within the packet, which would result in less error from noise sources deriving from quantum effects \[19\].

2.1.2 Representations & Energy

The wave function may be described in terms of its eigenfunctions,

\[ \Psi_N = \sum_{i=0}^{n} C_n \cdot \psi_n, \]  

(2.7)

where \((C_i)\) are the coefficient of the eigenfunction, and their total is constrained by,

\[ \sum_{i=0}^{\infty} |C_i|^2 = 1 \]  

(2.8)

Furthermore, calculation of operators allow definition of the physical observables of a system \[20\] \[21\]. Fourier transforms may be used for spectral analysis of the wave function, giving the eigenfrequencies \[17\]. Fourier analysis may then be run at desired frequencies to determine how much of the total wave function is comprised of particular eigenfrequencies \[22\].

\[ \Phi_{f_n} = \int_{0}^{\infty} \psi(t) \cdot e^{i2\pi f_n t} \cdot \delta t < n = 1, 2, 3, \cdots, N >, \]  

(2.9)

The contribution of each eigenfrequency component to the total allows us to define the system’s harmonic output \[23\]. To calculate the energy we use the effective potential operator and kinetic energy operator. The expectation value of the energy in the system may then be obtained \[14\],

\[ \langle E \rangle = \frac{\langle \psi \mid \hat{H} \mid \psi \rangle}{\langle \psi \mid \psi \rangle} = \frac{\int \psi^* \cdot \hat{H} \cdot \psi}{\int \psi^* \cdot \psi}. \]  

(2.10)

Here \(\langle E \rangle\) signifies the statistical average, or most likely value of \(E\), at a given point in time over a given space.
2.1.3 Energy States: Bound vs. Continuum

The energy an electron possesses is related to its momentum, and distance from any potential sources nearby. This is in direct analogy to the energy a rock possesses when situated on a hill. The rock’s total energy is the sum of kinetic and potential energies.

Electrons remain in bound states when the potential field exerted on them is greater than the energy they possess themselves. These states are discrete and specifically defined for each system (described later in Chapter 5), specifically as the eigenstates of that system. When the electron obtains enough energy to jump to a higher state, it will do so, unable to exist in the space between states for longer than the time dictated by the uncertainty principle,

\[ \Delta E \Delta t \geq \frac{\hbar}{2} . \]  

If the electron gains more energy than the potential holding it in place, it will ionize, or leave its system. Its net potential became positive. It is then said to be in a continuum of states, since the states are no longer discrete, but continuous.

\[ E = h\omega_p = \Delta E = E_{\text{current}} - E_{\text{new}} . \]  

2.2 Energy Processes

When the electrons energy increases, it is absorbing photons supplied by the external field \[E_p = h\omega_p = \frac{2\pi hc_0}{\lambda_p} .\]  

When the electron’s energy decreases, it releases a photon with energy equal to loss in its own energy. Figure 2.1 shows the energy a photon possesses vs the wavelength it will exhibit.

2.2.1 Absorption

When a photon strikes an electron, it is usually first absorbed. Figure 2.2 is a diagram of an electron absorbing a photon, and moving from the ground to the 1st excited energy state.

More than one photon may be absorbed at a time, though the process here is slightly more complex, and is discussed in 2.3.3.
2.2.2 Stimulated Emission

Stimulated emission, sometimes called photon duplication, is much more clear a concept from the alternative name. Consider a system which exists in a bound state other than the ground state. The energy difference between that state and the ground state (or another bound state with less energy than the current state) corresponds to a wavelength of photon, as seen in Figure 2.1. If a photon strikes the system with this wavelength, the transition frequency between the states is met. The electron is then induced to the lower state, emitting a photon in the same direction as the incident photon, and with the exact same wavelength and frequency characteristics \cite{12}.

Unlike absorption, there is no multi-photon version. More photons would either interfere, or cause a gain in energy right after the initial loss from the system’s perspective.

2.2.3 Spontaneous Emission

Spontaneous emission arises from interactions between energy states and vacuum excitations in the background \cite{24}. An accurate account may only be realized within a quantum electrodynamics formulation, and is ignored for now \cite{25}. Future iterations of this simulation will need to take into account both relativistic effects, field theory concepts from quantum elec-
CHAPTER 2. NONLINEAR OPTICS

![Diagram of 1-Photon Absorption example](image)

![Diagram of 2-Photon Absorption example](image)

Since it is not taken into account in the simulation except incidentally, a brief description and mathematical background is given in Appendix C.

2.2.4 Resonant vs. Non-Resonant

The diagrams of state transitions in Chapter 2 were all of resonant cases. In fact unless we design an experiment in the laboratory, we are far more likely to see nonresonant cases than resonant ones. If an electron gathers too little energy, it will simply decay to the lower state it was just in. If it gathers too much energy, it will emit the excess in the form of a photon. However, the dynamics in nonresonant transitions can become quite complex and difficult to trace, unless one observed the event as it took place. For example, several photons striking a system may induce stimulated emission, and initially succeed in duplicating a photon. However, if the external source continues to pump energy into the system in the form of photons, one of the next photons to strike
the system may actually be absorbed and excite the system to a completely different energy state, or a virtual state which collapses due to an insufficient amount of energy received to make the transition to a real state.

Resonance isn’t a matter of just matching the energy of photons, it’s a matter of matching the energy and Intensity (or arrival rate, when taking into account the system and beam dimensions in concert with intensity). This is why very intense sources of lower wavelength can still produce significant effects on their targets.

2.3 Excitation and Ionization Mechanics

Excitation is the phenomenon where an electron moves from a lower energy state to a higher energy state, as it was excited, or gained energy, immediately prior to doing so. Afterwards de-excitation will occur, when the electron drops from a higher energy state to a lower energy state, releasing energy in the form of photons in the process.

Ionization is defined as the electron leaving the potential well, having obtained more energy
than the well exerts on it. It is not guaranteed that the photon will return, but if so, it will nearly always release much more energy than excitation.

2.3.1 Quantum Tunneling

Tunneling ionization, as shown in Figure 2.6, is the only process to occur when the force exerted by the potential is much larger than the electron’s energy. The wave function is unable to move to any higher states, let alone leave the system under normal circumstances. However, a small yet nonzero chance remains that part of the wave function will escape regardless, to higher energy states or a smaller chance still to leave the system on a whole.

An external source is not necessarily required, but it makes the process much more likely. If the source is very strong we begin to see over barrier ionization, as shown in Figure 2.7, where the system ionizes extremely quickly.

2.3.2 Single Photon

Single photon excitation, as seen in Figure 2.8, describes the process where a photon with sufficient energy strikes a bound electron, giving it enough energy to jump to a higher bound state.
CHAPTER 2. NONLINEAR OPTICS

Single photon ionization, displayed in Figure 2.9, describes the process where a photon with sufficient energy strikes a bound electron, giving it enough energy to break free of its nucleus entirely. The photon energy defines which process will occur.

2.3.3 Multi-Photon

Multiple photons may strike the electron in a very short time. If the total energy collected within that time is sufficient in order to induce a transition between a lower bound state to a higher bound states, such as in Figure 2.10. If however the energy is large enough, complete ionization from the well will occur, demonstrated in Figure 2.11. Stark shifts and other phenomena can affect ionization in more extreme conditions, such as higher intensities.
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Figure 2.10: Multi-Photon Excitation example

If the total energy collected from those photons is large enough to induce a transition between a lower bound state to a higher bound states, or complete ionization from the well, it will occur just as if the energy was contained within one photon.

Figure 2.11: Multi-Photon Ionization example

However, the length of time in which the photons are absorbed is important. If the electron does not absorb enough energy to completely transition states, it enters a virtual state. This virtual state may only exist for a time period related to the energy absorbed thus far, and dictated by the uncertainty principle.

\[
\Delta E + p \Delta t \geq \hbar \rightarrow \Delta t \Delta \omega_p \leq 1 \rightarrow \Delta t \leq \frac{1}{\Delta \omega_p}.
\]  

(2.14)
CHAPTER 2. NONLINEAR OPTICS

If an absorbed photon has less energy, the electron has a shorter allowable lifetime for a virtual state. Therefore unless one uses truly high energy sources, virtual states requiring large numbers of photons to complete the transition to the next real state will decay very quickly. This is why high order harmonic generation is a very rare event, and why the infrared photons striking all around us do not spontaneously combine into hard X rays. Actually this is statistically likely to occur on a classical size scale, only very infrequently.

To demonstrate the constraints and requirements in concert together, Figure 2.12 portrays an energy vs. time diagram of two-photon absorption. It shows the competing forces, gap in energy, and net result from the electron’s point of view.

\[
\begin{align*}
E^- & \quad \omega_{p,\alpha} + \omega_{p,\alpha} = \omega_{p,2\alpha} = \\
\Delta E_e / 2 & \quad \Delta t_{vs} \quad \ldots
\end{align*}
\]

Figure 2.12: Two-Photon example
Chapter 3

Laser Matter Interaction

3.1 External Field

3.1.1 Source Type

This study used several different linearly polarized sources. Predominantly continuous-wave-like sources were used, which may be described as sinusoidal with respect to the frequency $\omega$ of the source,

$$\tilde{E}(\hat{r},t) = E_0 \sin(\omega t). \quad (3.1)$$

$E_0$ signifies the maximum amplitude the pulse may reach. Chirped pulse sources were also simulated, but tend to induce stronger and more abrupt effects, trending towards higher ordered harmonics and total ionization even before the source intensity strays too far into the strong field regime [26] [27].

$$\tilde{E}(\hat{r},t) = E_0 \sin^2\left(\frac{n\omega}{T}\right) \sin(\omega t). \quad (3.2)$$

Due to the variety and nature of effects in the results of simulations with chirped-pulse sources, they are recommended in studies focusing more on ionization dynamics into the continuum, rather than excitation dynamics between discrete bound states [26] [28] [27].
3.1.2 Intensity Regime

Focused laser sources can be characterized by irradiance, or power per unit area per time interval.

\[ I_0 = \left[ \ldots \right] \frac{W}{cm^2} \]  

We are most interested in the range between \( 5 \cdot 10^{11} \leq I_0 \leq 5 \cdot 10^{14} \). There are three broad ranges that intersect this range; the perturbative regime, the non-perturbative regime, and the strong field regime. Beyond \( I_0 \leq 10^{18} \) lies the relativistic regime, and beyond \( I_0 \leq 10^{22} \) the super-relativistic regime, in which some exciting recent work in high energy systems has been done.

In the perturbative regime, the source intensity is \( I_0 \leq 10^{11} \). The contribution to the effective potential from the external source is then much less than the contribution from the coulomb potential from the nucleus. Therefore, the electron is likely to remain trapped, unless tunneling ionization occurs, or at ranges closer to the non-perturbative regime, the electron experiences occasional multi-photon excitation. The effects seen will depend much more heavily on the system than on the laser source, which is merely an afterthought at these ranges. This regime has been explored extensively, especially since analytical techniques work quite well, until you reach \( I_0 \approx 10^{11} \), and the assumptions behind perturbation theory begin to break down \[29\].

In the non-perturbative regime, the source intensity is \( 10^{12} \leq I_0 \leq 10^{14} \). The contribution to the effective potential from the external source is then around the same order of magnitude as the contribution to the coulomb potential from the nucleus. We will then see effects such as single photon excitation and ionization, multi photon excitations or possibly ionization in the form of low order harmonic generation, tunneling ionization. The effects seen will depend on both the system and the source parameters, which compete for dominance of the electron behavior. The assumptions for this regime are the strictest in many ways, since ignoring either contributing factor as the other regimes do will lead to error \[11\].

