Modelling of Ultrafast X-ray Experiments Probing Charge Carrier Dynamics in Solar Cells

Khalili, Khadijeh

Publication date: 2020

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Modelling of Ultrafast X-ray Experiments
Probing Charge Carrier Dynamics
in Solar Cells

Khadijeh Khalili

Lyngby 2020
Improvements of currently achievable power efficiency in solar cells require, as a key prerequisite, a thorough understanding of the evolution of photoexcited electronic states in the presence of strong coupling to nuclei. Methods, which enable such understanding empower the application of common strategies for development and discovery of novel solar cell systems, such as introduction of new functional materials and device architectures as well as directed application of synthesis methods. Tracking the dynamics of a molecule initiated in an excited electronic state constitutes a rather challenging task for both theory and experiment. On the one hand the established theoretical methods, which rely on the Born–Oppenheimer approximation are not sufficient to describe such processes. Nonadiabatic molecular dynamics, which takes into account the coupling between the nuclear and electronic sub-systems is thus a natural choice to attack the problem theoretically. On the other hand, for experimental investigations, real-time imaging techniques are required. Recent advances in time-resolved x-ray science made new real-time imaging of ultrafast processes with sub-femtosecond temporal resolutions available.

In this thesis, I theoretically explore ultrafast charge and nuclear dynamics in a model electron donor-acceptor (D−A) conjugated compound using nonadiabatic molecular dynamics simulations. To this aim, I investigate the use of ultrafast x-ray absorption spectroscopy experiments to directly observe dynamics at the atomic level in which a nonstationary state, initiated by a UV-Vis pump pulse, is tracked by means of a suitable x-ray probe pulse arriving with some time delays.

This thesis involves a new expansion to an in-house software XMOLECULE (developed at CFEL-theory division at DESY in Hamburg) for a mixed quantum-classical treatment of molecular dynamics in electronically excited states. As the first project and in order to validate the code, I considered a scenario of investigating ultrafast hole dynamics after photoionization. I demonstrated how changes in the spectral features of the x-ray absorption spectrum at different time delays can be attributed to the ultrafast charge dynamics in the molecule. In the next step, more realistic process of photoexcitation, relevant to photovoltaic applications, is considered. Results showed how the time-resolved x-ray absorption spectroscopy is able to track electronic and structural dynamics during the excited-state relaxation occurring on a timescale of a few tens of femtoseconds.
Opnåelsen af en detaljeret forståelse af dynamikken i et fotoexciteret, elektronisk system er udgangspunktet til at introducere nye strategier til at forøge effektiviteten af solceller, fx gennem nye funktionelle materialer, nye syntesemetoder og nye komponentarkitekturer. At følge dynamikerne af et molekyle initieret i en exciteret elektronisk tilstand udgør en forholdsvis udfordrende opgave for både teori og eksperimenter. Ved hjælp af non-adiabatisk molekylær dynamik kan man simulere sådanne dynamiker, der har en stærk kobling mellem nuklære bevægelser og elektroniske tilstande, som leder til sammenbruddet af Born-Oppenheimer-approksimationen. I eksperimenter kræver afbildningen af disse dynamikker teknikker, som kan undersøge dem i realtid. Fremragende fremskridt i tidsopløste røntgenteknikker har muliggjort undersøgelser af ultrahurtige processer med tidsopløsninger på mindre end ét femtosekund.

I denne afhandling studerer jeg ultrahurtige ladnings- og nukleardynamikker i et modelsystem af et elektronisk, konjugeret donor-acceptor-molekyle (D−A) ved hjælp af non-adiabatiske molekylær dynamik-simuleringer. Med dette mål undersøger jeg brugen af ultrahurtige røntgenabsorptionsspektroskopieksperimenter til direkte at observere dynamikker på det atomistiske niveau, hvor en ikke-stationær tilstand, initieret af en UV-Vis-pumpepuls, bliver fulgt ved hjælp af egnede røntgenprobepulser, der ankommer med en given forsinkelse.

Denne afhandling inkluderer en ny tilføjelse til et internt udviklet stykke software ved navn XMOLECULE (udviklet i CFEL-teoridivisionen på DESY i Hamborg), der kan behandle molekylær dynamik i elektronisk exciterede tilstande fra en vinkel, der kombinerer kvantemekanik og klassisk mekanik. Som det første projekt, og for at validere koden, undersøger jeg ultrahurtige huldynamikker efter fotoionisering og demonstrerer, hvordan ændringer i de spektrale sæpræg af røntgenabsorptionsspektret ved forskellige forsinkelser kan kobles til de ultrahurtige dynamikker i molekylet. I det næste skridt undersøger jeg en mere relevant proces for solcelleapplikationer, nemlig fotoexcitering. Resultaterne viser, hvordan tidsopløst røntgenabsorptionsspektroskopi er i stand til at følge elektroniske og nuklære dynamikker under relakseringen af exciterede tilstande, der sker på tidsskalærer ned til få tiendedele af et femtosekund.
Preface

This thesis is prepared based on main results obtained during the three years of studies at the Technical University of Denmark (DTU), from 15\textsuperscript{th} of January 2017 to 14\textsuperscript{th} of January 2020, in fulfilment of the requirements for acquiring a PhD degree in the Chemistry, Biotechnology and Chemical Engineering PhD school. The majority of the work was carried out at the section for Imaging and Structural Analysis (ISA) in the Department of Energy Conversion and Storage (DTU-Energy), located at Risø Campus, Roskilde, Denmark. Moreover, the work is based on close collaborations with the CFEL-Theory Division at Deutsches Elektronen-Synchrotron (DESY) in Hamburg, Germany (corresponded to 1 year external stay), where the new extension of an \textit{ab-initio} code was performed. This work was funded by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant Agreement No. 681881).

Structure and scope of this thesis

The scope of this thesis is to develop a new theoretical scheme to probe ultrafast photoinduced processes in organic \textit{c}o-polymers with photovoltaic applications. It is an attempt to address experimental results and also propose experiments that will allow to directly benchmark the theoretical calculations and, in this way, bridge the gap between experiments and theory. In order to address photoinduced ultrafast dynamics, a scenario based on time-resolved x-ray absorption spectroscopy has been considered in the simulations. Because of the high computation cost, an oligomeric model compound (as fragment of the polymer chain) is chosen to study the relevant photoinduced dynamics in the conjugated polymers.

In Chapt. 1, I explain why and how I want to address ultrafast dynamics in organic conjugated molecules. In Chapt. 2, theory of light and matter interactions and formulae to calculate photoabsorption cross-sections are covered. Focus of Chapt. 3 is on the main concepts behind the electronic structure and molecular dynamics methods considered within this thesis. This chapter also explains the new extension of the code, \textit{e.g.}, coupled-perturbed Hartree-Fock method and its derivations. Chapters 4 and 5 present the findings of the charge-transfer and excited-state dynamics simulations in organic D–A molecules and liquid water. A conclusion and an outlook on future directions of research is given in Chapt. 6. As scattering signal calculation is not the core topic of the current thesis, theoretical aspects of scattering processes (first- and second-order) are presented in Appendix A. In addition, an overview of a beamtime
proposal related to my calculations and the original publications are presented in Appendix B and Appendix C, respectively.

**Acknowledgement**

I would like to thank my supervisor, Prof. Jens Wenzel Andreasen, for the guidance and encouragement he has provided throughout my PhD research studies. He cared so much about my work and responded to my questions and queries so promptly and patiently, especially when I was on pressure due to my family situation.

I would like express my deepest gratitude to my supervisor, Prof. Robin Santra, for his precious guidance during my PhD studies, as well as his inspiring personality, scholarly knowledge and enthusiasm.

I would like to say a very big thank you to Dr. Luise Theil Kuhn, head of ISA section, for keeping the doors open for me to bring my concerns to her and for giving always the best advice on my study path and challenges.

I gratefully acknowledge the funding sources, European Research Council (ERC), that made my PhD work possible and the Danish Agency for Science, Technology, and Innovation for funding the instrument center, DanScatt, for financial supports for my beam times.

Completing this work would have been all the more difficult were it not for the support and friendship provided by all my colleagues at SEEWHI and CFEL-theory groups, particularly, Dr. Tiago Ramos as my mentor, Anders Skovbo Gertsen for translating summary, proof-reading of this thesis, and useful endless scientific discussions, Dr. Ludger Inhester for his great support during new extension of XMOLECULE, Dr. Caroline Arnold for working together on the code extension, and Dr. Sophia Bazzi for fruitful discussions on chemistry topics.

I must express my gratitude to my husband, Dr. Vitalij Lutsker, for his continued support and encouragement. I was continually amazed by his willingness to answer my countless programming and data analysis questions.

And last, but not least, a very special word of thanks goes for my parents, sister, and brother for their unconditional love and encouragement.

Lyngby, January 14, 2020

Khadijeh Khalili
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CHAPTER 1

Introduction and Motivation

This first chapter is dedicated to give a short overview of the available renewable energy resources. Furthermore, a brief background of the global solar energy generation and solar cell production is presented. Importance of the organic photovoltaics (OPV) and their efficiency improvements are mentioned. In order to improve efficiencies of OPVs, it is important to understand the fundamental processes in such devices. X-rays and their main sources are introduced as a valuable tool to reach this goal. A short description of time-resolved x-ray techniques to study photoinduced femtosecond dynamics is the focus of the last part of this chapter.

1.1 Solar cells

The growth of industrial societies, the increasing need for energy and the limitation and unequal dispersion of fossil resources (oil, gas, and coal) to the world’s energy, along with the environmental concerns of excessive consumption of fossil fuels such as greenhouse gases from combustion of fuel have made humans think about alternative energy sources. Sources that are replaceable, clean, available, and renewable. Hence, energy from the wind, the sun, biomass, geothermal as well as water (hydroelectric or sea waves) are considered as replacement of fossil fuels in human planning for alternative energy sources.

Table 1.1 presents a comparison between the potential of finite resources and renewable alternatives in the world. The world’s required energy is estimated 16 Terawatt-years. The finite reserves are able to cover the global required energy but they are suffering from their environmental concerns. Among the renewable energies, wind energy has the potential to supply all of the required energy. However, it faces some challenges, e.g. cost and noise pollution, which limits using wind energy to meet global energy demand. As it is seen from Table 1.1, the potential of solar energy in comparison to the annual energy consumption of the world is so high that, despite the constraints, it is capable of supplying a considerable portion of the energy mix of the future [1]. Therefore, the energy applications based on the solar energy has gained a great deal of attention.

Solar energy, the light emitted from the sun, is the result of the continuous process of nuclear fusion in the sun and can be harvested in the form of heat and/or electricity. Photovoltaics (PV) is one of the most widely employed technologies to
Tables 1.1: 2009 estimate of finite and renewable planetary energy reserves (Terawatt-tyears) (Adapted from [1]).

<table>
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<th>Resource Type</th>
<th>Amount (TW-Yr)</th>
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<tr>
<td>Solar</td>
<td>23000</td>
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<tr>
<td>Wind</td>
<td>25-70</td>
</tr>
<tr>
<td>Biomass</td>
<td>2-6</td>
</tr>
<tr>
<td>OTEC</td>
<td>3-11</td>
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<tr>
<td>HYDRO</td>
<td>3-4</td>
</tr>
<tr>
<td>Geothermal</td>
<td>0.3-2</td>
</tr>
<tr>
<td><strong>Finite</strong></td>
<td></td>
</tr>
<tr>
<td>Natural gas</td>
<td>215</td>
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<tr>
<td>Petroleum</td>
<td>240</td>
</tr>
<tr>
<td>Uranium</td>
<td>300</td>
</tr>
<tr>
<td>Coal</td>
<td>900</td>
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generate electricity directly from the solar radiation. PV technologies are usually classified into three main categories or generations. First generation includes monocrystalline and poly-crystalline solar cells, which are produced on wafers and then assembled into panels to increase power. Silicon-based solar cells are by far the most produced in the world, over 80% of the PV market [2, 3]. Thin film solar cells, such as amorphous silicon (a-Si) and copper indium gallium selenide (CIGS) based solar cells, are categorized as the second generation having lower efficiencies than the first generation but with cheaper production costs and the possibility of growth on large areas. Third generation of solar cells have emerged to overcome shortcomings of the previous two categories, such as high costs of first generation and toxicity and limited availability of materials for the second-generation solar cells. This new generation includes dye-sensitized solar cell (DSSC), perovskite solar cells (PSCs), and organic photovoltaics (OPVs) [4, 5]. Among them, OPV cells are considered to be a promising choice to address the increasing demands for renewable energy due to their advantages such as inexpensive large scale production, non-toxic materials, transparency, flexibility, and light weight [6].

1.1.1 Polymer solar cells

A polymer solar cell, as one of the most attractive types of OPV, typically consist of a blend of two materials: an optically active electron donor and an electron acceptor (which may also be optically active, as the advantage of the non-fullerene acceptors). After absorbing sunlight by the light-absorbing donor polymer, the photogenerated bound electron-hole pair, in a simple picture, diffuses randomly until meeting a donor-acceptor interface in which it separates into free charges and will be collected at electrodes [7, 8]. Great efforts have been devoted to the improvement of the power conversion efficiencies (PCEs) of polymer solar cells (their ability to convert light
into electricity), which was low compared to the average of other kind of cells for many years. In order to achieve higher efficiency, several strategies have been taken into account including introduction of new materials, improvement of properties of the existing materials, advances in synthesis processes, and device architecture. Such efforts have increased power conversion efficiency of polymer solar cells substantially from $\sim 5\%$ to a current value of $\sim 17\%$ for the lab-scale devices within less than a decade [9–11]. What is required now is not only to improve further the efficiency but also to improve the stability of the OPVs for the large-scale purposes to be able to compete with conventional silicon cells [12].

Development of new materials have been done through the low-band gap polymers and, particularly, the use of conjugated polymers bearing electron-donating (D) and electron-withdrawing (A) compounds along their backbone and with a possibility to tune the bandgap to better match and harvest the solar spectrum [13–15]. Some of the efficient D-A conjugated polymers are PCDTBT [16, 17], PCPDTBT [18], and PBDTTTPD [19] (shown respectively in Fig. 1.1), which have been widely used as electron donating polymer in OPV devices.

![Figure 1.1: Schematic of (a) PCDTBT, (b) PCPDTBT, and (c) PBDTTTPD polymers (Images from [20–22]).](image)

Besides PCE, performance of PV cells is evaluated by quantum efficiency, which is the ability to separate the photoinitiated electron-hole pairs when arriving at the electron-donor interface and can be limited by some fast excited state relaxation processes such as charge recombination. On the other hand, achieving optimization of the quantum efficiency can give rise to higher PCE. Therefore, it is extremely
important to understand the photoinduced excited-state relaxation processes when designing and developing new PV materials and devices. However, typical timescales for the initial relaxation dynamics and charge-transfer process in OPVs are observed to be hundreds of femtoseconds \[23–25\], which makes it a challenge for theory and experiment to monitor. Atomic nature of the excited-state dynamics, \(i.e.\) ultrashort length and ultrafast time scales, demands theoretical and experimental methods that are sensitive to both the electronic and nuclear degrees of freedom. In theory, detailed exploration of photoinduced dynamics is feasible by using nonadiabatic molecular dynamics simulations. Experimentally, time-resolved techniques are required, in which a pump pulse initiates an excitation and a probe pulse is used for tracking the excited sample after an adjustable delay time (shown schematically in Fig. 1.2). However, time-resolved (pump-probe) experiments using visible light do not necessarily give the full information and in order to gain a clear interpretation of the underlying dynamics, x-ray based setups are attractive.

![Figure 1.2: Time-resolved experimental scheme in which a pump pulse excite the sample and the created excitations are monitored using a probe pulse arriving with some time delays.](image)

### 1.2 X-rays sources and techniques

The rapid development of new ultrafast extreme vacuum ultraviolet (XUV) and x-ray sources, both in laboratories and at large facilities, makes it possible to monitor electronic and nuclear dynamics in real time \[26, 27\]. The use of x-rays are appealing because of high degree of atom specificity as well as its ability to probe ultrafast dynamics. Prominent examples of techniques proposed to probe ultrafast nonadiabatic dynamics in photoexcited molecules are time-resolved x-ray absorption spectroscopy (TRXAS), time-resolved x-ray scattering (TRXS), time-resolved x-ray emission spectroscopy (TRXES), and time-resolved x-ray photoelectron spectroscopy (TRXPS) \[28–31\]. Of these, TRXAS, owning the advantage of probing electronic dynamics, structural dynamics, and the coupling between these two \[32\], is the focus of the present study and is explained in detail in the following.
1.2 X-rays sources and techniques

1.2.1 Synchrotron and free-electron lasers

Synchrotron radiation is the electromagnetic radiation emitted from electrons travelling at high speed, close to the speed of light, c. The travelling path of the electrons is given under the effect of magnetic field from (bending) magnets placed along the curved path of an evacuated storage ring of a synchrotron (Fig. 1.3). Accelerating the electrons emitted from a source (e.g. a heated filament in an electron gun), to reach the expected high energy, has been done by a linear accelerator or linac and then by an evacuated booster ring. In this way, energy of the electrons reaches from millions of electron volts (after linac) to giga electron volts (after booster) before entering the storage ring [33, 34]. Since x-ray phase produced by each electron is random, synchrotron radiation is not highly coherent. Enhanced transverse coherence of x-rays requires a long source-sample distance [35]. One of such facilities is Spring8 in Japan with 1 km long beamline.

Another possibility to enhance the transverse coherence of x-rays is to use free-electron lasers (FELs). The main difference between a FEL and a conventional optical laser is the laser medium that is replaced by free electrons in an accelerator as proposed for the first time in 1971. Besides that, a new scheme called self-amplified spontaneous emission (SASE) is used in FELs instead of the optical cavity. As shown in Fig. 1.4, propagation and transverse acceleration of initially random-phase electrons is carried out along a sinusoidal trajectory, forced by an alternating magnetic field (undulator). The electron micro bunches, created due to the interaction of electrons with the emitted radiation from relativistic electrons onto the electron beam, wiggle coherently in the undulator giving rise to emission of x-ray radiation. This radiation is similar to synchrotron radiation into a narrow forward cone, however, coherent and more intense at the end of the undulator when the electrons are strongly bunched [35, 36].
Figure 1.4: Sketch of a typical x-ray free electron laser showing an increase in the x-ray radiation coherency towards end of the undulator due to interaction of the electrons with the synchrotron radiation they emit (Image from [36]).

Time-resolved x-ray studies of the dynamics of photoexcited materials require instruments with intense and very short x-ray pulses [37]. Brilliance, or brightness has been introduced as a figure of merit for the performance of x-ray facilities and is defined as photons per second, per unit source size and divergence in a given bandwidth (photons/(sec.mrad$^2$.mm$^2$.0.1%bw)). Another important factor is photon flux. The relation between brilliance and photon flux is that the brilliance is given by the spectral flux divided by the transverse photon phase space [38]. Since their discovery in 1895, x-ray sources have been experiencing an increase in their average brilliance by more than 3 orders of magnitude every 10 years [37]. The peak brilliance of today’s state-of-the-art synchrotron radiation and FEL facilities are compared in Fig. 1.5. It is shown that the peak brilliance (brilliance scaled to the length of a single pulse) of FEL radiations are higher than synchrotron radiations. Such that peak brilliance of European x-ray free-electron laser (XFEL) (Hamburg, Germany) is about four orders of magnitude higher than Spring8 and PETRA III (DESY, Hamburg) synchrotron radiations [38]. Therefore, XFELs facilitate probing the structural dynamics of molecules at atomic size and timescales by generating very short pulse duration, extreme peak brilliance and high spatial coherence, which make them distinguishable from synchrotron radiations [39, 40].
1.2.2 Time-resolved x-ray absorption spectroscopy

Core-level transitions (transition of core-level electrons into the valence states) in x-ray absorption spectroscopy (XAS) makes it an element-specific technique and sensitive to local electronic structure. Moreover, the sensitivity of the core-level energies to change in internuclear separation deliver geometric information during the dynamics. A typical x-ray absorption spectrum (as shown in Fig. 1.6 at Pt L$_3$ edge) is characterised by absorption edges and is generally separated into two regimes: x-ray absorption near edge structure (XANES) in a region of photon energy within ±50 eV of the absorption edge; and (b) extended x-ray absorption fine structure (EXAFS) at photon energies more than up to 500 eV above the edge. Pre-edge region of XANES contains information about bound-bound transitions if not forbidden. In the XANES region, created photoelectrons after absorbing x-rays have rather low energies and high scattering cross sections and, therefore, undergo multiple scattering events. Hence, it is possible to extract geometrical structure information around the absorbing atom, *i.e.* bond angles and bond lengths from XANES. In the high energy region of EXAFS, however, the photoelectrons experience single scattering events due to their lower scattering cross sections and deliver information about the local geometric structure around the absorbing site [42–45]. The main focus of this thesis is to calculate XANES features of an x-ray spectrum.
In a time-resolved XANES spectroscopy, a UV/Vis pump pulse excites a valence electron followed by an x-ray probe pulse, which promotes a core-level electron into the created valence vacancy and, in this way, track the photoinduced dynamics. Schematic of a time-resolved XANES spectroscopy technique is illustrated in Fig. 1.7. Temporal resolution of a time-resolved XANES experiment is mostly dependent on the x-ray pulse duration apart from the size of the sample (e.g. a liquid jet) and the degree of precision with which the pump and probe pulses are aligned in time and space. Whereas synchrotron radiations are mostly suitable because of their stability and high photon flux, they have pulse duration of $>30$ picoseconds. It is possible to overcome the temporal limitation of storage ring employing femtosecond slicing techniques to obtain pulse duration in range of tens to hundreds of femtoseconds. However, it reduces the photon flux substantially [42, 43, 46]. With their ultrashort x-ray pulse duration, FELs offer the opportunity to probe photoinduced dynamics in real time. Rapid advances in XFELs offer a potential pulse duration of just a few femtoseconds enabling a rapid growth in time-resolved applications [47].
CHAPTER 2

Theory of Light-Matter Interaction

X-rays, a form of short-wavelength and high-energy electromagnetic radiation, are able to excite an electron from energetically inner shells and act as a selective technique for chemical elements. An x-ray photon can interact with matter within two main mechanisms: scattering and absorption. In the case of scattering and dependent on the energy of incident photon, coherent scattering (e.g. Thomson scattering) and Compton scattering can happen [34, 48]. Aspects and theoretical basis of x-ray scattering cross-sections are presented in Appendix A. This chapter introduces theoretical aspects of the photon-matter interactions focusing on x-ray absorption. For the sake of clarity, it is worth to mention that the derivation of x-ray absorption cross-section is based on the concepts introduced in the PhD tutorial in Ref. [49] and the course report prepared by myself (with the aim of using in thesis) and submitted in May 2017.

By the assumption that the x-ray photon energy is small in comparison to the electron rest energy and the relativistic effects are neglected, we utilize the non-relativistic quantum electrodynamics in order to describe the photon-matter coupled system. Here, the cross-section of absorption process will be presented as the central concept. Atomic units are employed, i.e. the electron charge $|e| = 1$, the electron mass $m_e = 1$, $\hbar = 1$, the speed of light in vacuum $c=1/\alpha$, where $\alpha$ is the fine-structure constant ($\approx 1/137$). The atomic unit of length is bohr, the atomic unit of cross-section is barn ($= 10^{-28} \text{ m}^2$), and the atomic unit of energy is Hartree ($\approx 27.2 \text{ eV}$).

2.1 Hamiltonian

In order to describe interaction of an electromagnetic field with a matter, one may solve the non-relativistic many-body Schrödinger equation (SE) as

$$\hat{H} |\Psi(t)\rangle = i \frac{\partial}{\partial t} |\Psi(t)\rangle$$

(2.1)

where $|\Psi(t)\rangle$ is the total state vector, which corresponds to the whole system and $\hat{H}$ is total Hamiltonian. The total Hamiltonian consists of three terms; many-body electronic Hamiltonian in the absence of an x-ray field ($\hat{H}_M$), photon Hamiltonian ($\hat{H}_{ph}$), and the minimal coupling interaction Hamiltonian between the matter and the
The electromagnetic field ($\hat{H}_{\text{int}}$) are given by

$$\hat{H}_M = \int \! dr \hat{\psi}^\dagger (\mathbf{r}) \left( -\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \right) \hat{\psi} (\mathbf{r})$$

$$+ \frac{1}{2} \int \! dr \int \! dr' \hat{\psi}^\dagger (\mathbf{r}) \hat{\psi}^\dagger (\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi} (\mathbf{r}') \hat{\psi} (\mathbf{r})$$

$$\hat{H}_{ph} = \sum_{k,\lambda} \omega_k \{ \hat{a}^\dagger_{k,\lambda} \hat{a}_{k,\lambda} + \frac{1}{2} \}$$

and

$$\hat{H}_{\text{int}} = \alpha \int \! dr \hat{\psi}^\dagger (\mathbf{r}) \left( \mathbf{p} \hat{A}(\mathbf{r}) \right) \hat{\psi} (\mathbf{r}) + \frac{\alpha^2}{2} \int \! dr \hat{\psi}^\dagger (\mathbf{r}) \hat{A}^2 (\mathbf{r}) \hat{\psi} (\mathbf{r}).$$

The second-quantization representation of electronic Hamiltonian introduced in (2.2) includes\(^1\) the electron kinetic energy, the electron-nucleus attraction, and the electron-electron repulsion, respectively. \(Z\) is the nuclear charge and \(\mathbf{R}_I\) is the position of \(I\)-th nucleus. The field operator \(\hat{\psi}^\dagger (\mathbf{r})/\hat{\psi} (\mathbf{r})\) (as a two-component spinor) creates/annihilates an electron at position \(\mathbf{r}\) (using \(\hat{c}^\dagger/\hat{c}\) operators),

$$\hat{\psi} (\mathbf{r}) = \sum_p \phi_p (\mathbf{r}) \hat{c}_p$$

$$\hat{\psi}^\dagger (\mathbf{r}) = \sum_p \phi_p^\dagger (\mathbf{r}) \hat{c}^\dagger_p,$$

where \(|\phi_p\rangle\) is a set of orthonormal spin orbitals.

In the formalism of second quantization, the photons can be interpreted as excitation of the electromagnetic quantum field, same as the electrons, which can be interpreted as excitations of a quantum field. Photon Hamiltonian (2.3) is given by the Hamiltonian for the free Maxwell’s field as a sum of independent harmonic-oscillator Hamiltonian. The contribution of the zero-point energy \(\sum_{k,\lambda} \omega_k^2 / 2\) could be dropped because only energy differences between states are measurable.

Finally, (2.4) represents the interaction Hamiltonian between the photon and electron fields, following the principle of minimal coupling in combination with the Coulomb Gauge. \(\mathbf{p} (= \nabla / i)\) is the canonical momentum of an electron and the vector potential, \(\hat{A}\), in the mode expression is

$$\hat{A} (\mathbf{r}) = \sum_{k,\lambda} \sqrt{\frac{2\pi}{V \omega_k \alpha^2}} \left[ \hat{a}^\dagger_{k,\lambda} \mathbf{e}_{k,\lambda} e^{ik \cdot \mathbf{r}} + \hat{a}_{k,\lambda}^\dagger \mathbf{e}_{k,\lambda}^* e^{-ik \cdot \mathbf{r}} \right],$$

which is characterized by wave vectors, \(\mathbf{k}\), and the normalized polarization vectors \(\mathbf{e}_{k,\lambda}\) (\(\lambda = 1, 2\)). \(V\) is the quantization volume.

\(^1\) The effect of nucleus is neglected and they only contribute to the potential.
2.2 Eigenstates

Before the interaction with photon, the molecule is considered to be in the ground state \(|\Psi_0^N_e\rangle\), where \(N_e\) denotes the number of electrons. Therefore, \(E_0^{N_e}\) will be the associated energy. In addition, we assume that the photon field is in the Fock state representation \(|\{N_{ph}\}\rangle\) containing \(N_{ph}\) photons in the mode \((k, \lambda)\). Hence, in the interaction picture, the eigenstates of \(\hat{H}_{ph} + \hat{H}_M\) may be written as the product states \(|\{N_{ph}\}\rangle |\Psi_0^{N_e}\rangle\) in which

\[
\left( \hat{H}_{ph} + \hat{H}_M \right) |\{N_{ph}\}\rangle |\Psi_0^{N_e}\rangle = \left( E_{\{N_{ph}\}} + E_0^{N_e} \right) |\{N_{ph}\}\rangle |\Psi_0^{N_e}\rangle,
\]

(2.7)

where \(E_{\{N_{ph}\}} = N_{ph}\omega_{in}\) is the eigenenergy of the photon Hamiltonian (the zero-point energy is dropped). These product states form a complete orthogonal set, and therefore, the eigenstates of \(\hat{H}\) (total interacting photon-electron states) may be expanded in the product basis \(|\{N_{ph}\}\rangle |\Psi_0^{N_e}\rangle\). Assuming the coupling described by \(\hat{H}_{int}\) is not permanently present and only induces a transition between one eigenstate of \(\hat{H}_{ph} + \hat{H}_M\) to another eigenstate of \(\hat{H}_{ph} + \hat{H}_M\), we can study photon absorption and photon scattering processes.

2.3 Time-dependent perturbation theory

Here, we use the time-dependent perturbation theory to find the transition rates and then determine the interaction cross-section. Although, time-dependent perturbation theory is generally used to treat time-dependent processes, it is also useful to treat the time evolution of a system exposed to time-independent perturbations, such as atomic decay or scattering problems.

We consider our coupled system consisting of an unperturbed quantum system with a time-independent Hamiltonian \(\hat{H}_0 = \hat{H}_{ph} + \hat{H}_M\) and a perturbation \(\hat{H}_{int}\) and assume that we know the stationary state vectors of the unperturbed system. When a photon pulse enters an interaction region, the interaction term \(\hat{H}_{int}\) induces a transition into scattering states. Replacing the interaction term \(\hat{H}_{int}\) with the product of \(\hat{H}_{int}\) and a temporal shape function \((\hat{H}_{int} \rightarrow \hat{H}_{int} f(t))\) helps us to introduce the interaction in which long before and long after the interaction, the perturbation disappears. There are some possible forms of \(f(t)\) to satisfy the condition of \(\lim_{t \to -\infty} \hat{H}_{int} f(t) = 0\): sudden, adiabatic, and finite duration temporal shape functions. The most appropriate shape function is adiabatic switching \((f(t) = e^{-\varepsilon |t|} with an infinitesimal \(\varepsilon > 0\), which avoids complications associated with a steep temporal shape function as from higher frequency Fourier components [50].

