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MMMGRUBS: MOLECULAR MOTION MOVIES AND GEOMETRY RECONSTRUCTION USING BAYESIAN STATISTICS

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Hakuna matata?

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TECHNICAL ABSTRACT

Ever since the early days of Coulomb explosion imaging, the direct imaging of the structure and dynamics of individual molecules has been promised; however, in practice no one has been able to accurately retrieve this structure and all imaging relies on plotting the momentum vectors of the fragments in different ways to infer crude changes in geometry. The momentum vectors tell a large part of the story but do not provide a clear picture of the molecular dynamics everyone seeks so an accurate method of retrieving the structure is highly desirable. I use Bayesian inference and Markov chain Monte Carlo methods to elucidate the molecular geometries, allowing for the study of larger systems than before and for the inclusion of measurement error in these studies for the first time. Using this method, the ultrafast isomerization of carbonyl sulfide and acetylene is imaged in position-space and showcased as a molecular movie. The method, however, is much larger in scope and is generalized to any problem involving a physical system described by a system of ordinary differential equations, where the final conditions are experimentally measured and inference of the initial conditions is desirable.

PLAIN LANGUAGE ABSTRACT

Insert better abstract.

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Part I

HOW TO EXPLODE A MOLECULE

To image the dynamics of a molecule by destroying it seems paradoxical. As we shall see, the molecule's structure is encoded in the atmoic shrapnel left behind after an explosion. However, to destroy one of nature's simplest creations is no easy task. Molecules are held together by strong chemical bonds. Our best line of attach is to shoot them with a short laser pulse—engulfing the molecule in an intense oscillating electric field will strip away its electrons and cause it to break up quickly. In these first few chapters, I will discuss how to create a short laser pulse and how these pulses interact with matter. Then I will introduce the technique of pump-probe Coulomb explosion imaging, which we will use to probe the dynamic structure of small molecules by studying the atomic fragments resulting from the explosion.

1 THE MAKING OF A SHORT LASER PULSE

1.1 SPONTANEOUS AND STIMULATED EMISSION

1.2 PROPERTIES OF A LASER

1.3 PRODUCING LASER LIGHT

1.4 MAKING LASER PULSES

1.5 MAKING SHORT LASER PULSES

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2.2.2 *Tunneling ionization*

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2.3 INTERACTION WITH SINGLE ELECTRONS

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3 COULOMB EXPLOSION IMAGING

3.1 EXPERIMENTAL SCHEME

In pump-probe Coulomb explosion imaging (CEI) one ultrashort laser pulse is split into two pulses through the use an asymmetric beam-splitter. One of the pulses, the pump pulse, is usually much weaker than the other, the probe pulse. A time delay τ between the pulses is then created such that the pump pulse goes first and the probe pulse second. The job of the pump pulse will be to initiate some change in the molecule. One example could include an isomerization of the molecule. Thus the pump pulse "pumps" the molecule into some excited state. The job of the powerful probe pulse is to engulf the molecule in an intense enough laser field such that multiple electrons are stripped off of it. The molecule's individual atoms are left in a highly-charged state and begin to behave as individual point charges in a purely Coulombic potential. The entire process occurs in the presence of a constant electric field and so the positively-charged ions all accelerate upwards towards a time- and position-sensitive detector. Thus the probe pulse allows for the "probing" of the excited state.

Testing this shit

$$\int_{-\infty}^{\infty} e^{-x^2}\,dx = \sqrt{\pi} \tag{3.1}$$

3.1.1 *Femtosecond Multiple Pulse Length Spectroscopy*

3.1.2 *Pump-probe Coulomb explosion imaging*

3.2 EXPERIMENTAL DETAILS

3.3 HISTORY AND ACCOMPLISHMENTS

CEI was first performed by **Vager89** whereby the Coulomb explosion was initiated by passing the molecule through a thin carbon film at high velocities.

3.4 OTHER WAYS OF INITIATING COULOMB EXPLOSIONS

There exist other methods of initiating CEI, among them thin foils, highly-charged ion impact, single X-ray photons from a synchrotron source.

3.5 TIME AND POSITION MEASUREMENT

3.6 CALCULATING ATOMIC FRAGMENT MOMENTA

3.7 UNCERTAINTY IN MOMENTUM MEASUREMENTS

Part II

HOW TO IMAGE A MOLECULE

Having destroyed a molecule and measured the momentum of each of its atomic fragments, we are left with the inverse problem of inferring its structure. While explosions proceed in a deterministic fashion, that is structures map bijectively to momentum measurements, the converse is not true. Two very different structures may produce the same momentum measurements. To make matters worse, there is no analytic solution to the problem and as the molecule grows, the problem of finding its structure becomes increasingly high dimensional. To combat this problem we will require the use of various mathematical and statistical methods. I first discuss some results from the theory of inverse problems to shed some general insight on these problems. I then follow with a discussion of optimization methods which may be used to tackle the problem for very small molecules. However, for full imaging of larger polyatomic molecules with an analysis of measurement error, Bayesian inference using Markov chain Monte Carlo methods is the way to go, which I discuss in the last chapter of this part.

Part III

SHOOTING THE MOVIE

Equipped with the means to explode a molecule and the necessary mathematical tools, we can now image the molecule's structure and shoot our molecular movie.

4 MOLECULAR MOVIES

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4.2 PREVIOUS ATTEMPTS

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