A Computational Approach to Ionized Molecular Diffraction

Introduction

Underlying in the molecular world, chemical processes such as photosynthesis and photodamage of DNA are governed by electron-nucleus interactions within the atoms of a molecule. To remediate our limited understanding of how this process occurs in nature, a method called gas-phase electron diffraction (GED) was proposed in 1930 to determine the structure of molecules and has since been enhanced by laser technology to capture images on ultrafast timescale. Despite significant advances, our current mathematical calculation fails to account for ionized molecules, which is more complicated regarding the scattering pattern and requires a more sophisticated theoretical model to simulate and interpret the diffraction data precisely. This research seeks to explore the methods of modifying the interference pattern calculation with the characteristics of ionized molecules to discover a more efficient model when analyzing data.

Research Question/Hypothesis

The chemical and mechanical energy produced as photons of light encounter a molecule is determined by forming and breaking atomic bonds and vibration, leading to energy dissipation (Centurion, 2021). However, this process wasn't fully understood at the nuclear level due to technological limitations in the early 20^{th} century. Despite significant advancement in gas-phase ultrafast electron diffraction (GUED) of our technology in the pursuit of understanding this process, current models struggle to accurately describe ionized molecules due to limitations in the scattering amplitude calculations.

According to our current theoretical model, the electron scattering signal can be calculated precisely using exact calculations. However, this approach is not highly accurate in practice for two reasons. First, it requires exact knowledge of the molecule's electronic and

nuclear charge density, which is often unavailable for the reaction intermediate. Second, it is highly inefficient in terms of computational power and time. Thus, we need a modified model to make the calculations more accurate and simplified.

This study aims to address this issue by modifying diffraction calculations to include the effects of ionization on scattering amplitudes. We hypothesize that adjusting the diffraction model to account for ionized molecules by incorporating it to the scattering amplitudes will enhance the accuracy of electron diffraction simulations and make the computations 100 times faster compared to traditional models.

Significance of Research

Although X-ray and electron diffraction are the two most powerful tools for understanding the structure and behavior of molecules, electron offers more advantages over X-ray diffraction for materials science and nanoscale characterization. Thus, a simplified model to account for ionized molecule scattering will not only revolutionize the methods of calculating the diffraction pattern, which allows effective determination of the crystalized structure of materials, but also contribute to other fields of science. The information obtained from diffraction experiments can also be used to develop more effective treatments for disease, create next-gen electronics, and clean energy technology.

Recently, Stanford researchers were able to gain new insight into cancer protein with a method called cryo-electron microscopy – an application of electron diffraction – to help develop drugs that are effective at lower doses (Collins, 2022). Moreover, the application of electron diffraction extends beyond Bioimaging to various other fields, such as Chemistry, where it provides the nature of chemical bonds and has been instrumental in establishing trends of structural variations in extended classes of compounds (M. Hargittai and I. Hargittai, 2010).

This project requires a sophisticated understanding of ultrafast science and interference phenomena to perform the calculations with a given set of data. While previous work within the field has examined the theoretical approach to calculating the scattering signals, this project uniquely focuses on the experimental result where ionized molecules play a major role during a chemical reaction such that an accurate model is needed to reduce precious computational time. Uniquely, this research utilizes computer programs to process the diffraction data, anticipating a significant reduction in computation time compared to traditional quantum mechanical scattering calculations.

This research builds on the theory of interference phenomena and molecular scattering, particularly under the mentoring of Dr. Martin Centurion from UNL's Physics Department. Centurion is an expert in this field and has contributed to the development of Ultrafast Imaging of Molecules theory, which has proven effective in determining molecular structures. By modifying the scattering calculation, this research aims to enhance its applicability in the real world and provide a more efficient method for analyzing electron diffraction data.

Method of Data Collection

It was not until the late 20th century that advanced laser technology enabled researchers to capture images under the ultrafast timescale (10^{-15} second). Such methods are called gas-phase ultrafast electron diffraction (GUED), which allows diffraction data retrieval at the intermediate instance of a chemical reaction. Among the models used for analyzing scattering patterns, the independent atomic model (IAM) approximation remains one of the simplest and most effective methods for calculating diffraction data, even though it carries a deficiency in accuracy.