In the strong field regime, the source intensity is \( 10^{15} \leq I_0 \leq 10^{17} \). The contribution to the effective potential from the external source will now vastly outweigh the contribution from the coulomb potential from the nucleus \[30\]. In fact, this regime is the beginning of the so-called ”free electron” regime, where the nucleic effects can be safely ignored, especially as one approaches the relativistic and super-relativistic regime \( I_0 \geq 10^{18} \). This regime however also assumes that the magnetic contribution may be ignored, as we could do so in the previous two. When nearing the
CHAPTER 3. LASER MATTER INTERACTION

relativistic regime \( I_0 \approx 10^{18} \), the magnetic terms start having a larger impact and can no longer be safely ignored [31].

3.1.3 Photon Description

Because of the number of photons generated and moving through the computational domain at a given time, it is reasonable to treat them collectively in a classical fashion. This is accurate owing to the correspondence principle, where individual photons may be relatively unpredictable due to their quantum nature, but in groups they will behave relatively orderly in a statistical manner [1].

To estimate the number of photons in the system at a given time, the target and its area must be known exactly. Since the targets used in this study are all smaller than the beam diameter, the beam may be treated as a plane wave from the target’s, and therefore the computational domain’s, point of view. The intensity over the target area yields the energy incident upon the system, and given the energy per photon at the source wavelength, we can calculate the average number of photons present within the system over a discrete unit of time.

3.2 Gauge Theory

Gauge theory is simply the exploitation of certain symmetry properties of a system, in order to simplify the math or reduce the number of variables to keep track of. It has a somewhat misleading name, owing to an initial slight misunderstanding when first being explored [32]. Lorenz actually stumbled upon some interesting coincidences long before this, and began to wonder, but could not definitively prove anything without some requisite theory which had not yet been discovered. We now know he was on the right track.

A fuller and more complete background is given in Appendix C but isn’t necessary for an understanding of the rest of the current work. However it is important for one to understand how each of the pieces of this puzzle fit together in a complete and mathematically rigorous fashion. Having this comprehension is paramount to understanding the next logical steps of this type of project. After all, realistic and relevant systems are much more complex.

3.2.1 Gauge Invariance

Gauge Invariance expresses the idea that one can use several related fields, such as Maxwell’s Equations, and simply apply unitary transforms to transfer from field to field with-
CHAPTER 3. LASER MATTER INTERACTION

out introducing error to our answer. The root of this phenomenon is the idea where all of these potential fields are really manifestations of the same potential field, with vector \((A)\) and scalar \((\phi)\) components [33] [34]. Maxwell’s equations are a good example of this in action,

\[ E \rightarrow H \]
\[ ↓ \quad \downarrow \cdot \]
\[ B \leftarrow D \]

To transform Maxwell’s equations into gauge invariant potentials, we convert the electric and magnetic field to scalar and vector potentials,

\[ E = -\nabla \phi - \frac{\partial A}{\partial t} \quad (3.4) \]
\[ B = \nabla \times A \quad (3.5) \]

This still defines an infinite number of potential gauge choices, so an additional constraint is needed for the solution to be unique.

3.2.2 Coulomb Gauge

The Coulomb Gauge in the length formulation is best used within the system’s potential well. It is a very good choice for semi-classical approaches [35]. To convert to the coulomb gauge, we simply apply the gauge fixing condition [36],

\[ \nabla \cdot A = 0 \quad (3.6) \]

From this condition, the scalar potential for the field is obtained [33],

\[ \phi(r, t) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(r', t)}{|r - r'|} d^3r' \quad (3.7) \]

Note that in higher intensity regimes, the Lorenz Gauge may be a better choice,

\[ \nabla \times \phi = 0 \quad (3.8) \]

While its fixing condition means essentially ignoring changes to the scalar potential, the external potential is assumed to vastly overwhelm the coulomb potential in these regimes anyways.
CHAPTER 3. LASER MATTER INTERACTION

3.2.3 Dipole Approximation

The dipole approximation allows direct interaction between the coulomb and laser fields,

\[ V_{\text{laser}}(\hat{r}, t) = -\hat{r} \cdot \tilde{E}(r_0, t) . \]  

(3.9)

This simplification is useful until we near the higher region of the strong field regime \( I_0 \leq 10^{16} \), where it starts becoming inaccurate. By the time we reach the relativistic regime \( I_0 \leq 10^{17} \), it is totally inaccurate. The electric quadripole and magnetic dipole terms are needed. Additionally, higher multipole terms are available for even greater intensities.

3.3 Simplifications and Symmetries

3.3.1 Long Wavelength Approximation

The last simplification used for this study was the long wavelength approximation \[33\]. This concept relies on the laser wavelength being much longer than the system length, a good rule of thumb being ten times longer. The laser would look essentially like a very slowly varying plane wave, uniform in all dimensions from the system’s point of view. This results from the change in potential being negligible from one side of the solution space to the other.

\[ \tilde{E}(\hat{r}, t) \rightarrow \tilde{E}(r_0, t) . \]  

(3.10)

3.3.2 Effective Potential

We are left then with a simplified term for the potential,

\[ V_{\text{eff}}(\hat{r}, t) = V_{\text{laser}}(\hat{r}, t) + V_{\text{coulomb}}(\hat{r}) . \]  

(3.11)

It is possible to represent a radially symmetric system under the influence of an external field as a 1 dimensional system. Since we studied square wells, Hydrogen atoms and a few specific instances of Hydrogen ions, our system was simplified to such a 1-D model.
Chapter 4

Numerical Simulation

Numerical approximations of analytical solutions have become a very important tool in the past few decades. Analytical answers offer a solution that is completely correct. However, they are often only possible for simplified scenarios, and rarely for situations one would find in the real world.

Parallelization of such methods has become a major breakthrough in recent years, speeding up calculations in some cases by thousands of times. This speedup requires meticulous work and effort, often along the same level as the initial math and physics themselves. As a result, it is not something to dive into unless one is willing to put an equal amount of work in. Parallelization is therefore discussed more in-depth in Appendix A but left out of this section to introduce core concepts first.

As one perfect example of this, we can only determine the analytical solution for the electron wave equations of Hydrogen atoms, Hydrogen molecular ions, Helium atoms for a few select scenarios, and Lithium atoms in extremely specific cases. Numerical approximations however allow us to set up reliability conditions and constraints, then solve the equations almost to the exact answer. Provided we stay within the confines of the conditions and constraints, the answer obtained will be reliably accurate.

4.1 FDTD-Q

The method utilized for this study is the 2nd order FDTD-Q. Here, the wave functions may be solved iteratively, real components on integer steps, and imaginary components on half-integer steps. In concept it is very similar to Yee’s cube, from classical electromagnetic simulations [37].
CHAPTER 4. NUMERICAL SIMULATION

In this study, the time steps use the indices \((n \cdot \delta t)\) and the space steps use \((k \cdot \delta r)\). The iterative stepping functions may be expressed as:

\[
\Psi_R^n = \psi_R^{n-1}(k) - \left( \frac{h \cdot \Delta t}{m_e \Delta r^2} \right)[\psi_I^{n-0.5}(k + 1) - 2\psi_I^{n-0.5}(k) + \psi_I^{n-0.5}(k - 1)] + \left( \frac{\Delta t}{h} V_{eff} \right) \psi_I^{n-0.5}(k).
\]

(4.1)

\[
\Psi_I^{n+0.5} = \psi_I^{n-0.5}(k) - \left( \frac{h \cdot \Delta t}{m_e \Delta r^2} \right)[\psi_R^{n}(k + 1) - 2\psi_I^{n}(k) + \psi_R^{n}(k - 1)] - \left( \frac{\Delta t}{h} V_{eff} \right) \psi_R^{n}(k).
\]

(4.2)

A visualization of this procedure is shown in Figure 4.1.

![Figure 4.1: FDTD-Q method](image)

The method is an explicit-staggered central differencing scheme, \((2^{nd} \text{ Order Space}, 1^{st} \text{ Order Time})\); starting at \(t_0\) solve the equations over each time half-step. A visualization of the stencil is shown in Figure 4.2.

![Figure 4.2: 2nd-Order Stencil](image)

This stencil is then applied to all spatial points on the grid, solving for the subsequent time points. An example of the method in action, stepping across space and time is shown in Figure 4.3.

Higher order methods were investigated and a generalized FDTD-Q method \((4^{th} \text{ Order Space}, 3^{rd} \text{ Order Time})\) was implemented \([38]\). However, time-dependent potentials can make this impractical, and parallelization becomes far more difficult. Therefore, only the \((2^{nd} \text{ Order Space}, 1^{st} \text{ Order Time})\) method was used here; for a description of higher order methods, see Appendix B.
4.2 Boundary Conditions

The question then remains as to what happens to the wave function when it strikes the boundaries of the grid. Ideally speaking, the solution space should be large enough so that the particle doesn’t reach the edge, but this is impossible to implement in practical problems. As a result, several boundary conditions were investigated, each of which under certain circumstances, would eliminate the outgoing wave before it hits the boundary, while leaving the interior grid solution all but untouched.

4.2.1 Dirichlet

Dirichlet boundaries are a commonly used boundary type for perturbation-regime problems. Dirichlet boundaries \[39\]. The solution at the boundaries itself is set to 0, corresponding roughly to an infinite well, or ”particle-in-a-box”. The ”weak formulation” of the boundaries is very simple to implement,
CHAPTER 4. NUMERICAL SIMULATION

\[ \Psi(r) = \begin{cases} 
0 & \text{for } r \leq -\frac{L}{2} \\
\Psi(r) & \text{for } |r| \leq \frac{L}{2} \\
0 & \text{for } r \geq \frac{L}{2}.
\end{cases} \]  (4.3)

"Weak formulation" simply means the boundaries work for general descriptions, but do not necessarily provide a unique solution [40]. It is often sufficient for shorter time durations or truly large solution spaces.

Provided the solution space is large enough, the weak solution will not corrupt the answer by a noticable amount if given conditions for target and source, such as the non-perturbative simple systems we worked with in this study. What can happen is for pieces of the answer to be removed, which is still a preferable scenario to spurious reflections. Because of the relative level of accuracy given compared to other methods, Dirichlet boundaries were used in this study.

A masking function is sometimes added to the homogenous Dirichlet conditions outlined above, It helps improve the boundaries and reduce the error from their presence. To implement it, we simply apply a cosine function starting a small distance (\(r_{abs}\)) from the edge (\(r_{BC}\)) starting at 1 and ending with 0 at the boundaries [41].

\[ r_{abs} < \hat{r} < r_{BC} \quad . \]  (4.4)

The original wave function then becomes,

\[ \Psi(\hat{r}) = \begin{cases} 
0 & \text{for } \hat{r} \leq r_{BC,1} \\
\cos^\alpha \left( \frac{\pi}{2} \frac{\hat{r} - r_{abs}}{r_{BC} - r_{abs}} \right) \cdot \Psi(\hat{r}) & \text{for } r_{BC,1} < \hat{r} \leq r_{abs,1} \\
1 \cdot \Psi(\hat{r}) & \text{for } r_{abs,1} < \hat{r} < r_{abs,2} \\
\cos^\alpha \left( \frac{\pi}{2} \frac{\hat{r} - r_{abs}}{r_{BC} - r_{abs}} \right) \cdot \Psi(\hat{r}) & \text{for } r_{abs,2} \leq \hat{r} < r_{BC,2} \\
0 & \text{for } \hat{r} \geq r_{BC,2}.
\end{cases} \]  (4.5)

This method isn’t quite as elegant as some of the other boundaries, but by experimenting with the (\(\alpha\)) parameter for each system, the boundaries can be made more accurate.