The initial state of the molecule-photon system in the interaction picture has a
form of

\[ |I\rangle = |N_{\text{ph}}\rangle |\Psi_0^{\text{el}}\rangle, \]

(2.8)

where the electronic ground state, \(|\Psi_0^{\text{el}}\rangle\), is assumed to be nondegenerate and the Fock state \(|N_{\text{ph}}\rangle\) represents the photon field. \(|I\rangle\) is an eigenstate of \(\hat{H}_0\) with eigenenergy \(E_I = N_{\text{ph}} \omega_{\text{in}} + E_0^{\text{el}}\). The state vector in the interaction picture

\[ |\Psi, t\rangle_{\text{int}} = e^{|i \hat{H}_0 t|} |\Psi, t\rangle \]

(2.9)

satisfies the initial condition \(\lim_{t \to -\infty} |\Psi, t\rangle_{\text{int}} = |I\rangle\) and the equation of motion,

\[ i \frac{\partial}{\partial t} |\Psi, t\rangle_{\text{int}} = e^{|i \hat{H}_0 t|} \hat{H}_{\text{int}} e^{-\varepsilon t} |e^{-i \hat{H}_0 t}| |\Psi, t\rangle_{\text{int}}, \]

(2.10)

which leads to an integral form for \(|\Psi, t\rangle_{\text{int}}\).

The \(\hat{H}_{\text{int}}\)-induced transition amplitude from \(|I\rangle\) to \(|F\rangle\) is given by

\[ S_{FI} = \lim_{t \to \infty} \langle F \mid |\Psi, t\rangle_{\text{int}} \]. \]

(2.11)

Using the orthogonality of eigenstates, \(\langle F \mid I \rangle = 0\), and following relations

\[ \delta (E_F - E_I) = \frac{1}{2\pi} \int dt e^{i(E_F - E_I) t} \]

(2.12)

\[ [\delta (E_F - E_I)]^2 = \delta (E_F - E_I) \frac{1}{2\pi} \int_{-T/2}^{T/2} dt e^{i(E_F - E_I) t} = \delta (E_F - E_I) \frac{T}{2\pi}, \]

(2.13)

we obtain the amplitude and the rate for an \(\hat{H}_{\text{int}}\)-induced transition, respectively, as

\[ S_{FI} = -2\pi i \delta (E_F - E_I) \]

\[ \times \left\{ \langle F \mid \hat{H}_{\text{int}} \mid I \rangle + \sum_M \frac{\langle F \mid \hat{H}_{\text{int}} \mid M \rangle \langle M \mid \hat{H}_{\text{int}} \mid I \rangle}{E_I - E_M + i\varepsilon} + \ldots \right\} \]

(2.14)

\[ \Gamma_{FI} = \frac{|S_{FI}|^2}{T} = 2\pi \delta (E_F - E_I) \]

\[ \times \left| \langle F \mid \hat{H}_{\text{int}} \mid I \rangle + \sum_M \frac{\langle F \mid \hat{H}_{\text{int}} \mid M \rangle \langle M \mid \hat{H}_{\text{int}} \mid I \rangle}{E_I - E_M + i\varepsilon} + \ldots \right|^2. \]

(2.15)

\[ \langle \Psi, t \rangle_{\text{int}} = |I\rangle - i \int_{-\infty}^{t} dt' e^{i \hat{H}_0 t'} \hat{H}_{\text{int}} e^{-\varepsilon |t'|} e^{-i \hat{H}_0 t'} |I\rangle - \int_{-\infty}^{t} dt' e^{i \hat{H}_0 t'} \hat{H}_{\text{int}} e^{-\varepsilon |t'|} e^{-i \hat{H}_0 t'} \times \int_{-\infty}^{t'} dt'' e^{i \hat{H}_0 t''} \hat{H}_{\text{int}} e^{-\varepsilon |t''|} e^{-i \hat{H}_0 t''} |I\rangle + \ldots \]
2.4 X-ray absorption

Here, we assumed the state of the system long before the collision is not equal to the state of the system long after the collision ($|I\rangle \neq |F\rangle$). The measured signal is proportional to the sum over all final states of interest, $\sum_F \Gamma_{FI}$. In general, at a given $E_I$, several processes can take place based on the two terms in $\hat{H}_{int}$: annihilation/creation of one photon following by a change in the state of one electron due to $p\hat{A}$ term as well as annihilation/creation of two photons or scattering of one photon from $\hat{A}^2$ term. In the next section, process to find the x-ray absorption cross-sections are explained and the scattering process will be covered in Appendix A.

2.4 X-ray absorption

In order to find the photoabsorption cross-section, the $\hat{H}_{int}$-induced transition rate in (2.15) must be first evaluated. Considering only the first order of $\hat{H}_{int}$ in $\Gamma_{FI}$,

$$\Gamma_{FI} = 2\pi \delta (E_F - E_I) \left| \langle F | \hat{H}_{int} | I \rangle \right|^2,$$

and exploiting only the $p\hat{A}$ term in $\hat{H}_{int}$ in (2.4), we have

$$\Gamma_{FI} = 2\pi \delta (E_F - E_I) \left| \langle F | \alpha \int dr \hat{\psi}^\dagger (r) (p\hat{A}(r)) \hat{\psi} (r) | I \rangle \right|^2. \quad (2.17)$$

Substituting of the initial state $|I\rangle$ with (2.8) and the final state $|F\rangle$ after absorption of x-ray with $|F\rangle = |N_{ph} - 1\rangle |\Psi_{N_{el}}\rangle$, (2.18)
as well as $\hat{A}$ and $p$ with (2.6) and $\nabla \overline{r}$, respectively, in (2.17) gives

$$\Gamma_{FI} = \frac{4\pi^2}{\omega_{in}} \alpha J_{ph} \delta (E_{N_{el}} - E_{N_{el}} - \omega_{in}) \times \left| \langle \Psi_{F}^{N_{el}} \rangle \int dr \hat{\psi}^\dagger (r) e^{ik_{in}.r} e^{ik_{in}.r} \nabla \overline{r} \hat{\psi} (r) |\Psi_{N_{el}}\rangle \right|^2, \quad (2.19)$$

by considering $\left| \langle N_{ph} - 1 | \hat{a}_{k_{in},\lambda_{in}} | N_{ph} \rangle \right|^2 = \delta_{k_{in}k_{in}} \delta_{\lambda_{in}\lambda_{in}} N_{ph}$ and $\left| \langle N_{ph} - 1 | \hat{a}_{k_{in},\lambda_{in}}^\dagger | N_{ph} \rangle \right|^2 = 0$ for the photon field. In (2.19), $J_{ph} = \frac{1}{\alpha} \frac{N_{ph}}{|\Psi_{N_{el}}\rangle}$ is the x-ray photon flux. We now consider the expansion of the field operators introduced in (2.5) and the electric dipole approximation, where $e^{ik_{in}.r} = 1$ and gives rise to disappearing of dependency on the x-ray direction, and we then have

$$\Gamma_{FI} = \frac{4\pi^2}{\omega_{in}} \alpha J_{ph} \delta (E_{F}^{N_{el}} - E_{0}^{N_{el}} - \omega_{in}) \times \sum_{p,q} \langle \phi_p | c_{k_{in},\lambda_{in}} \nabla \overline{r} | \phi_q \rangle \left| \langle \Psi_{F}^{N_{el}} \rangle | c_{p} c_{q} |\Psi_{N_{el}}\rangle \right|^2. \quad (2.20)$$
Here, we assume an independent-electron picture, characterized by one-body Hamiltonian $\hat{F}$, and a closed-shell system in which the orbitals are doubly occupied. We can find the ground-state energy as

$$E_0^{N_{el}} \approx \langle \Phi_0^{N_{el}} | \hat{F} | \Phi_0^{N_{el}} \rangle = \sum_{i=1}^{N_{ph}} \varepsilon_i,$$  \hspace{1cm} (2.21)

where the $N_{el}$-electron ground state, 0-particle-0-hole state, is expressed in terms of a single Slater determinant, $|\Psi_0^{N_{el}}\rangle \approx |\Phi_0^{N_{el}}\rangle$, and $\varepsilon_i$ ($i = 1, ..., N_{el}$) are the occupied orbital energy as the spin orbitals $|\phi_p\rangle$ are called occupied orbitals here. Any other $n$-particle-$n$-hole state, $|\Phi_{a,b,...}^{_{\text{\prime},\text{\prime},...}}\rangle$ ($a, b, ...$ being the virtual orbitals indices), can be constructed based on the ground-state eigenstate of $\hat{F}$. In the independent-electron level, only 1-particle-1-hole excitations (meaning $q = i$ for state $i$ and $p = a$ for state $a$ in (2.20)) of $|\Phi_0^{N_{el}}\rangle$ are accessible (refer to [49] for more details). The singly excited states are obtained by adding one electron to one-hole state, $|\Phi_0^{N_{el}-1} \rangle \equiv \hat{c}_i^\dagger \hat{c}_a |\Phi_0^{N_{el}}\rangle$, as

$$|\Psi_F^{N_{el}}\rangle = |\Phi_i^{a}\rangle \equiv \hat{c}_a^\dagger \hat{c}_i |\Phi_0^{N_{el}}\rangle.$$  \hspace{1cm} (2.22)

We can then rewrite (2.20) as

$$\Gamma_{FI} = \frac{4\pi^2}{\omega_{in}} \alpha J_{ph} \delta(\varepsilon_a - \varepsilon_i - \omega_{in}) \times \left| \langle \phi_a | \mathbf{e}_{k_{in},\lambda_{in}} \cdot \nabla_i | \phi_i \rangle \right|^2,$$  \hspace{1cm} (2.23)

where $\varepsilon_a$ is the orbital energy of virtual orbitals, $|\phi_a\rangle$, in which the additional electron occupied. Hence, the x-ray photoabsorption cross-section for bound-to-bound transitions is

$$\sigma_i^{a}(k_{in},\lambda_{in}) = \frac{\Gamma_{FI}}{J_{ph}} = \frac{4\pi^2}{3\omega_{in}} \alpha \delta(\varepsilon_a - \varepsilon_i - \omega_{in}) \times \left| \langle \phi_a | \mathbf{e}_{k_{in},\lambda_{in}} \cdot \nabla_i | \phi_i \rangle \right|^2.$$  \hspace{1cm} (2.24)

In order to average over spacial orientations of molecules, we sum up over three different polarization directions and divide it by 3. Moreover, the formula is in the velocity gauge and by transforming it to the length gauge, by considering $\langle \phi_a \nabla_i | \phi_i \rangle = i(\varepsilon_a - \varepsilon_i) \langle \phi_a | r_i | \phi_i \rangle$ in atomic units [51, 52], we have

$$\sigma_i^{a}(k_{in},\lambda_{in}) = \frac{4\pi^2}{3\omega_{in}} \alpha \delta(\varepsilon_a - \varepsilon_i - \omega_{in}) \times \sum_{r=x,y,z} \left| (\varepsilon_a - \varepsilon_i) \langle \phi_a | r_i | \phi_i \rangle \right|^2.$$  \hspace{1cm} (2.25)

Since $\varepsilon_a - \varepsilon_i = \omega_{in}$, we rewrite the equation for a general form of transition from molecular orbital $\phi_I$ to $\phi_F$

$$\sigma = \frac{4\pi^2}{3\omega_{in}} \sum_{r=x,y,z} \left| \langle \phi_F | r_i | \phi_i \rangle \right|^2 \delta(\varepsilon_F - \varepsilon_I - \omega_{in}),$$  \hspace{1cm} (2.26)
where $\langle \phi_F | r | \phi_I \rangle$ are transition dipole matrix elements. Satisfying the Einstein relation, $\varepsilon_a = \omega_{in} - I_i$ ($I_i = -\varepsilon_i$ being the ionization potential of a hole in the spin orbital $\phi_i$) by the orbital energy $\varepsilon_a$, can define edge in the x-ray absorption spectrum [49]. Such that, if

- $\omega_{in} < I_i$: in pre-edge region, electron excitation takes place into partially occupied orbitals.
- $\omega_{in} = I_i$: at threshold, the absorption cross-section is finite.
- $\omega_{in} > I_i$: excitation takes place into virtual orbitals $\phi_a$, which oscillates in space more rapidly with increasing $\omega_{in}$ and, therefore, the transition matrix elements decreases.

Equation (2.26) is used to calculate photoabsorption cross-sections in Chapters 4 and 5 using two different electronic structure methods, Hartree-Fock and Configuration-Interaction Singles, respectively. Basis of the used methods are covered in the next chapter.
CHAPTER 3
Computational Framework

In this chapter, basics of the electronic-structure and molecular dynamics methods considered throughout this thesis are briefly reviewed. Current chapter is mainly based on the course report prepared by myself and defended on August 2017 at DTU and the lecture note by Prof. Santra on the theory of photon-matter interactions.

3.1 Electronic-structure methods

Electronic properties of matter are determined by its electronic structure. In molecules, it is described by electronic energy levels and corresponding states. In order to calculate the electronic structure, one needs to solve a many-body Schrödinger equation (SE) associated with the molecular Hamiltonian. In general, the exact solution (exact eigenstate or wavefunction) is not possible and great effort has been made to solve it approximately. Important requirement to an approximate solution is its correct physical behavior. Some of the most important characteristics of the exact state, which should be satisfied by the approximate wavefunction and introduced into the models, are (1) antisymmetry with respect to the permutation of any pair of electrons, (2) square-integrability everywhere in space (and hence normalizability), (3) size-extensivity meaning that for a system containing non-interacting subsystems the total energy is equal to the sum of the energies of the individual systems, (5) variational stability, as well as (6) spin and spatial symmetry. Apart from all characteristics mentioned, the wavefunction describes the electronic structure and properties of the systems which contains \( N \) electrons. Therefore, the approximate wavefunction should be defined in a way to describe the same number of electrons (as an eigenfunction of the number operator). Throughout this thesis, Hartree-Fock (HF) and Configuration-Interaction Singles (CIS) methods, as explained in the following, are used to obtain required electronic structure data for two different study cases.

Before beginning the discussion, I define some important concepts:

- In Born-Oppenheimer (BO) approximation, the nuclei are heavier than the

---

1 With a reasonable level of accuracy and efficiency.
2 It ensures that for all possible variations \( \delta \Psi \), which are orthogonal to the wavefunction, the energy remains unchanged. This condition represents an upper bound to the true ground-state energy (the difference to the exact ground-state energy is the correlation energy). Not all methods guarantee variational stability.
electrons and they can be considered fixed while we solve the electronic Hamiltonian.

- **Inactive orbitals** refer to the orbitals that are doubly occupied in all determinants (e.g., the core orbitals) and are labelled $i, j, k, l$.

- **Active orbitals** are partially occupied and are distinguished (e.g., the valence orbitals) by the labels $v, w, x, y, z$.

- **Virtual or secondary orbitals**, which are unoccupied in all determinants, shown by the indices $a, b, c, d, e$.

- In so-called **closed-shell configuration**, each occupied spatial orbital contains a pair of electrons with opposite spin projections. Such a ground configuration is non-degenerate.

We start from the nonrelativistic molecular electronic Hamiltonian introduced in (2.2),

$$
\hat{H}_M = \int dr \, \hat{\psi}^\dagger(r) \left( -\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|r - R_I|} \right) \hat{\psi}(r)
+ \frac{1}{2} \int dr \int dr' \, \hat{\psi}^\dagger(r) \hat{\psi}^\dagger(r') \frac{1}{|r - r'|} \hat{\psi}(r') \hat{\psi}(r) + V_{N-N},
$$

(3.1)

where $V_{N-N} = \sum_{I,J} \frac{Z_I Z_J}{|R_I - R_J|}$ is nuclear-nuclear repulsion. By expanding the Schrödinger field operators in terms of spin orbitals ($\hat{\psi}_p(r) = \sum \hat{c}_p \phi_p(r)$ in (2.5)), one can rewrite the molecular Hamiltonian as

$$
\hat{H}_M = \hat{h} + \hat{g} + V_{N-N},
$$

(3.2)

where $\hat{h}$ and $\hat{g}$ are one- and two-electron operators, respectively,

$$
\hat{h} = \sum_{pq} \int dr \, \phi_p \left[ -\frac{\nabla^2}{2} - \sum_I \frac{Z_I}{|r - R_I|} \right] \phi_q^\dagger \hat{c}_p \hat{c}_q = \sum_{pq} h_{pq} \hat{c}_p \hat{c}_q = \sum_{pq} h_{pq} E_{pq},
$$

(3.3)

$$
\hat{g} = \frac{1}{2} \sum_{pqrs} \int dr \int dr' \phi_p^*(r) \phi_q^*(r') \frac{1}{|r - r'|} \phi_r(r) \phi_s(r') \hat{c}_p \hat{c}_q \hat{c}_s \hat{c}_r
= \frac{1}{2} \sum_{pqrs} g_{pqrs} \hat{c}_p \hat{c}_q \hat{c}_s \hat{c}_r
= \frac{1}{2} \sum_{pqrs} g_{pqrs} F_{pqrs},
$$

(3.4)

The mixed or general indices $m, n, o, p, q, r, s, t, u$ are used for orbitals of arbitrary or unspecified occupancies.
3.1 Electronic-structure methods

Spin orbitals are spinor eigenstates of an effective one-electron SH,

\[
\left\{ -\frac{\nabla^2}{2} - \sum_{I} \frac{Z_I}{|r - R_I|} + V \right\} \phi_p(r) = \varepsilon_p \phi_p(r), \tag{3.5}
\]

where \(\varepsilon_p\) is called the orbital energy associated with the spin orbital \(\phi_p(r)\). Orbitals with \(\varepsilon_p < 0\) may generally be classified as bound. While unbound orbitals are characterized by \(\varepsilon_p \geq 0\). \(V\) is a mean-field chosen to appropriate the interaction of the electron with all the other electrons in the system. A typical requirement is that \(V\) reflects the symmetry of the spacial arrangement of the nuclei [49].

It is now convenient to represent the electronic Hamiltonian \(\hat{H}_M\) in (3.2) as

\[
\hat{H}_M = \hat{H} + \hat{V}_{res} + V_{N-N}, \tag{3.6}
\]

where

\[
\hat{H} = \hat{h} + \hat{V} \tag{3.7}
\]

and

\[
\hat{V}_{res} = \hat{g} - \hat{V} \tag{3.8}
\]

describe the electronic system at the mean-field level (Fock operator) and the residual electron-electron interaction after subtraction of the mean-filed Fock potential, \(\hat{V}\), respectively. To reach an exact solution of the SE, one must not only construct eigenstates of \(\hat{H}\), which can then be used as a basis for determining eigenstates of \(\hat{H}_M\), but also determine \(\hat{V}\) such as to minimize the impact of \(\hat{V}_{res}\).

3.1.1 Hartree-Fock approximation

Hartree-Fock (HF) model has the simplest wavefunction among the standard models of quantum chemistry [53]. The HF energy is obtained by minimizing the expectation value of the electronic energy (variation principle) with respect to the orbitals occupying a single Slater determinant (a single configuration of spin orbitals or a single space- and spin- adapted configuration state function, CSF\(^4\)) as

\[
E_{HF} = \min \langle \Phi_0^N | \hat{H}_M | \Phi_0^N \rangle, \tag{3.9}
\]

where \(|\Phi_0^N\rangle\) is a single Fock state that provides an optimal approximation to the non-degenerate ground state. As HF is a “mean-field” theory, it may be used for the second goal (an appropriate choice for \(\hat{V}\) and hence for \(\hat{H}\)). The Fock operator (or

\(^4\) A linear combination of Slater determinants that fulfill spin and spatial symmetry constraints: \(|\text{CSF}\rangle = \sum_i C_i |i\rangle\), where \(|i\rangle\) and \(C_i\) are Slater determinants and coefficients with fixed spin symmetry of the wavefunction, respectively.
the associated Hamiltonian) in the HF equations (or the effective one-electron SE), in second quantization representation, is
\[ \hat{H} = \hat{F} = \sum_{pq} f_{pq} c^\dagger_p c_q, \]
where the elements \( f_{pq} \) constitute the Fock matrix. The diagonalization of the Fock matrix gives the solution of the Fock equations with the canonical spin orbitals\(^5\) as the eigenvectors and the orbital energies, \( \varepsilon_p \), as the eigenvalues (\( f_{pq} = \delta_{pq} \varepsilon_p \)). However, by means of an iterative procedure, where the reconstruction and diagonalization of the Fock matrix is repeated until the spin orbitals generated by its diagonalization become identical to those from which the Fock matrix has been constructed. This iterative procedure, and in general, HF method is referred to as the self-consistent field (SCF) method\(^53\).

Similarly, \( \hat{V} \) is written as
\[ \hat{V} = \sum_{pq} V_{pq} c^\dagger_p c_q \]
where
\[ V_{pq} = \sum_i (g_{pqui} - g_{piiq}). \]

The summation over \( i \) in (3.12) means that the Fock potential depends on the form of the occupied spin orbitals. \( g_{pqui} \) and \( g_{piiq} \) are the classical Coulomb interaction and the exchange correction term, respectively, which have a form of two-electron integral
\[ g_{pqrs} = \int dr \int dr' \hat{\phi}^*_p(r) \hat{\phi}^*_q(r') \frac{1}{|r - r'|} \hat{\phi}_r(r) \hat{\phi}_s(r'). \]

The Coulomb interaction is between the electron and the charge distribution of the occupied spin orbitals and the exchange term arises from the antisymmetry of the wavefunction. One can then obtain the HF energy as
\[ E_{HF} = \langle \Phi^N_0 | \hat{H}_M | \Phi^N_0 \rangle = \langle \Phi^N_0 | \hat{H} | \Phi^N_0 \rangle + \langle \Phi^N_0 | \hat{V}_{res} | \Phi^N_0 \rangle + V_{N-N} \]
\[ = \sum_i h_{ii} + \frac{1}{2} \sum_{i,j} (g_{ijij} - g_{iijj}) + E_{N-N} \]
\[ = \sum_{p,q} \varepsilon_p \delta_{pq} - \frac{1}{2} \sum_{p,q} (g_{pqpq} - g_{pqqp}) + E_{N-N}, \]
where from (3.5), \( \varepsilon_p = \langle \phi^*_p | \hat{F} | \phi^*_p \rangle = \hbar^2 + \sum_{q=1}^N (g_{pqpq} - g_{pqqp}). \)

\(^5\)In a canonical representations, which is a diagonal representation, the electrons move independently and occupy the spin orbitals by taking into account the Pauli principle and is only one possible choice of spin orbitals.
3.1 Electronic-structure methods

3.1.1 Restricted Hartree-Fock theory

The restricted Hartree-Fock (RHF) approximation arises from this fact that, in the non-relativistic treatment, there is no mixture of spatial and spin degrees of freedom and we shall write the spin orbitals as a product of a spatial and a spin part [53, 54]. Since we have two eigenvalues, $\pm \frac{1}{2}$, for $\hat{S}_z$, we consider two spin orbitals with the same spatial part but two spin parts of $\alpha$ and $\beta$,

$$\varphi_i(r) = \phi_i(r)\alpha(\sigma) \quad \text{or} \quad \varphi_i(r) = \phi_i(r)\beta(\sigma).$$  \hspace{1cm} (3.15)

Further restriction is to consider the system with an even number of electrons in which, because of doubly occupation of spatial orbitals, causes the total spin to be zero, i.e., a singlet wavefunction. In such a case, we can split the two-electron integrals in (3.13) into two integrals each of which with a summation over $\frac{N}{2}$ spacial orbitals of $\alpha$- and $\beta$-spins. Applying these procedures, the total HF energy becomes

$$E_{RHF} = 2 \sum_i h_{ii} + \sum_{ij} (2g_{ijij} - g_{ijji}) + E_{N-N},$$  \hspace{1cm} (3.16)

which depicts different relative weights of the one- and two-electron contributions in comparison to (3.14). We consider here the orbital energy

$$\varepsilon_i = h_{ii} + \sum_j (2g_{ijij} - g_{ijji}),$$  \hspace{1cm} (3.17)

which yields

$$E_{RHF} = \sum_i (\varepsilon_i + h_{ii}).$$  \hspace{1cm} (3.18)

As a conclusion of this section, the HF wavefunction of a closed-shell electronic system is an antisymmetrized product of independent-particle solutions of the effective one-electron SEs arising from the fact that each electron in the system behaves independently.

3.1.1.1 Koopmans’ theorem

Calculation of all valence-hole states (corresponding to an $(N-1)$-electron system) throughout this thesis has been carried out by employing Koopmans’ theorem [55], a consistent and, at the same time, efficient way to address holes in the outer valence. The method is based on the hypothesis that the single particle electrons do not change in the process of removing one electron from the $N$-electron system (frozen orbital approximation). Let us assume that one electron is removed from the spin orbital $\phi_i$ to produce the $(N-1)$-electron state as [56],

$$|\Phi_i^{N-1}\rangle = \hat{c}_i |\Phi_0^N\rangle,$$  \hspace{1cm} (3.19)
with the expectation value of the energy

\[ E_l^{N-1} = \langle \Phi_l^{N-1} | \hat{H}_M | \Phi_l^{N-1} \rangle. \]  

(3.20)

The ionization potential of this process is then

\[ IP_l = E_l^{N-1} - E_0^N, \]  

(3.21)

where \( E_0^N = \langle \Phi_0^N | \hat{H}_M | \Phi_0^N \rangle = \sum_i h_{ii} + \frac{1}{2} \sum_i \sum_j (g_{ijij} - g_{ijji}) \) is the total electronic energy of the neutral \( N \)-electron system with \( i, j, \ldots \) refer to spin orbitals occupied in \( |\Phi_0^N\rangle \). Similarly, \( E_l^{N-1} = \sum_{i \neq l} h_{ii} + \frac{1}{2} \sum_{i \neq l} \sum_{j \neq l} (g_{ijij} - g_{ijji}) \). We can then find the ionization potential in (3.21) as

\[ IP_l = -h_{ll} - \frac{1}{2} \sum_i (g_{iiii} - g_{i4i}) - \frac{1}{2} \sum_j (g_{ljlj} - g_{ljlj}) \]  

(3.22)

\[ = -\varepsilon_l. \]

Therefore, the negative of the occupied spin orbital energies represents the energy required to remove an electron from that spin orbital. The energy surface of the ionized state (\( N - 1 \) electrons) with a vacancy in orbital \( l \) is, therefore, given by

\[ E_l^{N-1} = E_0^N - \varepsilon_l. \]  

(3.23)

### 3.1.2 Configuration-interaction theory

In configuration-interaction (CI) method, the exact \( N \)-electron wavefunction can be represented as a linear combination of all determinants constructed from a complete set of one-electron basis in the \( N \)-electron Fock space \([53, 57]\). Because of the simple structure of the wavefunction, the CI method has been extensively and successfully applied for small closed- and open-shell molecular systems. However, because of the large number of variables in this method, one should include all configurations generated from the reference space by carrying out excitations up to a given excitation level in the CI expansion. The simplest truncated CI method is configuration-interaction singles (CIS) in which the excited-state wavefunction is written as a linear combination of all possible singly-excited determinants \( |\Phi_1^a\rangle = c_1^a \hat{c}_i^\dagger |\Phi_0^N\rangle \),

\[ |\Psi_{\text{CIS}}\rangle = \sum_{i,a} C_i^a |\Phi_i^a\rangle, \]  

(3.24)

with \( C_i^a \) as the CIS coefficients. This means that there are only particle-hole excitations in addition to the reference HF ground state for the representation of \( \hat{H}_M \). As a consequence of the Brillouin theorem, which states that the CIS wavefunction is
orthogonal to the HF ground state, \( \langle \Psi^a | \hat{H} | \Psi^N \rangle = 0 \), there are no coupling matrix elements between the ground state (zero-particle zero-hole) and the single excitation (one-particle and one-hole) and, therefore, at the CIS level, the HF ground state is an eigenstate of \( \hat{H}_M \). The CIS matrix thus has the following block structure [56]

\[
M = \begin{bmatrix}
\langle \Psi^N | \hat{H}_M | \Psi^N \rangle & 0 \\
0 & \langle \Psi^b | \hat{H}_M | \Psi^a \rangle 
\end{bmatrix}.
\] (3.25)

The zero-particle zero-hole block in (3.25) gives the RHF ground-state energy. The procedure of calculating the one-particle and one-hole block includes considering any pair of occupied and unoccupied orbitals, which leads to an \((n \times n)\)-sized matrix \((n = n_{\text{occ}} \times n_{\text{unocc}})\) with \((\varepsilon_a - \varepsilon_i) + A g_{aiia} - g_{aiii}\) as diagonal \((a = b, i = j)\) and \(A g_{aijb} - g_{abij}\) as off-diagonal \((a \neq b, i \neq j)\) elements, or in a general form as

\[
\langle \Psi^b_j | \hat{H}_M | \Psi^a_i \rangle = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} + A g_{aijb} - g_{abij},
\] (3.26)

where \(A\) can be equal to 2 or 0 for singlets and triplets [58], respectively. The resulting matrix is diagonalized to find the eigenvalues as \(E_{\text{CIS}}\) (electronic excitation energies in the CIS method). CIS is a size-consistent method and leads to a well-defined wavefunction and differentiable energy [59]. Analytical gradient of CIS energy to determine the excited-state geometry is presented in Sec. 3.2.2.

3.2 Molecular dynamics

Ab initio molecular dynamics (AIMD), which mixes the traditional molecular dynamics (MD) and the electronic structure methods, computes the forces acting on the nuclei from state-of-the-art electronic structure theory when MD trajectories are being analyzed. Therefore, AIMD eliminates the need to obtain an empirical or predefined potential, which is usually used in the classical MD. AIMD can tackle a collection of problems, e.g., systems with different atom or molecule types and chemically complex systems. Born-Openheimer molecular dynamics (BOMD) is the basis and one example of adiabatic AIMD [60, 61]. On the other hand, nonadiabatic molecular dynamics (NAMD) has been developed to overcome the breakdown of the methods based on single Born-Openheimer (BO) potential energy surface (PES) in studying some processes involving nonadiabatic electronic transitions between PESs. Such a transition happens when a sufficient population of excited electronic state exists, for instance, during radiation decay or energy and charge transfer. In addition, systems with very small (or zero) energy band gap such as metals break down the BO criterion in which electronic states are widely separated in energy. In NAMD, multiple PESs must be considered to study nonadiabatic transitions leading to understanding their effects on atomic pathways. An adiabatic PES \((E(R))\) is a function of all nuclear positions and brings a \(3N\)-dimensional hypersurface of the electronic energy of an \(N\)-atom system [62, 63].
Among two different representations of wavefunctions, adiabatic and diabatic, the former is more available in standard electronic structure states by solving the electronic Schrödinger equation (SE) and minimizing the number of transitions at low energies [64]. In addition to quantum-mechanically solving the time-dependent electronic SE for fixed nuclear positions, there are several approaches to address the nuclear equation of motion. These approaches can be divided into three categories: fully quantum (e.g., time-dependent Hartree (TDH) and multi-configurational time-dependent Hartree (MC-TDH)), semiclassical (e.g., density matrix and quantum Liouville), and mixed quantum-classical (e.g., Ehrenfest MD and surface hopping (SH)) methods. There are some issues which should be considered in choosing an appropriate molecular-dynamics method. Both TDH and Ehrenfest MD are based on a single effective PES and are not able to describe quantum entanglement, e.g., the correlation between electronic states and the nuclear path when the ground and excited PESs have a significant population [63]. Another issue is the quantum back-reaction problem arising from changing in the forces, that govern the classical nuclear motion, due to the changes of quantum states. Only adiabatic representation based SH adequately described this feedback between the quantum transitions and the classical trajectories [64]. In addition, SH approximately satisfy detailed balance, which means that the population of different quantum states approach the correct Boltzmann probabilities and will be in Boltzmann equilibrium in the long time limit and at a given temperature [65].