In the IAM, the molecule is treated as a collection of non-interacting atoms such that the elastic scattering intensity of a molecule that is comprised of N atoms can be expressed as

$$I_{mol}(s) = \sum_{i=1}^{N} \sum_{j=1, j\neq i}^{N} |f_i(s)||f_j(s)| \cos(n_i - n_j) \exp\left(-\frac{1}{2} l_{ij}^2 s^2\right) \frac{\sin(sr_{ij})}{sr_{ij}}, \quad (1)$$

where $f_n(s)$ is the atomic form factor (AFF) of the n^{th} atom as a function of momentum transfer s, η_n is the phase shift of the n^{th} atom, and r_{ij} and the internuclear distance (Centurion, 2021). The term $\exp\left(-\frac{1}{2} l_{ij}^2 s^2\right)$ is used for a Gaussian-shaped probability density to model low amplitude vibration.

In cases of photochemically excited molecules involving significant structural arrangements, this becomes insufficient and requires a more general calculation with time-dependent diffraction patterns

$$I_{mol}(s,t) = \sum_{i=1}^{N} f_i^*(s,t) f_i(s,t) + \sum_{j=1, j\neq i}^{N} f_i^*(s,t) f_j^*(s,t) \frac{\sin(sr_{ij})}{sr_{ij}}. \quad (2)$$

As such, the total intensity of the electron scattering can be computed by

$$I_{total}(s,t) = I_{atom}(s,t) + I_{mol}(s,t), \quad (3)$$

where

$$I_{atom}(s,t) = \sum_{i=1}^{N} |f_i(s,t)|^2 . \quad (4)$$

Note that Equation (1) is a derivation of Equation (2) to account for the electronic and thermal effect, with the AFF becoming complex under the first-order correction to the Born approximation,

$$f_i(s,t) = |f_i(s,t)| e^{i\eta_j}. \quad (5)$$

Since $f_n(s,t)$ can be computed with reasonable confidence, we only need to evaluate r_{ij}, the time-dependent internuclear distances to reproduce the experimental diffraction intensities.

Here, the research goal is to modify Equation (1) to account for ionized molecules by applying quantum mechanical theory to calculate the AFF of an atomic ion. To accomplish this, the first step involves developing a Python program that takes the atomic configuration of a gas molecule as input and outputs a simulated diffraction pattern, represented as one- and two-dimensional graphs *(Figure 1)*. Numerical methods will be optimized for computational efficiency, using libraries such as NumPy and SciPy, and validated by comparing simulated diffraction patterns with experimental data, ensuring accuracy in the modified model.