4.2.2 Neumann

Neumann boundaries essentially involve setting the change in wave function to a value [42]. They are much more organic to the problem than Dirichlet conditions, but require more work
CHAPTER 4. NUMERICAL SIMULATION

to acquire, even in the case of weak formulation.

\[ \frac{\partial \Psi}{\partial r} = g \]  \hspace{1cm} (4.6)

Instead of simply being able to set the solution to 0 at the boundaries as with the weak Dirichlet formulation, we must solve an integral problem on the boundaries at each time step to solve even the weak Neumann formulation. Unique solutions often require more complex variations on this base, such as very large matrix multiplication or convolution kernels to obtain an answer, which for practical solution spaces become very computationally expensive very quickly. Worse yet, time-dependent potentials add even more complexity.

4.2.3 Open and Transparent

Open and Transparent Boundaries essentially absorb the wave function as it passes through the boundary, which looks very much like the wave is traveling outside the grid, never to be seen again. They work well for stationary problems, in which the system stays put while the external field passes through. They are often the best attempts currently to reduce error [43]. However, they often must be developed for each individual problem, and involve other assumptions as well [44].

4.2.4 Complex Absorber

Complex absorbing "sponges" must be tailored to each problem individually [18]. A number of adjacent grid points near the boundary are given complex potentials. This removes a fraction of the wave function as it passes through these points and approaches the boundary, but at the expense of removing part of the solution permanently. These are the most inaccurate, but often the easiest to employ, and are best used when debugging code or testing scenarios.

4.2.5 Exterior Complex Scaling

Exterior complex scaling involves rotating the solution into a complex coordinate plane, so that the inbound reflections do not interfere with the outbound excited solution [45].

4.2.6 Selection Process

Boundary conditions are still a subject of much debate in finite difference methods, and even more so amongst quantum finite difference methods. There are no perfect boundary conditions,
since most will still have some reflection, and others will remove chunks of the solution itself, making it inaccurate the more time passes in the simulation. Generally speaking, boundaries for particle wave functions requires a level of mathematical rigor and assumptions which make each type useful for relatively specific problem formulations only.

However without any boundary conditions, the solution will be plagued with spurious reflections from the boundaries, which lead to aberrant answers. Therefore perfect or not, to obtain a reasonably accurate solution some boundary method must be chosen. As previously mentioned, Dirichlet conditions were used in this study, because they introduced the least error in our solution.
Chapter 5

System Setup

5.1 Solution Space

5.1.1 Grid Discretization

The solution space of the problem is defined by the system under study and the external source parameters. We first decide the spatial step size, chosen to be small enough as to allow for accurate iterations across the space, but not so small that calculation across space for each time step takes an unreasonable amount of time.

\[ \Delta r = \frac{\mathbb{R}^1}{n_{steps}}, \]  

(5.1)

where \( \Delta r \) is the length of spatial step, \( \mathbb{R}^1 \) is the system length, and \( n_{steps} \) is the number of spatial steps in which to discretize the system.

5.1.2 Stability Conditions

Stability of the scheme ultimately rests on the size of time step used. Then, using the space step and the effective potential from the system and influence on it from the external source, we can calculate the time step. It must be small enough so the solution does not diverge, but not so small that calculating the solution does not take an unreasonable amount of time. In explicit methods, the time step is not calculated inherently by the method itself, and must be determined carefully.
CHAPTER 5. SYSTEM SETUP

\[ \Delta t_{\text{max}} \leq \frac{\hbar}{\frac{\hbar^2}{m_e \Delta r^2} + V_{\text{max}}} \]  \hspace{1cm} (5.2)

where \( (V_{\text{max}}) \) is the maximum potential the system experiences during simulation, and \( (\Delta t_{\text{max}}) \) is the maximum allowable time step in which the system remains stable. If the time step is greater than this, the solution will diverge. Provided the time step is not larger than described above, the solution will remain accurate. In this study, 10\% of the maximum critical value across all simulations was used, or \( (0.1 \cdot \Delta t_{\text{max}}) \).

5.1.3 Initial Setup

To start our iterative solution, we must specify the initial state of the system. This means setting the electron wave function to a position and momentum corresponding to an energy eigenstate of the system. The position and momentum formulation will differ depending on the layout of the system potential.

5.2 Square Well

Square well potentials, when coupled with Dirichlet boundaries, become the proverbial "particle-in-a-box" type problem and are among the simplest to define since we can solve them analytically with ease. They have a potential of \( (V = 0) \) inside the boundaries, and \( (V = \infty) \) outside the boundaries, as shown in Figure 5.1.

Figure 5.1: Infinite Square Well potential
5.2.1 State Formulation

An initial state may be defined which remains in a stable configuration despite oscillations. These special states are the bound states of the system, and may be found with harmonic analysis techniques \(^{22}\). Because infinite square wells have a potential of 0, their bound states’ eigenfunctions are defined only by frequency of oscillation (energy) and distance between system walls.

\[
\Psi_n(r,t_0) = \left(\frac{\sqrt{2}}{L}\right) \cdot \sin \left(\frac{n\pi x}{L}\right) \quad <n = 1, 2, 3...>
\]  

The energy of an eigenfunction for a system of length \((L)\) in energy state \((n)\) is defined as \(^{14}\)

\[
E_n = \frac{n^2\pi^2\hbar^2}{2m_eL^2}
\]  

5.2.2 Resonance Conditions

For example, if \(L = 20 \cdot a_0\) the first two energy states of the well and their resonant energy are calculated to be:

\[
\begin{align*}
E_1 &= 0.3366\text{eV} \\
E_2 &= 1.3465\text{eV}
\end{align*}
\]

\[
\Rightarrow \Delta E_{1,2} = 1.0099\text{eV}
\]  

The resonant wavelengths between these states are then multiples of 1227.8nm depending on the number of photons involved in the excitation:

\[
\Delta \lambda_{1,2} = N_{\text{photons}} \cdot (1227.8 \cdot 10^{-9})
\]  

5.2.3 Superposition of States

To define a system as a combination of two states, perhaps partially excited or due to uncertainty, we simply add the two states together, and normalize. This process is unusually simple in an infinite square well system,

\[
\Psi_{a,b} = \frac{\Psi_a + \Psi_b}{\sqrt{2}}
\]
CHAPTER 5. SYSTEM SETUP

Superpositions of states may also be defined for any other system, by combining eigen-function formulations in the quantities desired, then normalizing so that the sum of the resulting wave function’s parts over all space is unity.

\[
\left[ \int_{\mathbb{R}^N} |\Psi_{a,b}|^2 \cdot (d^N\mathbb{R}) \right] \rightarrow 1 .
\] (5.8)

5.3 Hydrogen Atom

5.3.1 Potential Map

As mentioned in 2.1.1, we must regularize the potential so we don’t end up with \(-\infty\) at the origin \([18]\). The nucleus is actually on the order of \(10^{-15}\) m in diameter, which would prevent reaching the ”singularity” that would otherwise manifest itself. The soft-core, or regularized coulomb potential, is an approximation which changes the system very little, and fixes the problem well enough so that more complex and drastic measures do not need to be taken.

\[
V_{\text{coulomb}}(r) = \frac{Z_{(\text{protons})}e_0^2}{\hat{r}} = \frac{Z_{(\text{protons})}e_0^2}{\sqrt{\hat{r}^2 + \kappa^2}} .
\] (5.9)

where \((Z_{\text{protons}})\) is the number of protons in the nucleus, and \(\kappa\) is the correction factor for the soft-core hydrogen atom. So we are solving not exactly for Hydrogen-1, but a facsimile different only noticably at the origin, where instead of dropping to \(\rightarrow -\infty\) it merely drops very low depending on the regularization parameter.

Atomic nuclei actually can trap electrons, but the energy required to do so for the smallest of atoms is \(I_{\text{trap}} \geq 1.3 MeV\). To accurately account for the nucleus, we need to account for the
CHAPTER 5. SYSTEM SETUP

baryons that comprise it, the protons and neutrons \[2\]. These in turn are made up of three quarks, one of each color (red, green and blue). Protons consist of two up and one down quark with charges \(2 \left(\frac{2}{3}\right) + 1 \left(-\frac{1}{3}\right)\), and neutrons of one up and two down quarks with charges \(1 \left(\frac{2}{3}\right) + 2 \left(-\frac{1}{3}\right)\). True accuracy would then only be found in a Quantum Chromodynamics formulation, although a full quantum electrodynamics formulation could approximate it well. As it stands, the simulation should not exceed \(2 \cdot 10^{-14} s\) or nucleic motion would need to be accounted for. Slight nuclear motion begins to occur at \(10^{-15} s\) with significant motion and molecular twisting occurring at \(10^{-12} s\) [46].

5.3.2 State Formulation

The Hydrogen atom is the only realistic atomic system we can solve for analytically, in all scenarios. Its eigenenergy functions have been known accurately for nearly a century, the first two of which are as follows: [14].

\[
\Psi_{100}(r, t_0) = \frac{1}{\sqrt{\pi} \cdot (a_0)^{3/2}} \cdot e^{-\frac{r}{a_0}}, \tag{5.10}
\]

\[
\Psi_{200}(r, t_0) = \frac{1}{4 \cdot \sqrt{4 \cdot (\pi) (a_0)^{3/2} \cdot (a_0)^{3/2}}} \cdot (2 - \frac{r}{a_0}) \cdot e^{-\frac{r}{2a_0}}, \tag{5.11}
\]

where the initial time \((t_0 = 0)\), and \((a_0 = \frac{\hbar^2}{me^2} \approx 52.9177 \cdot 10^{-12} m)\). The only other analytically solvable real world problems are Helium for some cases, and a very few special cases of Lithium may be solved for without approximation.

5.3.3 Resonance Conditions

Resonance conditions for hydrogen are more complex than those for infinite square wells, since the potential is more complicated. The energy gaps between bound states influence which wavelengths of photons are desirable in order to induce change,

\[
\Delta \lambda_{1,2} = \frac{2 \cdot \pi \cdot \hbar \cdot c_0}{|E_2 - E_1|}. \tag{5.12}
\]

where \((\Delta \lambda_{1,2})\) is the resonance wavelength between states \((E_1)\) and \((E_2)\), and \((c_0)\) is the speed of
light in vacuum. Hydrogen’s \([1s]\) and \([2s]\), essentially the ground and 1st excited states in terms of principle quantum number only, are 13.6\,eV and 3.4\,eV. The resonant wavelengths between these states are then multiples of 121.2\,nm depending on the number of photons \(N_{\text{photons}}\) involved in the excitation:

\[
\Delta \lambda_{1,2} = N_{\text{photons}} \cdot (121.2 \cdot 10^{-9} \text{m}).
\] (5.13)

### 5.4 Arbitrary Potential Wells

A primary goal of this project was to be able to apply the solution methods to essentially arbitrary potentials, or wells complex enough to be considered arbitrary, from multiple atoms forming a chain of molecules.