### 3.2.1 Surface hopping

The starting point to derive MD equations is the time-dependent non-relativistic electronic SE [66]

\[ i \frac{\partial}{\partial t} \Psi(r, t; R(t)) = H \Psi(r, t; R(t)) \]  

(3.27)

with \( r_i \) and \( R_I \) as electronic and nuclear degrees of freedom, respectively, and the total molecular Hamiltonian,

\[ H = - \sum_I \frac{\nabla_i^2}{2M_I} - \sum_i \frac{\nabla_i^2}{2} + \sum_{i<j} \frac{1}{|r_i - r_j|} - \sum_{I,i} \frac{Z_I}{|R_I - r_i|} + \sum_{i<j} \frac{Z_I Z_J}{|R_I - R_J|} \]

\[ = - \sum_I \frac{\nabla_i^2}{2M_I} + H_e(\{r_i\}, \{R_I\}), \]  

(3.28)

where the two first terms are kinetic energy of the electrons and nuclei, respectively, \( I \) and \( J \) refer to the the nuclei with atomic number \( Z_I \) and \( Z_J \), and \( i \) and \( j \) refer to the the electrons at positions \( r_i \) and \( r_j \). \( H_e = - \sum_i \frac{\nabla_i^2}{2} + V(\{r_i\}, \{R_I(t)\}) \) is the electronic part of the molecular Hamiltonian, at the nuclear position \( \{R_I\} \), with taking into account the nuclear-nuclear repulsion in addition to electron-electron repulsion and electron-nuclear attraction in \( V \). We now need to choose a suitable representation for...
the electronic part as well as an accurate method for computing the required diagonal and off-diagonal PESs.

SH method (here, trajectory surface hopping), which compromise between accuracy and efficiency, is based on classical treatment of nuclei with considering the nonadiabatic transfer of “amplitude” between electronic states as the only nuclear quantum effect. SH is based on a multi-configurational expansion of the molecular wavefunctions using the ansatz \[ [66, 67] \]

\[
\Psi(r, t; R(t)) = \sum_{k=0}^{\infty} c_k(t) \psi_k(r; R(t)), \tag{3.29}
\]

where \(\psi_k(r; R)\) is adiabatic electronic wavefunction, which depends parametrically on the nuclear coordinates \(R(t)\), and \(c_k\) is the time-dependent expansion coefficient. When we insert (3.29) into the time-dependent electronic SE (3.27),

\[
i \frac{\partial}{\partial t} \sum_k c_k(t) \psi_k(r; R) = H \sum_k c_k(t) \psi_k(r; R) \tag{3.30}
\]

and projecting on each adiabatic electronic state,

\[
\langle \psi_l \big| i \frac{\partial}{\partial t} \sum_k c_k(t) \psi_k(r; R) \rangle = \langle \psi_l \big| H \sum_k c_k(t) \psi_k(r; R) \rangle, \tag{3.31}
\]

we find the LHS and RHS of (3.31), respectively, as

\[
\langle \psi_l \big| i \frac{\partial}{\partial t} \sum_k c_k(t) \psi_k(r; R) \rangle = i \sum_k \frac{dc_k(t)}{dt} \langle \psi_l \big| \psi_k \rangle + i \sum_k c_k(t) \langle \psi_l \big| \frac{\partial}{\partial R} \psi_k \rangle = i \frac{dc_l(t)}{dt} + i \sum_k c_k(t) \psi_l \frac{\partial}{\partial R} \psi_k \tag{3.32}
\]

and

\[
\langle \psi_l \big| H \sum_k c_k(t) \psi_k(r; R) \rangle = \sum_k c_k(t) \langle \psi_l \big| H \psi_k \rangle = \sum_k c_k(t) H_{kl}. \tag{3.33}
\]

Using the chain rule

\[
\langle \psi_l \big| \frac{\partial}{\partial R} \psi_k \rangle = \langle \psi_l \big| \frac{\partial}{\partial \mathbf{R}} \psi_k \rangle \cdot \frac{d\mathbf{R}}{dt} = \mathbf{d}_{kl} \cdot \dot{\mathbf{R}}, \tag{3.34}
\]

and putting (3.32)-(3.34) into the time-dependent SE (3.31), we find a set of coupled equations of motions for \(c_k(t)\) as the time-dependent complex state amplitude for each trajectory as

\[
i \frac{dc_l(t)}{dt} = \sum_{k=0}^{\infty} c_k(t) \left( H_{kl} - i d_{kl} \cdot \dot{\mathbf{R}} \right) \tag{3.35}
\]
where \( \mathbf{d}_{kl}(\mathbf{R}) \) is the first-order nonadiabatic couplings vector (NACV) and account for the finite kinetic energy of the nuclei. \( \eta_{kl} = \mathbf{d}_{kl} \cdot \dot{\mathbf{R}} \) is considered as the first-order derivative coupling between BO states. It is convenient here to define the electronic density matrix \([68]\) as

\[
\rho_{kl}(t) = c_k(t) \cdot c_l^*(t)
\]

with diagonal elements, \( \rho_{kk} \), as state population and off-diagonal elements, \( \rho_{kl} \), as the coherence and rewrite (3.35)

\[
i \frac{\partial \rho_{kl}}{\partial t} = \sum_j \{ \rho_{jl}[H_{kj} - i\mathbf{R} \cdot \mathbf{d}_{kj}] - \rho_{kj}[H_{jl} - i\mathbf{R} \cdot \mathbf{d}_{jl}] \}.
\]

### 3.2.1 Fewest switches algorithm

Generally, adiabaticity is introduced by allowing the trajectory to hop between surfaces. In early days, only electronic population, \( \rho_{kk} \), were considered so that hops occurs when the population of the current state lowers under certain threshold. It means that switches could occur at any point of the configurational space. Now, we derive an algorithm which minimize the number of state switches. Starting point is to consider the number of trajectories assigned to state \( k \), out of \( N \) trajectories at time \( t \) \([68, 69]\),

\[
N_k(t) = \rho_{kk}(t)N.
\]

If the population of \( k \) decreases at a short time later \( t' = t + \Delta t \), then \( N_k(t') < N_k(t) \) or \( \delta N = N_k(t) - N_k(t') > 0 \) which \( \delta N \) is the minimum number of hops from \( k \) to any other \( l \neq k \). The minimum number of hops from \( l \neq k \) to \( k \) is zero. The probability that one of \( N_k \) trajectories will switch is

\[
P_k(t)dt = \frac{\rho_{kk}(t) - \rho_{kk}(t')}{\rho_{kk}} \approx -\dot{\rho}_{kk}\delta t \rho_{kk}
\]

where

\[
\dot{\rho}_{kk} = c_k^*c_k + c_k^*c_k^* + c_k^*c_k^* = 2\Re(c_k^*c_k).
\]

Inserting (3.35), in the form of \( \frac{\partial c_k(t)}{\partial t} = -\sum_l c_l(t) \left( iH_{lk} - \mathbf{d}_{lk} \cdot \dot{\mathbf{R}} \right) \), into (3.40) gives rise to

\[
\dot{\rho}_{kk} = -2\Re \sum_{l \neq k} c_l(t) \left[ iH_{lk} - \mathbf{d}_{lk} \cdot \dot{\mathbf{R}} \right]
\]

\[
= -2 \sum_{l \neq k} [\Im(\rho_{kl}H_{kl}) - \Re(\rho_{kl}\mathbf{d}_{kl} \cdot \dot{\mathbf{R}})].
\]

Substituting (3.41) into (3.39) and integrating over time then leads to

\[
P_k = -2 \sum_{l \neq k} \int_{t}^{t+\Delta t} dt \left[ \frac{\Im(\rho_{kl}H_{kl}) - \Re(\rho_{kl}\mathbf{d}_{kl} \cdot \dot{\mathbf{R}})}{\rho_{kk}} \right]
\]
3.2 Molecular dynamics

Sum in (3.42) means that $P_k$ is the probability to hop from state $k$ to any state. The probability of hop from state $k$ to a particular state $l$ is then

$$P_{k\rightarrow l} = -\frac{2\int_{t}^{t+\Delta t} dt [\Im(\rho_{kl}H_{kl}) - \Re(\rho_{kl}d_{kl} \cdot \dot{R})]}{\rho_{kk}}. \quad (3.43)$$

In an adiabatic representation $H_{kl} = 0$ and

$$P_{k\rightarrow l} = \frac{2\int_{t}^{t+\Delta t} dt [\Re(\rho_{kl}d_{kl} \cdot \dot{R})]}{\rho_{kk}} \Delta t. \quad (3.44)$$

where integrating over a small time step gives rise to

$$P_{k\rightarrow l} = \frac{2\Re(\rho_{kl}d_{kl} \cdot \dot{R})}{\rho_{kk}} \Delta t. \quad (3.45)$$

By considering a positive number of hops (population decreasing),

$$g_{kl} = \max(P_{kl}, 0) \quad (3.46)$$

and comparing the hopping probability with a random number $\zeta \in [0, 1]$, a hop from state $k$ to $l$ occurs when

$$\sum_{i \leq l-1} g_{ki} < \zeta < \sum_{i < l} g_{ki}. \quad (3.47)$$

This algorithm, which is called “fewest switches (FS) algorithm”, guarantees that minimum number of hops is preformed along each trajectory. Between hops, the classical trajectories evolve on a single adiabatic (BO) PES at any given time according to Newtonian equation of motion. For PES $k$, the nuclei experience forces are then given by

$$F_I = -\frac{\partial E_k(R)}{\partial R_I}. \quad (3.48)$$

3.2.1.1 Velocity adjustment

If a stochastic hop is accepted, a new scaling for the momenta of the nuclei along $d_{kl}(R)$ is required to conserve the total energy. When the system jumps from a state $k$ to a state $l$, the velocity of each nucleus $I$ will be re-scaled by

$$\dot{R}_I^{(l)} = \dot{R}_I^{(k)} - \gamma_{kl} \frac{d_{kl}^I}{M_I} \quad (3.49)$$

where $\gamma_{kl}$ is a scaling factor to be determined, and the overall kinetic energy change is then

$$\Delta K = \frac{1}{2} \sum_I M_I \left(\dot{R}_I^{(l)}\right)^2 - \frac{1}{2} \sum_I M_I \left(\dot{R}_I^{(k)}\right)^2 = a_{kl}\gamma_{kl}^2 - b_{kl}\gamma_{kl} \quad (3.50)$$
where

\[ a_{kl} = \frac{1}{2} \sum_I \left( \frac{d_{kl}^I}{M_I^2} \right)^2, \]  

(3.51)

\[ b_{kl} = \sum_I \mathbf{R}_I^{(k)} \cdot \mathbf{d}_{kl}^I. \]  

(3.52)

By considering the total energy conservation (\(\Delta K = \Delta E\))

\[ a_{kl} \gamma_{kl}^2 - b_{kl} \gamma_{kl} - (E_l - E_k) = 0, \]  

(3.53)

we can find that if \(b_{kl}^2 + 4a_{kl}(E_l - E_k) < 0\), a switch cannot happen because there are no real solutions to (3.53). Therefore, the nuclear velocities are reversed\(^6\) by setting \(\gamma_{kl} = b_{kl}/a_{kl}\). This situation is similar to the back reflected density due to the lack of quantum effects such as tunneling arises from classical nature of nuclear subsystem in the mixed quantum-classical calculations [71]. In the case of \(b_{kl}^2 + 4a_{kl}(E_l - E_k) \geq 0\), the scaling factor is the solution and ensures that the total energy is conserved exactly [72].

3.2.1.III Frustrated hops

A hop, which is not allowed energetically, is called frustrated and will be ignored: if the target state has an energy greater than the total energy of the system, hop will be energetically forbidden. It means that the kinetic energy of the initial state \(k\) is less than the energy gap between the two potential energy surfaces,

\[ T_h(k) < E(l) - E(k), \]  

(3.54)

where \(\mathbf{h} = \frac{\mathbf{d}_{kl}}{d_{kl}}\) is a unit vector in the direction of the nonadiabatic coupling vector. In this case, the nuclear velocity should be reversed along the hopping vector [73, 74].

3.2.1.IV On-the-fly surface hopping algorithm

Figure (3.1) depicts the basic FSSH algorithm. Let consider the state \(k\) as the current state and state \(l \neq k\) as any other state, each iteration of FSSH algorithm will then have the steps listed below:

1. There are different ways to generate the initial conditions, \(e.g.,\) nuclear coordinates and momenta. In this thesis, the sampling has been done using the vibrational ground state distribution of neutral molecule. By employing the microcanonical normal mode sampling, a zero-point energy is assigned to each

\(^6\)Or the velocities will not be adjusted [70].
3.2 Molecular dynamics. The ensemble of the coordinates and conjugated momenta for the classical trajectories are calculated, respectively, by

\[ q_i = \sqrt{\frac{2E_i}{f_i}} \cos (2\pi \zeta_i) \] (3.55)

\[ p_i = \sqrt{2m_iE_i} \sin (2\pi \zeta_i) \] (3.56)

where \( i = 1, \ldots, N \) is the number of normal modes. \( E_i, f_i, \) and \( m_i \) are the zero-point energy, the force constant, and the mass of the \( i \)th normal mode, respectively. \( \zeta \) is a uniformly distributed random number in the \([0,1]\) interval.

2. Find the energies and energy gradients from the electronic structure methods as a function of time and nuclear degrees of freedom.

3. Use of Velocity-Verlet algorithm \([77]\) to propagate nuclear coordinates (in (3.48)) at each time step \( \Delta t \)

\[ v(t + \frac{\Delta t}{2}) = v(t) + \frac{1}{2}a(t)\Delta t \] (3.57)

\[ x(t + \Delta t) = x(t) + v(t + \frac{\Delta t}{2})\Delta t \] (3.58)

\[ a(t + \Delta t) = \nabla E(t + \Delta t) \] (3.59)

\[ v(t + \Delta t) = v(t + \frac{\Delta t}{2}) + \frac{1}{2}a(t + \Delta t)\Delta t \] (3.60)

which give rise to

\[ \mathbf{R}(t + \Delta t) = \mathbf{R}(t) + v(t)\Delta t + \frac{\nabla E(t)}{2M} \Delta t^2 \] (3.61)

\[ v(t + \Delta t) = v(t) + \frac{\nabla E(t) + \nabla E(t + \Delta t)}{2M} \Delta t. \] (3.62)

4. Propagate quantum amplitude in (3.35) at each electronic time step \( \delta t \).

5. Generate a random number \( \zeta \in [0,1] \) and compare it to (3.47) to figure out whether or not a hop occurs. If not, return to step 2. and recalculate required parameters for the next time step.

6. Check the occurrence of a frustrated hop using (3.54) and reject hop if it is energetically forbidden. Then, return to step 2. and recalculate required parameters for the next time step.

7. If hop is not forbidden, adjust velocities using the procedure in section (3.2.1.II) to conserve the total energy of the system.

8. Consider the state after hop as the current state and go to step 2.
Initial condition generation

Calculate $E_k$ and $\nabla E_k$ as a function of nuclear coordinates and time.

Set new $k$

Propagate nuclei.

Propagate quantum amplitude and compute $P_{k\rightarrow l}$

Generate random number and compare to FS algorithm.

Adjust velocities.

Yes

Enough $T$?

Yes

No

Yes

Hop?

No

Reject hop and reverse velocities.

Figure 3.1: Flow chart of the FS algorithm.
3.2 Molecular dynamics

3.2.2 Evaluation of coupling matrix elements and energy gradients

The procedure in (3.2.1.IV) involves, in each iteration, evaluation of energy gradients and the nonadiabatic couplings between different electronic states. Analytic calculations of these parameters are implemented in XMOLECULE by L. Inhester, C. Arnold, and myself based on coupled-perturbed Hartree-Fock (CPHF) method introduced in [78–80]. The procedure covered here is adapted from derivation by L. Inhester. In this section, Greek subscripts refer to spin-orbital basis functions (atomic orbitals) and indices $i, j, k, l$ are used for molecular orbitals of arbitrary occupancy.

3.2.2.1 Energy gradient

**A. RHF**

In the Roothaan-Hall formulation, which is normally applied to the HF theory, the molecular orbitals (MOs), $\phi_p$, are expanded in a set of atomic orbitals (AOs), $\chi_p$,

$$\phi_p = \sum_{\mu} C_{\mu p} \chi_{\mu},$$

(3.63)

where the MO coefficients, $C_{\mu p}$, may be used as the variational parameters to optimize the HF energy. Minimization of the RHF energy in (3.16) with respect to the linear coefficients $C_{\mu p}$ in (3.63) leads to the RHF Fock-type equation

$$\sum_{\nu} (F_{\mu \nu} - \varepsilon_p S_{\mu \nu}) C_{\nu p} = 0$$

(3.64)

where $S_{\mu \nu}$ is overlap between AOs. The coefficients $C_{\nu p}$ are subject to the orthonormalization condition of the spin orbitals, which requires the condition

$$\sum_{\mu \nu} C_{\mu p}^* S_{\mu \nu} C_{\nu p} = \delta_{pq}.$$  

(3.65)

In (3.64), $F_{\mu \nu}$ is the $N \times N$ RHF Fock matrix elements given by

$$F_{\mu \nu} = h_{\mu \nu} + \sum_{0}^{n} (2(\mu \nu | oo) - (\mu o | \nu o))$$

(3.66)

where the sum is over the number of occupied orbitals and, in AO space,

$$h_{\mu \nu} = \int d\mathbf{R} \chi_{\mu}^*(\mathbf{R}) \hat{h} \chi_{\nu}(\mathbf{R})$$

(3.67)

$$(\mu \nu | \kappa \lambda) = \int d\mathbf{R} \int d\mathbf{R}' \chi_{\mu}^*(\mathbf{R}) \chi_{\nu}^*(\mathbf{R}) \frac{1}{|\mathbf{R} - \mathbf{R}'|} \chi_{\kappa}(\mathbf{R}') \chi_{\lambda}(\mathbf{R'}).$$

(3.68)
Now, the goal is to find solutions of the Fock equations (3.64) for values of \( R = R_0 + \delta R \), the molecular geometry, in the vicinity of \( R_0 \), undisturbed geometry, for which solutions are already available. Therefore, we write the Fock equation (3.64) for parameter \( R \) in the matrix form

\[
F(R)C(R) = S(R)C(R)E(R) \tag{3.69}
\]

with the orthonormality condition between spin orbitals for all values of \( R \)

\[
C^\dagger(R)S(R)C(R) = 1. \tag{3.70}
\]

\( C(R) \) is the full matrix and \( C_p(R) \) (coefficients of the spin orbitals \( \phi_p \)) as its columns and \( E(R) \) is the diagonal matrix of one-electron orbital energies, \( \epsilon_p(R) \). For the simplicity, transformation of the spin orbitals is considered via

\[
C(R) = C(R_0)U(R), \tag{3.71}
\]

where \( U(R_0) \) is the unit matrix (\( U_{ij}(R_0) = \delta_{ij} \)). For further simplification, we can write the Fock and overlap matrix elements transformed by \( C(R_0) \) (in MO space) given, respectively, by

\[
\mathfrak{F}(R) = C^\dagger(R_0)F(R)C(R_0) \tag{3.72}
\]

\[
\mathfrak{S}(R) = C^\dagger(R_0)S(R)C(R_0). \tag{3.73}
\]

Substituting (3.71) in (3.69), multiplying on the left by the Hermitian conjugate \( C^\dagger(R_0) \), and considering (3.72) and (3.73), we obtain the HF equations in the matrix form at geometry \( R \) as

\[
\mathfrak{F}(R)U(R) = \mathfrak{S}(R)U(R)E(R) \tag{3.74}
\]

\[
U^\dagger(R)\mathfrak{S}(R)U(R) = 1. \tag{3.75}
\]

Now, in order to solve the basic equations (3.74) and (3.75) for small \( R \), we expand the main matrices in powers of \( R \) to the second order as

\[
\mathfrak{F}(R) = \mathfrak{F}(R_0) + \delta R \mathfrak{F}^{(1)} + (\delta R)^2 \mathfrak{F}^{(2)} + O((\delta R)^n) \tag{3.76}
\]

\[
\mathfrak{S}(R) = \mathfrak{S}(R_0) + \delta R \mathfrak{S}^{(1)} + (\delta R)^2 \mathfrak{S}^{(2)} + O((\delta R)^n) \tag{3.77}
\]

\[
U(R) = U(R_0) + \delta R U^{(1)} + (\delta R)^2 U^{(2)} + O((\delta R)^n) \tag{3.78}
\]

\[
E(R) = E(R_0) + \delta R E^{(1)} + (\delta R)^2 E^{(2)} + O((\delta R)^n), \tag{3.79}
\]

where, as already mentioned, \( \mathfrak{S}(R_0) = 1, U(R_0) = 1 \), and \( \mathfrak{F}(R_0) = E(R_0) \) \( (\mathfrak{F}_{kj}(R_0) = \epsilon_j(R_0)\delta_{kj}) \). \( O((\delta R)^n) \) are the \( n \)th order of \( \delta R \). Substituting (3.76)-(3.79) into (3.74)
and (3.75) and equating the terms with the same order of $\delta R$, we obtain the coupled-perturbed Hartree-Fock (CPHF) equations and overlap criterion as

$$
\mathbf{\tilde{S}}^{(1)} + \mathbf{E}(R_0) \mathbf{U}^{(1)} = \mathbf{\tilde{S}}^{(1)} \mathbf{E}(R_0) + \mathbf{U}^{(1)} \mathbf{E}(R_0) + \mathbf{E}^{(1)}
$$

(3.80)

and

$$
\mathbf{U}^{(1)\dagger} + \mathbf{\tilde{S}}^{(1)} + \mathbf{U}^{(1)} = 0.
$$

(3.81)

We now write the two CPHF equations in the subscript notation for off-diagonal elements of $i \neq j$ as

$$
du_{ij} \frac{d}{dR} \bigg|_{R_0} = \frac{d\tilde{S}_{ij}}{dR} \bigg|_{R_0} \frac{\varepsilon_j(R_0) - \varepsilon_i(R_0)}{\varepsilon_j(R_0) - \varepsilon_i(R_0)}
$$

(3.82)

and diagonal elements with $i = j$ as

$$
du_{ii} \frac{d}{dR} \bigg|_{R_0} = -\frac{1}{2} \frac{d\tilde{S}_{ii}}{dR} \bigg|_{R_0}.
$$

(3.83)

In order to reach a complete solution, we need then to find the first-order Fock matrix contribution $\mathbf{\tilde{S}}^{(1)}$. The Fock matrix elements in MO space is given by

$$
\tilde{S}_{ij}(R) = h_{ij}(R) + g_{ij}(R)
$$

(3.86)

where $h_{ij}$ is an element of the matrix of the operator $\hat{h}$ in the MO basis. From (3.66) and (3.67),

$$
h_{ij} = \sum_{\mu\nu} C_{\mu i}(R) h_{\mu \nu} C_{\nu j}(R)
$$

(3.87)

and similarly,

$$
g_{ij} = \sum_{\mu\nu} C_{\mu i}(R) g_{\mu \nu} C_{\nu j}(R)
$$

(3.88)

where, from (3.66),

$$
g_{\mu \nu} = \sum_o \sum_{\kappa \lambda} C_{\kappa o}(R) C_{\lambda o}(R) [2(\mu \nu | \kappa \lambda) - (\mu \kappa | \nu \lambda)].
$$

(3.89)

The matrix elements of the first-order Fock contribution may be then written by

$$
d\tilde{S}_{ij} \bigg|_{R_0} = \frac{dh_{ij}}{dR} \bigg|_{R_0} + \frac{dg_{ij}}{dR} \bigg|_{R_0}.
$$

(3.90)
The derivative of the transformed (MO basis) one-electron part is simply

$$\frac{dh_{ij}(R)}{dR} \bigg|_{R_0} = \sum_{\mu\nu} [C_{\mu i}(R_0) \frac{dh_{\mu\nu}}{dR} \bigg|_{R_0} C_{\nu j}(R_0)] + \sum_k \left[ \frac{du_{kj}}{dR} \bigg|_{R_0} h_{kj} \right] + \sum_k \left[ h_{ik} \frac{du_{kj}}{dR} \bigg|_{R_0} \right].$$

(3.91)

The two-electron part $g_{ij}^{(1)}$ can be found by starting from (3.89)

$$\frac{dg_{\mu\nu}}{dR} = \sum_o \sum_{\kappa\lambda} [C_{\kappa o}(R) \frac{d}{dR} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] C_{\lambda o}(R)]$$

$$+ \sum_{\kappa\lambda} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \sum_o \frac{dC_{\kappa o}(R)}{dR} \times \sum_k C_{\kappa k}(R_0) \frac{du_{ko}}{dR} \bigg|_{R_0}$$

$$+ \sum_{\kappa\lambda} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \sum_j C_{\lambda j}(R) \times \sum_o \frac{dC_{\lambda o}(R)}{dR} \bigg|_{R_0} C_{\kappa o}(R_0) \frac{du_{ko}}{dR} \bigg|_{R_0}.$$  

(3.92)

We have then the second and the third terms in RHS, respectively, as

$$\sum_o \sum_k \sum_{\kappa\lambda} C_{\kappa k} C_{\lambda o} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] = \sum_o \sum_k [2(\mu\nu|ko) - (\mu k|\nu o)]$$

(3.93)

$$\sum_o \sum_k \sum_{\kappa\lambda} C_{\kappa o} C_{\lambda k} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] = \sum_o \sum_j [2(\mu\nu|ok) - (\mu o|\nu k)].$$

(3.94)

Considering the symmetry of the two-electron integrals toward interchange,

$$\frac{dg_{\mu\nu}}{dR} \bigg|_{R_0} = \sum_o \sum_{\kappa\lambda} [C_{\kappa o}(R_0) \frac{d}{dR} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] C_{\lambda o}(R_0)]$$

$$+ \sum_o \sum_k \frac{du_{ko}(R)}{dR} \bigg|_{R_0} [4(\mu\nu|ko) - (\mu k|\nu o) - (\mu o|\nu k)].$$

(3.95)

From (3.90), (3.91), and (3.95), we can then write

$$\frac{d\mathcal{F}_{ij}}{dR} \bigg|_{R_0} = \sum_{\mu\nu} [C_{\mu i}(R_0) \frac{dh_{\mu\nu}}{dR} \bigg|_{R_0} C_{\nu j}(R_0)]$$

$$+ \sum_{\mu\nu} \sum_o \sum_{\kappa\lambda} [C_{\mu i}(R_0) C_{\nu j}(R_0) C_{\kappa o}(R_0) C_{\lambda o}(R_0) \times \frac{d}{dR} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \bigg|_{R_0}$$

$$+ \sum_{\mu\nu} \sum_o \sum_k \sum_{\kappa\lambda} [C_{\mu i}(R_0) C_{\nu j}(R_0) \frac{du_{ko}}{dR} \bigg|_{R_0} \times [4(\mu\nu|ko) - (\mu k|\nu o) - (\mu o|\nu k)] R_0.$$

(3.96)
and in a compact form, for $i \neq j$, as

$$\left. \frac{d\mathcal{F}_{ij}}{d\mathbf{R}} \right|_{\mathbf{R}_0} = \sum_{\mu\nu} \left[ C_{\mu i}(\mathbf{R}_0) \frac{dh_{\mu\nu}}{d\mathbf{R}} \left|_{\mathbf{R}_0} C_{\nu j}(\mathbf{R}_0) \right] + \sum_{\mu\nu} \sum_{o} \sum_{\kappa\lambda} \left[ C_{\mu i}(\mathbf{R}_0) C_{\nu j}(\mathbf{R}_0) C_{\kappa o}(\mathbf{R}_0) C_{\lambda o}(\mathbf{R}_0) \times \frac{d}{d\mathbf{R}} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \right|_{\mathbf{R}_0} \right]$$

$$+ \sum_{o} \sum_{k} \left[ \frac{du_{ko}}{d\mathbf{R}} \right|_{\mathbf{R}_0} \times [4(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \right]_{\mathbf{R}_0}.$$  

(3.97)

Note that $\frac{du_{ko}}{d\mathbf{R}}$ depends only on the virtual-occupied matrix elements and not other combinations of orbitals. Moreover, $\frac{du_{ko}}{d\mathbf{R}}$ again depends on $\frac{d\mathcal{F}}{d\mathbf{R}}$ through (3.82) and, therefore, can be determined by an iterative procedure. The derivative of the energy eigenvalues (the diagonal Fock matrix elements) are given by

$$\left. \frac{d\mathcal{F}_{ii}}{d\mathbf{R}} \right|_{\mathbf{R}_0} = \sum_{\mu\nu} \left[ C_{\mu i}(\mathbf{R}_0) \frac{dh_{\mu\nu}}{d\mathbf{R}} \left|_{\mathbf{R}_0} C_{\nu i}(\mathbf{R}_0) \right] + \sum_{\mu\nu} \sum_{o} \sum_{\kappa\lambda} \left[ C_{\mu i}(\mathbf{R}_0) C_{\nu i}(\mathbf{R}_0) C_{\kappa o}(\mathbf{R}_0) C_{\lambda o}(\mathbf{R}_0) \times \frac{d}{d\mathbf{R}} [2(\mu\nu|\kappa\lambda) - (\mu\kappa|\nu\lambda)] \right|_{\mathbf{R}_0} \right]$$

$$+ \sum_{o} \sum_{k} \left[ \frac{du_{ko}}{d\mathbf{R}} \right|_{\mathbf{R}_0} \times [4(ii|\kappa\lambda) - (ik|i\lambda) - (io|jk)] \right]_{\mathbf{R}_0}.$$  

(3.98)

In order to find the total energy derivative of RHF energy via

$$E(\mathbf{R}) = \sum_{i} \langle \phi_i | \hat{\mathcal{H}}_i | \phi_i \rangle + \mathcal{F}_{ii}(\mathbf{R}),$$  

(3.99)

we need to start from Lagrangian function,

$$L(\mathbf{C}) = E(\mathbf{C}) - \sum_{ij} \lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}),$$  

(3.100)

where $E(\mathbf{C}) = E_{\text{RHF}}(\mathbf{C})$ in (3.99). The Lagrangian parameters $\lambda_{ij}$ are introduced to enforce the normalization condition, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ and play the role of orbital energies ($\lambda_i = \varepsilon_i$). The Lagrangian function can be then written in AO space as

$$L(C_{\mu i}, \varepsilon_{i}) = E(C_{\mu i}, \varepsilon_{i}) - \sum_{ij} \varepsilon_{ij} \sum_{ij} C_{\mu i} C_{\nu j} S_{\mu\nu} - \delta_{ij},$$  

(3.101)
with a derivative respect to the geometry parameters as

\[
\frac{dL}{dR} = \sum_{\mu i} \frac{\partial L}{\partial C_{\mu i}} \frac{\partial C_{\mu i}}{\partial R} + \sum_{ij} \frac{\partial L}{\partial \varepsilon_{ij}} \frac{\partial \varepsilon_{ij}}{\partial R} + \frac{\partial E(C_{\mu i}, \varepsilon_i)}{\partial R} - \sum_{ij} \varepsilon_{ij} \sum_{\mu \nu} C_{\mu i} C_{\nu j} \frac{dS_{\mu \nu}}{dR} = \frac{dE}{dR}. \tag{3.102}
\]

Considering the variational condition and if \(C_{\mu i}\) and \(\varepsilon_{ij}\) solve the HF equations, \(\frac{\partial L}{\partial C_{\mu i}} = 0\) and \(\frac{\partial L}{\partial \varepsilon_{ij}} = 0\) and then \(L(C_{\mu i}, \varepsilon_i) = E\) and, therefore, \(\frac{dL}{dR} = \frac{dE}{dR}\). In canonical SCF, where \(\varepsilon_{ij} = \varepsilon_i \delta_{ij}\), the derivative of the Lagrangian function and, therefore, total energy derivative of RHF energy can be written as

\[
\frac{dE}{dR} = \frac{\partial E(C_{\mu i}, \varepsilon_i)}{\partial R} - \sum_i \varepsilon_i \sum_{\mu \nu} C_{\mu i} C_{\nu i} \frac{dS_{\mu \nu}}{dR}, \tag{3.103}
\]

where \(\frac{\partial E(C_{\mu i}, \varepsilon_i)}{\partial R} = \sum_{\text{occ.}} \delta h_{\mu i}(R) + \frac{\partial \xi_{\mu i}(R)}{dR}\) from (3.99).