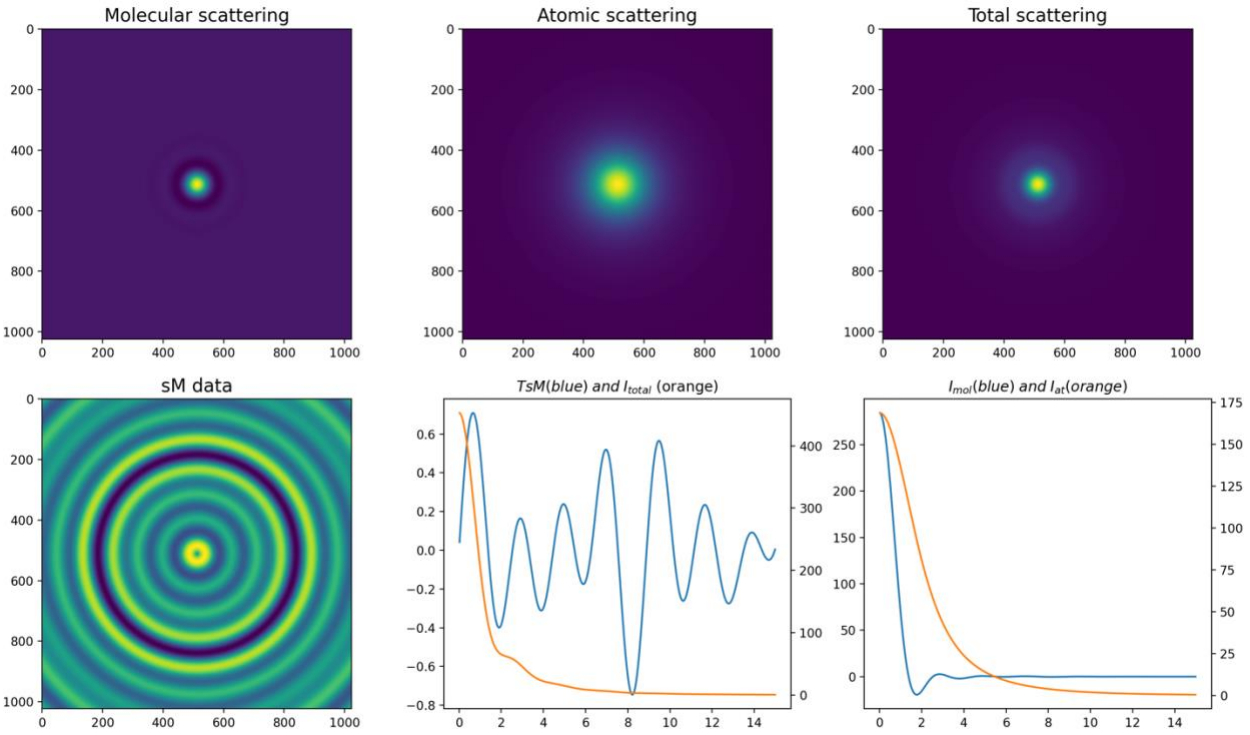

Figure 1. Example Diffraction Output of Trifluoromethyl Iodide (CF3I). Calculations were performed using a program from Cuong Le, a graduate student from the Centurion Group.

Data for the calculations will be sourced from Dr. Centurion's lab using a GUED setup, where ionized molecules are generated and probed using femtosecond electron pulses. *Figure 2* illustrates the setup and execution of these experiments. The analyzed data will then be used to

calculate the AFF of an ionized atom using quantum mechanical scattering theory. Equation (5) will be modified to reflect its properties. This modification will then be generalized and incorporated into Equation (1) through Python simulation.

The outcome is expected to offer a promising solution to the research question by extending the applicability of scattering models to ionized molecules.