#### 5.4.1 Gaussian Pulse

Gaussian pulses are useful tools for generating an initial electron wave packet, corresponding to a system state. The state generated from the gaussian pulse actually contains components from many different states. Depending on the potential, it should contain components from all eigenstates which are able to exist within the solution space.

\[
\psi_0(r, t_0) = e\left(\frac{r^2 (r-r_0)^2}{4(\sigma r)^2}\right) \cdot e^{(i-k_0 \cdot r)}.
\] (5.14)

where \(r\) is the current grid point, \(r_0\) is the center of the pulse’s starting location, \(\sigma r\) is the initial pulse width, and \(k_0\) is the initial momentum of the pulse \[18\]. Gaussian pulses are quite adept at generating an initial wave function containing component wave functions from as many eigenfunctions as possible. Furthermore, they can be used on any of the aforementioned wells, or any arbitrary well and still retain at least some of each component.

#### 5.4.2 Imaginary Time Propagation

While several methods of determining eigenfunctions exist, the most promising for this particular application is Imaginary Time Propagation \[47\]. Especially important, the method works
for molecules and larger systems, such as a $[\text{C}^{60}]$ molecule in one recent study \[48\]. Strategy and relevant specific information is discussed here, but a more in-depth look is included in Appendix B.2.

It may be argued that there is physical significance to this procedure. Dr. Stephen Hawking wrote a paper popularizing the concept of imaginary time in the early 1980’s, and subsequently mentioned it in a book in the late 1990’s about various models of the universe, \[49\] \[50\]. In a subsequent book in the late 2000’s, he further suggested that if a model satisfied the criteria in Table 5.1 then it fulfilled the requirements in order to be considered a good and valid conceptual framework of how the universe operates \[51\].

<table>
<thead>
<tr>
<th>Table 5.1: Model Criteria &amp; Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Is elegant</td>
</tr>
<tr>
<td>(2) Contains few arbitrary or adjustable elements</td>
</tr>
<tr>
<td>(3) Agrees with and explains all existing observations</td>
</tr>
<tr>
<td>(4) Makes detailed predictions about future observations that can disprove or falsify the model if they are not borne out.</td>
</tr>
</tbody>
</table>

For our purposes, imaginary time propagation is a very useful mathematical trick which allows us to convert the Schrodinger wave equation from a diffusion-like equation into one of exponential decay \[47\], albeit one that does not work on the time axis we grew up on.

First, perform a Wick transform of the time axis onto the imaginary plane. At $t_0$, this is quite easy to do,

$$ t \rightarrow i \cdot t = \tau . \quad (5.15) $$

The effects on the Schrodinger wave equation are quite profound. What was once a diffusion-like equation now much more closely resembles exponential decay \[47\].

$$ \psi_n(r, t) = C_n \cdot \varphi_n \cdot e^{-i \cdot \frac{E_n}{\hbar} t} \rightarrow \psi_n(r, \tau) = C_n \cdot \varphi_n \cdot e^{-\tau \cdot \frac{E_n}{\hbar}} . \quad (5.16) $$

The important change is the removal of the imaginary component. Before, a high energy state would simply oscillate rapidly as $(t \rightarrow \infty)$ on the real time axis, as can be seen from observing the left hand equation above. Now on the right hand equation, a high energy state means the component associated with that state decays and asymptotically approaches 0 as $(\tau \rightarrow \infty)$ on the
CHAPTER 5. SYSTEM SETUP

imaginary time axis. Lower energy states follow suit at a slower pace, and since the ground state by
definition is the lowest energy state, it will be the last to decay [47].

Since the total wave function may be described as a sum of its eigenfunctions and coeffi-
cients, if the initial wave function could be separated, the eigenfunctions and the amount of each
present could be determined.

\[ \Psi_N = \sum_{n=0}^{N} C_n \psi_n \] \hspace{1cm} (5.17)

To obtain the first several eigenfunctions of a solution space, we follow the Gram-Schmidt
orthonormalization scheme [36]. There are several methods available, but Gram-Schmidt is the best
general method, and most of the other schemes only yield accurate results for the specific sets of
circumstances they were designed to exploit [52].

Use a generating function, either random noise or a Gaussian if the eigenstates are not
known, or if the eigenstate is known approximately, the process may be accelerated by formulating
the initial guessing as near to the eigenstate as possible. Propagate the initial wave function in
time along the imaginary axis, \[ \Psi(r, n\Delta \tau) \rightarrow \Psi(r, [n + 1]\Delta \tau) \] . Continue this until convergence,
repeating to the point where only the lowest energy state remains,

\[ \lim_{\tau \to \infty} \Psi_N(r, \tau) \rightarrow C_0 \cdot \varphi_0 \] \hspace{1cm} (5.18)

The propagators for the 2nd order non-implicit version change slightly from the original
iterative equations, but are still identifiable as the FDTD-Q stepping equations.

Renormalizing the remaining wave function and then gives us the coefficient of the ground
state component, and subtracting the renormalized wave function from the initial wave function gives
us the ground state component of our wave function.

\[ C_1 \psi_1 = \Psi_N - C_0 \phi_0 \] \hspace{1cm} (5.19)

We simply repeat this process for additional energy states, starting with the same original
wave function, for any states desired.

\[ C_n \psi_n = \Psi_N - C_{n-1} \phi_{n-1} \hspace{1cm} < n = 1, 2, 3, \cdots, N > \] \hspace{1cm} (5.20)
CHAPTER 5. SYSTEM SETUP

However unless using a higher order method, it is advised that only the first five states are grabbed, as Gram-Schmidt orthonormalization propagates and increases error for each term discovered; higher energy states will therefore inevitably have larger error than lower energy states obtained with the procedure [36]. This may be mitigated with higher order methods, which allow for increased accuracy and potentially reducing calculation time, provided the computational cost to calculate is not greater than lower order methods [48] [53].

5.4.3 ITP Example: Hydrogen Atom (soft-core)

Hydrogen atoms were also investigated in this study with the same variety of methods used on the Square Well. The results were analogous to the square well system, albeit somewhat more noisy and prone to errors from spurious reflections and slightly noisier than the simpler, essentially linear or quadratic systems which may be found in the introductory lessons and chapters of many courses and books about Quantum Mechanics [24] [14]. Table 5.2 shows the first five principle energy states as calculated by the Imaginary Time Propagation method, and the increasing error as the method is used to obtain successively higher states.

The system was formulated with the parameters outlined in 6.1.1. An initial trial function was generated as random noise, normalized within the solution space, in order to provide as many eigenstates as possible while maintaining orthogonality between different components [36]. The eigenfunctions and eigenenergies were then calculated with a 4th-Order variable time-stepping algorithm, similar to the one derived in Appendix B.2.

<table>
<thead>
<tr>
<th>Energy State</th>
<th>ITP Result</th>
<th>Exact Value</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1s]</td>
<td>-13.103 (eV)</td>
<td>-13.606 (eV)</td>
<td>3.70 (%)</td>
</tr>
<tr>
<td>[2s]</td>
<td>-3.741 (eV)</td>
<td>-3.402 (eV)</td>
<td>9.96 (%)</td>
</tr>
<tr>
<td>[3s]</td>
<td>-1.712 (eV)</td>
<td>-1.529 (eV)</td>
<td>11.97 (%)</td>
</tr>
<tr>
<td>[4s]</td>
<td>-0.954 (eV)</td>
<td>-0.848 (eV)</td>
<td>12.50 (%)</td>
</tr>
<tr>
<td>[5s]</td>
<td>-0.656 (eV)</td>
<td>-0.543 (eV)</td>
<td>12.89 (%)</td>
</tr>
</tbody>
</table>

Table 5.2: Hydrogen Atom: Calculated Energy States
Chapter 6

Results and Analysis

6.1 System and Source Parameters

6.1.1 Space/Time Discretization

Our model was simulated with a target in the center of a spatial grid. The grid itself was a radially symmetric sphere of $2 \cdot r = D = 40 \cdot \alpha_0$ with $n_{steps} = 2048$ and $\Delta r = 1.0327 \cdot 10^{-12}(m)$. As a result, a 1-dimensional approximation was used for simplicity.

Since an explicit-staggered finite difference scheme was used, the time step size for the 2nd-Order method was set to $0.1 \cdot \Delta t_{critical}$, or $\Delta t = 184.23 \cdot 10^{-18}(s)$ to keep the model stable and prevent the solution from diverging. Each experiment was run for a total time of $T_{total} = 20 \cdot 10^{-15}(s)$ so a total of $(10^7)$ steps were required. The time limit was imposed to ensure that nuclear motion is very unlikely to occur, yet allowing plenty of time for electron motion to take place.

6.1.2 Initial System Formulation

Two systems were chosen for this study. First, a square well was used to show the ideas worked in a perfect-world scenario [11]. This was then compared with a hydrogen atom (soft-core).

Each system was simulated a large number of times, in states varying from its ground state, 1st excited state, gaussian ensemble of states, and a superposition of the ground and 1st excited states. The majority of results displayed are from the square well, due to the lack of noise and ease of transitioning from basic math and theory to immediately quantifiable results.
CHAPTER 6. RESULTS AND ANALYSIS

6.1.3 External Source Parameters

All targets were exposed to an external source, a (simulated) laser positioned so the beam was normal to the target. A train of between one and four continuous-like pulses passed through the system. Several combinations of source irradiance were tested, varying the duration of effect, intensity and wavelength, and therefore the arrival rate as well as energy per photon. The irradiance was varied between the high end of the perturbative regime \( I_0 = 5 \cdot 10^{11} \, \text{(W cm}^2 \text{)} \) to the high end of the nonperturbative regime \( I_0 = 5 \cdot 10^{14} \, \text{(W cm}^2 \text{)} \). The higher end of the perturbative regime, where perturbation theory begins to break down, was expected to encourage more stimulated emission-type transitions, while higher intensities were expected to encourage more absorption-type transitions.

6.2 Simulation Results

All systems were placed in their ground state and excited, and observed through continued excitation from the source, then relaxation after the source was shut off. The initial state formulation of the system in concert with the external source parameters was expected to define which transition took place.

Important to note, because no spontaneous emission can occur in this model, slight relaxation was expected, followed by oscillation between a combination of states which the system was partially excited or induced towards. If a resonant transition occurred, with no excess or deficit of energy, only one state was expected to remain visible after the source turned off.

6.2.1 Determination of Energy States

The results from the Square Well were very clean, and indeed almost free of noise due to the essentially "ideal" conditions within the system. The only real difference between results from each system under study was the level of noise from spurious reflections off the boundaries. Table 6.1 shows the first five principle energy states as calculated by the Imaginary Time Propagation method.

The system was formulated with the parameters outlined in 6.1.1. An initial trial function was formulated as random noise, normalized within the solution space, in order to provide as many eigenstates as possible while maintaining orthogonality between different components \[. \] The eigenfunctions and eigenenergies were then calculated with a 4th-Order variable time-stepping algorithm, similar to the one derived in Appendix B.2.
CHAPTER 6. RESULTS AND ANALYSIS

<table>
<thead>
<tr>
<th>Energy State</th>
<th>ITP Result</th>
<th>Exact Value</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0857 (eV)</td>
<td>0.0842 (eV)</td>
<td>∼ 1.78 (%)</td>
</tr>
<tr>
<td>2</td>
<td>0.3703 (eV)</td>
<td>0.3366 (eV)</td>
<td>∼ 10.01 (%)</td>
</tr>
<tr>
<td>3</td>
<td>0.8159 (eV)</td>
<td>0.7574 (eV)</td>
<td>∼ 7.72 (%)</td>
</tr>
<tr>
<td>4</td>
<td>1.4785 (eV)</td>
<td>1.3465 (eV)</td>
<td>∼ 9.80 (%)</td>
</tr>
<tr>
<td>5</td>
<td>2.3885 (eV)</td>
<td>2.1038 (eV)</td>
<td>∼ 13.53 (%)</td>
</tr>
</tbody>
</table>

Table 6.1: Square Well: Calculated Energy States

6.2.2 Resonant Absorption

The system was initially set to the ground state. Since the goal was to induce absorption to a higher state, in this case the 1st excited state, the laser was set up accordingly. The external source shown in Figure 6.1 was set to \( I_0 = 1 \cdot 10^{13} \text{ (W/cm}^2\text{)} \) at a wavelength of \( \lambda = 1227.8 \text{ (nm)} \).