### B. CIS

As introduced in Sec. 3.1.2, in CIS method, the electronic wavefunction is approximated by a linear expansion of electron configurations, considering only single particle-hole excitations relative to HF ground state. The CIS matric elements in (3.26) can be expanded in AOs as \((a, b\) and \(r, s\) are occupied and unoccupied indices here)

\[
\langle \Psi_s^r | \hat{H}_{MN} | \Psi_a^r \rangle = (\varepsilon_r - \varepsilon_a) \delta_{a,b} \delta_{r,s} + \sum_{\mu \nu \kappa \lambda} C_{\mu r} C_{\nu a} C_{\kappa b} C_{\lambda s} [A(\mu \nu | \kappa \lambda) - (\mu \lambda | \kappa \mu)]. \tag{3.104}
\]

Substituting (3.104) into the expectation value of the CIS excited state,

\[
E = \langle \Psi_{\text{CIS}}^r | H | \Psi_{\text{CIS}}^r \rangle = \sum_{a,r} \sum_{b,s} C_{a}^r C_{b}^s \langle \Phi_{\mu}^s | H | \Phi_{\lambda}^r \rangle, \tag{3.105}
\]

one can find the corresponding energy gradient (for \(A=2\) given by

\[
\frac{dE}{dR} = \sum_{a, r} \sum_{b, s} C_{a}^r C_{b}^s \left( \frac{d \varepsilon_r}{dR} - \frac{d \varepsilon_a}{dR} \right) \delta_{a,b} \delta_{r,s}
+ 2 \sum_{\mu \nu \kappa \lambda} \frac{dD_{\mu \nu}}{dR} D_{\kappa \lambda} [2(\mu \nu | \kappa \lambda) - (\mu \lambda | \kappa \mu)] + \sum_{\mu \nu \kappa \lambda} D_{\mu \nu} D_{\kappa \lambda} \left[ 2 \frac{d(\mu \nu | \kappa \lambda)}{dR} - \frac{d(\mu \lambda | \kappa \mu)}{dR} \right], \tag{3.106}
\]

which is simplified using the abbreviation of

\[
D_{\mu \nu} = \sum_{a, r} C_{a}^r C_{\mu r} C_{\nu a} \tag{3.107}
\]
with a gradient of

\[
\frac{dD_{\mu\nu}}{d\mathbf{R}} = \sum_{a,\sigma} C_a^\sigma \left( \frac{dC_{\mu\sigma}}{d\mathbf{R}} C_{\nu a} + C_{\mu\sigma} \frac{dC_{\nu a}}{d\mathbf{R}} \right) \\
= \sum_{a,\sigma} C_a^\sigma \sum_j \left( C_{\mu j} C_{\nu a} \frac{du_{jr}}{d\mathbf{R}} + C_{\mu j} C_{\nu j} \frac{du_{ja}}{d\mathbf{R}} \right).
\]

(3.108)

The energy gradients in (3.106) are computed analytically based on CPHF equations.

3.2.2.2 NACME

Considering the transition density matrix in MO space for transition from determinant \(k\) to \(l\), \(\gamma_{ij}^{kl} = \langle \psi_l | c_i^\dagger c_j | \psi_k \rangle\) with \(c_i^\dagger/c\) as electron creation/annihilation basic operator for excitation manifold [81], one can write elements of the non-adiabatic coupling matrix vector (NACV) in (3.34), \(d_{kl}(\mathbf{R}) = \langle \psi_l | \frac{\partial}{\partial \mathbf{R}} | \psi_k \rangle\), as \(\sum_{ij}^{MOS} \gamma_{ij}^{kl} \langle \phi_i | \frac{\partial}{\partial \mathbf{R}} | \phi_j \rangle\), where derivative of the orbital overlap in AO space (using (3.63) and (3.83)) is given by CPHF equations as

\[
\langle \phi_i | \frac{\partial}{\partial \mathbf{R}} | \phi_j \rangle = \sum_j \int d\mathbf{r} C_{\mu i} \chi_{\mu}(\mathbf{r}, \mathbf{R}) \\
\times \left( \frac{dC_{\nu j}(\mathbf{R})}{d\mathbf{R}} \chi_{\nu}(\mathbf{r}, \mathbf{R}) + C_{\nu j}(\mathbf{R}) \frac{d\chi_{\nu}(\mathbf{r}, \mathbf{R})}{d\mathbf{R}} \right) \\
= \frac{1}{2} \frac{d\mathbf{S}_{ij}}{d\mathbf{R}} + \frac{du_{ij}}{d\mathbf{R}} \\
= -\frac{du_{ji}}{d\mathbf{R}} + \frac{du_{ij}}{d\mathbf{R}}.
\]

(3.109)
CHAPTER 4

Ultrafast Hole Dynamics

This chapter covers the calculation procedure and the results of the new extension of XMOLECULE [82, 83] with two application examples: (1) hole dynamics in a photoionized donor-acceptor molecule (paper I) and (2) ultrafast dynamics in liquid water after strong-field ionization (paper II).

4.1 Hole dynamics in a photoionized donor-acceptor molecule

Investigation of the potential of probing charge transfer dynamics in the conjugated benzothiadiazole-thiophene (BT-1T) molecule with time-resolved x-ray absorption spectroscopy has been carried out here for a simpler scenario of photoionization instead of the relevant process of photoexcitation. Interaction of a vacuum ultraviolet (VUV) probe pulse creates a valence vacancy, which can be filled by a promoted core electron after absorption of an x-ray probe pulse arriving with some delay (schematically shown in Fig. 4.1). As shown in Fig. 4.2, BT-1T has two sulfur atoms with different chemical environments, which make them distinguishable in the core absorption spectrum and makes the molecule appropriate for the charge transfer study.

Figure 4.1: Schematic of photoionization scenario considered in this chapter.

The non-adiabatic dynamics of photoionized BT-1T is modelled using on-the-fly
non-adiabatic molecular dynamics simulations based on Tully’s surface hopping approach (as explained in section 3.2.1) using the XMOLECULE electronic structure toolkit. Following the surface hopping algorithm in Fig. 3.1, 100 initial conditions (atomic coordinates and momenta) are first generated from the equilibrium geometry of BT-1T in the ground electronic state using CDTK toolkit (an in-house chemical dynamics toolkit at CFEL-Theory group). The next step is to calculate energy and energy gradients, at each 0.5 fs time steps and overall time of 400 fs, at the HF level of electronic structure theory using Koopmans’ theorem. Analytic calculation of HF energy gradients (as the new implementation in the code) is explained in detail in Sec. 3.2.2. Note that Chapt. 2 ultimately focuses on the derivation of cross-sections for stationary targets. However, when a system is ionized or excited using a pump pulse, the remaining system will be in a non-stationary state [84]. In other words, the equilibrium geometry of the ground state does not correspond to an equilibrium geometry of the excited states. In the adiabatic representation, the nuclear wave packets move independently of each other on their respective PESs [85]. Propagation of trajectories (along a PES) and the quantum amplitude determine the nuclear geometry of the molecule and its electronic state at each time step. Knowing this information, one can calculate the time-dependent absorption cross-section (using Eq. (2.26)). The molecular orbitals are described as linear combinations of atomic orbitals. The test calculation, to validate the code and investigate potential of charge transfer in the molecule, is carried out using the minimal basis set, STO-3G, giving the possibility for debugging the code. The results are presented here.

### 4.1.1 Test calculations

Table 4.1 presents the electronic-structure calculation results at the HF level of theory using STO-3G basis set. It shows that the binding energies of the four highest occupied MOs in the BT-1T molecule are relatively close to each other (∼2 eV from HOMO to HOMO-3 orbital) at the equilibrium geometry of BT-1T in the ground electronic state and will be considered in the current research study. The visualization (using VMD-1.9 [86]) and the partial population (from Mulliken population analysis

![Figure 4.2: Schematic of the BT-1T molecule highlighting the two sulfur atoms.](image)
of the four molecular orbitals indicates that they have different degrees of contribution on the two sulfur atoms. Whereas the HOMO-3 and HOMO-2 orbitals have higher population on $S_{BT}$ and HOMO-1 orbital on $S_T$, the HOMO orbital has almost no population on the two sulfur atoms.

**Table 4.1:** Orbital energies ($E_b$), isosurfaces, and partial hole populations on the sulfur atoms $S_{BT}$ and $S_T$ for the least bound orbitals of the BT-1T molecule at the ground state equilibrium geometry.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>HOMO</th>
<th>HOMO-1</th>
<th>HOMO-2</th>
<th>HOMO-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_b$ (eV)</td>
<td>6.05</td>
<td>7.27</td>
<td>7.80</td>
<td>8.01</td>
</tr>
<tr>
<td>Isosurface ($\pm 0.01$ au)</td>
<td><img src="image" alt="IsoSurfaces" /></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Part. Pop. on $S_{BT}$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.410</td>
<td>0.118</td>
</tr>
<tr>
<td>Part. Pop. on $S_T$</td>
<td>0.004</td>
<td>0.635</td>
<td>0.002</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Considering ionization from each of the four valence orbitals in Table 4.1, the x-ray absorption cross-sections have been calculated using Eq. (2.26) at sulfur K-edge shown in Fig. 4.3. The test calculations are done using the ground-state geometry of the BT-1T molecule. Two features are observed in Fig. 4.3. First, strength of the core transitions are in consistency with the localization of the valence orbitals on the two sulfur atoms such that transition to the HOMO-1 orbital with a large localization of $S_T$ has the largest strength among other transitions. Second, transition energies from the two core orbitals have $\sim 2$ eV distance, which makes them distinguishable in the spectrum. Therefore, we conclude that the BT-1T molecule has the potential of investigation of the charge transfer using x-ray absorption spectroscopy at S K-edge.

The next step is to plot the time-resolved x-ray absorption spectrum of BT-1T molecule after photoionization from each of the valence orbitals. First of all and in order to examine the number of trajectories and estimate error of the calculated absorption cross-section, the bootstrapping methodology has been applied, which is very useful when there is no information about the underlying distribution of the sample in an ensemble. The method is based on random resampling from an ensemble of the $n$ trajectories ($n = 100$ here). The resampling is carried out by randomly drawing of the trajectories with possibility of replacement [88]. From 500 resamples of 100 trajectories, the error of the absorption cross section has been computed, which gives the uncertainty in the calculated cross section due to the finite number of trajectories.
Figure 4.3: Static S K-edge absorption cross-section of the transitions from two core orbitals localized on the two sulfur atoms to four valence orbitals in Table 4.1. Transitions from the core orbital number 1 (localized on $S_{BT}$) are shown in red and from the core orbital number 2 (localized on $S_T$) are in blue.

and not the systematic errors due to the level of theory and the dynamics method [89]. The analysis has been performed on trajectories ionized from the HOMO-3 orbital (as an example) and at their time zero as shown in Fig. 4.4. Broadening of the transition lines is carried out using a Gaussian function and a standard deviation of $\sigma = 0.2$ eV to account for finite lifetime effects. The average cross-section from the resampling (dashed green line) matches exactly with the average curve from the original trajectories (solid red line) showing a reasonable size of the ensemble. The statistical error is the largest at the position of the highest peak, however, small compared to the peak height.

4.1.1 Time-resolved studies

We now turn to the calculation of time-resolved parameters after ionization of the BT-1T molecule from HOMO-3 valence orbital. Figure 4.5(a) shows the time evolution of the electronic-state populations during the relaxation. An ultrafast decay of the HOMO-3 orbital with the half lifetime of 6 fs is followed by an increase in the population of the HOMO-2 and HOMO-1 orbital until 10 fs. After that the HOMO-2 orbital starts to deplete. Increase in the population of the HOMO orbital starts simultaneously with decrease in population of the HOMO-1 orbital after $\sim 50$ fs such that around 200 fs there is a very low portion of the latter. Figure 4.5(b) depicts the evolution of the partial hole population on the two sulfur atoms in time. The fast decrease in the population on $S_{BT}$ until 50 fs is in consistency with the time that both the HOMO-3 and the HOMO-2 orbitals (with the larger localization on $S_{BT}$)
Figure 4.4: Time-zero x-ray absorption cross-section of BT-1T molecule ionized from HOMO-3 orbital averaged over the generated trajectories (solid red line) and bootstrapping resampling.

are depleted as shown in Fig. 4.5(a). Similarly, increase in S\textsubscript{T} population is due to the increase in the HOMO-1 population with the larger localization on S\textsubscript{T} and there is almost no hole population on the two sulfur after 200 fs.

Figure 4.5: (a) Electronic-state relaxation dynamics and (b) time evolution of partial hole population on the two sulfur atoms after ionization of the HOMO-3 orbital.

Figure 4.6 further shows the time-resolved sulfur K-edge x-ray absorption spectrum following VUV photoionization of the HOMO-3 orbital, inspected in a specific energy window below the excitation threshold for the neutral molecule. The S 1s
ionization potentials of the two sulfur atoms are 2473.00 and 2471.07 eV within the current framework (HF level of theory and using STO-3G basis set). All resonant absorption is restricted to a few eV right below the 1s binding energy (known from Koopmans’ theorem). Here, they are at least 6 eV below the S 1s ionization threshold of the neutral BT-1T molecule. Hence, all absorption of the neutral molecule, in the spectral vicinity of the resonances we are considering, comes from nonresonant and, therefore, spectrally featureless absorption. This makes a cation distinguishable from x-ray absorption in a neutral system in experiments [90, 91]. Considering this specific energy window below the sulfur K-shell excitation threshold for the neutral molecule in our calculations is advantageous because in this energy window there is no resonant signal from unpumped molecules. Accordingly, at time t<0 (before the pump) there is no resonant XAS signal in this energy window [92].

Figure 4.6 shows appearance of a peak at around 2465 eV assigned to $S_{BT} \rightarrow$ HOMO-3 transition (see Fig. 4.3 for the position of the transitions). This peak goes down almost immediately followed by appearance of another peak at slightly below 2464 eV, which is assigned to transitions from $S_T$ to HOMO-1 orbital. The observed timescales in Fig. 4.6 perfectly match with those reported in Figures 4.5(a) and (b) showing charge (hole) transfer from $S_{BT}$ to $S_T$ within $\sim$50 fs. The results indicate the ability of time-resolved x-ray absorption spectroscopy to track ultrafast charge transfer dynamics in molecules.

![Absorption cross-section](image)

**Figure 4.6:** Sulfur K-edge x-ray absorption spectrum of BT-1T at the selected delay times.

### 4.1.2 Final calculations

So far, we established a theoretical foundation for experiments that will allow us to track the mechanisms and dynamics of charge carrier transfer in organic conjugated
molecules as a fragment of D–A conjugated polymers. We now repeat the calculations using a larger basis set. Figure 4.7 compares HF values (Koopmans’ theorem) of the valence ionization potentials calculated using four different basis sets. It shows an almost consistent shift in the ionization energy of the four valence orbitals as well as 6-31G basis set to be a reasonable compromise in terms of accuracy and computational cost for the final calculations. Further analysis showed that the current framework (using 6-31G basis set) is able to reproduce the PES calculated at the level of Density Functional Theory (DFT) and the configuration showed in Fig. 4.2 is the most likely representative for the majority conformer in the experiment at room temperature [92].

**Figure 4.7:** HF values of the valence ionization potentials with four different basis sets (Image from [92]).

4.1.2.1 Time-resolved x-ray spectroscopy

The same scenario that is explained in Fig. 4.1 is employed here such that the primary molecular dynamics after ionization from a valence hole using a VUV pump pulse is followed by an x-ray pulse for up to 400 fs. Figure 4.8 depicts time-resolved x-ray absorption spectrum at the sulfur K-edge showing an ultrafast movement in the position of the peak at 2494.22 eV to 2393.07 within <20 fs. This sensitivity to the position of the valence hole due to a chemical shift between sulfur atoms at two separated sites can facilitate tracking the charge transfer from one sulfur to the other one. In order to better understand the charge transfer process, the XAS is decomposed into the signals from the core orbitals that are localized on the two sulfur atoms (core orbital 1 on S_{BT} in Fig. 4.9(a) and core orbital 2 on S_{T} in Fig. 4.9(b)). The high intensity peak that appears immediately after the pump pulse at t = 0 fs in Fig. 4.9(a) decreases rapidly and vanishes mostly after 150 fs. An intense peak in Fig. 4.9(b) appears after a time delay at lower energies and decreases on a timescale of several
hundred fs. The low intensity region in Fig. 4.9(b) is associated to excitations from the core orbitals into the HOMO orbital that is populated at later time delays during the relaxation process.

Figure 4.8: Time-resolved x-ray absorption spectrum of BT-1T molecule after photoionization of the HOMO-3 orbital.

Figure 4.9: Decomposition of the calculated time-resolved x-ray absorption spectrum of the BT-1T molecule after ionization of the HOMO-3 orbital into two spectra associated with transitions from (a) core orbital 1 and (b) core orbital 2, which are localized on $S_{BT}$ and $S_{T}$, respectively (Images from [92]).

Further calculations inspected the x-ray absorption spectrum after ionization from the HOMO orbital (all the trajectories start the relaxation dynamics from the HOMO orbital). In contrast to the spectrum in Fig. 4.8, the x-ray absorption spectrum of the molecule after photoionization of the HOMO orbital in Fig. 4.10 shows no sign of charge transfer in the molecule showing rather constant absorption strength for the two sulfur atoms due to the low overlap of the HOMO orbital with them (the same as the test calculation results shown in Table 4.1). Dynamics following photoionization
of the HOMO orbital can be compared with the late-time delay dynamics in the case of photoionization of the HOMO-3 orbital, *e.g.*, after 200 fs when population of the HOMO orbital starts to increase. However, for the case of HOMO orbital, the spectrum is sharper compared to the HOMO-3 spectrum, which indicates that the amount of vibrational energy in the molecule (less vibrational energy for the case of the HOMO orbital) can be inferred from the particular changes in the x-ray absorption (near-edge) spectrum. Further analysis can be done on the oscillation of the spectrum in Fig. 4.10. For instance, Fourier transform analysis, \( f(\nu) = \int_0^T \exp\{i2\pi\nu t\} f(t) \), of the peak position of the x-ray absorption signal, \( f(t) \), shows dominant frequencies equal to 10, 20, 25, 45, and 50 THz. The same Fourier analysis on the specific coordinates that describe the local chemical environment around the two sulfur atoms as well as the bond connecting the two units has been carried out to find the origin of the frequencies of the oscillation in the peak position of the x-ray absorption signal in Fig. 4.10. The investigations show that the bond distance \( d_{\text{C-C}} \) (connecting the two units) oscillates with frequencies of 10 and 50 THz. The oscillation frequencies are equal to 20 and 45 THz for the angle \( \angle \text{C-C-S}_T \) (angle from the middle C-C bond connected to \( S_T \)). The oscillation frequencies of 20 and 25 are also originated from the bonds connected to the two sulfur atoms, \( S_T - \text{C} \) and \( S_{\text{BT}} - \text{N} \) bonds. We therefore conclude that the observed oscillations in the x-ray absorption spectrum for the ionization of HOMO orbital can be attributed to specific vibrations in the molecule. This finding demonstrates that TRXAS also allows us to resolve local geometrical changes in the molecule.

![Figure 4.10: Time-resolved x-ray absorption spectrum of BT-1T molecule after photoionization of the HOMO orbital (Image from [92]).](image)

### 4.1.3 Conclusion

With the new theoretical framework in XMOLECULE, we demonstrated that absorption of x-ray light that excites the sulfur core level into a previously created valence vacancy by VUV light can identify the position of the valence hole. We could moni-
tor the movement of the valence vacancy from the vicinity of one sulfur atom to the other, which occurs on a time scale of few tens of fs. We demonstrated that time-resolved x-ray absorption technique allows us to address the ultrafast dynamics in molecular building blocks of a family of conjugated polymers with sensitivity toward both electronic and nuclear structures.

Original Publication: Paper I

K. Khalili, L. Inhester, C. Arnold, R. Welsch, J. W. Andreasen, and R. Santra

*Hole Dynamics in a Photovoltaic Donor-Acceptor Couple Revealed by Simulated Time-Resolved X-Ray Absorption Spectroscopy,*

Structural Dynamics 6, 044102 (2019); [https://doi.org/10.1063/1.5097653](https://doi.org/10.1063/1.5097653)


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**Statement of Contributions**

All calculations and generation of the figures were done by myself. The implementation of CPHF in XMOLECULE was done by myself, L.I., and C.A.. The manuscript was written by myself with input by L.I and corrections from C.A., R.W., J.W.A. and R.S. The results were obtained by myself and discussed with L.I., C.A., R.W., J.W.A. and R.S.

4.2 Ultrafast dynamics in liquid water

Strong-field ionization of liquid water produces the $\text{H}_2\text{O}^+$ radical cation and the hydrated electron, both being highly reactive. Rapid ion-molecule reaction of $\text{H}_2\text{O}^+$ with a neighboring water molecule yields $\text{H}_3\text{O}^+$ and $\text{OH}$ as reaction products [93] and in contrast to the hydrated electron, dynamics of the radical cation has not yet been fully elucidated. An ultrafast x-ray probe (based on x-ray absorption spectroscopy) has been introduced to track the ultrafast hole dynamics (that are a part of the early-time dynamics of liquid water, but not everything) with time resolution of few tens of fs [94]. Therefore it is suitable for studying proton transfer. In order to gain a comprehensive insight of the underlying dynamics, theoretical approaches are required, which is carried out in the same work as the second application of the XMOLECULE new extension presented throughout this thesis. The ultrafast
molecular dynamics of liquid water and the x-ray absorption probe signal simulations following strong-field ionization have been performed using a two-layered QM/MM approach considering 12 water molecules as a core region treated quantum-mechanically (QM) and surrounding 1012 water molecules described with classical molecular modeling (MM). The electronic structure of core 12 radical cation was obtained at the HF level of theory employing Koopmans’ theorem, to obtain singly-ionized states, and 6-31G basis set using XMOLECULE. To describe nuclear dynamics, Tully’s FSSH approach is used to take into account non-BO effects considering 107 initial geometries of liquid water. The evolution of the state populations for trajectories initiated in HOMO-6 showed ultrafast relaxation to cationic ground state within 25 fs. In addition, separation of charge (on $\text{H}_3\text{O}^+$) and hole (on OH), as a measure of proton transfer, occurs in a timescale of 60 fs. The theoretical analysis revealed that x-ray absorption spectroscopy is indirectly sensitive to the proton transfer. The relevant time scale is therefore not extracted from the charge/hole separation diagram, but from the diagram showing the distances between neighboring oxygen atoms. The experimental timescale that is relevant for the agreement with the calculations is not directly seen in the 2D absorption spectrum, but has been extracted from selected time traces. X-ray absorption lines of the hole is not the same as the pre-edge feature and is separated from the edge (around 526 eV).

Original Publication: Paper II


Science 367(6474) 179-182; https://doi.org/10.1126/science.aaz4740

Supplemental material available online: https://science.sciencemag.org/content/suppl/2020/01/08/367.6474.179.DC1.

Statement of Contributions

My contribution in the paper is related to the new extension of XMOLECULE for the hole dynamics simulations, along with C.A. and L.I.. Experimental results gathering and analysis, theoretical calculations, and manuscript preparation is done within a collaboration with several groups. The manuscript was written by both experimental and theoretical parties and I was involved in the two iterations through internal review and then revised versions.
CHAPTER 5

Ultrafast Particle-Hole Dynamics

Excited-state relaxation following photoexcitation can occur through the electronic and vibrational energy relaxation and redistribution, which lead to the changes in the charge localization on the subunits of the conjugated molecule. These changes can give rise to ultrafast structural reorganization through, for instance, torsion of one unit or planarization of the molecule. Subsequently, ultrafast charge transfer can occur in the molecule [95, 96]. This chapter is dedicated to the investigation of the excited-state dynamics, charge transfer and conformational changes, of a photoexcited BT-1T conjugated molecule because of its attractive properties such as asymmetrical subunits, each of them having one sulfur atom but in different chemical environments as introduced in Chapt. 4.

5.1 Computational details

Nonadiabatic molecular-dynamics simulations based on the Tully’s FSSH approach in combination with excited-state calculations at the CIS level of theory have been performed to address excited-state dynamics of BT-1T after excitation to the lowest excited state. For this purpose, we calculated the gas-phase XAS spectrum at the carbon K-edge (nitrogen K-edge, and sulfur L- and K-edges are presented in Paper III [97]) as a function of time.

The same ensemble of 100 initial nuclear conditions as for the photoionization calculations in Chapt. 4 are used for the photoexcitation calculations. The sampled geometries are propagated in time independently starting from the lowest excited state. The FSSH algorithm in Fig. 3.1 is employed for each 0.5 fs timestep during the dynamics for a total propagation time of 400 fs (giving rise to 800 geometries for each trajectory). Two of the trajectories are not propagated for the full 400 fs due to SCF convergence problems and the averaged parameters presented in the following are from 98 trajectories. The post-processing processes include x-ray absorption cross-sections calculation (using (2.26)) for each geometry using the CIS wavefunctions and the 6-31G basis set [97]. Note that within the CIS expansion, calculation of the transition dipole moments between the involved CI eigenvectors to determine absorption line strengths in (2.26) are given for the ground state as \( \sum_{i,a} C_i^a \langle \Phi_0 | r | \Phi_i^a \rangle \) and for an excited state as \( \sum_{i,a} \sum_{j,b} C_i^a^* C_j^b \langle \Phi_i^a | r | \Phi_j^b \rangle \) (\( r = x, y, z \)).
5.2 Ultrafast excited-state dynamics

Electronic-state population for trajectories initiated in S₁ in Fig. 5.1 shows a relatively slow decay in the population of the S₁ state with no upward hop to the S₂ state. The lifetime of the S₁ state is estimated ~2.14 ps by fitting an exponential function.

![Graph showing state population over time](image)

**Figure 5.1:** Time evolution of the population of the ground and first two excited states of BT-1T after excitation to the lowest excited state.

The low-lying absorbing singlet state S₁ of BT-1T is attributed to the HOMO→LUMO transition. Figure. 5.2 shows the orbitals involved in the transition and depicts high localization of the LUMO of the benzothiadiazole unit versus the HOMO that is more distributed on the two units. In other words, Fig. 5.2 suggests that the S₁ state has an excess negative charge at the BT unit and, thus, the T unit must have an excess positive charge. Therefore, it is expected that the nonadiabatic transition during the relaxation process from S₁ to S₀ to be associated with electron transfer from BT to T unit. This is exactly seen in Fig. 5.3 showing slow decay in the population on the BT unit that is happening simultaneously with an increase in the electronic population on the T unit.

![Molecule orbitals](image)

**Figure 5.2:** Molecule orbitals contributed in the first excitation, S₀ → S₁ (The orbitals are visualized using VMD-1.9 [86] .).
We now further investigate the ability of tracking the excited-state dynamics using the XAS. Figure 5.4(left) shows the numbering scheme of the BT-1T as used in the analysis. The calculated static ground- and excited-state C $K$-edge XAS at the ground-state geometry of BT-1T is shown in Fig. 5.4(right). The excited-state XAS spectrum shows up red shifted compared to the ground-state spectrum. Vertical lines in Fig. 5.4(right) are oscillator strength of each core transition showing that the two electronic states have different shapes because of the different localization on the carbon atoms (as expected from Fig. 5.2). The core transitions associated with carbon atoms $C_{10}$, $C_3$, and $C_5$ have the main contribution in the first absorption band in the excited-state spectrum.
Figure 5.5 shows the time-resolved XAS at the carbon $K$-edge. The excited-state absorption (ESA) peak appears immediately at energies $\sim 5$ eV below the first ground-state absorption band as shown in Fig. 5.4(right). A quick move to higher energies is seen in the position of ESA, which then oscillates with almost the same amplitude until 50 fs. The same behavior is seen for the time delays between 100 and 200 fs but with lower amplitude compared to the earlier time delays. After that, the ESA features decrease with higher rate. All these changes are followed by an increase in ground-state features at around 285 eV. All the observed time scales are in a good agreement with the changes in Figures 5.1 and 5.3 showing subtle variation in the state and electronic populations before 200 fs and larger changes after that. Therefore, the shift and any changes in the ESA bands can be attributed to the local electronic population on the absorbing atoms $[98, 99]$. We then conclude that appearing of the ground-state features during the relaxation gives a fingerprint of the charge transfer from the BT to the T unit.

![Figure 5.5: Normalized carbon $K$-edge XAS intensity (shifted by -11 eV) versus photon energy for different time delays after photoexcitation.](image)

In order to understand specific behaviors of the XAS spectrum in detail, we investigate the time evolution of the structural features relevant to the carbon atoms with higher contributions in the absorption bands. For instance, the sharp oscillation in the $C_5$-$C_{10}$ bond length (change in the electron density) before 200 fs and slow decrease in the magnitude towards the ground-state value after 200 fs in Fig. 5.6 is in agreement with the observations in Fig. 5.5.
5.3 Conclusion

Understanding photoexcitation dynamics in conjugated compounds in detail is essential to have a control over optoelectronic properties as a requisite for a variety of applications based on polymers. It has been shown here that the new introduced theoretical framework, based on FSSH approach in combination with CIS electronic-structure method, can give a reasonably good picture of time-resolved XAS spectrum with a focus on the low-lying absorption-band features. With the proven potential of time-resolved XAS in predicting changes in the electronic structure and structural dynamics, we were able to track excited-state dynamics in BT-1T D-A molecule. We showed that the excited-state relaxation is associated with not only the ultrafast structural dynamics but also the ultrafast charge transfer between the two units in the molecule. We could probe those changes with a timescale of a few tens of fs. Knowing ~2 ps lifetime of the BT-1T excited state along with the possible dynamics during the relaxation can help to successfully design of new photovoltaic materials and architectures, as an application of organic devices.