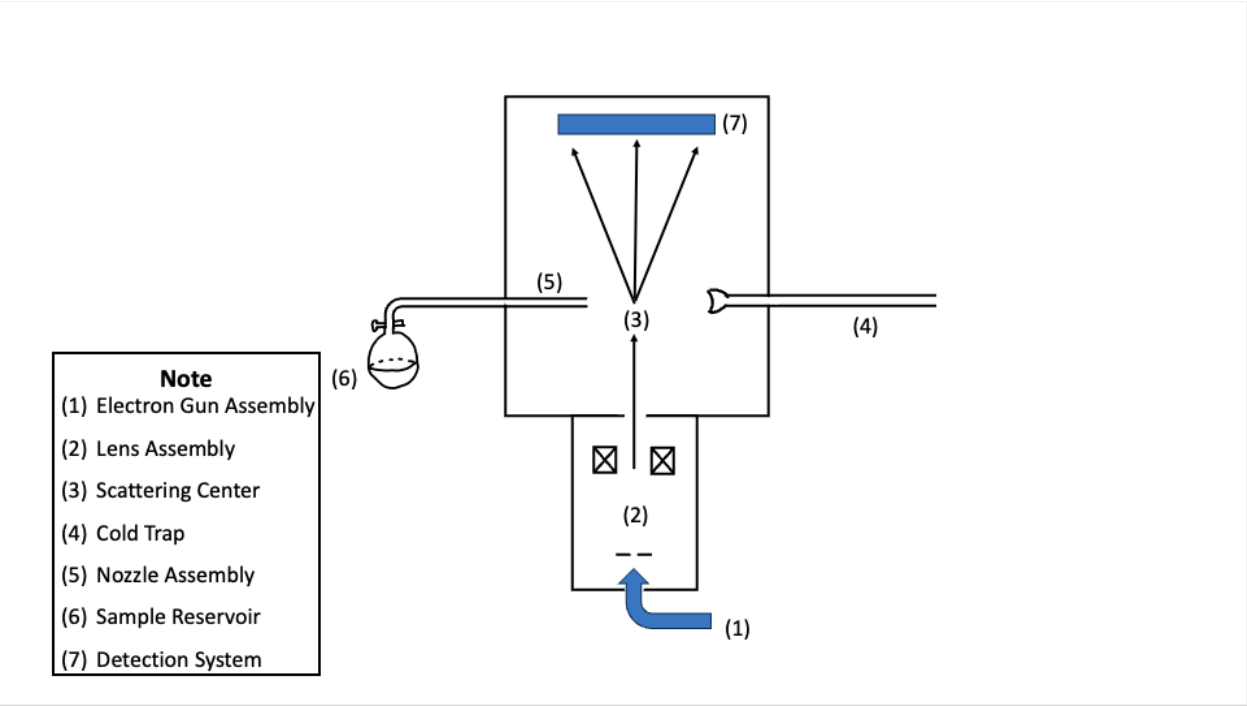

Figure 2. Electron Diffraction Unit

Analysis of Data

In most GUED and GED experiments, the orientations of the molecules are random, resulting in an isotropic diffraction pattern. Since $I_{mol}(s)$ from Equation (2) exhibits a nominal s^{-5} dependence, the intensity decreases rapidly as s increase, causing significant variation in signal levels across the data sets. To address this, a more suitable representation of the scattering intensity is given by

$$sM(s) = s\frac{I_{mol}(s)}{I_{atom(s)}}, \tag{6}$$

and the real-space pair distribution function (PDF) can be found by taking the Fourier transform of $sM(s)$ over a finite range of s

$$P(r) \approx r \int_{s_{min}}^{s_{max}} sM(s) \sin(sr)\, e^{-\alpha s^2} ds\,. \tag{7}$$

Here, $e^{-\alpha s^2}$ is a damping factor to minimize sharp-edged sine-transform effects at high s value (Centurion, 2021).

This study focuses on the structural changes of the molecule during a chemical reaction process by observing the plotted data of Equation (7) with the time-dependent correction to both Equation (6) and (7).

$$sM(s) = s\frac{I_{mol}(s,t)}{I_{atom}(s,t)} \quad and \tag{8}$$

$$P(r;t) = r \int_{s_{min}}^{s_{max}} sM(s,t) \sin(sr)\, e^{-\alpha s^2} ds. \tag{9}$$

These two equations will hence provide the observable outcomes needed to refine Equation (5) and solve the initial research question.

Benchmark

This project will be divided into the following benchmarks:

1. Phase 1 – Foundational Research & Preparation (5/10/2025-7/4/2025): Develop a strong theoretical foundation and computational framework.
2. Phase 2 – Python Program Development & Initial Testing (7/5/2025-9/26/2025): Develop and test the core diffraction model before incorporating ionization effects.
3. Phase 3 – Computing the AFF for Ionized Molecules (9/27/2025-2/27/2026): Perform the most complex computational task – calculating the AFF of ionized atoms.

4. Phase 4 – Integrating AFF into Diffraction Model (2/28/2026-3/26/2026): Modify diffraction equations to incorporate ionized AFF values and analyze the impact on accuracy.
5. Phase 5 – Final Report and Publication (3/27/2026-5/2/2026): Summarize findings and publish results in a physical chemistry journal.

Additionally, progress will be tracked through weekly meetings with the advisor, and updates will be shared via interim reports.

Conclusion

In summary, this research aims to improve the efficiency of the diffraction data in GUED and GED by exploring the method of modifying the AFF of an atomic ion, thereby optimizing computational resources. This project is significant not only in the field of physics but also in contributing to advancements in scientific instruments. With a detailed plan and structured benchmarks, it is positioned for successful completion, ultimately advancing the tools to unlock the universe’s deepest mysteries.

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