![Figure 6.1: Resonant Absorption, Square Well (External Field)](image)

The frequency response of the system displayed in Figure 6.2 shows much a wilder response during the pulse itself, but this is expected. In fact, the more intense nonlinear effects such as HOHG (High Order Harmonic Generation) often occur during the pulse itself, and fade after the source is shut off [26]. We are more interested in LOHG (Low Order Harmonic Generation), which much more commonly originates from bound state transitions.

![Figure 6.2: Resonant Absorption, Square Well (Frequency Response)](image)

Figure 6.3 sheds more insight into the sequence of events in the system. After the source
is shut off, the response relaxes slightly and stabilizes, in a higher frequency mode than the system started in.

![Figure 6.3: Resonant Absorption, Square Well (Population of States)](image)

It is the population of states where one can most easily identify what happened. First, the system is started with the ground state in a nearly completely dominant role, and the 1st excited state population negligible. Rapid oscillations occur during the source excitation itself. Then after the source is shut off, the population of states stabilizes with the roles reversed; the 1st excited state is dominant, and the ground state population is quite negligible. Clearly a resonant transition occurred.

Therefore, we successfully induced a resonant transition with this combination of system and source parameters, exciting an infinite square well from its ground state to its 1st excited state.

6.2.3 Resonant Stimulated Emission

The system was initially set to the 1st excited state. Since the goal was to induce stimulated emission to a lower state, in this case the ground state, the laser was set up accordingly. The external source shown in Figure 6.4 was set to \( I_0 = 5 \cdot 10^{11} \text{ (W/cm}^2\text{)} \) at a wavelength of \( \lambda = 1227.8 \text{ (nm)} \) and was only sent once.

![Figure 6.4: Resonant Stimulated Emission, Square Well (External Field)](image)

The frequency response of the system displayed in Figure 6.5 shows a much tamer response than with absorption. Even during the pulse, one complete transition got started but only truly completed by the end of the simulation, gradually shifting from the 1st excited to the ground
CHAPTER 6. RESULTS AND ANALYSIS

frequency component, increasing until energy was actually lost from the system, released as a photon.

Figure 6.5: Resonant Stimulated Emission, Square Well (Frequency Response)

The population of states graph as displayed in Figure 6.6 sheds more insight into the sequence of events in the system. matched the frequency response, showing gradual but steady change until it ended up effectively with totally inverted state probabilities. Since stimulated emission is when a photon strikes an electron with an energy equal to a state transition to a lower state, and incuces the electron to drop to that state and emit another photon with energy equal to the gap between its starting state and ending state.

Figure 6.6: Resonant Stimulated Emission, Square Well (Population of States)

Again, a resonant transition was induced here, the system dropping from the 1st excited to its ground state, presumably having released the excess energy as a photon.

6.2.4 Nonresonant Absorption

The off-resonant cases moved the system to a combination of states, none of which could be discharged, so the system looked very noisy after the source turned off. If spontaneous emission allowed energy to be discharged, the system would revert back to the ground state, since it did not completely enter into another eigenstate.

The system was initially set to the ground state. Since the goal was to induce absorption to a higher state, in this case the 1st excited state, the laser was set up accordingly. The external source,
CHAPTER 6. RESULTS AND ANALYSIS

shown in Figure 6.7 was set to \( I_0 = 2.5 \times 10^{12} \, \text{W/cm}^2 \) at a wavelength of \( \lambda = 2455.6 \, \text{nm} \). The wavelength is double the resonant case, but there are two pulses so the energy based on intensity would be the same. Because the intensity is cut to one fourth, we saw an electric field half as powerful as the resonant case.

![Figure 6.7: Non-Resonant Absorption, Square Well (External Field)](image)

The frequency response of the system, displayed in Figure 6.8 shows much a wilder response during the pulse itself, but this is expected. After the source is shut off, the response relaxes slightly stabilizes, but remains in a combination of two frequency modes, oscillating between the two.

![Figure 6.8: Non-Resonant Absorption, Square Well (Frequency Response)](image)

It is the population of states, as can be seen in Figure 6.9 that once again tells the most explicit tale. First, the system is started with the ground state in a nearly completely dominant role, and the 1st excited state population negligible. Rapid oscillations occur during the source excitation itself. Then after the source is shut off, the population of states does stabilize, but with the roles only somewhat changed; the 1st excited state has increased in population, and the ground state decreased, but neither is completely dominant.

Essentially we have induced partial absorption, but the system did not receive enough energy to jump to the next state.
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![Figure 6.9: Non-Resonant Absorption, Square Well (Population of States)](image)

6.2.5 Nonresonant Stimulated Emission

The system was initially set to the 1st excited state. Since the goal was to induce stimulated emission to a lower state, in this case the ground state, the laser was set up accordingly. The external source is shown in Figure 6.10 was set to $I_0 = 2.5 \times 10^{12} \ (W/cm^2)$ at a wavelength of $\lambda = 2445.6 \ (nm)$ and only one pulse was sent. The wavelength is double the resonant case, but there are two pulses so the energy based on intensity would be the same. Because the intensity is cut to one fourth, we saw an electric field half as powerful as the resonant case.

The observant reader will note this is the same external field as the non-resonant absorption case.

![Figure 6.10: Non-Resonant Stimulated Emission, Square Well (External Field)](image)

The frequency response of the system, displayed in Figure 6.11 shows the same basic story as non-resonant absorption, except with the roles reversed. During the pulse, a complete transition occurred, but then after stabilization when the source was shut off, it appears to oscillate between two frequency modes.

![Figure 6.11: Non-Resonant Stimulated Emission, Square Well (Frequency Response)](image)

The population of states, which may be seen in Figure 6.12 shows what actually happened: Stimulated emission did take place here, but afterwards energy was still being fed into the system. Therefore, once the stimulated emission occurred, absorption started, but not enough energy was provided to induce full transition back to the 1st excited state. The system then remains trapped between the two states.
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Figure 6.11: Non-Resonant Stimulated Emission, Square Well (Frequency Response)

Figure 6.12: Non-Resonant Stimulated Emission, Square Well (Population of States)
Chapter 7

Conclusion

7.1 Goals Achieved

We successfully simulated our model and induced both resonant and non-resonant absorption and stimulated emission from several simple 1-electron simulated systems using external sources operating in the non-perturbative intensity regime. We observed system state changes and the results implied that with spontaneous emission, permeable boundaries or both, the system would relax to the ground state. When these are taken into account the system should emit a photon containing the energy between the final energy state achieved in simulation and the system ground state.

We have successfully demonstrated a working model of 1-electron systems for arbitrary wells. The examples here have radial symmetry for simplicity’s sake, but other geometric constructs work equally well. An external source from a laser may be turned on and off at different times, with different pulse shapes. The source and system potentials interact in an effective potential defined by the gauge coupling method, which impacts the wave function propagation.

Parallelization of algorithms and schemes led to a substantial reduction in the compute time, of $4 - 10x$ for pre-built MATLAB methods, up to $40 - 1000x$ using custom-built MEX C-libraries and CUDA Kernels. As a result, larger spaces with more discrete points, and a more descriptive time domain with more discrete points up to the limit of $25 \cdot 10^{-15}$ were possible to simulate in a vastly reduced amount of time. The simulation time limit of $25 \cdot 10^{-15}$ is a function of forces not accounted for, specifically the nuclear motion, which would require a QCD approach to incorporate with complete accuracy.

Our model was able to switch from the Ground to 1st Excited states, and from the 1st Excited to Ground states, with each system simulated. From these state transitions an accurate
CHAPTER 7. CONCLUSION

formulation of energy output may be interpreted. When compared to the input, the harmonic output can be calculated.

7.2 Next Steps

The next steps for this project are to derive more realistic solution space boundaries, and to develop a full quantum electrodynamics formulation [54] [55] [56]. The former would allow accurate simulation of ionization. The latter would enable not only spontaneous emission, but with the appropriate wave equations, allow an accounting of relativistic effects, particle spin, and interactions between electrons [57]. This will allow for larger structures to be modeled, potentially fulfilling the Pauli Exclusion Principle [58]. DFT makes for a good approximation in many circumstances, to either construct, work with or verify results [59].

Spontaneous Emission results from interactions with the quantum vacuum, and needs a QED formulation to be accurately accounted for [24]. Furthermore, spin and relativistic effects in the system can’t be taken into account in the current model. A Quantum Field Theory approach is needed for this, where locality descriptions of particles have 4-vector components [2]. Interactions between particles may be treated more accurately in this case [60].

Without accurate boundaries, spurious reflections and other kinds of interference from the boundaries can occur. Allowing wave function to pass through the boundaries would allow for ionization calculations, and better accuracy overall.

7.2.1 Other Thoughts

Despite the enormous amount of work and effort put into this project, there is still a ways to go before it can simulate physically relevant structures beyond Hydrogen, Helium or Lithium atoms, Hydrogen-2 or Helium-Hydrogen molecules.

The author is eager to see what will happen in the coming years, and how the substantial potential of this type of simulation will be borne out, grow and progress.
Bibliography


BIBLIOGRAPHY


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Appendix A

Parallelization

A.1 Introduction

Graphical processing units have come a long way in the decades since their invention. Originally designed for processing the massive amounts of data destined for a computer monitor, people swiftly realized they could be used for other tasks which benefited from a parallel processing approach.

Learning how to effectively parallelize an algorithm is key. There are many who believe this new trend to be a useless fad, but this is mostly due to lack of intensive investigation as to what truly offers a speedup, and what is merely a gimmick. Utilizing the hardware effectively and efficiently, as well as choosing problems which can actually achieve a large speedup, is just as important as what hardware one uses.

If done properly, the time savings alone is often worth the effort, from $\approx 1\% - 10\%$ of the original serial code. For larger projects, the energy savings is extremely significant, and can be even larger than the time savings, $\approx 0.5\% - 10\%$ of the original usage.

A.1.1 Hardware

Whichever the application or, budget, the common building block is the parallel processing card. There are very specialized versions for highly specific purposes, but in this study we focused on the GPGPU, or General Purpose Graphics Processing Unit. Not all versions may even be used as graphics cards now, such as NVidia’s high performance Tesla cards, which are for calculation purposes only. A cluster of computers may be built to work together for truly massive tasks, but
for this project a single machine was used, since the parallelization was not intended to be the main focus.

### A.1.2 CUDA vs OpenCL

At the time of writing, there are two main companies that specialize in parallel computing. ATI (now part of AMD)’s OpenCL, and NVidia’s CUDA. OpenCL cards are generally more powerful in terms of raw numbers, but are significantly more difficult to program for. Also, there is no competitor to NVidia’s flagship Tesla card, so if the build is to be used in an environment such as a parallel computing center, this is an important consideration.