Original Publication: Paper III


*Simulation of Time-Resolved X-ray Absorption Spectroscopy of Ultrafast Dynamics in Particle-Hole-Excited 4-(2-Thienyl)-2,1,3-benzothiadiazole*

Final draft.
Statement of Contributions

All the calculations and generation of the figures were done by myself. The implementation of CIS formalism in XMOLECULE was done by myself and L.I. The manuscript was written by myself with input by L.I and corrections from A.S.G., J.W.A. and R.S. The results were obtained by myself and discussed with L.I., A.S.G., J.W.A. and R.S. Scattering calculations were performed by B.L.H and K.F.N. based on the geometries from my trajectory calculations.
Conclusion and Outlook

In this thesis, a theoretical framework for the time-resolved x-ray absorption spectroscopy was developed. An expression for the x-ray absorption cross-section of the stationary states was derived based on quantum electrodynamics and perturbation theory, and was further used for nonstationary states in the framework of nonadiabatic dynamics calculations. The theoretical scheme (employed as a new extension in an in-house software package, XMOLECULE, at the CFEL-Theory division) is used for two different photo-induced processes: photoionization and photoexcitation. In both cases, the calculations address time-resolved x-ray absorption spectroscopy experiments, which trigger the nonstationary states using an appropriate pump pulse and track them by an x-ray probe pulse arriving after some delay times.

4-(2-Thienyl)-2,1,3-benzothiadiazole molecule (called BT-1T here), bearing benzothiadiazole as an electron-withdrawing and thiophene as an electron-donating unit along its backbone, is chosen as a model to address ultrafast charge-transfer and excited-state dynamics in \( \pi \)-conjugated polymers with photovoltaic applications. Chapters 2 and 3 cover details on the computational methods used throughout the thesis. Chapter 4 presented findings on the study of the ultrafast hole and nuclear dynamics in BT-1T following photoionization with a VUV pulse. The results are found using the on-the-fly nonadiabatic molecular dynamics simulations based on Tully’s FSSH approach and calculation of the valence-hole states at the HF level of theory and employing Koopmans’ theorem. We showed in Paper I through nonadiabatic molecular dynamics calculations that the hole transfer, as a result of the electronic-state relaxation to the ground state (hole in the HOMO), occurs within a few tens of femtoseconds after ionization from the HOMO-3 orbital. While ionization from the HOMO orbital (the highest valence orbitals) causes ultrafast structural dynamics as a result of the vibrationally hot molecule. Both the ultrafast hole-transfer and structural dynamics were inspected theoretically by time-resolved x-ray absorption spectroscopy exploiting its atomic site-specificity.

In addition to the BT-1T in Chapt. 4, the new capabilities of XMOLECULE to investigate electron-hole dynamics has been used for the case of the ionized liquid water, as a result of interaction of high-energy radiation with matter in aqueous environments. In Paper II, the x-ray absorption spectroscopy is used as a probe to track the ultrafast hole dynamics, which is considered as a part of the early-time dynamics of liquid water. The theoretical analysis revealed that x-ray absorption spectroscopy is indirectly sensitive to the proton transfer (separation of charge and
hole), which occurs on a timescale of 60 fs.

The same gas-phase BT-1T (in Paper I) is considered to study particle-hole dynamics after photoexcitation. As presented in Chapt. 5, in the case of excitation, Tully’s FSSH approach is combined with excited-state calculations at the CIS level of theory. Considering only the first absorption band (populating the $S_1$ state) in Paper III, we calculated the gas-phase x-ray absorption spectrum at the carbon $K$ edge, nitrogen $K$ edge, and sulfur $L$ and $K$ edges as a function of time after excitation by a UV femtosecond laser. The calculation results show a lifetime of the first excited state of $\sim 2$ ps. Along with the charge transfer from the benzothiadiazole to thiophene unit, the excited-state relaxation is accompanied by the bond elongation in the benzothiadiazole unit as well as thiophene ring puckering.

As the ultimate result of this thesis, we have shown in our calculations that in addition to sensitivity to the structural features, it is exactly the electronic-structure changes that XAS is sensitive to, whereas nonresonant x-ray scattering is not.

**Outlook**

The time-resolved x-ray absorption simulation framework has been successfully implemented in the XMOLECULE. In Chapt. 5, describing charge-transfer excitations can be improved in two ways: (1) improving the two-electron transformation algorithm such that one can use larger basis set and (2) adding the second excitation to the CIS matrix (CISD method) within XMOLECULE. Using higher level of theory and larger basis set were not computationally feasible to use for the simulations presented throughout this thesis and the study presented must be considered as a quantitative study. One can also consider using the XMOLECULE XAS simulation interface with other available electronic-structure software.
APPENDIX A

Photon Scattering

In Chapt. 2, equ. (2.15) has been used to find photoabsorption cross-section in Sec. 2.4. Here, theory of light-matter interaction is extended for the case of x-ray scattering and its aspects. The derivations are mainly based on my report submitted in May 2017, lecture notes by Prof. Santra on the theory of photon-matter interactions, and [49].

Consider the initial state $|I\rangle$ in (2.8), which photons are in the mode $(k_{in}, \lambda_{in})$. After a photon has been scattered into the mode $(k_F, \lambda_F)$, the final state of the system is

$$|F\rangle = \hat{a}_{k_F,\lambda_F}^\dagger |N_{ph} - 1\rangle |\Psi_{F}^{N_{el}}\rangle .$$

The transition from $|I\rangle$ to $|F\rangle$ is mediated by $\hat{A}^2$ in first order and by $p \cdot \hat{A}$ in second order. We consider the states of $|N_{ph} - 1\rangle |\Psi_{M}^{N_{el}}\rangle$ and $\hat{a}_{k_F,\lambda_F}^\dagger |N_{ph}\rangle |\Psi_{M}^{N_{el}}\rangle$ as the intermediate states $|M\rangle$ for second order $p \cdot \hat{A}$. Therefore, the transition rate from $|I\rangle$ to $|F\rangle$ is

$$\Gamma_{FI} = 2\pi \delta(E_{F}^{N_{el}} + \omega_F - \omega_{in} - E_{0}^{N_{el}})$$

$$\times \left| \sum_{p,q,k,\lambda,k',\lambda'} \frac{2\pi}{V\sqrt{\omega_k\omega_{k'}}} \langle N_{ph} - 1 | \hat{a}_{k_F,\lambda_F}^\dagger \hat{a}_{k_k,\lambda_k}^\dagger |N_{ph}\rangle \right|^2 \times \langle \Psi_{F}^{N_{el}} | \hat{a}_{k_F,\lambda_F}^\dagger |N_{ph}\rangle$$

$$\times \langle \phi_{p} | e^{ik\cdot r} \hat{p} \epsilon_{k,\lambda}^* | \phi_{q}\rangle \langle \Psi_{F}^{N_{el}} | \hat{c}_{q}^\dagger |\Psi_{0}^{N_{el}}\rangle$$

$$\times \left| \sum_{M} \sum_{p,q,k,\lambda,k',\lambda'} \frac{2\pi}{V\sqrt{\omega_k\omega_{k'}}} \left\{ \langle N_{ph} - 1 | \hat{a}_{k_F,\lambda_F}^\dagger \hat{a}_{k_k,\lambda_k} |N_{ph} - 1\rangle \right. \right.$$}

$$\times \left. \langle \phi_{p} | e^{-ik\cdot r} \hat{p} \epsilon_{k',\lambda'}^* | \phi_{q}\rangle \langle \Psi_{M}^{N_{el}} | \hat{c}_{q}^\dagger |\Psi_{0}^{N_{el}}\rangle \right\}$$

$$\times \langle \Psi_{M}^{N_{el}} | \hat{c}_{q}^\dagger |\Psi_{0}^{N_{el}}\rangle \right\}^2$$

(A.1)
Here, \( \{\phi_p(r)\} \) is a basis of orthogonal spin orbitals, where \( r \) is the position. The index \( p \) (as well as \( q \) in (A.2)) comprises both spatial and spin quantum numbers and \( \hat{c}^\dagger/\hat{c} \) are the electron creation/annihilation operators. The transition rate \( \Gamma_{FI} \) in (A.2) leads to the three diagrams contributing to photon scattering in Fig. A.1. In the first term, there is no intermediate state, which represents the scattering via the \( \hat{A}^2 \) term in which one photon is absorbed and one emitted at the same point (Fig. A.1a). The second term is showing the absorption-first process in which the initial state photon is absorbed at initial time, leaving the atom in an intermediate state with no photon (Fig. A.1b). The final term depicts the emission-first process in which the atom emits the final state photon at initial time, leaving the atom in some intermediate state (with two photons in the field). At final time, the atom absorbs the initial state photon (Fig. A.1c). We can now find the differential scattering cross-section associated with the electronic channel \( |\psi_{Ne}^a\rangle \)

\[
\frac{d\sigma_F}{d\Omega_{k_F}} = \frac{V}{(2\pi)^3\alpha^3} \sum_{\lambda_F} \int_0^\infty d\omega_F \omega_F^2 \frac{\Gamma_{FI}}{J_{ph}}, \tag{A.3}
\]

which is based on the assumption that the polarization of the scattered photon remains unobserved. In (A.3), \( J_{ph} = \frac{1}{\alpha} \frac{N_{ph}}{V} \) is the x-ray photon flux, number of photons per unit time and unit area. The rate of scattering divided by the incoming photon flux is defined as the scattering cross-section

\[
\sigma_F = \frac{\Gamma_{FI}}{J_{ph}}. \tag{A.4}
\]
A.1 Elastic x-ray scattering

In elastic scattering, (with final state $|F⟩ = \hat{a}_{k_F,\lambda_F}^\dagger |N_{ph}⟩ - 1 |Ψ_0^{N_{el}}⟩$), only $\hat{A}^2$ conserves the total number of photons (at least to the first order with respect to $\hat{H}_{int}$) in the transition rate (2.15) leading to

$$\Gamma_{FI} = \frac{(2\pi)^3 N_{ph}}{V} \frac{1}{\omega_F \omega_{in}} |\epsilon_{k_F,\lambda_F}^* \epsilon_{k_{in},\lambda_{in}}|^2 \times |f^0(Q)|^2 \delta(\omega_F - \omega_{in})$$

(A.5)

where $Q = k_F - k_{in}$ is the photon momentum transfer and $|k_F| = |k_{in}|$. This transition rate describes the elastic x-ray scattering (e.g. Rayleigh and Thomson scattering) which gives direct information about the atomic structure of crystals. Note that

$$\rho(r) = \langle \Psi_0^{N_{el}} | \tilde{\psi}(\mathbf{r}) \tilde{\psi}(\mathbf{r}) | \Psi_0^{N_{el}} \rangle$$

(A.6)

is the electron density in the state $|\Psi_0^{N_{el}}⟩$. With this relation, we obtain the elastic scattering factor as

$$f^0(Q) = \int d\mathbf{r} \rho(\mathbf{r}) e^{iQ \cdot \mathbf{r}}$$

(A.7)

which is the Fourier transform of the electron density. Hence, the differential cross-section for elastic scattering simplifies to

$$\frac{d\sigma}{d\Omega_{k_F}} = \alpha^4 |f^0(Q)|^2 \sum_{\lambda_F} |\epsilon_{k_F,\lambda_F}^* \epsilon_{k_{in},\lambda_{in}}|^2 .$$

(A.8)

If $|f^0(Q)|^2 = 1$, (A.8) leads to the differential cross-section for Thomson scattering,

$$(\frac{d\sigma}{d\Omega})_T = \alpha^4 \sum_{\lambda_F} |\epsilon_{k_F,\lambda_F}^* \epsilon_{k_{in},\lambda_{in}}|^2 ,$$

for which momentum transfer is negligible. Assuming kinetic approximation (no multiple scattering of the detected photon) and neglecting the resonant scattering effects, the elastic scattering factor depends only on $Q$ (not explicitly on $k_{in}$) and we can write the molecular scattering factor as

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

(A.9)

The scattering pattern has to be recorded for variety of propagation directions of the incoming x-ray beam with respect to the target, which is possible in practice by rotating the target. In view of the fact that $(\frac{d\sigma}{d\Omega})_T$ is straightforward to calculate\(^1\), the experimental $\frac{d\sigma}{d\Omega_{k_F}}$ may be divided by $(\frac{d\sigma}{d\Omega})_T$ to give $|f^0(Q)|^2$. If $Q$ tends to infinity, $f^0(Q)$ tends to zero and in the forward direction, $Q = 0$,

$$f^0(Q) = \int d\mathbf{r} \rho(\mathbf{r}) = Z$$

(A.10)

\(^1\)For instance, we can calculate $\sum_{\lambda_F} |\epsilon_{k_F,\lambda_F}^* \epsilon_{k_{in},\lambda_{in}}|^2$ for linearly polarized as well as unpolarized x-rays as a function of the polar and azimuthal angles.
so that the differential cross-section is proportional to $Z^2$ for small $Q$.

The effect of the second order $p\hat{A}$ in the x-ray scattering can be included using a dispersive correction giving two additional factors (real $\Delta f'$ and imaginary $\Delta f''$) to the elastic scattering factor. Dispersion corrections are energy-dependent and can be considered as the resonant scattering terms if they take on their extreme values at the absorption edges. However, the Thomson term, $f^0(Q)$, depends on the scattering vector. In resonant scattering, an electron jumps to a higher lying level, and then decays back to the initial state in which the photon emission can be taken via some intermediate states. Hence, the resonant scattering can probe the intermediate states, which can be found using the second-order perturbation theory. Note that the dispersive correction become relevant at small photon energy. While at sufficiently high-photon energy, the dominant contribution to elastic x-ray scattering comes from $f^0(Q)$ [49].

### A.2 Inelastic x-ray scattering

Inelastic scattering dominated by second-order $p\hat{A}$ is generally called Raman scattering and the inelastic scattering via $\hat{A}^2$ Compton scattering. Here, we illustrate the application of the non-relativistic treatment of Compton scattering by a free electron initially at rest. In Compton scattering, the incident photon energy is substantially greater than the electron binding energies. Generally, in inelastic scattering experiments, in addition to the differential scattering cross-section measurement, the doubly differential scattering cross-section for the scattering of a photon can be obtained. The doubly differential scattering cross-section for Compton scattering by the first-order perturbation theory and (A.2) is

$$
\frac{d^2\sigma}{d\Omega_{k_F} d\omega_F} = \frac{\alpha^4 \omega_F}{\omega_{in}} \sum \lambda_F \sum F \delta(E_{F el} + \omega_F - \omega_{in} - E_{0 el}^N) \times \left| \epsilon_{k_F, \lambda_F} \epsilon_{k_{in}, \lambda_{in}} \langle \Psi_F^{N_{el}} | \int d\mathbf{r} \psi_\uparrow (\mathbf{r}) e^{i(k_{in} - k_F)\cdot \mathbf{r}} \psi(\mathbf{r}) | \Psi_0^{N_{el}} \rangle \right|^2 .
$$

(A.11)

Let the electron wave function be

$$
\langle \mathbf{r} | \mathbf{q} \rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{q} \cdot \mathbf{r}}
$$

(A.12)

where $\mathbf{q}$ is the electron momentum. Now, we consider zero momentum for target electron $\mathbf{q}_0 = 0$ for the initial state $|I\rangle = |N_{ph}\rangle |\mathbf{q}_0\rangle$ and the final state as $|F\rangle = \hat{a}_{k_F, \lambda_F}^\dagger |N_{ph} - 1\rangle |\mathbf{q}_F\rangle$. Using the definition of square of delta function (2.12) as well as (A.11) and (A.12), we have

$$
\mathbf{q}_F = k_{in} - k_F
$$

(A.13)
and then transition rate follows

\[ \frac{d^2\sigma}{d\Omega_{k_F} d\omega_F} = \alpha^4 \frac{\omega_F}{\omega_{in}} \sum_{\lambda_F' \lambda_F} |\epsilon^*_{k_F, \lambda_F'} \cdot \epsilon_{k_{in}, \lambda_{in}}|^2 \times \delta \left( \frac{|k_{in} - k_F|^2}{2} + \omega_F - \omega_{in} \right) \]  

(A.14)

where the delta function restricts the summation to those states accessible with energy and momentum conservation. In order to find an expression for \( \omega_F \), we define

\[ f(\omega_F) = \frac{1}{2} (\alpha^2 \omega_{in}^2 + \alpha^2 \omega_F^2 - 2\alpha^2 \omega_{in} \omega_F \cos(\theta_F) ) + \omega_F - \omega_{in} \]  

(A.15)

which is found by using (A.13), the concept of energy conservation, and definition of the scattering angle \( \theta_F \) as

\[ \cos(\theta_F) = \frac{k_{in} \cdot k_F}{|k_{in}| \cdot |k_F|}. \]  

(A.16)

Hence, \( f(\omega_F) \) in (A.15) has a non-negative root

\[ \tilde{\omega}_F = \omega_{in} \{ 1 + \alpha^2 \omega_{in} (1 - \cos(\theta_F)) \}^{-1}. \]  

(A.17)

In the non-relativistic theory \( \alpha^2 \omega_{in} \) must be much less than one. On the other hand, \( \tilde{\omega}_F \) gives a relation between energy of scattered photon and scattering angle. For instance, for small scattering angle, \( \tilde{\omega}_F \) is equal to the energy of incoming photon. And the maximum energy transfer is obtained in the backward direction for \( \theta_F \approx \pi \).

Now, we can find the differential scattering cross-section by integrating (A.14) with respect to \( \omega_F \)

\[ \frac{d\sigma}{d\Omega_{k_F}} = \left( \frac{d\sigma}{d\Omega} \right)_T \times \int_0^\infty d\omega_F \frac{\omega_F}{\omega_{in}} \delta(f(\omega_F)) \]  

\[ = \left( \frac{d\sigma}{d\Omega} \right)_T \times \int_0^\infty d\omega_F \frac{\omega_F}{\omega_{in}} \frac{\delta(\omega_F - \tilde{\omega}_F)}{|df(\omega_F)/d\omega_F|}_{\omega_F = \tilde{\omega}_F} \]  

(A.18)

Using \( \frac{df(\omega_F)}{d\omega_F} = \alpha^2 \omega_F - \alpha^2 \omega_{in} \cos(\theta_F) + 1 \), and

\[ |1 + \alpha^2 \tilde{\omega}_F - \alpha^2 \omega_{in} \cos(\theta_F)|^{-1} = 1 - \alpha^2 \tilde{\omega}_F + \alpha^2 \omega_{in} \cos(\theta_F) \]  

\[ \approx 1 - \alpha^2 \omega_{in} + \alpha^2 \omega_{in} \cos(\theta_F) \]  

\[ = 1 - \alpha^2 \omega_{in} [1 - \cos(\theta_F)] \approx \frac{\omega_F}{\omega_{in}} \]  

(A.19)

we can find

\[ \frac{d\sigma}{d\Omega_{k_F}} = \left( \frac{d\sigma}{d\Omega} \right)_T \times \left( \frac{\tilde{\omega}_F}{\omega_{in}} \right)^2 \]  

(A.20)
which leads to Thomson scattering in lower momentum transfer limit, \( \theta_F = 0 \).

In the case of interaction between an incoming photon and a moving electron in the Compton scattering, one has to consider the electron’s ground-state momentum (\( p \)), which makes an energy shift as an additional term into delta function in (A.14),

\[
\Delta \omega = \frac{q_F^2}{2} + q_F \cdot p.
\]

When the electron is not at rest, but has an energy greater than photon energy, a transfer of energy can happen from the electron to the photon. This process is called inverse Compton scattering distinguishable from the direct Compton scattering, in which the electron is at rest [50, 101].

### A.3 Resonant scattering

Resonant x-ray Scattering (RXS) is a technique capable to probe elementary (intrins-)ic excitations in complex materials by measuring changes in the energy, momentum, and polarization of the scattered photon [102, 103]. In a resonant scattering, the incident x-ray energy is close to an absorption edge of the sample. One can tune the x-ray photon’s energy to match the value required to excite an inner-shell electron into a valence state of the atom of interest, which enhances the scattering cross-section in comparison to the non-resonant scattering.

When the incoming x-rays are in resonance with specific transition, the second term in the transition rate (A.2) becomes large. In addition, in a resonant scattering, the absorption-first term is larger than the emission-first term and one can neglect the latter in the transition rate calculation. Moreover, if the resonance happens in a pre-edge region, one can consider only one intermediate state and drop the sum over \( M \). Therefore, the doubly differential scattering cross-section from the resonant part of the second order term in (A.2) is given by

\[
\frac{d^2 \sigma}{d \Omega_{k_F} d \omega_F} = \alpha^4 \sum_F \frac{\omega_F}{\omega_{in}} \times \delta(E_{F}^{N_{el}} + \omega_{F} - \omega_{in} - E_{0}^{N_{el}}) \times \left| \sum_{p,q} \sum_{p',q'} \langle \Psi_{F}^{N_{el}} \mid \hat{c}_{p}^{\dagger} \hat{c}_{q} \mid \Psi_{M}^{N_{el}} \rangle \langle \Psi_{M}^{N_{el}} \mid \hat{c}_{p'}^{\dagger} \hat{c}_{q'} \mid \Psi_{0}^{N_{el}} \rangle \right|^2
\]

(A.21)

which shows the role of intermediate state by excitation of a core electron into an intermediate state through absorption of the first photon, followed by re-emission of a (scattered) photon once the core hole is filled back.
A.4 Optical coherence

Our knowledge of the condition of a dynamical system, with an infinite number of degrees of freedom, is not so precise, in practice, by using a pure quantum state $|\psi\rangle$. To treat a system in mixed state, for instance, the radiation field with a large number of degrees of freedom, it is required to use statistical methods \[104\]. In this case, the density operator $\hat{\rho}$ helps to obtain the probabilities to find the system in certain quantum state

$$\hat{\rho} = \sum_{i,j} P_{i,j} |\psi_i\rangle \langle \psi_j|.$$ \hspace{1cm} (A.22)

The diagonal elements of the density matrix for any state $|\psi\rangle$ (e.g. Fock state $|N_{ph}\rangle$ for a photon field), lie between zero and 1 in any representations and give the probability of occupying a quantum state. For this reason, diagonal elements are referred to as populations (where $0 \leq P_i \leq 1$ and satisfies $\sum_i P_i = 1$). Off-diagonal elements describe the evolution of coherent superpositions and are referred to as coherences. In this case, $P_{i,j}$ are the elements of the density operator in the basis of the $|\psi_i\rangle$. We use the latter property to describe the role of coherence in scattering process.

In addition, for a system in a pure quantum state $|\psi\rangle$, $\langle \psi | \hat{o} | \psi \rangle = \langle o \rangle$ is the ensemble average of the observable $o$ (represented by the Hermitian operator $\hat{o}$). For a system in a mixed state (as a series of pure states $|\psi_i\rangle$), the average expectation value of the observable (from (A.22)) can be written as

$$\langle o \rangle = \text{Tr} \{ \hat{\rho} \hat{o} \}$$ \hspace{1cm} (A.23)

where the symbol ‘Tr’ is cyclic and stands for the trace, or the sum of the diagonal matrix elements.

On the other hand, coherence -as an inherent concept- is related to the statistical variation of the radiation field. To characterize the fluctuations and coherence properties of the electromagnetic field, we use the correlation functions. As the first step of finding the correlation function, we write the Hermitian transversal electric field in the Heisenberg picture as

$$E^{\pm} = \sum_{k,\lambda} \sqrt{\frac{2\pi\omega_k}{V}} \left[ i\hat{\alpha}_{k,\lambda}^{\dagger} \epsilon_{k,\lambda} e^{i(k \cdot r - \omega_k t)} - i\hat{\alpha}_{k,\lambda} \epsilon_{k,\lambda}^{*} e^{-i(k \cdot r - \omega_k t)} \right]$$ \hspace{1cm} (A.24)

which can be considered as the sum of a positive and a negative frequency part $E^{\pm} = E^{(+)}(r, t) + E^{(-)}(r, t)$ which contain the photon annihilation and photon creation operators, respectively. By introducing the symbols $E^{(+)}$ and $E^{(-)}$ for the projections of the complex fields in the polarization direction $\epsilon_{k,\lambda}$ and $\epsilon_{k,\lambda}^{*}$, we have\[2\]

$$\hat{E}^{(+)}(r, t) = \epsilon_{k,\lambda}^{*} E^{(+)}(r, t)$$ \hspace{1cm} (A.25)

\[2\]Remind that each mode is characterized by wave vectors, $k$, and a polarization vector $\epsilon_{k,\lambda}(\lambda = 1, 2)$.
\[
\hat{E}^{(-)}(\mathbf{r}, t) = \varepsilon_{k, \lambda} E^{(-)}(\mathbf{r}, t).
\]  
(A.26)

We shall define a correlation function of the complex fields at separated positions and times at the first-order, \(G^{(1)}\), for the \(\varepsilon\) components of the complex fields as

\[
G^{(1)}(\mathbf{r}, t; \mathbf{r}', t') = \text{Tr}\{\hat{\rho}\hat{E}^{(-)}(\mathbf{r}, t)\hat{E}^{(+)}(\mathbf{r}', t')\}
\]  
(A.27)

which can be generalized to higher order correlations. Now, we consider the role of coherence in the scattering process. Let \(\hat{o}(t)\) be the observable in the interaction picture

\[
\hat{o}(t) = e^{i\hat{H}_0 t}\hat{o} e^{-i\hat{H}_0 t}
\]  
(A.28)

with the expectation value at time \(t\) (the probability of observing a scattered photon) as

\[
\langle\hat{o}\rangle_t = \text{Tr}\{\hat{\rho}(t)\hat{o}(t)\}.
\]  
(A.29)

Now, we consider the observable as

\[
\hat{o}_{k_F} = \sum_j \sum_{\lambda_{F'}} \sum_n \langle \Psi_{N_{el}}^0, \{n\}_{k_F, \lambda_F} | \Psi_{N_{el}}^0, \{n\}_{k_{F'}, \lambda_{F'}} \rangle
\]  
(A.30)

where \(|\{n\}_{k_F, \lambda_F}\rangle\) is a Fock state with exactly one photon in the mode \((k_F, \lambda_F)\). \(\langle\hat{o}_{k_F}\rangle_t\) can be considered as the probability to find exactly one photon with momentum \(k_F\).

We assume that long before the collision between photons and electronic system, the two subsystems are not entangled which leads to the initial state of the entire system as

\[
\lim_{t \to -\infty} \hat{\rho}(t) = \hat{\rho}_{ph} \otimes \hat{\rho}_m \equiv \hat{\rho}_{in}
\]  
(A.31)

where

\[
\hat{\rho}_{ph} = \sum_{\{n\}, \{n'\}} \hat{\rho}_{\{n\}, \{n'\}} |\{n\}\rangle \langle\{n'\}|.
\]  
(A.32)

and

\[
\hat{\rho}_m = |\Psi_{N_{el}}^0\rangle \langle\Psi_{N_{el}}^0|
\]  
(A.33)

The \(\{n\}\) and \(\{n'\}\) are complete sets that satisfy the number of photons in all initially field modes with a distribution \(\hat{\rho}_{\{n\}, \{n'\}}\). \(\hat{\rho}(t)\) is the state of the system at time \(t\), so that \(\hat{\rho}(t) = \hat{U}_{int}(t, -\infty)\hat{\rho}_{in}\hat{U}_{int}^\dagger(t, -\infty)\). \(\hat{U}_{int}(t, t_0)\) is the time evolution operator in the interaction picture and satisfies the equation of motion\(^3\) \(\hat{H}_{int}(t)\hat{U}_{int}(t, t_0) = i \frac{\partial}{\partial t} \hat{U}_{int}(t, t_0)\) and \(\hat{H}_{int}(t) = e^{i\hat{H}_0 t}\hat{H}_{int} e^{-i\hat{H}_0 t}\) is the interaction Hamiltonian in the interaction picture. We further assume that the modes \((k_F, \lambda_F = 1, 2)\) are unoccupied in the initial states, \(i.e., \hat{a}_{k_F, \lambda_F} \hat{\rho}_{ph} = 0, \hat{\rho}_{ph} \hat{a}_{k_F, \lambda_F}^\dagger = 0\).