### A.2 Strategy for Finite Difference Methods

The algorithm to be parallelized is just as important a consideration as the hardware, when looking for a speed up in computation time. Finite Difference Methods are more difficult than many algorithms to parallelize, simply because each time step must be calculated in its entirety before moving onto the next, and no step may be skipped.

#### A.2.1 Orthogonal Operators

Two methods to sidestep this problem are discussed. The first is shown in Figure A.1. It involves taking advantage of operator orthogonality, and is best used in cartesian, polar, cylindrical or spherical coordinates. Dimensions may be calculated independently, and the result added together.

![Figure A.1: Parallelization Strategy #1: Dimensions and Particles](image-url)
A.2.2 Grid Division

A second method, shown in Figure A.2, is less efficient but a general solver; it will work for cases where operators might not be orthogonal, or where such constraints break down. Simply divide the grid into sections, and solve independently:

Communication must still take place between grid sections, and time steps must still be completely solved before moving onto the next. However, this method allows full advantage to be taken of the hardware, and is far more scalable than the other method. The only issue is when communication time between sections becomes larger than the speedup itself. For one machine this would be a remote concern, but when dividing amongst a cluster, it is a problem which must be considered.

A.3 Implementation and Effectiveness

A.3.1 Methodology & Process

Parallelization strategy 2 was used (grid division), since any future iterations would be more likely to use it. The grid division and communication was handled by an update function, and kernels were written to handle each piece. The source code may be found in Appendix E.
APPENDIX A. PARALLELIZATION

For a much faster speedup, the configuration of hardware on the chip itself must be utilized [62]. There are different types of memory within the GPGPU, and to get a speedup of hundreds, sometimes thousands of times, each must be properly used and the relevant data allocated to each. System crashes are quite possible here, since the card’s internal memory is very unlikely to have error checking of its own. Such an in-depth study of the chip architecture often requires just as much work as the science and math sections of a project, so unless an interdisciplinary team is involved, it is best to stick to one or the other. Otherwise the time to completion estimate must be doubled at minimum.

A.3.2 Benchmarks & Algorithm Speedup

Our parallel algorithm ran much faster than the serialized version in all cases, as is clearly shown in table A.1. "CPU-only" means purely serial, "Pre-built" refers to the reasonable CUDA functionality already built into MATLAB, and "MEX + Kernel" is the custom-made MEX library and CUDA Kernel(s) from the libraries provided by NVidia and MATLAB.

<table>
<thead>
<tr>
<th></th>
<th>Initialize</th>
<th>FDM &amp; Post-Proc.</th>
<th>Save to Disk</th>
<th>TOTAL Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CPU-Only]</td>
<td>0.7945 (s)</td>
<td>1618.1650 (s)</td>
<td>5.5689 (s)</td>
<td>≈ 1628.2828 (s)</td>
</tr>
<tr>
<td>[Pre-built]</td>
<td>0.1324 (s)</td>
<td>282.4023 (s)</td>
<td>35.6382 (s)</td>
<td>≈ 328.5522 (s)</td>
</tr>
<tr>
<td>[MEX + Kernel]</td>
<td>0.0117 (s)</td>
<td>0.0056 (s)</td>
<td>37.4994 (s)</td>
<td>≈ 38.1373 (s)</td>
</tr>
</tbody>
</table>

Table A.1: Algorithm Runtimes: Serial(CPU) vs Parallel (GPU) Methods

Worthy of note is how specific tasks run faster on the different pieces of hardware. Different operations ran at different speeds, but the main bottleneck was transfer from GPU to CPU. The actual finite difference algorithm ran on average ≈ 2117.5418 times faster on the GPU kernel than the CPU, provided the memory available on the GPU was sufficient to hold all the recorded data at once. If not, then a relatively significant slowdown took place whenever data transfers were needed. Even so, the GPU was still exponentially faster than the CPU overall.

A.3.3 Thoughts & Conclusion

Context is very important here, something often lost on the ”casual” engineer or physicist. While an enormous amount of time was saved in running the actual simulation in a parallelized setup compared to a serialized setup, it may be argued that in some cases, the time to build and debug the
APPENDIX A. PARALLELIZATION

parallel version was not worth the time and computational savings. Studies that will not be repeated more than a few times certainly fall under this category, for example.

This study was performed with one-dimensional methods, with a relatively in-depth analysis of the card and proper usage of memory types. It is higher dimensions where vectorized, parallelized code truly shines, and indeed such a study would only be possible with such measures if undertaken on higher dimensional or multi-particle systems. Such an in-depth study of the hardware and time to both learn and implement effective code often takes as long as the physics and math portions of the project.
Appendix B

Higher Order Methods

Numerical schemes based on the 2nd order central difference operator and using sufficiently small time steps yield an approximately accurate answer, within the constraints of the problem they are calculating. However, depending on the number of steps to solve, the computation time may be prohibitively slow. It is possible to derive higher order methods, which may reduce computation time significantly depending on the problem they are used on, by allowing larger time steps [38] [63] [64]. This way despite the longer time on each step, the reduced number of steps to reach the desired length of simulation time will reduce the computation time overall. Care must be taken in their use, since if used improperly they can actually increase the computation time.

B.0.4 Strengths and Weaknesses

The biggest obvious benefit to using a higher order scheme is the possibility of larger time steps, thus reducing the total number of time steps while still so

B.1 Generalized FDTD-Q Scheme

B.1.1 Derivation

The generalized version of the 2nd order operator take the form of \((2 \cdot N)\) th-Order Space, 
\((2 \cdot N - 1)\) th-Order Time. A detailed derivation of this formulation may be found in both [64] and [38].
APPENDIX B. HIGHER ORDER METHODS

\[ \Psi^n_R = \psi^{n-1}_R(k) + 2 \left\{ \sum_{p=0}^{N} \left( \frac{\Delta t}{2} \right)^{2p+1} \left( \frac{(-1)^{p+1}}{(2p+1)!} \right) \left[ \left( \frac{h}{2m_e \Delta x^2} \right) \mathcal{D}^2_r - \frac{V_{eff}}{h} \right]^{2p+1} \psi^{n-0.5}_I(k) \right\} \]  

(B.1)

\[ \Psi^{n+\frac{1}{2}}_I = \psi^{n-\frac{1}{2}}_I(k) + 2 \left\{ \sum_{p=0}^{N} \left( \frac{\Delta t}{2} \right)^{2p+1} \left( \frac{(-1)^{p}}{(2p+1)!} \right) \left[ \left( \frac{h}{2m_e \Delta x^2} \right) \mathcal{D}^2_r - \frac{V_{eff}}{h} \right]^{2p+1} \psi^{n}_R(k) \right\} \]  

(B.2)

The operator itself is represented as \( \mathcal{D}^n_r \). As an example, the 4th order operator would be

\[ \mathcal{D}^2_r = \frac{1}{12} \left[ -(1)\psi(k - 2) + (16)\psi(k - 1) - (30)\psi(k) + (16)\psi(k + 1) - (1)\psi(k + 2) \right] \]  

(B.3)

This means the stencil for the 4th order operator would look something like Figure B.1.

![Figure B.1: 4th-Order Stencil](image)

B.1.2 Strengths and Weaknesses

The biggest obvious benefit to using a higher order scheme is the possibility of larger time steps, thus reducing the total number of time steps while still solving for the same length of time. The solution at time step is more complex, but stable reductions to \( 1\% - 0.01\% \) of the time step used in the 2nd order formulation have been realized [38].

The only real weaknesses have to do with increased complexity for each computation, which can make parallelization more difficult, not to mention when time-dependent potentials are implemented.
B.2 Nth-Order Imaginary Time Propagation

B.2.1 Derivation

Higher order imaginary time propagation schemes are more complex in derivation and execution than real time methods \cite{48}. Instead of using a constant time step, a variable step size is often best \cite{53}. Propagate at the initial step size, and when this solution converges, reduce the step size and keep going at the smaller step size. Continue until some final convergence criteria are met.

The Nth order schemes we focus on involve operator splitting. For a more detailed derivation of the higher order operator, see \cite{48}. First, start with the initial Hamiltonian, with kinetic energy $T$ and potential energy $V$ \cite{48},

\[
H = -\frac{\hbar^2}{2m_e} \nabla^2 + V = T + V \tag{B.4}
\]

With time evolution operator $(\epsilon = -\Delta t)$ and $\mathcal{T}(\epsilon) = e^{\epsilon(T + V)}$, the 2nd order split operator method is \cite{48},

\[
\mathcal{T}_2(\epsilon) = e^{\frac{1}{2} \epsilon V} e^{\epsilon T} e^{\frac{1}{2} \epsilon V} \tag{B.5}
\]

Past 2nd order it is very possible to wind up with complex coefficients, thus making the solution quite unstable \cite{48}. Higher orders can be solved by approximation of the single-product expansion into a sum of products \cite{48},

\[
e^{\epsilon(T + V)} = \sum_{k=1}^{n} c_k \mathcal{T}_2^k \left( \frac{\epsilon}{k} \right) \tag{B.6}
\]

With coefficients for each term defined by,

\[
c_i = \prod_{j=1, j \neq i}^{n} \frac{k_i^2}{k_i^2 - k_j^2} \tag{B.7}
\]

The common theme here is splitting the 2nd order operator, which only contains odd powers of the evolution operator, and so we will only be able to derive even order operators which contain various coefficients of the 2nd order operator to different powers. Using the above method, we can derive the 4th order operator, which was used for this study.
APPENDIX B. HIGHER ORDER METHODS

\[ T_4(\epsilon) = -\left(\frac{1}{3}\right)T_2(\epsilon) + \left(\frac{4}{3}\right)T_2^2(\epsilon) \]  \hspace{1cm} (B.8)

B.2.2 Variable Time Step

As with the higher order method in real time, we can increase the time step size. Here, since we are solving the eigenfunction and eigenenergy problem, we do not need evenly spaced steps. Using variable time steps gets us to the solution faster. A step-by-step procedure is given below starting with an initial time step and repeating for each eigenfunction.

Table B.1: Variable-Time-Step ITP Scheme: Strategy

- **(1) Check for local energy convergence at each step**
  - \( \cdots \) If not reached... continue propagating with current time step
  - \( \cdots \) If reached... retreat one step, cut step size in half, and propagate

- **(2) Check for global energy convergence**
  - \( \cdots \) If not reached... continue propagating with current time step
  - \( \cdots \) If reached... save value for eigenfunction, subtract from total and resume from beginning

The math behind the procedure is similar to the 1st order method in 5.4.2. First, we use the idea of the wave function described by its eigenvectors\[53\],

\[ \Psi_n = \sum_{i=0}^{N-1} d_i \cdot \varphi_i \]  \hspace{1cm} (B.9)

where \( (d_i) \) are the component coefficients of each eigenfunction \( (\varphi_i) \), adding up to the total wave function \( (\Psi_n) \). A constraint on the eigenfunctions is,

\[ \sum_{i=0}^{N-1} |d_i^2| = 1 \]  \hspace{1cm} (B.10)

Additionally, we can find the first components for the first two from the following equations\[53\],

\[ d_i = O(h^p) \]
\[ d_0 = 1 + O(h^{2p}) \], \( for(i > 1) \).  \hspace{1cm} (B.11)
where \((h)\) is the step size. The energy may be estimated from the wave function and system hamiltonian,

\[
E_{h,1} \equiv \Psi_n^T H \Psi_n = E_0 + \mathcal{O}(h^{p+1})
\]  
(B.12)

where \((\Psi_n^T)\) signifies the transpose of \((\Psi_n)\). Another estimate is needed for global convergence,

\[
\tilde{\psi}_{n+1} = e^{-hH} \psi_n + \mathcal{O}(h^{p+1}) = e^{-hE_0} \varphi_0 + \mathcal{O}(h^{p+1})
\]  
(B.13)

The second energy estimate is then obtained with the relation,

\[
E_{h,2} \equiv \frac{\log(||\tilde{\psi}_{n+1}||)}{h} = E_0 + ch^p + O(h^{p+1})
\]  
(B.14)

where \((c)\) is the number of steps taken. An amalgamation of the estimates gives an error estimate for the total energy,

\[
\Delta E_h \equiv E_{h,2} - E_{h,1} = ch^p + \mathcal{O}(h^{p+1})
\]  
(B.15)

Convergence is determined by comparing subsequent steps,

\[
\delta E_h^n \equiv E_{h,1}^n - E_{h,1}^{n-1} = ch^{2p} + \mathcal{O}(h^{2p+1})
\]  
(B.16)

This is checked for each step, and if it drops below \(|\delta E| < (\Delta E)^2\), then convergence is deemed reached. A good estimate (and the one used in this study) is \(\Delta E < 10^{-10}\).

**B.2.3 Strengths and Weaknesses**

The Nth order ITP method by itself provides much better solutions than the initial ITP method, but can take a very long time to run. With variable time stepping, the Nth order ITP method is clearly superior, taking less time and providing more accurate eigenfunctions and eigenenergies [48].
APPENDIX B. HIGHER ORDER METHODS

There are even parallelization methods which offer further improvements, such as a general grid segmentation strategy described in [61]. However some strategies, while at first glance offer seemingly significant speedups, at closer inspection rely on specific conditions to function [52]. Great care must be taken when investigating higher order methods, due to any unspoken assumptions which may not play a major part in lower order method, but will invalidate certain approaches to a higher order formulation.
Appendix C

Gauge Invariance in Classical & Quantum Electrodynamics

In this section, a somewhat more detailed and in-depth exploration of electrodynamics and its gauge symmetries is explored, both from a classical and quantum standpoint. For an even more rigorous derivation, the reader is advised to look through the references within this section, as well as the books on the subject within those references.

C.1 Overview

Building any system, mathematical or physical, requires an understanding of the parts and components within that system, and how they interact with each other. In an electrodynamics system, classical or quantum, the components consist of electrons and photons. It is the interaction between each component, both with similar components and those of the other type, that must be accounted for.

C.1.1 Electrons

Electrons are leptons in the fermion group, and are influenced by the electromagnetic, weak and gravitational forces only. Their fermionic heritage means they must obey the Pauli exclusion principle, which is what gives atoms their electronic structure via electron shells. They have mass \( 9.109 \cdot 10^{-31} \) and spin \( \left(\frac{1}{2}\right) \). They may be modeled with the Schrödinger
APPENDIX C. GAUGE INVARIANCE IN CLASSICAL & QUANTUM ELECTRODYNAMICS

(both relativistic and non-relativistic), Dirac, Bethe-Salpeter, and other wave and field equations which describe fermions of spin $\left(\frac{1}{2}\right)$.

C.1.2 Photons

Photons are bosons $[68]$. They are carriers of the electromagnetic force with spin $\left(\frac{1}{2}\right) [69]$. They officially have no mass, but have an effective rest mass which has meaning within whichever gauge symmetry one chooses to describe a volume of space.

C.1.3 Derivation Strategy

Derivation is relatively straightforward, despite not being immediately obvious at first. One standard method merely takes three steps $[70]$:

Table C.1: General Strategy for Formulation of Gauge Invariant Equations of Motion

1. **Formulate terms for source and kinetic energy by vector and scalar components**
   - ··· Using the potential field $(\Phi)$, formulate scalar contributions
   - ··· Using the potential field $(A)$, formulate vector contributions

2. **Ensure formulation will yield unique solution**
   - ··· Use Action Principle (Fixing Conditions) & apply to terms
   - ··· If solution not unique, formulation is NOT a Gauge!

3. **End result should be Maxwell’s equations in potential form, modified by gauge condition**

There are formulations which do not result in unique solutions and are therefore not considered a Gauge, yet still remain useful tools. A good example of this is the Kramers-Henneberger representation, sometimes inaccurately called the ”acceleration gauge” $[18]$. It does not yield unique solutions, and one must be very careful when transforming into and out from it. However, it is very useful for reducing erroneous reflections at the solution boundaries, since only the acceleration matters.

Essentially, the gauge invariance of electrodynamics results from the freedom to choose an arbitrary frame of reference in quantum physics $[70]$. 
C.2 Gauge Theory

The origins of Gauge Theory are rooted in the discovery of the rules around Maxwell’s equations, which are only truly meaningful on a classical scale \[71\]. We assume here that signals and waves travel through the vacuum, and the causes of phenomena can be explained in a clear mathematical basis. This causality is reconstructed mathematically with retarded potentials, which in turn come from the D’Alembert equations for field strengths of potentials. If these potentials are used for a mathematical description of the system, we end up with a complicated system of coupled partial differential equations (PDEs). To simplify, differential conditions are used, which we call a gauge.

C.2.1 Electrodynamics

We begin by studying Maxwell’s equations,

\[
\begin{align*}
\nabla \cdot E &= \frac{1}{\epsilon_0} \rho \\
\nabla \times B &= 0 \\
\n\nabla \times E + \frac{\partial}{\partial t} B &= 0 \\
\n\nabla \times B - \frac{1}{c^2} \frac{\partial}{\partial t} E &= \frac{1}{c^2 \epsilon_0} J
\end{align*}
\tag{C.1}
\]

On classical scales, electromagnetic fields are not quantized, so we are much more free in how we may treat them. Regardless of quantization, different fields describing different potentials are connected by gauge transformations \[32\]. Each has a scalar \( \Phi(r, t) \) and vector \( A(r, t) \) component, corresponding in the case of electromagnetic fields to the electric \( E(r, t) \) and magnetic \( B(r, t) \) field, respectively \[72\].. The homogeneous, or first two Maxwell’s equations may formulated as scalar and vector potentials in order to express the field strengths,

\[
\begin{align*}
E &= -\nabla \Phi - \frac{\partial}{\partial t} A \\
B &= \nabla \times A
\end{align*}
\tag{C.2}
\]

The inhomogeneous, or last two of Maxwell’s equations may be used to formulate equations of motion using the scalar and vector potentials,

\[
\begin{align*}
\Delta \Phi + \frac{\partial}{\partial t} (\nabla \cdot A) &= -\frac{1}{\epsilon_0} \rho \\
\Delta A - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} A - \nabla (\nabla \cdot A + \frac{1}{c^2} \frac{\partial}{\partial t} \Phi) &= \frac{c^2}{\epsilon_0} J
\end{align*}
\tag{C.3}
\]

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APPENDIX C. GAUGE INVARIANCE IN CLASSICAL & QUANTUM ELECTRODYNAMICS

Important to realize however, is while these potentials determine the strength of the fields, the various fields do not uniquely define the potentials \[70\]. For example, with \( U(r,t) \) as an arbitrary field,

\[
\Phi'(r,t) = \Phi(r,t) + \frac{\partial}{\partial t} U(r,t) \quad \text{(C.4)}
\]

\[
A'(r,t) = A(r,t) - \nabla \cdot U(r,t) \quad \text{(C.5)}
\]

The fields \( \Phi' \) and \( A' \) result in the same electric and magnetic fields as \( \Phi \) and \( A \) \[32\]. In order to obtain unique solutions, additional constraints are needed.

C.2.2 Field Quantization

Gauges in quantum electrodynamics follow the same general format as those in classical, except the vector potential gains new meaning \[34\]. A four-vector potential is used to define the 3+1 dimensions of space-time, thus also opening the door to relativistic formulations. A Gauge field in four-vector potential notation is described as,

\[
A^\mu \equiv (\Phi, A) \quad \text{(C.6)}
\]

In terms of field strength,

\[
F^{\mu\nu} = -F^{\nu\mu} \equiv \partial^\mu A^\nu - \partial^\nu A^\mu \quad \text{(C.7)}
\]

The new form of the equations then becomes,

\[
\begin{align*}
\left\{ \begin{array}{l}
\nabla \cdot E = \frac{1}{\varepsilon_0} \rho \\
\nabla \cdot B = 0 \\
\nabla \times E + \frac{\partial}{\partial t} B = 0 \\
\n\nabla \times B - \frac{1}{c^2} \frac{\partial}{\partial t} E = \frac{1}{c^2\varepsilon_0} J
\end{array} \right. \\
\rightarrow \left\{ \begin{array}{l}
\partial_\mu F^{\mu\nu} = 0 \\
\epsilon_{\mu\nu\rho\sigma} \partial^\rho F^{\mu\nu} = 0
\end{array} \right. \\
\rightarrow \left\{ \begin{array}{l}
\partial_\mu F^{\mu\nu} = J^\nu \\
\epsilon_{\mu\nu\rho\sigma} \partial^\rho F^{\mu\nu} = 0
\end{array} \right. \quad \text{(C.8)}
\end{align*}
\]

Finally, we can describe a gauge transformation with arbitrary field \( \mathcal{U} \) in four-vector notation,
APPENDIX C. GAUGE INVARIANCE IN CLASSICAL & QUANTUM ELECTRODYNAMICS

\[ F'_{\mu\nu} = F_{\mu\nu} - (\partial^\mu \partial^\nu - \partial^\nu \partial^\mu) \cdot U(r, t) \rightarrow F'_{\mu\nu} = F_{\mu\nu} \]  \hspace{1cm} (C.9)

Since the derivatives commute in the right-hand term multiplied by the arbitrary function, we end up with a field strength which is gauge invariant. To formulate the results in a specific gauge, we want to find equations of motion which describe Maxwell’s equations. An alternative description of this is an ”action”, and is often described by Lagrangian equations of motion.

\[ \mathcal{L} = \frac{1}{4} F^{\mu\nu} F_{\mu\nu} + J^\mu A_\mu \]  \hspace{1cm} (C.10)

The Lagrangian may be described in terms of the gauge field itself,

\[ \mathcal{L} = \frac{1}{2} \partial^\mu A^\nu \partial_\mu A_\nu + \partial^\mu A^\nu \partial_\nu A_\mu + J^\mu A_\mu \]  \hspace{1cm} (C.11)

To simplify further, the equation of motion may be described as a combination of the first two of Maxwell’s equations in four-vector form,

\[ [g^{\mu\nu} \partial^2 - \partial^\mu \partial^\nu] \cdot A_\nu + J^\mu = 0 \]  \hspace{1cm} (C.12)

This yields a more easily accessible formulation of the Lagrangian, which also happens to be Lorentz invariant, Gauge invariant, parity invariant and time-reversible invariant,

\[ \mathcal{L} = \left( \frac{1}{2} \cdot A_\mu [g^{\mu\nu} \partial^2 - \partial^\mu \partial^\nu] A_\nu \right) + \left( J^\mu A_\mu \right) - \left( \frac{1}{2} \cdot \partial^\mu A^\nu [\partial_\mu A_\nu - \partial_\nu A_\mu] \right) \]  \hspace{1cm} (C.13)

C.2.3 Quantum Electrodynamics

In simplest terms, a Lagrangian in Quantum Electrodynamics is the interaction between a bosonic field (photons), such as the massless Klein-Gordon equation, coupled to a fermionic field (electrons), such as the spin \( \frac{1}{2} \) field here potentially describable by the Schrodinger, Dirac or Bethe-Salpeter equations [60].

\[ \mathcal{L}_{QED}^{int} = -\mathcal{H}_{QED}^{int} = -q A_\mu \bar{\psi} \gamma^\mu \psi \]  \hspace{1cm} (C.14)
APPENDIX C. GAUGE INVARIANCE IN CLASSICAL & QUANTUM ELECTRODYNAMICS

The electric four-vector in this Lagrangian is,

\[ j^\mu = q \bar{\psi} \gamma^\mu \psi \]  

where the charge is \( q = e_0 \) for one electron. Of course, with an interacting theory, entirely new problems arise [60]. Exact calculation is practically impossible for most problems, making it a prime candidate for numerical approximation methods.