\(^3\hat{U}_{int}(t, -\infty) = 1 - i \int_{-\infty}^{t} dt' \hat{H}_{int}(t') - \int_{-\infty}^{t} dt' \hat{H}_{int}(t') \int_{-\infty}^{t'} dt'' \hat{H}_{int}(t'') + \cdots = \hat{U}_{int}^{(0)}(t, -\infty) + \hat{U}_{int}^{(1)}(t, -\infty) + \hat{U}_{int}^{(2)}(t, -\infty) + \cdots\)
Through second order in $\hat{H}_{\text{int}}$,
\[
\langle \hat{o}_{k_F} \rangle = \text{Tr} \left\{ \hat{U}_{\text{int}}^{(1)}(t, -\infty) \hat{\rho}_{\text{in}} \hat{U}_{\text{int}}^{(1)\dagger}(t, -\infty) \hat{o}_{k_F}(t) \right\}.  \tag{A.34}
\]
All terms that involve $\hat{U}_{\text{int}}^{(0)} = \hat{U}_{\text{int}}^{(0)\dagger} = 1$ vanish. Then, if $\hat{o}_{k_F}(t) = \hat{\rho}_{\text{in}}$, the expectation value of the observable in the interaction picture reads
\[
\langle \hat{o}_{k_F} \rangle = \lim_{t \to \infty} \langle \hat{o}_{k_F} \rangle_t = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 \text{Tr} \left\{ \hat{H}_{\text{int}}(t_1) \hat{\rho}_{\text{in}} \hat{H}_{\text{int}}(t_2) \hat{o}_{k_F} \right\}.  \tag{A.35}
\]
Here,
\[
\hat{n}(r, t) = e^{i \hat{H}_{\text{mt}} t} \hat{n}(r) e^{-i \hat{H}_{\text{mt}} t}  \tag{A.36}
\]
\[
\hat{A}(r, t) = \hat{A}^{(+)}(r, t) + \hat{A}^{(-)}(r, t)  \tag{A.37}
\]
\[
\hat{A}^2(r, t) = e^{i \hat{H}_{\text{ph}} t} \hat{A}^2(r) e^{-i \hat{H}_{\text{ph}} t} = e^{i \hat{H}_{\text{ph}} t} \hat{A}(r) e^{-i \hat{H}_{\text{ph}} t} \hat{A}(r) e^{-i \hat{H}_{\text{ph}} t}  \tag{A.38}
\]
+ terms do not consider a photon-in-photon-out process
and $\hat{n}(r) = \hat{\psi}^\dagger(r) \hat{\psi}(r)$ is the electron density operator. The expectation value from the second term in (2.4) can be written as
\[
\langle \hat{o}_{k_F} \rangle = \int dt_1 \int dr_1 \int dt_2 \int dr_2 \text{Tr} \left\{ \alpha^4 [\hat{n}(r_1, t_1) \hat{A}^{(-)}(r_1, t_1) \hat{A}^{(+)}(r_1, t_1) \hat{\rho}_{\text{in}} \right.
\]
\[
\times \hat{n}(r_2, t_2) \hat{A}^{(-)}(r_2, t_2) \hat{A}^{(+)}(r_2, t_2) \hat{o}_{k_F})] \right\}
\]
\[
= \alpha^4 \sum_{\lambda_F} \sum_{\{n\}_{k_F}, \lambda_F} \langle \{n\}_{k_F}, \lambda_F | \hat{A}^{(-)}(r_1, t_1) \hat{A}^{(+)}(r_1, t_1) \right.
\]
\[
\times \hat{n}(r_2, t_2) \hat{A}^{(-)}(r_2, t_2) \hat{A}^{(+)}(r_2, t_2) | \{n\}_{k_F}, \lambda_F \rangle.  \tag{A.39}
\]
The electronic part is
\[
\sum_F \langle \Psi_F^{N_{el}} | \hat{n}(r_1, t_1) \hat{n}(r_2, t_2) | \Psi_F^{N_{el}} \rangle
\]
\[
= \sum_F \langle \Psi_F^{N_{el}} | \hat{n}(r_1, t_1) | \Psi_0^{N_{el}} \rangle \langle \Psi_0^{N_{el}} | \hat{n}(r_2, t_2) | \Psi_F^{N_{el}} \rangle
\]
\[
= \sum_F \langle \Psi_F^{N_{el}} | \hat{n}(r_2, t_2) | \Psi_F^{N_{el}} \rangle \langle \Psi_F^{N_{el}} | \hat{n}(r_1, t_1) | \Psi_0^{N_{el}} \rangle  \tag{A.40}
\]
\[
= \langle \Psi_0^{N_{el}} | \hat{n}(r_2, t_2) \hat{n}(r_1, t_1) | \Psi_0^{N_{el}} \rangle.
\]
The photon part will be evaluated by considering the fact that \( \hat{\mathbf{A}}^{(+)\downarrow} (\mathbf{r}, t) \) and \( \hat{\mathbf{A}}^{(-)\downarrow} (\mathbf{r}, t) \), which contains the photon annihilation and creation operator, acts on \( |\Psi_j^{N_{\mathbf{d}}}; \{n\}_{k_F, \lambda_F}\rangle \) and \( \langle |\Psi_j^{N_{\mathbf{d}}}; \{n\}_{k_F, \lambda_F}\rangle \), respectively. Then, we have

\[
\sum_{\lambda_F} \sum_{\{n\}_{k_F, \lambda_F}} \left\langle \{n\}_{k_F, \lambda_F} \right| \hat{\mathbf{A}}^{(\downarrow)} (\mathbf{r}_1, t_1) \hat{\mathbf{A}}^{(+)} (\mathbf{r}_1, t_1) \hat{\rho}_{ph} \hat{\mathbf{A}}^{(-)} (\mathbf{r}_2, t_2) \hat{\mathbf{A}}^{(+)} (\mathbf{r}_2, t_2) \left| \{n\}_{k_F, \lambda_F} \rightangle 
\]

\[
= \sum_{\lambda_F} \frac{2\pi}{\sqrt{a^2 \omega_F}} \frac{1}{\sqrt{\alpha}} e^{-i(k_F \cdot r_1 - \omega_F t_1)} e^{i(k_F \cdot r_2 - \omega_F t_2)} \text{Tr} \left\{ \hat{\rho}_{ph} \hat{\mathbf{A}}^{(-)} (\mathbf{r}_1, t_1) \hat{\mathbf{A}}^{(+)} (\mathbf{r}_2, t_2) \right\} 
\]

\[
= \frac{2\pi}{\sqrt{a^2 \omega_F}} \frac{1}{\sqrt{\alpha}} e^{-i(k_F \cdot r_1 - \omega_F t_1)} e^{i(k_F \cdot r_2 - \omega_F t_2)} \sum_{\lambda_F} \sum_{i,j} \left( \epsilon^*_{k_F, \lambda_F} \right)_i \left( \epsilon_{k_F, \lambda_F} \right)_j \text{Tr} \left\{ \hat{\mathbf{A}}^{(-)} (\mathbf{r}_2, t_2) \hat{\mathbf{A}}^{(+)} (\mathbf{r}_1, t_1) \right\} \left( \epsilon^*_{k_F, \lambda_F} \right)_j \left( \epsilon_{k_F, \lambda_F} \right)_j ,
\]

(A.41)

which depends on the first-order correlation function

\[
G^{(1)}_{ij} (\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) = \text{Tr} \left\{ \hat{\rho}_{ph} \hat{\mathbf{A}}^{(-)} (\mathbf{r}_2, t_2) \hat{\mathbf{A}}^{(+)} (\mathbf{r}_1, t_1) \right\} 
\]

\[
= \frac{1}{\omega_{in} \alpha^2} \left( \epsilon^*_{k_F, \lambda_F} \right)_i \left( \epsilon_{k_F, \lambda_F} \right)_j \text{Tr} \left\{ \hat{\rho}_{ph} \hat{E}_i^{(+)} (\mathbf{r}_2, t_2) \hat{E}_j^{(+)} (\mathbf{r}_1, t_1) \right\} 
\]

\[
= \frac{1}{\omega_{in} \alpha^2} \left( \epsilon^*_{k_F, \lambda_F} \right)_i \left( \epsilon_{k_F, \lambda_F} \right)_j G^{(1)}_{ij} (\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) .
\]

(A.42)

Equation (A.42) shows the connection between \( G^{(1)}_{ij} (\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) \) and the standard first-order correlation function of the electromagnetic field in (A.27). Here, we first assumed that the spectral bandwidth, \( \Delta \omega \), in the initial state of the electromagnetic field is small in comparison to the mean photon energy, \( \omega_{in} \), and \( G^{(1)}_{ij} (\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) = \frac{1}{\omega_{in} \alpha^2} G^{(1)}_{ij} (\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) \), where \( G^{(1)}_{ij} (\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) = \text{Tr} \left\{ \hat{\rho}_{ph} \hat{E}_i^{(+)} (\mathbf{r}_2, t_2) \hat{E}_j^{(+)} (\mathbf{r}_1, t_1) \right\} \). Then, we assumed further that the spread of incoming \( k \) vector is small in comparison to the mean photon momentum \( k_{in} \), and that the spread of incoming polarization, \( \epsilon_{k,\lambda} \), is small in comparison to \( \epsilon_{k_{in},\lambda_{in}} \).

As for the expectation value from the first term in (2.4), it is expected to find an electronic correlation function differs from the density-density correlation function derived for pure first-order \( \hat{\mathbf{A}}^2 \), which is covered in the following. Considering only the term of first-order \( \hat{\mathbf{A}}^2 \), which leads to the doubly differential scattering probability in (A.39), and based on (A.40—A.42), the one-photon scattering is a function of the density-density correlation function of the initial electron state and of the first-order correlation function of the initial photonic state.
So far, the role of coherence for the $A^2$ term has been considered in the interaction Hamiltonian, which is a first-order process and dominates for high-energy non-resonant x-ray scattering \[105\]. The role of coherence in one-photon scattering via second-order process of $p\cdot A$ is now taken into account. Here, the expectation value of the observable is studies, which can be used to find the doubly differential scattering probability, $\frac{d^2p}{\delta k_F \delta \omega_F} = \frac{V}{(2\pi)^3} \alpha^3 \omega_F^2 \langle \hat{a}_{k_F} \rangle$, of time-resolved resonant (inelastic) x-ray scattering (RIXS) from quantum electromagnetics. RIXS probe pulse induces a transition of an electron from atomic core shell to valence band, and then, the created core vacancy is filled by an electron accompanied by the emission of a photon that contributes to the scattering pattern.

Observation of a photon in the scattering mode $k_F$ introduced in (A.30) has, in the case of second-order process (compared to (A.34)), the probability of

$$\langle \hat{a}_{k_F} \rangle = \text{Tr} \left\{ \hat{U}^{(2)}_{int}(t, -\infty) \hat{\rho}_{in} \hat{U}^{(2)\dagger}_{int}(t, -\infty) \hat{a}_{k_F}(t) \right\}. \quad \text{(A.43)}$$

where $\hat{U}_{int}(t, -\infty)$ is the time evolution operator in the interaction picture,

$$\hat{U}(t, -\infty) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_n \ldots \int_{-\infty}^{t_2} dt_1 \hat{H}(t_n) \hat{H}(t_{n-1}) \ldots \hat{H}(t_1). \quad \text{(A.44)}$$

The Hermitian conjugate of $\hat{U}(t, -\infty)$ is

$$\hat{U}^\dagger(t, -\infty) = 1 + \sum_{n=1}^{\infty} (i)^n \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_n \ldots \int_{-\infty}^{t_2} dt_1 \hat{H}(t_n) \hat{H}(t_{n-1}) \ldots \hat{H}(t_1), \quad \text{(A.45)}$$

which has a negative-time ordering, meaning that $\hat{H}(t_i)$ act on the left, and has the equation of motion

$$\frac{\partial}{\partial t} \hat{U}^\dagger(t, t_0) = + \frac{i}{\hbar} \hat{U}^\dagger(t, t_0) \hat{H}(t). \quad \text{(A.46)}$$

From (A.44), the second-order evolution operator can be written as

$$\hat{U}^{(2)}_{int}(t, -\infty)_{t \to \infty} = - \int_{-\infty}^{\infty} dt' \int_{-\infty}^{t'} dt'' \hat{H}_{int}(t') \hat{H}_{int}(t'') \quad \text{(A.47)}$$

and

$$\hat{U}^{(2)\dagger}_{int}(t, -\infty)_{t \to \infty} = - \int_{-\infty}^{\infty} dt' \int_{-\infty}^{t'} dt'' \hat{H}_{int}(t') \hat{H}_{int}(t''), \quad \text{(A.48)}$$

where Hamiltonian is itself Hermitian and, as already mentioned, $\hat{H}_{int}(t) = e^{i\hat{H}_{int}t} \hat{H}_{int} e^{-i\hat{H}_{int}t}$. $t$ tends to infinity, which means that the time to detect a scattering signal is
much larger than the time interval during the process that the photonic and electronic systems collide with each other. From (A.43), (A.47), and (A.48),

\[
\langle \hat{o}_{k_F} \rangle = \int_{-\infty}^{\infty} dt'_1 \int_{-\infty}^{\infty} dt'_2 \int_{-\infty}^{t'_1} dt'_1 \int_{-\infty}^{t'_2} dt''_2 \text{Tr} \left\{ \hat{H}_{\text{int}}(t'_1) \hat{H}_{\text{int}}(t''_1) \hat{\rho}_{\text{in}} \hat{H}_{\text{int}}(t''_2) \hat{H}_{\text{int}}(t'_2) \right\}.
\]

(A.49)

Using the mode expression of vector potential in (2.6), second-order term of \(\hat{H}_{\text{int}}\) in (2.4) can be rewritten as

\[
\hat{H}_{\text{int}} = \sum_{k,\lambda} \sqrt{\frac{2\pi}{V \omega_k}} \left\{ \int dr \hat{\psi}^\dagger(r) \hat{a}_{k,\lambda} p \epsilon_{k,\lambda} e^{ik \cdot r} \hat{\psi}(r) + \int dr \hat{\psi}^\dagger(r) \hat{a}^\dagger_{k,\lambda} p \epsilon_{k,\lambda} e^{-ik \cdot r} \hat{\psi}(r) \right\}.
\]

(A.50)

From the density operator for the radiation field in (A.32), \(\hat{\rho}_{\text{ph}} = \sum_{\{n'\},\{n''\}} \hat{\rho}_{\{n'\},\{n''\}} \langle \{n'\} | \langle \{n''\} \rangle \), and for the matter system in (A.33), \(\hat{\rho}_{\text{m}} = \sum_{N,M} P_{N,M} | \Psi_{N}^{\text{el}} \rangle \langle \Psi_{M}^{\text{el}} | \), the initial density operator of the whole system can be given by

\[
\hat{\rho}_{\text{in}} = \hat{\rho}_{\text{m}} \otimes \hat{\rho}_{\text{ph}} = \sum_{\{n'\},\{n''\}} \hat{\rho}_{\{n'\},\{n''\}} \sum_{N,M} P_{N,M} | \Psi_{N}^{\text{el}} \rangle \langle \Psi_{M}^{\text{el}} | \langle \{n'\} | \langle \{n''\} \rangle .
\]

(A.51)

It is now convenient to define

\[
\hat{D}_{k,\lambda} = \int dr \hat{\psi}^\dagger(r) p \epsilon_{k,\lambda} e^{ik \cdot r} \hat{\psi}(r)
\]

(A.52)

and substitute (A.50) in (A.49) (while considering \(\hat{o}_{k_F}(t) = \hat{o}_{k_F}\)) to find

\[
\langle \hat{o}_{k_F} \rangle = \int_{-\infty}^{\infty} dt'_1 \int_{-\infty}^{\infty} dt'_2 \int_{-\infty}^{t'_1} dt'_1 \int_{-\infty}^{t'_2} dt''_2 \sum_{\lambda_p=1}^{2} \sum_{k_1,\lambda_1} \sum_{k_2,\lambda_2} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \sqrt{\omega_1 \omega_2}}
\]

\[
\times \text{Tr} \left\{ e^{i H_0 t'_1} \left( \hat{a}_{k_F,\lambda_F} \hat{D}_{k_F,\lambda_F} + \hat{a}^\dagger_{k_F,\lambda_F} \hat{D}^\dagger_{k_F,\lambda_F} \right) e^{i H_0 (t'_1-t''_1)} \right\}
\]

\[
\times \left( \hat{a}_{k_1,\lambda_1} \hat{D}_{k_1,\lambda_1} + \hat{a}^\dagger_{k_1,\lambda_1} \hat{D}^\dagger_{k_1,\lambda_1} \right) e^{i H_0 t''_1} \times \hat{\rho}_{\text{in}} \times e^{i H_0 t''_2}
\]

\[
\left( \hat{a}_{k_2,\lambda_2} \hat{D}_{k_2,\lambda_2} + \hat{a}^\dagger_{k_2,\lambda_2} \hat{D}^\dagger_{k_2,\lambda_2} \right) e^{i H_0 (t''_2-t'_2)}
\]

\[
\left( \hat{a}_{k_F,\lambda_F} \hat{D}_{k_F,\lambda_F} + \hat{a}^\dagger_{k_F,\lambda_F} \hat{D}^\dagger_{k_F,\lambda_F} \right) e^{i H_0 t'_2} \hat{o}_{k_F}. \]

(A.53)
Equation (A.53) can be more expanded after substituting (A.51) as

\[
\langle \hat{o}_{k_F} \rangle = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt'_2 \int_{-\infty}^{t_1} dt''_1 \int_{-\infty}^{t_2} dt''_2 \sum_{\lambda_F=1}^{2} \sum_{F, k_1, \lambda_1 k_2, \lambda_2} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \sqrt{\omega_1 \omega_2}} P_{N,M} \rho_{\{n'\}, \{n''\}} \sum_{N, M} \langle \Psi_{N, \lambda_F}^{\text{est}} ; \{n\}_{k_F, \lambda_F} | \{\psi_{\lambda_F}^{\text{est}} \} \rangle \langle \hat{a}_{k_F, \lambda_F} \hat{D}_{k_F, \lambda_F} | \hat{D}_{k_F, \lambda_F}^{\dagger} \rangle e^{iH_{0}(t'_1-t''_1)} \langle \hat{a}_{k_1, \lambda_1} \hat{D}_{k_1, \lambda_1} | \hat{D}_{k_1, \lambda_1}^{\dagger} \rangle e^{iH_{0}t''_1} \\
+ \left\{ e^{iH_0t'_1} \langle \hat{a}_{k_1, \lambda_1} \hat{D}_{k_1, \lambda_1}^{\dagger} \rangle e^{iH_0(t'_1-t''_1)} \langle \hat{a}_{k_1, \lambda_1} \hat{D}_{k_1, \lambda_1}^{\dagger} \rangle e^{iH_0t''_1} \right\} \\
+ \left\{ e^{iH_0t'_1} \langle \hat{a}_{k_2, \lambda_2} \hat{D}_{k_2, \lambda_2}^{\dagger} \rangle e^{iH_0(t'_1-t''_1)} \langle \hat{a}_{k_2, \lambda_2} \hat{D}_{k_2, \lambda_2}^{\dagger} \rangle e^{iH_0t''_1} \right\} \\
+ \left\{ e^{iH_0t'_1} \langle \hat{a}_{k_3, \lambda_3} \hat{D}_{k_3, \lambda_3}^{\dagger} \rangle e^{iH_0(t'_1-t''_1)} \langle \hat{a}_{k_3, \lambda_3} \hat{D}_{k_3, \lambda_3}^{\dagger} \rangle e^{iH_0t''_1} \right\} \langle \Psi_{N}^{\text{est}} ; \{n'\} \rangle \langle \hat{a}_{k_1, \lambda_1} \hat{D}_{k_1, \lambda_1} | \hat{D}_{k_1, \lambda_1}^{\dagger} \rangle e^{iH_0t''_1} \\
+ \left\{ e^{iH_0t'_1} \langle \hat{a}_{k_2, \lambda_2} \hat{D}_{k_2, \lambda_2}^{\dagger} \rangle e^{iH_0(t'_1-t''_1)} \langle \hat{a}_{k_2, \lambda_2} \hat{D}_{k_2, \lambda_2}^{\dagger} \rangle e^{iH_0t''_1} \right\} \langle \Psi_{N}^{\text{est}} ; \{n'\} \rangle \langle \hat{a}_{k_2, \lambda_2} \hat{D}_{k_2, \lambda_2} | \hat{D}_{k_2, \lambda_2}^{\dagger} \rangle e^{iH_0t''_1} \\
+ \left\{ e^{iH_0t'_1} \langle \hat{a}_{k_3, \lambda_3} \hat{D}_{k_3, \lambda_3}^{\dagger} \rangle e^{iH_0(t'_1-t''_1)} \langle \hat{a}_{k_3, \lambda_3} \hat{D}_{k_3, \lambda_3}^{\dagger} \rangle e^{iH_0t''_1} \right\} \langle \Psi_{N}^{\text{est}} ; \{n'\} \rangle \langle \hat{a}_{k_3, \lambda_3} \hat{D}_{k_3, \lambda_3} | \hat{D}_{k_3, \lambda_3}^{\dagger} \rangle e^{iH_0t''_1} \}
\]

Now, one can separate the photonic and the electronic terms,

\[
\langle \hat{o}_{k_F} \rangle = \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt'_2 \int_{-\infty}^{t_1} dt''_1 \int_{-\infty}^{t_2} dt''_2 \sum_{\lambda_F=1}^{2} \sum_{F, k_1, \lambda_1 k_2, \lambda_2} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \sqrt{\omega_1 \omega_2}} P_{N,M} \rho_{\{n'\}, \{n''\}} \sum_{N, M} \langle \Psi_{N, \lambda_F}^{\text{est}} ; \{n\}_{k_F, \lambda_F} | \{\psi_{\lambda_F}^{\text{est}} \} \rangle \langle \hat{a}_{k_F, \lambda_F} \hat{D}_{k_F, \lambda_F} | \hat{D}_{k_F, \lambda_F}^{\dagger} \rangle e^{iH_{0}(t'_1-t''_1)} \\
\times \left\{ e^{iH_0t'_1} \langle \hat{a}_{k_1, \lambda_1} | \hat{D}_{k_1, \lambda_1}^{\dagger} \rangle e^{iH_0(t'_1-t''_1)} \langle \hat{a}_{k_1, \lambda_1} | \hat{D}_{k_1, \lambda_1}^{\dagger} \rangle e^{iH_0t''_1} \right\} \\
\times \left\{ \langle \{n\}_{k_F, \lambda_F} | \hat{a}_{k_F, \lambda_F} \hat{a}_{k_1, \lambda_1} | \{n'\} \rangle \langle \Psi_{N}^{\text{est}} | e^{iH_0t'_1} \hat{D}_{k_F, \lambda_F} e^{iH_0(t'_1-t''_1)} \rangle \right\} \\
\times \left\{ \langle \{n'\}_{k_F, \lambda_F} | \hat{a}_{k_F, \lambda_F} \hat{a}_{k_1, \lambda_1} | \{n''\} \rangle \langle \Psi_{N}^{\text{est}} | e^{iH_0t''_1} \rangle \right\}
\]

(continued on next page)
which gives rise to 16 terms after multiplying two brackets. Among non-zero photonic terms, one represents the absorption-first process: Assuming that the scattered mode is initially unoccupied, an annihilation operator is required to absorb one photon. This state is not stable and so emits the photon to \( |\{n'\}\rangle \) via \( a_{k_F,\lambda_F}^\dagger \) operator. The absorbed photon goes back to the scattered mode via emission process, which is done using \( a_{k_F,\lambda_F}^\dagger \) operator. Therefore, the photonic term is given by

\[
\sum_{\{n\}_F,\lambda_F \{n'\}_F} \sum_{\{n''\}_F} \rho_{\{n',\lambda_F\}} \langle \{n\}_F,\lambda_F | a_{k_F,\lambda_F}^\dagger a_{k_1,\lambda_1} | \{n'\}_F \rangle \langle \{n''\}_F | a_{k_2,\lambda_2}^\dagger a_{k_F,\lambda_F} \rangle
\]

(A.56)

and (A.54) can be written as

\[
\langle \hat{a}_{k_F} \rangle = \int_{-\infty}^\infty dt' \int_{-\infty}^\infty dt'' \int_{-\infty}^{t_1'} dt'_1 \int_{-\infty}^{t_2'} dt'_2 \sum_{\lambda_F=1}^2 \sum_{k_1,\lambda_1} \sum_{k_2,\lambda_2} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \sqrt{\omega_1 \omega_2}} \sum_{N,M} P_{N,M} \text{Tr} \left\{ \hat{P}_{\rho} a_{k_2,\lambda_2}^\dagger a_{k_1,\lambda_1} \right\} e^{-i\omega_1 t_1' e^{i\omega_2 t_2} e^{i\omega_F (t_1' - t_2')}}
\]

(A.57)

classifying \( \hat{H}_0 = \hat{H}_m + \hat{H}_{ph} \). The term \( \text{Tr} \left\{ \hat{P}_{\rho} a_{k_2,\lambda_2}^\dagger a_{k_1,\lambda_1} \right\} e^{-i\omega_1 t_1' e^{i\omega_2 t_2} e^{i\omega_F (t_1' - t_2')}} \) resembles the correlation function, \( G^{(1)}(r, t; r', t') = \text{Tr} \left\{ \hat{P} \hat{E}(r, t) \hat{E}^+(r', t') \right\} \) in (A.27), except for the positional factor \( e^{-i\mathbf{k}_1 r_1 e^{i\mathbf{k}_2 r_2'}} \), which is tied up in the operators \( \hat{D}_{k_2,\lambda_2}^\dagger \) and
\( \hat{D}_{k_1, \lambda_1} \) respectively. Now, it is convenient the expand (A.57) by replacing \( \hat{D}_{k, \lambda} \) by its definition in (A.52) and write in a tensorial form as

\[
\langle \hat{a}_{k_F} \rangle = \int_{-\infty}^{\infty} dt_1' \int_{-\infty}^{\infty} dt_2' \int_{-\infty}^{t_1'} dt_1'' \int_{-\infty}^{t_2'} dt_2'' \sum_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \sum_{F} \sum_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \omega_{i_{\perp}}}
\]
\[
\int dr_1' \int dr_2' \int dr_1'' \int dr_2'' \sum_i \sum_j \sum_l \sum_h \Tr \left\{ \tilde{\rho}_{ph} \hat{a}_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \hat{a}_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \right\}
\]
\[
e^{-i\omega_{i_{\perp}} t_1''} e^{i\omega_{i_{\perp}} t_2''} e^{i\omega_{i_{\perp}} (t_1' - t_2')} (e_{k_{i_{\perp}}, \lambda_{i_{\perp}}})_i (e_{k_{i_{\perp}}, \lambda_{i_{\perp}}})_j e^{-i k_1 r_1'}
\]
\[
(e_{k_{i_{\perp}}, \lambda_{i_{\perp}}})_l e^{-i k_2 r_2'} \sum_{N, M} P_{N, M}
\]
\[
\langle \Phi_{N_{\perp}}^{N_{\perp}} \right| e^{i H_m t_1''} \tilde{\psi}(r_1') P_{j_{\perp}} \tilde{\psi}(r_1') e^{-i H_m (t_1'' - t_2'')} \tilde{\psi}(r_1'') P_{j_{\perp}} \tilde{\psi}(r_1'') e^{-i H_m t_2''} \left| \Phi_{N_{\perp}}^{N_{\perp}} \right\rangle
\]
\[
\langle \Phi_{M_{\perp}}^{N_{\perp}} \right| e^{i H_m t_2''} \tilde{\psi}(r_2'') P_{j_{\perp}} \tilde{\psi}(r_2'') e^{-i H_m (t_2'' - t_1'')} \tilde{\psi}(r_2') P_{j_{\perp}} \tilde{\psi}(r_2') e^{-i H_m t_1''} \left| \Phi_{M_{\perp}}^{N_{\perp}} \right\rangle
\]
\[
(A.58)
\]

Equation (A.58) is written based on the assumption that the spectral bandwidth and angular spread of the beam around a mean \( k_{i_{\perp}} \) are small and the beam is nearly polarized with polarization vectors that are close to \( e_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \). Then, \( \omega_1 \omega_2 \approx \omega_{i_{\perp}}^2 \), \( k_1, k_2 \approx k_{i_{\perp}} \), and \( e_{k_2, \lambda_2} \approx e_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \). In addition, \( t_1 - t_2'' \) is not large (initial state is localized) and \( e^{-i H_m (t_1'' - t_1')} \) can be ignored [105]. Therefore, there are two space-time points at the end similar to photonic part. Using some completeness relations and move desired \( \langle \Phi_{I_{\perp}}^{N_{\perp}} \right| d \left| \Phi_{I_{\perp}}^{N_{\perp}} \right\rangle \) to its appropriate position, we can find an electronic correlation function (in second-order) and obtain

\[
\langle \hat{a}_{k_F} \rangle = \int_{-\infty}^{\infty} dt_1' \int_{-\infty}^{\infty} dt_2' \int_{-\infty}^{t_1'} dt_1'' \int_{-\infty}^{t_2'} dt_2'' \sum_{\lambda_{i_{\perp}}} \sum_{k_{i_{\perp}}, \lambda_{i_{\perp}}} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \omega_{i_{\perp}}}
\]
\[
\int dr_1' \int dr_2' \int dr_1'' \int dr_2'' \sum_i \sum_j \sum_l \sum_h G^{(1)}(r_2', t_2''; r_1', t_1''') e^{i\omega_F (t_1'' - t_2'')} e^{-i k_1 r_1'} e^{-i k_2 r_2'} \sum_{N, M} P_{N, M}
\]
\[
\Tr \left\{ \tilde{\rho}_{ph} d_i(r_2'') d_j(r_1', t_1') d_h(r'2', t_2') d_j(r''', t_1''') \right\}
\]
\[
(A.59)
\]

With same polarization vector, one can find a scalar correlation function in (A.42),
\[
\rho^{G^{(1)}_{ij}}(r_2', t_2''; r_1', t_1''') = (e_{k_{i_{\perp}}, \lambda_{i_{\perp}}})_i (e_{k_{i_{\perp}}, \lambda_{i_{\perp}}})_j G^{(1)}_{ij}(r_2', t_2''; r_1', t_1''').
\]

If we don’t consider the
same incoming polarization vector, we have to return to

\[ p_h G_{t_3}^{(1)}(r_2''; t_2''; r_1'; t_1') = \text{Tr}\{ \hat{\rho}_{ph} \hat{E}_i^{(-)}(r_2''; t_2'') \hat{E}_j^{(+)}(r_1'; t_1') \} \]

\[ = \sum_{k_1, \lambda_1, k_2, \lambda_2} \left( \frac{2\pi}{V} \right) \frac{1}{\omega_F(\omega_1 \omega_2)} \langle \epsilon_{k_2, \lambda_2}^* l \rangle \langle \epsilon_{k_1, \lambda_1}^* \rangle \]

\[ \times e^{-i\epsilon(k_2, \omega_2) t_2''} e^{i\epsilon(k_1, \omega_1) t_1'} \]

\[ \times \text{Tr}\{ \hat{\rho}_{ph} \hat{a}_{k_2, \lambda_2}^+ \hat{a}_{k_1, \lambda_1} \} \]

(A.60)

and use relevant indices for tensorial correlation function for photonic subsystem and rewrite (A.57),

\[ \langle \hat{\rho}_{k_F} \rangle = \int_{-\infty}^{t_1'} dt_1' \int_{-\infty}^{t_2'} dt_2' \int_{-\infty}^{t_1''} dt_1'' \int_{-\infty}^{t_2''} dt_2'' \sum_{\lambda_F=1}^{\lambda_F} \sum_{k_{in}, \lambda_{in}} \left( \frac{2\pi}{V} \right)^2 \frac{1}{\omega_F \omega_{in}} \]

\[ \int dr_1' \int dr_2' \int dr_1'' \int dr_2'' \sum_i \sum_j \sum_l \sum_h \sum_{\epsilon_{k_F, \lambda_F}} G_{ij}^{(1)}(r_2''; r_1', t_1') \]

\[ e^{i\omega_F(t_1' - t_2')} e^{-i\epsilon_{k_F, \lambda_F}(r_1' - r_2')} \left( \epsilon_{k_F, \lambda_F}^* \right)_i \left( \epsilon_{k_F, \lambda_F} \right)_h \]

\[ \text{Tr}\{ \hat{\rho}_{ph} d_i(r_2''; t_2'') d_i(r_1', t_1') d_h(r_2', t_2') d_h(r_1'', t_1'') \} \]

(A.61)
In order to visualize the theoretical observations from my calculations in real experiments, a beamtime experiment has been proposed, which is explained here. Based on the type of the experiment and the required time resolution, SwissFEL is chosen as the most appropriate facility.

SwissFEL’s x-ray beamline ARAMIS, that has been launched for the first time in 2017, has two experimental stations, Alvra and Bernina. The Alvra beamline specializes in measuring the ultrafast dynamics of photochemical and photobiological systems using a variety of x-ray scattering and spectroscopic techniques and consists of two instruments: Alvra Prime and Alvra Flex. Alvra-Prime is particularly suited for the measurements that provide information on the local electronic and geometric structure around the absorbing species with a few tens of fs temporal resolution, namely, using time-resolved near-edge x-ray absorption spectroscopy [106–108] and, therefore, suited for the current study.