C.3 Gauge Fixing and Constraints

C.3.1 Coulomb Gauge

The Coulomb Gauge, otherwise known as “minimal coupling”, requires an additional constraint to be imposed,

\[ \nabla \cdot A = 0 \]  

Maxwell’s equations are then transformed into equations of motion of the form,

\[ \Delta \Phi = -\frac{1}{\epsilon_0} \rho \]  

\[ \frac{\partial}{\partial t} A - c^2 \Delta A + \nabla \frac{\partial}{\partial t} \Phi = \frac{1}{\epsilon_0} J \]  

This is the gauge to use when the coulomb field is at around the same order of magnitude, or larger than the external field.

C.3.2 Lorenz Gauge

The Lorenz Gauge, known for being manifestly covariant, requires an additional constraint,

\[ \frac{\partial}{\partial t} \Phi + c^2 \nabla \cdot A = 0 \]  

Maxwell’s equations are then transformed into equations of motion of the form,

\[ \frac{\partial^2}{\partial t^2} \Phi - c^2 \Delta \Phi = \frac{\epsilon_0^2}{\epsilon_0} \rho \]  

\[ \frac{\partial^2}{\partial t^2} A - \Delta A + \nabla \frac{\partial}{\partial t} \Phi = \frac{1}{\epsilon_0} J \]
APPENDIX C. GAUGE INVARIANCE IN CLASSICAL & QUANTUM ELECTRODYNAMICS

This is the gauge to use for strong field approximation, when the external field outweighs the coulomb field by a large margin.

C.3.3 Other Gauges

There are literally an infinite number of gauges to choose from. Simply pick a constraint, apply to Maxwell’s equations to derive the equations of motion, and formulate the system with the new description. The former two gauge choices are the most popular for the type of problem at the focus of this study. Although for a QED formulation, other gauges would potentially see more use, as their benefits are more likely to come into play.
Appendix D

The Unit Cell

D.1 Basic Theory

Unit cells allow a simpler description of a structure. Essentially they rely on a concept from crystallography, where repeating blocks of simpler, smaller structures can be placed adjacent to one another in order to reconstruct the larger pattern. Interestingly enough, there are organic structures which may be described using this concept as well, among them some varieties of collagen [9].

This is by no means an exhaustive resource of the fundamental biology or even crystallography at the heart of the theory behind unit cells themselves. Instead this chapter is provided to give the interested reader a background on one strategy to understand and quantify these structures.

D.1.1 Size Scale

A larger structure which we say is comprised of collagen is really constructed of collagen fibrils [73]. These are themselves ropes of collagen fibers, which in turn are constructed of proteins, made up of amino acids, made up of molecules and finally made of atoms. By now we have seen the relative size scale of atoms and molecules, which can range from $10^{-12}m$ to roughly $10^{-9}m$ in size, depending on complexity and the number of particles involved. Figure [D.1] shown the scale of several larger combinations of these structures.

Larger networks of collagen fibers form relatively expansive extracellular matrices, such as those in eyes, skin, and many other organic structures. These networks can be any size really, but to ignore effects which are quantum in origin and treat the medium as a classical system, generally a
structure of $\sim 0.1 \cdot 10^{-3} m$ or greater is needed for consistent statistical accuracy.

D.1.2 Atoms & Molecules

Using MATLAB’s Bioinformatics Toolbox, one can load in organic structures and view them using their physical descriptions. Figure [D.2] shows the unit cell from one perspective, with the average electron clouds of each atom displayed, while Figures [D.3] and [D.4] show the structure length-wise, with atomic symbols and bonds only, respectively.

These chains of molecules are the basic building blocks of the larger pattern of collagen.
APPENDIX D. THE UNIT CELL

Figure D.3: Collagen Structure: Horizontal view, atomic description (image taken with MATLAB)

Figure D.4: Collagen Structure: Horizontal view, atomic bonds (image taken with MATLAB)

D.1.3 Acids, Fibrils & Fiber Clusters

Now that the individual pieces are known, its time to construct some amino acids. The basic amino acids comprising collagen type-1-α are Proline, Glycine and Hydroxypoline [75]. Figure D.5 shows an example of several acids joining together in a chain.

Figure D.5: Collagen Structure: Proteins and Amino Acid Formulation (source: [76])

A cross section of what this might look like may be seen in Figure D.6.
APPENDIX D. THE UNIT CELL

D.1.4 Crystalline Structures

Using a group of fibers, larger structures are built. Figure D.7 shows how the fibers twist and turn around each other.

The result of this behavior en masse will look similar to Figure D.8. It is clear that more considerations will be needed when the final structure is derived. However, using this basic framework, relatively simple descriptions can be used to create more complex models.
D.2 Repeating Patterns

All of these structures repeat themselves to make larger structures, which repeat to make even larger structures. Based on this, if the simplest structure is known which can uniquely generate the pattern sought after, then a tessellation of this structure is all that is needed in order to replicate the entire pattern.

However, care must be taken since there may be some deviations when scaling up to larger patterns, as deviations in the actual structure from a model may add up to a somewhat different pattern than what occurs in nature. Testing for aberrations becomes important at each step, and should not be neglected if accuracy is a concern [75].

D.2.1 Symmetry

Collagen has cylindrical symmetry, repeating the same building blocks after several iterations of them. Figure D.9 shows this for $(7/2)$ cylindrical symmetry.

A radial projection of this with approximate size given may be observed in Figure D.10. Care must be taken when considering symmetry properties and conditions, since there is some disagreement as to the exact symmetry for some biological structures. In some cases, average symmetry can even disagree with the general consensus on the specific symmetry type of a particular structure [75] [76].

While each piece may be cylindrically symmetric, different angles of fibers might result in a different answer than one generated assuming perfect construction [78]. In fact, recent work...
quantifying these differences has revealed quite a few discrepancies [79] [80]. This makes classical descriptions quite difficult, albeit possible with a great deal of work [8].

### D.2.2 Unit Cells

All of these properties are considered when constructing the final unit cell. In concept, the result should be similar to that displayed in Figure D.11.
APPENDIX D. THE UNIT CELL

D.2.3 Organic Structures as Repeating Crystals

The concept of the unit cell is key to the field of crystallography, the study of repeating atoms in a structure. Once a unit cell of the desired structure has been obtained, a statistical description may be derived. Any discrepancies between the result found in nature and the derived result in the laboratory would mean a flaw in the understanding of the pattern, or body of knowledge about the structure.

The mere fact that one may describe biological structures as "crystals" is in itself quite fascinating. Being able to determine or estimate their behavior from the context of a rather different field of study presents many exciting possibilities for the future.
Appendix E

Source Code

E.1 Language Fundamentals

Each language used in this study tended to be very good for a specific strategy or ideology in which they performed their instructed tasks. As a result, the final product uses them all, rather than one unified language for everything.

E.1.1 MATLAB

MATLAB’s strength is prototyping. It is precompiled, so it will inevitably be significantly slower than any compiled language such as the C-based languages, including MEX Libraries and CUDA Kernels. However, based on how code is formulated and the leniency of syntax relative to the other two languages used here, it is hands down the best for testing new ideas and devising new algorithms.

E.1.2 MEX

MEX, or properly speaking C, is a compiled language, and therefore is formulated for how to run best on the user’s specific hardware setup at compile time. Once a method has been sufficiently polished and tested in MATLAB, it should be moved to a C-function and turned over to MEX. The MEX version of the MATLAB algorithm will often run several times faster than its MATLAB counterpart.
APPENDIX E. SOURCE CODE

E.1.3 CUDA

CUDA Kernels are the very last step. Under no circumstances should an algorithm be parallelized before it is polished, or the results will almost invariably end in disaster. Once a method has been abstracted to a MEX C-based library, a CUDA Kernel may be constructed for it. If devised properly, the resulting Kernel will be many times faster than its original serial MEX cousin, and exponentially faster than its original ancestor implemented in MATLAB.

E.2 Program Structure

E.2.1 Overview

The software developed for this study was left relatively open-ended, with priorities weighted towards relevant scientific results and rapid development speed. This meant relative ease of access in terms of adding new components or algorithms, not to mention modification of existing algorithms. Abstraction was attempted for every piece implemented, but there are improvements and modifications which could be made if a particular version or algorithm is to be used over and over again for the foreseeable future.
APPENDIX E. SOURCE CODE

E.2.2 Flowchart: Serial Algorithms Only

Using serial methods (CPU-algorithms only), the flowchart representing the system is shown in Figure E.1.

Figure E.1: System Flowchart (Serial): CPU-methods only
APPENDIX E. SOURCE CODE

E.2.3 Flowchart: Parallelized Algorithms

When using parallel methods (Custom-built MEX Library and CUDA Kernel(s) on a GPGPU), the flowchart changes in a significant, but simple way, as can be seen in Figure E.2.

Figure E.2: Custom-built MEX Library & CUDA Kernel(s) on GPGPU
APPENDIX E. SOURCE CODE

E.3 Raw Code

Please refer to the packaged source code with its included "ReadMe" file for a much more exhaustive commentary, description and functionality. Here the names of files and their general purpose are given.

E.3.1 MATLAB: Master Function

MASTER CONTROL PROGRAM.m

E.3.2 MATLAB: Memory Indices and Book-keeping

GENERATE SETTINGS.m
DATA STORAGE.m
MemAnalysis.m
createMemIndex.m
VarInitialize.m
LoadFormat.m
SaveFormat.m

E.3.3 MATLAB: FDTD-Q

FDM run.m
FDM fdtdq 1D.m
FDM BCs 1D.m

E.3.4 MATLAB: Post-Processing and Data Analysis

FFT run.m
FFT EnergyCalc.m
FFT StatePopulation.m

E.3.5 MATLAB: Observable System Parameters

PotentialCoulomb.m
Psi0 Generate.m
ITP EigenFinder.m
APPENDIX E. SOURCE CODE

Nth Order ITP EigenFinder.m
PotentialLaser.m

E.3.6 MATLAB: Graphics Generation

GRAPH .m
GRAPH SaveGraphicName.m
GRAPH Potential VS Laser.m
GRAPH SpectralAnalysis.m
GRAPH PopulationState.m
GRAPH PopulationStateNorm.m

E.3.7 MATLAB: AVI Creation

RECORD MOVIE.m
animateWaveFunction.m

E.3.8 MEX: C-Libraries

FDTD PAR.mex64

E.3.9 CUDA: Kernels

FDTD GPGPU.cu