A UV-Vis absorption spectrum\(^1\) of the BT-1T molecule in toluene is shown Fig. B.1. The absorption band for the BT-1T molecule centered at slightly below 400 nm can be assigned to an intramolecular charge transfer state between the thiophene and benzothiadiazole unit. By adding a thiophene unit (with hexyl sidechains) on both sides of the BT monomer, the absorption band shows a red shift, as also expected for BT-T based low bandgap polymers in actual solar cell devices. For the experiment, I suggested BT-1T (with molecular formula \(\text{C}_{10}\text{H}_{6}\text{N}_{2}\text{S}_{2}\)) in solution (Toluene, \(\text{C}_{7}\text{H}_{8}\)) and the use of standard liquid jet setup with He atmosphere. Other proposed beamline’s specifications are listed in the following:

**Proposal title:** Time resolved x-ray study of charge-transfer and excited-state dynamics in donor-acceptor type conjugated materials

**Co-proposers:** Prof. Dr. Jens W Andreasen (Principal investigator, DTU-Energy), Prof. Dr. Martin M Nielsen (DTU-Physics), Dr. Kristoffer Haldrup (DTU-Physics), Dr. Christian Rein (DTU-Energy), Dr. Chris J Milne (Photon Science (PSD), Paul Scherrer Institut)

**Proposal abstract:** Ultrafast time-resolved x-ray absorption near-edge structure

\(^1\)The experiment has been done by Ole Hagemann at DTU-Energy, Riss campus.
Figure B.1: UV-Vis absorption spectrum of the BT-1T molecule (blue) and BT-1T plus thiophene unit (with hexyl sidechains) on both sides (red) in toluene (Inset: Schematic of BT-1T highlighting the two sulfur atoms).

(XANES) spectroscopy is proposed to characterize the photo-excitation dynamics of benzothiadiazole-thiophene (BT-1T) in solution. A fundamental understanding of photoinduced charge-transfer dynamics is an essential requirement for developing and improving new types of organic photovoltaics. Ultrafast pump-probe techniques such as time-resolved x-ray absorption spectroscopy (TRXAS), using an x-ray free electron laser in combination with a femtosecond laser, present desirable probes of charge carrier dynamics as they can track the nuclear dynamics coupled to electronic excitation. Thiophene-based molecules and polymers are important components of emerging organic photovoltaics, and we here propose to study the BT-1T model compound, which is the fundamental building block of a family of low band-gap donor-acceptor type conjugated polymers widely used in organic photovoltaics. Based on our theoretical findings, the changes in the time-resolved x-ray absorption spectrum at the sulfur K-edge are sensitive probes of the excited state evolution of BT-1T occurring on the femtosecond time scale. The BT-1T molecule has two distinct sulfur atoms identifiable in XAS due to their different chemical environments, making the molecule an ideal sensor for detecting charge leaving one sulfur centre and arriving at the other.

**Experimental method:** In order to study the ultrafast dynamics in detail, we consider here a TRXAS experiment employing a 400 nm pulsed pump beam in combination with a tender x-ray probe pulse with an energy range near the sulfur K-edge. The laser photon will be absorbed by one of the electrons in the HOMO orbital of BT-1T and thereby promoting it to the LUMO (HOMO-LUMO excitation around 400 nm in Fig. 1), and a neutral excited state is formed. Subsequent absorption of an x-ray photon (arriving at delay $t$), can promote an electron into the created valence hole (in the HOMO state) and the absorption is thereby sensitive to the localization
of the valence hole on the atom in which the K-shell is localized. The sample will
be circulated in a liquid jet of 50 \(\mu\)m thickness at sufficient flow speed to ensure full
sample replenishment between successive pump/probe cycles. Laser excitation will
be at 400 nm with 10 \(\mu\)J/pulse on a 100 \(\mu\)m spot using the laser system installed
at the beam line. Assuming homogeneous distribution of the molecules in solution
(ca. 1 mg/ml) and light absorption (ca. 6.7\% of the \(2 \times 10^{13}\) photons/pulse gener-
ates charge separation), this would generate ca. 0.2 charge separations per molecule.
Depending on the pump-probe overlap (a rather small x-ray spot (30 \(\mu\)m) in a signif-
icantly larger laser spot (\(\sim\)100 \(\mu\)m)), we should be able to probe a large population of
photoexcited molecules and achieve a strong shift of the sulfur edge if 75\% of excitons
is localized as predicted from theory. The pump photon energy (400 nm) is slightly
more than the energy needed to create photocarriers in BT-1T \([17]\), which neglects
complicated kinetics with “hot carriers”. The sample to be used in the experiment
is BT-1T (C\(_{10}\)H\(_{6}\)N\(_{2}\)S\(_{2}\)) in toluene. Toluene is not a toxic liquid but suspected car-
cinogenic and brings some chemical hazards that should be taken into account during
the sample preparation and disposal (based on safety data sheet). If possible, we
prefer to receive toluene at the beam time directly from supplier. The solutions will
be prepared in the fume hood of the chemistry lab, and the samples will carried to
the beamline hutch in closed containers.

Proposed experimental conditions:

Table B.1: Experimental conditions.

<table>
<thead>
<tr>
<th>Laser requirements</th>
<th></th>
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<tbody>
<tr>
<td>Laser wavelength</td>
<td>0.4 (\mu)m</td>
</tr>
<tr>
<td>Laser pulse energy</td>
<td>0.01 (\mu)J</td>
</tr>
<tr>
<td>Laser spot size</td>
<td>100 (\times) 100 (\mu)m(^2)</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>35 fs at 800 nm and best effort at other wavelengths</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Timing requirements</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Desired best time resolution</td>
<td>150 fs</td>
</tr>
<tr>
<td>Maximum time delay</td>
<td>10 ps</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X-ray parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray focus size</td>
<td>50 (\times) 50 (\mu)m(^2)</td>
</tr>
<tr>
<td>X-ray bandwidth</td>
<td>Pink beam (0.5%)</td>
</tr>
<tr>
<td>X-ray energies ranges</td>
<td>2.460-2.480 keV and 2.480-2.490 keV</td>
</tr>
<tr>
<td>X-ray repetition rate</td>
<td>25 Hz</td>
</tr>
</tbody>
</table>

Expected results: We expect experimental data that will allow us to directly
benchmark our theoretical calculations, in particular: An absorption spectrum recorded
at different time delays shows changes of spectral features. These features can be in-
dividually attributed to the ultrafast charge and structural dynamics in the molecule that appears on a time scale of 100s of fs.

**Summary:** The lack of a fundamental understanding of charge transfer dynamics in organic photovoltaics has long been recognized as a barrier for the further development of these complex devices. We therefore propose that time-resolved x-ray absorption spectroscopy using an x-ray probe in combination with a laser pump allows us to address the ultrafast carrier dynamics in such devices with sensitivity towards both electronic and nuclear structure. As a model building block for donor-acceptor type polymers, we study the BT-1T molecule. During the relaxation process after absorption of 400 nm laser pump beam, the created valence hole leaves the surroundings of the sulfur atom in benzothiadiazole. Moreover, structural evolution gives a clear fingerprint in the XAS spectrum.
APPENDIX C

Publications

Paper I

1Because of the copyright policies, the full articles of Papers I and III are presented here.
Hole dynamics in a photovoltaic donor-acceptor couple revealed by simulated time-resolved X-ray absorption spectroscopy

Cite as: Struct. Dyn. 6, 044102 (2019); https://doi.org/10.1063/1.5097653
Submitted: 27 March 2019 . Accepted: 27 June 2019 . Published Online: 23 July 2019

Khadijeh Khalili, Ludger Inhester, Caroline Arnold, Ralph Welsch, Jens Wenzel Andreasen, and Robin Santra

COLLECTIONS

This paper was selected as Featured
Hole dynamics in a photovoltaic donor-acceptor couple revealed by simulated time-resolved X-ray absorption spectroscopy

Khadijeh Khalili,1,a) Ludger Inhester,2,3 Caroline Arnold,2,5,4 Ralph Welsch,3,5 Jens Wenzel Andreasen,1,b) and Robin Santra2,3,4

AFFILIATIONS
1Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark
2Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany
3The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany
4Department of Physics, Universität Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany

a)khdkh@dtu.dk
b)jewa@dtu.dk

ABSTRACT
Theoretical and experimental methodologies that can characterize electronic and nuclear dynamics, and the coupling between the two, are needed to understand photoinduced charge transfer in molecular building blocks used in organic photovoltaics. Ongoing developments in ultrafast pump-probe techniques such as time-resolved X-ray absorption spectroscopy, using an X-ray free electron laser in combination with an ultraviolet femtosecond laser, present desirable probes of coupled electronic and nuclear dynamics. In this work, we investigate the charge transfer dynamics of a donor-acceptor pair, which is widely used as a building block in low bandgap block copolymers for organic photovoltaics. We simulate the dynamics of the benzothiadiazole-thiophene molecule upon photoionization with a vacuum ultraviolet (VUV) pulse and study the potential of probing the subsequent charge dynamics using time-resolved X-ray absorption spectroscopy. The photoinduced dynamics are calculated using on-the-fly nonadiabatic molecular dynamics simulations based on Tully’s Fewest Switches Surface Hopping approach. We calculate the X-ray absorption spectrum as a function of time after ionization at the Hartree-Fock level. The changes in the time-resolved X-ray absorption spectrum at the sulfur K-edge reveal the ultrafast charge carrier dynamics in the molecule occurring on a femtosecond time scale. These theoretical findings anticipate that ultrafast time-resolved X-ray absorption spectroscopy using an X-ray probe in combination with a VUV pump offers a new approach to investigate the detailed dynamics of organic photovoltaic materials.

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I. INTRODUCTION
The charge transfer from a donor to an acceptor plays a central role in photoinduced processes in both natural and artificial light harvesting systems. Therefore, achieving fundamental insight into the charge transfer dynamics is essential for many applications. One of the challenges associated with that comes from the atomic nature of these dynamics, which occurs on very short length and time scales, angstroms to nanometers and femtoseconds to picoseconds. The detailed exploration of photoinduced processes requires experimental methods that are sensitive to both the electronic and nuclear degrees of freedom. Time-resolved, pump-probe techniques involve a nonstationary state initiated by a pump pulse and probed by means of a suitable probe pulse arriving with some time delay. However, pump-probe spectroscopy with visible light does not always yield a clear interpretation of the underlying dynamics. X-ray free-electron lasers, capable of producing femtosecond pulses of X-rays, are promising tools for enabling investigations of few-femtosecond nonequilibrium dynamics.7,10 The use of X-rays is appealing, because of not only their atom specificity due to localization of core transitions but also their ability to probe ultrafast dynamics.12 There are a growing number of time-resolved experiments for probing ultrafast nonadiabatic dynamics in photoexcited molecules.13 Of these, time-resolved X-ray
absorption spectroscopy (TRXAS) has the advantage of detecting the local geometric structure of the system under study and, at the same time, the underlying electronic structure changes that drive the structural dynamics.\textsuperscript{14,15} Only a few theoretical studies have investigated the opportunities of TRXAS for studying ultrafast dynamics in molecules.\textsuperscript{21–23} For instance, a theoretical study of the use of ultrafast pre-edge TRXAS for probing nonadiabatic effects in the molecular dynamics of photoexcited molecules was done by Neville and co-workers.\textsuperscript{26} They investigated the sensitivity of the calculated TRXAS spectra to both geometric distortions and the electronic character of the initial state, demonstrating the potential of TRXAS for probing excited-state nonadiabatic molecular dynamics. Here, we use the localization of core orbitals, resulting in atomic-site specificity of TRXAS to track ultrafast charge transfer dynamics in real space. We study the time evolution of the location of the valence hole by exploiting the well-separated core-level absorption edges of the two sulfur atoms in benzothiadiazole-thiophene (BT-1T) and the atomic site-specificity of X-ray spectroscopy.

BT-nT (n being the number of thiophene units) is one of the favored combinations of monomers in the light absorbing polymers\textsuperscript{27–29} (Fig. 1). Easy synthesis, flexible processing, and a bandgap matching the solar spectrum makes π-conjugated polymers attractive as structural building blocks in organic photovoltaic (OPV) applications.\textsuperscript{30} A typical polymer solar cell, as one of the most attractive types of OPV, has an active layer composed of a π-conjugated polymer as an electron-donating component and another polymer or a small molecule as an electron-accepting component.\textsuperscript{31,32} To achieve a desired bandgap, the polymer is often composed of two or more appropriate monomers with different electron affinities. Both the BT and T units in BT-1T contain a sulfur atom (shown as S_BT and S_T in Fig. 1). The different chemical environments of these sulfur atoms give rise to distinct core-level binding energies and, consequently, distinguishable X-ray absorption signals. This prototypical conjugated monomer therefore exemplifies a wide class of π-conjugated polymers, with two sulfur atoms in distinctly different chemical environments.

The functioning of a polymer solar cell depends on the successful dissociation of sunlight-generated electron-hole pairs into charge carriers and further requires migration of these pairs in the electron-donating polymer toward a donor-acceptor interface.\textsuperscript{33,34} We here present a strategy to study hole carrier dynamics of donor-acceptor type conjugated materials containing sulfur using the model monomer compound BT-1T in the gas phase. In a previous work, Scarongella et al.\textsuperscript{35} showed that studying the fragments of the polymer chains can give rise to fundamental insight into the charge transfer character of oligomeric/polymeric systems. By using time-resolved femtosecond transient absorption spectroscopy, they found that charge transfer relaxation in their model polymer compound occurs on time scales of a few picoseconds. In order to study the ultrafast dynamics in detail, we here consider a TRXAS scenario employing a vacuum ultraviolet (VUV) pump pulse beam for initial photoionization in combination with a tender X-ray probe pulse with an energy range near the sulfur K-edge (~2.5 keV with tuning capability). A VUV photon will be absorbed by one of the electrons in the valence orbitals and thereby generates an ionized state by leaving a valence hole behind. Absorption of the X-ray light promotes an electron from the K-shell into the previously created valence hole and is thereby sensitive to the distance of the valence hole to the atom in which the K-shell is localized. Instead of the photoexcitation process relevant to photovoltaic applications, we here investigate the simpler process of photoionization as a model for the isolated hole dynamics in the case of photoexcitation.

After ionization through absorption of a single VUV photon, the molecule is vibrationally excited and the molecular geometry starts to rearrange. The electronic subsystem dynamics follow the nuclear rearrangement adiabatically, as long as electronic states are energetically separated. When electronic states come close to each other, nonadiabatic effects become relevant, which promotes the transfer of electronic excitation energy to the vibrational degrees of freedom. This process describes an electronic rearrangement that shifts the initially created charge in the molecule from one spatial position to another. We demonstrate that an X-ray absorption spectrum recorded at different time delays shows changes of spectral features that can be attributed to the ultrafast charge dynamics in the molecule which occur on a time scale of tens of femtoseconds.

II. METHODS

A. Nonadiabatic molecular dynamics

In order to obtain a time-resolved X-ray absorption spectrum of the VUV-pumped BT-1T molecule, we conduct mixed quantum-classical molecular dynamics simulations employing Tully’s Fewest Switches Surface Hopping (FSSH) approach. FSSH is based on classical propagation of the nuclei and transitions between electronic quantum states.\textsuperscript{36–38} Starting from the equilibrium geometry of BT-1T in the ground electronic state, quasiclassical sampling is employed to generate 100 initial conditions (atomic coordinates and momenta). Each of the 100 initial conditions is then independently propagated with a time step of 0.5 fs and a total propagation time of 400 fs. Switching between the electronic potential energy surfaces is determined via probabilities calculated on-the-fly according to the FSSH algorithm. If a stochastic hop is accepted, the momenta of nuclei are scaled along the nonadiabatic coupling vector to conserve the total energy. We do not employ any decoherence corrections as these are not relevant for the irreversible electronic decay processes addressed in this work. The velocity Verlet algorithm\textsuperscript{39} is employed for propagating
the nuclei. The implementation follows previous work by Subramanian et al.\(^{40}\)

### B. Electronic structure

All the electronic-structure and X-ray-absorption calculations are carried out using the XMOLCEULE toolkit,\(^{44}\) at the level of the restricted closed-shell Hartree-Fock (RHF) method and using the 6-31G Gaussian basis set. In order to have a consistent and, at the same time, efficient way to model all valence-hole states relevant for this study, we employ Koopmans’ theorem, i.e., the potential energy surface of the ionized state (N-1 electrons) with a vacancy in orbital \(i\) is given by \(E_i = E_{RHF} - E_i\), where \(E_i\) is the energy of the \(i\)th occupied orbital and \(E_{RHF}\) is the ground-state RHF energy of the neutral (N-electron) system. We note that as long as the RHF method remains valid for the neutral ground state and we address holes in the outer valence, this model should give a qualitatively and semiquantitatively correct picture of the electronic structure and the dynamics in the hole state. The accuracy of the applied electronic structure method is further discussed in the supplementary material. This approach has been tested before in several previous studies addressing ionized state dynamics.\(^{43,44}\) We therefore expect this method to provide a model that is sufficient for the qualitative understanding of the molecular dynamics and its impact on the X-ray absorption spectrum. The energy gradients and nonadiabatic coupling matrix elements for the ionized states are calculated analytically based on the coupled perturbed Hartree-Fock (CPHF) theory,\(^{45-47}\) which is part of a new implementation in the XMOLCEULE toolkit. The molecule is in the gas phase, and no solvent environment is considered in the current study.

The electronic-structure calculation shows that the four highest occupied molecular orbitals (MOs) in the BT-1T molecule are relatively close in energy at the equilibrium geometry of BT-1T in the ground electronic state. The considered valence orbitals and their corresponding energies are illustrated in Table I. The visualization of the molecular orbitals indicates that the four highest occupied orbitals have different degrees of contribution on the two sulfur atoms. This observation is quantified by the partial population of the molecular orbitals indicates that the four highest valence orbitals. Figure 2(a) shows the time evolution of the sulfur K-edge X-ray absorption spectrum following VUV photionization of the HOMO-3 orbital. The spectra have been obtained by convolution with a Gaussian function with a standard deviation of \(\sigma = 0.2\) eV to account for finite lifetime effects. We inspect in our calculation the specific energy window below the excitation threshold for the neutral molecule, because in the neutral molecule, X-ray absorption resonances associated with sulfur K-shell excitation are located within just a few electronvolts below the S 1s ionization threshold (2503.14 and 2505.00 eV for the two sulfur atoms within the current

![Isosurface](image)

#### TABLE I. Orbital energies (\(E_i\)), isosurfaces, and partial hole populations on the sulfur atoms S\textsubscript{BT} and S\textsubscript{T} for the least bound orbitals of the BT-1T molecule at the ground state equilibrium geometry.

<table>
<thead>
<tr>
<th>MO</th>
<th>HOMO</th>
<th>HOMO-1</th>
<th>HOMO-2</th>
<th>HOMO-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_i) (eV)</td>
<td>8.10</td>
<td>9.60</td>
<td>10.06</td>
<td>10.31</td>
</tr>
<tr>
<td>Isosurface (±0.01 au)</td>
<td><img src="image" alt="Isosurface" /></td>
<td><img src="image" alt="Isosurface" /></td>
<td><img src="image" alt="Isosurface" /></td>
<td><img src="image" alt="Isosurface" /></td>
</tr>
<tr>
<td>Part. Pop. on S\textsubscript{BT}</td>
<td>0.000</td>
<td>0.006</td>
<td>0.248</td>
<td>0.256</td>
</tr>
<tr>
<td>Part. Pop. on S\textsubscript{T}</td>
<td>0.006</td>
<td>0.611</td>
<td>0.014</td>
<td>0.000</td>
</tr>
</tbody>
</table>
The resonances that we are considering are at least 8 eV below the S 1s ionization threshold of the neutral molecule. Therefore, the neutral molecule does not display any resonant features in the spectral region that we are considering. For this reason, we note that at a negative time delay \( t < 0 \) (before the pump), there is no resonant X-ray absorption signal in this energy window (black part at negative time delays). This energy range is very advantageous for the experimental data collection since the X-ray absorption in a cation is distinguishable from X-ray absorption in a neutral system, as it has been demonstrated in several studies before.\(^{49-51}\) At \( t \geq 0 \), two distinct features can be seen in the time evolution of the absorption spectrum in Fig. 2(a). The first feature is a peak around 2494.2 eV (labeled A) that appears with the arrival of the pump pulse. After a short delay (<20 fs), a second feature appears in the region around 2493.1 eV (labeled B) and peak A starts to become weaker. Beyond the 50 fs time delay, the intensity of peak B goes down but with a much slower rate than peak A. At the position of peak A, we can see some remaining low absorption for \( t > 100 \text{ fs} \). In Fig. 2(b), snapshots of the spectrum at selected times are shown. Peak A and peak B can be directly attributed to the X-ray absorption on sulfur atoms S\(_{BT}\) and S\(_T\), respectively. Because of the different chemical environment, S\(_{BT}\) has a slightly higher K-edge binding energy, which gives rise to absorption at higher X-ray energies. S\(_T\) has a lower K-shell binding energy, and therefore, the X-ray absorption is at slightly lower energies.

The quick changes in the X-ray absorption spectrum can be understood from the electronic state populations from the FFSH calculations. Figure 3(a) shows the time evolution of the electronic state population after initial ionization of the HOMO-3 orbital. A very fast decay of the population in the HOMO-3 hole state with a half-lifetime of 8 fs can be seen. Subsequently, the HOMO-2 hole state and later the HOMO-1 hole state are populated. The decrease in the population of the HOMO-1 hole state after 50 fs leads to an increase in the cationic ground state (HOMO) population. This picture is also confirmed by inspecting the time evolution of the population of the valence hole on the two sulfur atoms as shown in Fig. 3(b). Initially, the hole is located close to S\(_{BT}\). Within 50 fs, it is transferred to S\(_T\) and later leaves the vicinity of both sulfur atoms. The changes in the absorption spectrum therefore directly reflect the movement of the valence hole from the vicinity of sulfur atom S\(_{BT}\) to sulfur atom S\(_T\) within less than 20 fs. The subsequent decrease in absorption peak B can be directly linked to the population of the HOMO hole state, in which the vacancy is not in the vicinity of either of the two sulfur atoms. From the orbital populations given in Table I, it can be inferred that the short-lived HOMO-3 and HOMO-2 hole states lead to X-ray absorption on sulfur atom S\(_{BT}\), whereas the later populated state (hole in HOMO-1) gives rise to absorption on S\(_T\). For a more detailed analysis of the X-ray absorption spectrum following VUV photoionization of the HOMO-3 orbital, see the supplementary material, Figs. S4 and S5.

Figure 4 shows that the relation between hole population dynamics and the X-ray absorption signal holds in a similar manner also for initial ionization on the HOMO-2, HOMO-1, and HOMO orbitals. We specifically inspect the X-ray absorption spectrum after ionization on the HOMO orbital. The calculated X-ray absorption spectrum and the partial hole population on the two sulfur atoms after

\[\text{EQ. (1)}\]
photoionization of the HOMO orbital are shown in Figs. 4(e) and 4(f), respectively. The spectrum in Fig. 4(e) shows a slight oscillation in the absorption signal with almost constant absorption strength. In this case, the hole is in the HOMO orbital, and thus, the absorption $S_T \rightarrow$ HOMO occurs at a higher energy relative to $S_T \rightarrow$ HOMO-1 [Fig. 4(c)]. As expected from the low overlap of the HOMO orbital with the two sulfur atoms (see Table I), the absorption is very low (note that the scale in the color bar is smaller by a factor 10 relative to Fig. 2). An even weaker signal can be seen at higher absorption energies, which can be identified as excitation from SBT to the HOMO hole. The time-dependent hole populations in Fig. 4(f) show the changes of the hole populations on SBT and $S_T$, indicating that the valence hole undergoes certain fluctuations even in the electronic ground state of the cation. Variations in the absorption signal over time shown in Fig. 4(e) are the result of the dynamical evolution of the vibrationally hot molecule. Moreover, the dynamics following photoionization of the HOMO orbital can be compared with the dynamics following photoionization of the HOMO-3 orbital after long delay times, when the electronic state has relaxed to the ground state (hole in the HOMO orbital). The key difference, however, is that in the latter case, the molecule has much more vibrational energy. Compared to the late-time X-ray absorption signal after ionization of the HOMO-3 orbital, the spectrum after ionization of the HOMO orbital is much sharper. This observation suggests that the amount of vibrational energy in the molecule can be inferred from the particular changes in the X-ray absorption (near-edge) spectrum.

We have conducted further analysis of the oscillations in the absorption signal for the simulations starting with a hole in the HOMO orbital. To that end, we have analyzed the Fourier transform, $f(\nu) = \int_0^\infty \exp(i2\pi\nu t)f(t)$, of the peak position of the X-ray absorption signal $f(t)$. The power spectrum, $|f(\nu)|^2 / \sum_{\nu} |f(\nu)|^2$, of the peak position in the X-ray absorption spectrum is shown in Fig. 5(a). In the figure, dominant frequencies are highlighted with dashed lines. In order to link these oscillations with vibrations of the molecular geometry, we also conducted a Fourier analysis of the selected structural parameters. For our analysis, we consider specific coordinates that describe the local chemical environment around the two sulfur atoms as well as the bond connecting the two units in BT-1T (see Fig. 1). The frequencies that describe...
oscillations of the bond distance \(d_{C_5-C_6}\) and the angle \(\angle C_5-C_6-C_9\) in thiophene and the oscillation of the selected structural parameters. The red lines in (a) and (b) highlight the same set of frequencies.

IV. CONCLUSION

The lack of a fundamental understanding of charge transfer dynamics in organic photovoltaics has long been recognized as a barrier for the further development of these complex devices. Therefore, we have undertaken a study to establish the theoretical foundation for experiments that will allow us to fully elucidate the mechanisms and dynamics of charge carrier transfer in organic heterojunctions. We demonstrate here that time-resolved X-ray absorption using an X-ray probe in combination with a VUV pump allows us to address the ultrafast carrier dynamics in molecular building blocks used for such devices with sensitivity toward both electronic and nuclear structures. As a model building block for donor-acceptor type polymers, we study BT-1T. After ionization in the HOMO-3 valence orbital, the electronic state quickly relaxes to the ground state (hole in the HOMO) and the molecule ends up in a highly excited vibrational state. During this relaxation process, the valence hole, initially created by VUV ionization, is transferred from one end (SBT) of the molecule to the other (S
d&C0), respectively. As can be seen, the X-ray absorption spectrum oscillates with the same frequencies as the investigated bond parameters. We therefore conclude that the observed oscillations in the X-ray absorption signal can be attributed to specific vibrations in the molecule. This finding demonstrates that TRXAS also allows us to resolve local geometrical changes in the molecule.

ACKNOWLEDGMENTS

This work received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant Agreement No. 681881) and was funded in part by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant No. DE-SC0019451, and by the Cluster of Excellence “The Hamburg Centre for Ultrafast Imaging” of the Deutsche Forschungsgemeinschaft (DFG) - EXC 1074 - project ID 194651731. K.K. thanks Dr. Kristoffer Haldrup and Anders Skovbo Gertsen for valuable and constructive discussions and comments during the preparation of this manuscript and ASAP for supporting DFT calculations [B3LYP/6-311++G(dp) level of theory]. The authors declare no competing financial interest.

REFERENCES


Supplementary Material:
Hole Dynamics in a Photovoltaic Donor-Acceptor Couple Revealed by Simulated Time-Resolved X-Ray Absorption Spectroscopy

Khadijeh Khalili,¹, a) Ludger Inhester,², ³ Caroline Arnold,², ³, ⁴ Ralph Welsch,², ³ Jens Wenzel Andreasen,¹, b) and Robin Santra², ³, ⁴
¹) Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksbergvej 399, 4000 Roskilde, Denmark
²) Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany
³) The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany
⁴) Department of Physics, Universität Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany

¹) khadkh@dtu.dk
²) jewa@dtu.dk
I. METHOD ANALYSIS

A. Electronic structure and basis set

In order to estimate the accuracy of the Koopmans’ theorem approach for the ionization potentials, we conducted ROHF SCF calculations for the ionized states. In Table S1, we compared the ionization potentials calculated from the orbital energies with the difference of neutral RHF and ionized ROHF state energies (so-called ΔSCF method). The ΔSCF calculation results in HOMO, HOMO-1, and HOMO-2 ionization potentials shifted by ~0.4 - 1.1 eV towards lower values (unfortunately, we have not been able to converge the SCF iterations for the HOMO-3 hole state). There are quantitative differences in the ionization potentials of the orbitals. However, we can see that the energy levels mainly shift consistently. Figure S1 depicts the comparison of four different basis sets showing an almost consistent shift in the ionization energy of the valence orbitals. It shows that the considered basis set is a reasonable compromise in terms of accuracy and computational cost.

Table S1: Comparison of the valence ionization potentials (in eV) from Koopmans’ theorem and ΔSCF calculations.

<table>
<thead>
<tr>
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<th>HOMO-1</th>
<th>HOMO-2</th>
<th>HOMO-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koopmans</td>
<td>8.10</td>
<td>9.60</td>
<td>10.06</td>
<td>10.31</td>
</tr>
<tr>
<td>ΔSCF</td>
<td>7.36</td>
<td>8.50</td>
<td>9.65</td>
<td>—</td>
</tr>
</tbody>
</table>

We have compared the potential energy surface (PES) of the ionized molecule from Koopmans’ theorem/6-31G (this work) with ROHF/6-31G and spin-unrestricted open-shell density functional theory (DFT) calculation using the UB3LYP hybrid functional and the 6-31G basis set, as implemented in the GAUSSIAN 09 package. Changing the C5-C6 bond (which is one of the relevant coordinates, see Fig. 1 in the manuscript), we determined the ionized ground-state energy. This produces the potential energy surfaces plotted in Fig. S2, which show almost identical shape. We therefore conclude that the shape and the relative energies between the potential energy curves are well described with the Koopmann’s theorem approach and we therefore obtain a qualitatively correct description of the dynamics.

In Fig. S3, we further compare the neutral ground state energy surface as a result of the relaxed scan of the BT-1T torsion angle from RHF/6-31G (used for the preparation of initial conditions...
FIG. S1: HF values of the valence ionization potentials with four different basis sets.

FIG. S2: Cut of the potential energy surface of the molecule in the ionized ground state along the C₅-C₆ bond using different electronic structure methods.

in this work), and DFT calculations employing the B3LYP functional and two different basis sets using the GAUSSIAN 09 package. The 6-31G and 6-311++G(d,p) basis sets are chosen as an example of low and high levels of theory, respectively. Although the curves in Fig. S3 have rather different shapes, all of them show the same global minimum. Within the region close to the minimum that is covered by our simulation all the employed electronic methods show a qualitative similar shape. This also supports the results from Fig. S2 comparing the PESs for the
FIG. S3: Cut of the potential energy surface of the molecule in the neutral ground state along the BT-1T torsion angle using different electronic structure methods and levels of theory.

The calculated PES along the torsion angle in Fig. S3, however, shows a second minimum, whose position is sensitive to the employed electronic structure model and basis set. Comparing RHF/6-31G and B3LYP/6-31G calculations shows that the PES barrier height depends strongly on the electronic structure method. Moreover, increasing the size of the basis set reduces the barrier height in B3LYP calculation but rather close to the RHF/6-31G results. The low position of the second minimum at 0.03 eV for B3LYP/6-311++G(d,p) suggests that depending on the temperature and sample preparation the molecule might occur in a mixture of conformers. Based on the Boltzmann distribution at room temperature this results in around 70% probability for the conformation to occur in the global minimum. It is thus to be expected that our simulation results will still be representative for the majority conformer.

B. XA spectrum

To assess the quality of our XAS data we also have calculated core excitation energies with the $\Delta$SCF method regarding the excitation of the sulfur $K$-shell to one of the valence holes. Our data in Table S2 indicates that the excitation energy evaluated via the $\Delta$SCF method is consistently shifted by $\sim$15 eV to lower energies compared to Koopmans’ theorem values. This shift is expected from
the large relaxation contributions accompanying the core vacancy.

Table S2: Comparison of the core→valence orbitals excitation energies (in eV) from Koopmans’ theorem and ∆SCF calculations.

<table>
<thead>
<tr>
<th>Excitation</th>
<th>Koopmans</th>
<th>∆SCF</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→HOMO</td>
<td>2496.43</td>
<td>2481.9</td>
<td>14.53</td>
</tr>
<tr>
<td>2→HOMO</td>
<td>2494.57</td>
<td>2480.26</td>
<td>14.31</td>
</tr>
<tr>
<td>1→HOMO-1</td>
<td>2494.93</td>
<td>2480.75</td>
<td>14.18</td>
</tr>
<tr>
<td>2→HOMO-1</td>
<td>2493.07</td>
<td>2479.11</td>
<td>13.96</td>
</tr>
<tr>
<td>1→HOMO-2</td>
<td>2494.47</td>
<td>2479.6</td>
<td>14.87</td>
</tr>
<tr>
<td>2→HOMO-2</td>
<td>2492.61</td>
<td>2477.96</td>
<td>14.65</td>
</tr>
<tr>
<td>1→HOMO-3</td>
<td>2494.22</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2→HOMO-2</td>
<td>2492.36</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

II. PARTIAL CONTRIBUTION OF EACH CATIONIC STATE TO THE FULL XA SPECTRUM

Here, we analyze the time evolution of the X-ray absorption spectrum of the BT-1T molecule after ionization of the HOMO-3 orbital in more detail. Figure S4 shows the XAS decomposed into the signals from the core orbitals that are localized on the two sulfur atoms (core orbital 1 on S_BT in Fig. S4(a) and core orbital 2 on S_T in Fig. S4(b)). The high intensity peak that appears immediately after the pump pulse at t = 0 fs in Fig. S4(a) decreases rapidly and vanishes mostly after 150 fs. An intense peak in Fig. S4(b) appears after a time delay at lower energies and decreases on a time-scale of several 100 fs. These observations are consistent with our interpretation of Fig. 3b. In order to explain the low intensity region in Fig. S4(b), we show here further analysis of the contributions of the different ionized orbitals to the XAS signal shown in Fig. S5. Figures S5(a-d) show the XAS signal associated with an excitation from one of the two sulfur core orbitals into the valence hole HOMO-3, HOMO-2, HOMO-1, and HOMO, respectively.

The signal in Fig. S5(a) that is associated with a S_BT → HOMO-3 transition disappears and the signal in Fig. S5(b) and Fig. S5(c) associated with transitions into HOMO-2 and HOMO-1 rises. These two signals appear almost simultaneously, but the one in Fig. S5(c) remains much
FIG. S4: Decomposition of the calculated time-resolved X-ray absorption spectrum of the BT-1T molecule after ionization of the HOMO-3 orbital for (a) core orbital 1 and (b) core orbital 2, which are localized on $S_{BT}$ and $S_T$, respectively.

FIG. S5: Decomposition of the calculated time-resolved X-ray absorption spectrum of BT-1T molecule after ionization of HOMO-3 orbital into the different ionized states with hole in the (a) HOMO, (b) HOMO-1, (c) HOMO-2, and (d) HOMO-3 orbital.
longer and can be mostly associated to the transition $S_T \rightarrow \text{HOMO-1}$ (left signal in Fig. S5(c)). For excitations into the HOMO orbital (Fig. S4(d)) only a weak contribution can be seen because of the very low population of the HOMO orbital on the sulfur atoms. Moreover, the signals in Fig. S5(d) appear at higher energy because of the higher excitation energy for the core to HOMO orbital as expected from Table S2.

This analysis confirms the interpretation of the XAS signal that is given in the main text: The individual signals in the XAS spectrum can be associated with individual core to valence transitions and follow the time-dependent population of the valence hole in our molecule.

REFERENCES

Paper III
Simulation of Time-Resolved X-ray Absorption Spectroscopy of Ultrafast Dynamics in Particle-Hole-Excited 4-(2-Thienyl)-2,1,3-benzothiadiazole

Khadijeh Khalili
Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark

Ludger Inhester
Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany and The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany

Anders S. Gertsen
Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark

Bianca Laura Hansen and Kristian Frellesen Nielsen
Department of Physics, Technical University of Denmark, Fysikvej, 2800 Kgs. Lyngby, Denmark

Jens Wenzel Andreasen
Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark

Robin Santra
Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany and The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany
Abstract

To date, alternating co-polymers based on electron-rich and electron-poor units are the most attractive materials to control functionality of organic semiconductor layers in which ultrafast excited-state processes play a key role. We present a computational study of the photoinduced excited-state dynamics of the 4-(2-Thienyl)-2,1,3-benzothiadiazole molecule, which is a common building block in the backbones of π-conjugated polymers used for organic electronics. In contrast to homo-polymer materials, such as oligothiophene, 4-(2-Thienyl)-2,1,3-benzothiadiazole has two non-identical units, namely thiophene and benzothiadiazole, making it attractive for intramolecular charge transfer studies. To gain a thorough understanding of the coupling of excited-state dynamics with nuclear motion, we consider a scenario based on femtosecond time-resolved X-ray absorption spectroscopy using an X-ray free-electron laser in combination with a synchronized ultraviolet femtosecond laser. Using the Tully’s Fewest Switches Surface Hopping approach in combination with excited-state calculations at the level of Configuration Interaction Singles, we calculate the gas-phase X-ray absorption spectrum at the carbon K edge, nitrogen K edge, and sulfur L and K edges as a function of time after excitation to the lowest electronically excited state. Our ab-initio MD simulations indicate that the excited-state relaxation processes involve bond elongation in the benzothiadiazole unit as well as thiophene ring puckering at a timescale of 100 fs. Furthermore, we show that these dynamical trends can be identified from the time-dependent X-ray absorption spectrum.

I. INTRODUCTION

The sub-femtosecond X-ray pulses provided by X-ray free-electron lasers enable investigations of ultrafast, non-equilibrium dynamics of functional materials as well as their electronic and geometric structure. By exploiting the atomic element specificity from inner-shell transitions as well as the sensitivity of the core-level energies to internuclear separation, X-ray absorption spectroscopy (XAS) is a promising tool to probe local geometric information of molecules [1–4]. Detailed exploration of ultrafast, nonadiabatic dynamics in photoexcited molecules requires an exploration of the underlying electronic structure changes that drive

* jewa@dtu.dk

2
the structural dynamics. This is feasible by using time-resolved (pump-probe) techniques in which a non-equilibrium state is initiated by a pump pulse and probed by means of a suitable probe pulse arriving with a given time delay [5–8].

In the last decade, organic photovoltaics (OPVs) have attracted increasing attention as an alternative to silicon-based solar cells due to their low cost and easy manufacturing [9, 10]. However, when upscaled to large-area cells with industrial relevance, OPVs have been suffering from low efficiencies compared to traditional, silicon-based photovoltaics [11]. Remarkable efforts have been made to increase OPV efficiencies, especially in terms of materials discovery and optimization; this includes improved alignment of energy levels through substitution, improved charge transfer dynamics through morphology optimization, and improved charge extraction through optimization of interfacial layers, giving rise to a drastic increase in power conversion efficiency, which now exceeds 17 % [12–15]. An early, but key, strategy to increase efficiency has been the lowering of the band gap of OPV absorber materials for better sunlight harvesting, leading to the synthesis of a wide range of low-band-gap donor co-polymers exhibiting charge-transfer absorption. The backbones of these consist of electron-rich aromatic units, often thiophene derivatives, accompanied by electron-deficient units, a building-block materials design principle which has proved advantageous for the screening of new donor materials with improved electronic properties [16–18].

The functioning of OPV active layer materials is based on the processes in their photoexcited states, and therefore, a fundamental understanding of these complex processes and their decay mechanisms can give rise to improvements in the efficiency of such devices. A popular way to study the excited-state relaxation of co-polymers is to study the dynamics of their donor-acceptor (D−A) backbones as oligomeric model compounds. Moreover, D−A π-conjugated molecules have attracted attention in the context of optoelectronics, where excited-state deactivation plays a key role. Benzo thiadiazole (BT) and thiophene (T), as fundamental units of a family of efficient low-band-gap electron-donating polymers [19–21] and a variety of polymers with applications in electronic devices [22], have already been investigated in a few studies separately or in a π-conjugated framework. Iagatti et al. [23] studied the relationship between the structural properties and the excited-state dynamics of dTBT (D−A−D framework based on an electron-withdrawing/accepting BT core connected to two flanking electron-donating T rings) in solution and solid state using ab initio
calculations and transient-absorption and time-resolved fluorescence measurements. They concluded that the main relaxation mechanism involves an intermolecular charge transfer accompanied by planarization of the molecule’s geometry. The same dTBT molecule has been considered as a model compound to study the charge-transfer relaxation in D–A type conjugated materials by Scarongella et al. [24]. Using time-resolved femtosecond transient-absorption spectroscopy in solution and in the solid state as well as density functional theory (DFT) calculations, they reported a planar backbone in both the ground and excited states and weak conformational relaxations including marginal contraction of the central benzene ring and elongation of the molecule along the short axis. They have also reported some spectral dynamics in the molecule occurring with time constants of a few picoseconds (ps), which are so far not fully elucidated. The discrepancy in the two reported structural relaxations of the molecule is controversial and requires more investigations. In order to overcome the limitations of optical transient-absorption spectroscopy for revealing the underlying dynamics, we consider time-resolved XAS to obtain complementary information on the excited-state dynamics in D–A type molecules.

In this paper, we study the excited-state dynamics of 4-(2-Thienyl)-2,1,3-benzothiadiazole (BT-1T) molecule, characterized by a D–A structure in which one T ring is connected to one BT unit (Fig. 1). In our previous work [25], we showed that there are two conformers, of which the one shown in Fig. 1 is the most energetically favorable. We then investigated the ultrafast charge transfer dynamics following the UV photoionization of this molecule. We showed that the charge transfer can be inspected by time-resolved XAS exploiting its atomic site specificity. Moreover, by ionizing from the highest occupied molecular orbital (HOMO), our earlier findings demonstrated that time-resolved XAS allows us to resolve local geometrical changes in the molecule. Here, we extend our earlier study by considering particle-hole photoexcitation instead of photoionization (pure hole formation), which is more relevant for PV applications. This way, we also strengthen our understanding of the main relaxation processes in the lowest excited state of the BT-1T molecule.

A great deal of work has already been carried out by means of time-resolved experiments to explore the complex excited-state relaxation dynamics of π-conjugated structures [26–28]. Experimental data are usually combined with theoretical investigations as an indispensable tool for a more detailed description of the observed dynamics. However, it has always been a challenge to theoretically describe excited-state dynamics of a molecule. Nonadiabatic
excited-state molecular-dynamics (NA-ESMD) calculations have been performed using time-dependent density functional theory (TDDFT) [29], algebraic diagrammatic construction to second order (ADC(2)) [30, 31] or configuration interaction singles (CIS) [32–34] to study excited-state deactivation mechanisms via internal conversion or relaxation to the ground state (GS). It was found that the choice of the excited-state computational method is crucial because the failures in, for instance, incorrect state ordering, poor distribution of oscillator strengths, and erroneous descriptions of the excited-state potential energy surfaces can give rise to problematic computed absorption spectra [31, 35]. Here, we carefully verify that the employed CIS method provides a computationally efficient and qualitatively accurate description of photoinduced dynamics in the energy region we are interested in. In the present work, we systematically investigate the photoabsorption spectra of the relevant D–A molecule, BT-1T, in gas phase by using the Tully’s fewest switches surface hopping (FSSH) approach [36–38] based on excited-state calculations at the level of CIS.

II. COMPUTATIONAL DETAILS

A. Nonadiabatic molecular dynamics

Throughout this work, the FSSH approach is employed to describe the nonadiabatic, ultrafast dynamics of BT-1T after photoexcitation. FSSH is based on a quantum-mechanical
treatment of the electronic subsystem, while the nuclear subsystem is treated classically, propagating along a classical trajectory. An ensemble of 100 nuclear initial conditions (i.e., coordinates and momenta) is obtained by quasiclassical sampling [39, 40] of the normal-mode coordinates of BT-1T in the ground state (GS). Each of the 100 initial conditions is then independently propagated with a time step of 0.5 fs and a total propagation time of 400 fs (as we are interested in the ultrafast timescales). The classical trajectories propagate on a single adiabatic potential energy surface and can switch between the electronic states based on the nonadiabatic hopping probability.

B. Electronic-structure calculations

Electronic-structure data, energies, energy gradients, and nonadiabatic couplings are determined on the fly at the level of CIS using the XMOLECULE toolkit [41]. In the CIS method, the electronic wavefunction is approximated by a linear expansion of electron configurations,

$$|\Psi\rangle = \sum_{a,r} C_{a}^{r} |\Phi_{a}^{r}\rangle,$$

where the $|\Phi_{a}^{r}\rangle$ are determinants with single particle-hole excitations relative to the Hartree-Fock (HF) ground state with amplitudes $C_{a}^{r}$. The particle-hole determinant describes an excitation from occupied molecular orbitals (MOs) labelled by $a,b,\cdots$ to virtual orbitals labeled by $r,s,\cdots$. As a consequence of the Brillouin theorem, which states that there are no coupling matrix elements between the ground state and the single excitation (or $\langle \Phi_{0}|\hat{H}|\Phi_{a}^{r}\rangle = 0$), CIS matrix has a block structure with the HF ground state as an eigenstate of $\hat{H}$ [42]. The ground-state block in the CIS matrix gives the restricted Hartree-Fock (RHF) ground-state energy, $E_{0} = \langle \Phi_{0}|H|\Phi_{0}\rangle$. The single-excitation block elements in the MO space are

$$\langle \Phi_{b}^{s}|H|\Phi_{a}^{r}\rangle = (\epsilon_{r} - \epsilon_{a})\delta_{a,b}\delta_{r,s} - (rs|ba) + 2(ra|bs)$$

with $(rs|ba)$ and $(ra|bs)$ being the two-electron integrals. The resulting matrix is then diagonalized to find the eigenvalues as the electronic excitation energies in the CIS method.
The corresponding CIS energy gradient is given by

$$\frac{dE_{\text{CIS}}}{\partial R} = \sum_{a,r} \sum_{b,s} C_{b}^{*} C_{r}^{a} \left( \frac{d\epsilon_{r}}{dR} - \frac{d\epsilon_{a}}{dR} \right) \delta_{a,b} \delta_{r,s} + \sum_{a,r} \sum_{b,s} C_{b}^{*} C_{r}^{a} \left( - \frac{d\langle rs|ba \rangle}{dR} + 2 \frac{d\langle ra|bs \rangle}{dR} \right).$$

(3)

In our approach, the energy gradients are computed analytically based on the coupled-perturbed Hartree-Fock (CPHF) theory [43–45] as implemented in XMOLECULE.

C. Photoabsorption cross sections

Our method for evaluating X-ray absorption cross sections was described in detail elsewhere [25, 46]. Calculated oxygen K-edge X-ray absorption spectra of formaldehyde in Fig. S3 in the electronic supporting information (ESI) show that by considering an absolute shift in the spectrum, the CIS method (with a relatively small basis set) provides a qualitatively correct spectrum in the energy range covering the first few absorption lines (higher absorption lines are out of the scope of the current study). More details on this can be found in the ESI.

The absorption line strengths are essentially determined by the transition dipole moments between the involved CI eigenvectors. Within the CIS expansion these are given for the ground state as \( \sum_{a,r} C_{a}^{s} \langle \Phi_{0} | \hat{\mu} | \Phi_{r}^{a} \rangle \) and for an excited state as \( \sum_{a,r} \sum_{b,s} C_{b}^{r} C_{a}^{s} \langle \Phi_{r}^{a} | \hat{\mu} | \Phi_{s}^{b} \rangle \) (\( \mu = x, y, z \)). We discuss the accuracy of the calculated absorption spectra for valence and core and core-valence excitation in the ESI.

III. RESULTS AND DISCUSSION

The lowest excited state transition energies, oscillator strengths, corresponding MOs, and CIS coefficients of BT-1T in gas phase are shown in Table I. Table I compares the results from the CIS calculation using XMOLECULE to two other levels of theory, namely complete-active-space self-consistent field (CASSCF) and complete-active-space second-order perturbation theory (CASPT2), using Molcas 8.2 [47] (restricted-active-space state interaction (RASSI) [48] is used to compute oscillator strengths). All calculations are performed using the 6-31G basis set, which is justified as a reasonable compromise between computa-
tional cost and precision for describing the lowest-energy transition by a basis-set analysis (cf. Fig. S3 in ESI). The lowest-excited-state calculations are carried out on the HF/6-31G-optimized geometry of BT-1T, which might be the reason why all the energies reported in Table I are so high compared to the experimentally measured value of 3.2 eV (however in solution). The role of the geometry in the excitation energy is further elucidated by repeating the CIS calculations on the HF/6-31+G(d)-optimized geometry, which gives 3.77 eV for the first transition energy (for more analysis, cf. Fig. S1 in ESI). The improved results show that the overestimated CIS values are mostly related to the basis set and not necessarily the method itself. With the computational limitations, molecular dynamics trajectories with larger basis sets are not currently feasible and the current study is considered as a quantitative study. We emphasize that the present work should be seen as a method development of XAS analysis within the XMOLECULE toolkit, and the overestimation of absolute values are thus not of great importance to the relevance of the simulation framework presented herein. The implementation of more precise quantum chemical methods for describing charge-transfer excitations into XMOLECULE is ongoing.

In Table I, the first absorption band in the gas-phase electronic spectrum of BT-1T is attributed to a low-lying absorbing singlet state (S$_1$) dominated in all three calculations by the HOMO $\rightarrow$ LUMO particle-hole configuration. The involved $\pi$ and $\pi^*$ orbitals are depicted in Fig. 2. While the LUMO is mostly localized on the BT unit with some localization on the BT sulfur, S$_{BT}$, the HOMO has a low localization on the two sulfur atoms.

<table>
<thead>
<tr>
<th></th>
<th>$E$(eV)$^a$</th>
<th>$f$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIS</td>
<td>4.08</td>
<td>3.88$\times 10^{-1}$</td>
<td>0.92</td>
</tr>
<tr>
<td>CASSCF/RASSI</td>
<td>4.61</td>
<td>4.07$\times 10^{-1}$</td>
<td>0.81</td>
</tr>
<tr>
<td>CASPT2/RASSI</td>
<td>3.93</td>
<td>4.07$\times 10^{-1}$</td>
<td>0.81</td>
</tr>
</tbody>
</table>

$^a$ Experimental UV-vis absorption spectrum of the BT-1T molecule in toluene shows the first absorption band at 3.2 eV.
FIG. 2: Molecular orbitals involved in the first excitation, $S_0 \rightarrow S_1$, considered in the current study. (The orbitals are visualized using VMD-1.9 [49].)

A. Electronic state population

In order to investigate the nonadiabatic excited-state dynamics of BT-1T, trajectories were initiated from the first absorption band populating the $S_1$ state. The evolution of the state populations for trajectories initiated in $S_1$ are shown in Fig. 3(a). As one can see, the $S_1$ state decays relatively slowly such that only 20% of the trajectories relax to the ground state within 400 fs. The simulations do not show any upward hops leading to population of the $S_2$ state. We divide the $S_1$ state population into two regions: one below 200 fs where it stays rather constant with a very small decay ($\sim 4\%$) and one after that when it starts to decay with a higher rate. By fitting an exponential decay for the second region to the population of the $S_1$ state, we obtain a lifetime of the first excited state of 2.14 ps. Figure 3(b) shows the dynamics of the electronic population in the BT-1T molecule after initial excitation to the $S_1$ state from the time-dependent Mulliken charge population [50]. As seen, the electronic population is mostly localized on the BT unit at time zero as expected due to the excitation to the LUMO orbital with high localization on BT. It then decreases slowly with time and is transferred to the T unit along with the decay of the $S_1$ state in Fig. 3(a).

B. Structural dynamics

Figure 4 shows the dynamics of selected geometrical features, averaged over the ensemble of trajectories, as a function of time. Specifically, the torsional angle $\delta_{C_{10}-C_{5}-C_{6}-C_{7}}$ (shown
FIG. 3: Time evolution of (a) the population of the ground and first two excited states and (b) the partial population for the trajectories started in the $S_1$ state.

in Fig. 1 as a criterion for the rotation of the thiophene unit) and the related bonds (for possible double bond shift or ring puckering), $C_6 - C_7$, $C_5 - C_6$, and $C_5 - C_{10}$, are chosen. Moreover, we show the structural parameters $\vartheta_{C_5-C_6-S_T}$ and $\delta_{C_6-S_T-C_9-H_4}$ (see Fig. 1) to discuss possible out-of-plane motions in the molecule. As can be seen, the initial excitation to $S_1$, as shown in Fig. 4(a), induces large fluctuations in the dihedral angle $\delta_{C_6-S_T-C_9-H_4}$, while the torsional angle $\delta_{C_{10}-C_5-C_6-C_7}$ stays rather constant indicating that the molecule stays rather planar during the relaxation. The $C-C$ bond lengths undergo oscillations with slowly decaying amplitudes, where the bonds $C_6 - C_7/C_5 - C_{10}$ oscillate anticyclic to $C_5 - C_6$ at very short time delays, which indicates a flip between single and double bonds between the corresponding units. Irregular oscillations at larger time delays are observed for all the three bonds leading to elongation of $C_5 - C_{10}$ and shortening of the two others. The $\vartheta_{C_5-C_6-S_T}$ angle (shown in Fig. 4(c)) oscillates around the ground-state value. Based on the results from Fig. 4, we conclude that excited-state relaxation leads to a ring puckering in the thiophene unit.

We further consider the time evolution of the structural features relevant to the two sulfur atoms such as the distance between them, $S_{BT} - S_T$, as well as the $S_{BT} - N$ and $S_T - C$ bond lengths. Figure 5(a) shows a rapid increase in the distance between the two sulfur atoms after the excitation. Also for $S_{BT} - N$ and $S_T - C$ a slight-bond length increase can be observed. Since almost all bonds become a bit larger, we plotted the shift in the molecule’s geometry (as collective deviation and calculated from the change in the geometry during
FIG. 4: Time evolution of selected structural parameters after excitation to the S\textsubscript{1} state. The arrows in (b) are guides to the eye for the initial and final values of the C – C bond lengths.

the dynamics compared to the GS geometry) as a function of time in Fig. 6, showing that the molecule expands overall. Moreover, it shows the characteristic 200 fs timescale after which the excited-state population in Fig. 3 is seen to decrease at high rate. In other words, the energy needed for the expansion comes from electronic deexcitation. Experimentwise, X-ray scattering is a natural choice to track time evolution of the molecular structures. Appendix A discusses that, considering BT-1T in experimental condition (e.g. in solution), the difference scattering signal of such structural changes during the relaxation are supposed to be observable.
FIG. 5: Time evolution of (a) $S_{BT} - S_T$ distance, (b) $S_{BT} - N$ and (c) $S_T - C$ bond lengths.

FIG. 6: Displacement in the molecular geometry (compared to the GS geometry) as a function of time.
C. Time-resolved X-ray absorption spectrum

We now turn to the time-resolved (pump-probe) X-ray absorption spectroscopy and discuss its ability to obtain detailed information on the previously discussed dynamical evolution underlying the excited-state relaxation dynamics. Figures 7(a) and 7(b) provide the carbon and nitrogen $K$ edge spectra, respectively, revealing instantaneous changes upon photoexcitation. The spectra are shown in the energy window focusing on the lowest ground-state (GS) absorption bands and a few eV below that to capture features that are specific to the excited-state (ES) XAS. In the top panels, showing the GS spectra, each transition line without broadening is shown with a red vertical line, from left to right, assigned to $C_{10}$, $C_4$, $C_3$, $C_7$, $C_9$, $C_8$, $C_5$, $C_2$, $C_1$, and $C_6$ for the $C K$ edge and $N_1$ and $N_2$ for the $N K$ edge. Two main dynamical features can be seen in the time evolution of the absorption spectra in the bottom panels of Figures 7(a) and 7(b). In both figures, an excited-state absorption (ESA) peak appears immediately at energies $\sim$5 eV below the first GS absorption band. This ES low-energy contribution moves quickly to higher energies and oscillates with high amplitude until 50 fs. At time delays between 100 and 200 fs, the ESA peaks show subtle variation in amplitude with small changes in the position of the peaks. At larger time delays (>200 fs), the ESA features decrease with higher rate, as expected from Fig. 3(a), followed by an increase in the GS features. The excited-state relaxation is associated with the charge transfer from the BT to the T unit, as seen in Fig. 3(b), meaning that the technique is able to track the electronic-structure changes going hand-in-hand with the charge transfer mediated by non-Born-Oppenheimer physics. Moreover, the shift of the ESA bands towards higher/lower energies can be explained by the behavior of the local electronic population on the absorbing atoms [51, 52]. Our calculations show that the transition lines associated with carbon atoms $C_{10}$, $C_3$, and $C_5$ have the main contribution in the ES absorption spectrum of BT-1T (see Fig. S12 in ESI). The bond-length analysis of $C_5 - C_{10}$ in Fig. 4(b) displays structural dynamics that perfectly match the small-time-delay behavior of the ESA $C K$ edge peaks shown in Fig. 8. The sharp oscillation in the $C_5 - C_{10}$ bond length (change in the electron density) before 200 fs is observed also in the position of the ES peak in the $C K$ edge spectrum.

A more detailed analysis is required here to elucidate the contribution of other parameters in the spectrum. Table II shows the different peaks in the power spectrum from the Fourier
FIG. 7: Normalized (a) carbon and (b) nitrogen $K$ edge XAS intensity versus photon energy for the ground state (vertical red lines represent oscillator strength) and for different time delays after photoexcitation. The C and N $K$ edge spectra are shifted by -11 and -16 eV, respectively, based on the analysis reported in the ESI. The horizontal arrows show the two first ultrafast move of the ESA peak.

analysis for the selected structural parameters as well as the ES peaks of the C and N $K$ edge spectra. As seen in Table II, the oscillation peaks at 20-25 THz appears more or less for all the reported parameters. It also seems that the presence of sulfur decreases the oscillation frequency such that $S_{BT} - S_T$ has the lowest-frequency contribution to the two spectra. The
FIG. 8: Position of ES peak in C $K$ edge spectrum of BT-1T in Fig. 7 versus time delay after excitation to the $S_1$ state.

larger frequencies of 45-50 THz in the edge spectra mostly originate from $C - C$ bonds and those parameters that involve carbon atoms. The oscillation peak at 22.5 THz in the $N$ $K$ edge spectrum is from $S_{BT} - N$ bonds and larger values must be from the bonds connected to carbon atoms.

The computed BT-1T sulfur $L$ and $K$ edge spectra are shown in Figures 9(a) and 9(b), respectively. The plots are in the energy range emphasizing the ES features. Moreover, the plots are shifted by -10 and -21.4 eV for the $S$ $L$ and $K$ edge spectra, respectively, as discussed in the ESI. BT-1T has two non-equivalent sulfur atoms (benzothiadiazole $S_{BT}$ and thiophene $S_T$) and each of them gives one dominant transition as shown in the upper panels of Figs. 9(a) and 9(b). The positions of the core transition thresholds for the $S_{BT}$ 2$p$ and the $S_T$ 2$p$ channels are located at 166.7 and 167.1 eV, respectively. The sulfur edge spectra show rather more complicated behavior compared to the C and N edges. The upper panel of Fig. 9(b) shows the static XAS spectrum of the first few eV of the $S$ $K$ absorption edge of BT-1T in gas phase. It is characterized by two features assigned to $S_{BT}$ 1$s$ and $S_T$ 1$s$ core transitions at 2472.7 and 2473.5 eV, respectively. In the lower panel of Fig. 9(b), the transient $S$ $K$ edge spectrum upon photoexcitation is presented. Similar to the $S$ $L$ edge spectrum, and early-time-delay oscillation occurs at lower energies compared to the time-zero ESA peak. Moreover, and in contrast to the other edge spectra, after $\sim 40$ fs, there is
TABLE II: Frequencies, in THz, of the peaks obtained by Fourier analysis of selected geometrical parameters as well as of the position of the ES peak in the C and N K edge spectra.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Peak #1</th>
<th>Peak #2</th>
<th>Peak #3</th>
<th>Peak #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{BT} - S_T$</td>
<td>10</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\vartheta_{C_5-C_6-S_T}$</td>
<td>10</td>
<td>20</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>$C_5 - C_6$</td>
<td>10</td>
<td>-</td>
<td>47.5</td>
<td>-</td>
</tr>
<tr>
<td>$C_5 - C_{10}$</td>
<td>15</td>
<td>25</td>
<td>45</td>
<td>52.5</td>
</tr>
<tr>
<td>$C_7 - C_6$</td>
<td>-</td>
<td>20</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>$S_{BT} - N_1$</td>
<td>12.5</td>
<td>22.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$S_{BT} - N_2$</td>
<td>15</td>
<td>22.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\delta_{C_{10}-C_5-C_6-C_7}$</td>
<td>15</td>
<td>25</td>
<td>35</td>
<td>-</td>
</tr>
<tr>
<td>$\delta_{C_6-S_T-C_9-H_4}$</td>
<td>5</td>
<td>12.5</td>
<td>42.5</td>
<td>50</td>
</tr>
<tr>
<td>$S_T - C_6$</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>$S_T - C_9$</td>
<td>20</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C K edge</td>
<td>-</td>
<td>22.5</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>N K edge</td>
<td>-</td>
<td>22.5</td>
<td>45</td>
<td>50</td>
</tr>
</tbody>
</table>

no clear energetic separation between ES and GS absorption lines, which also makes it hard for a Fourier analysis. As already observed, most information about the structural changes appeared in the C K edge spectrum.
FIG. 9: Normalized sulfur (a) L and (b) K edge XAS intensity versus photon energy for the ground state (vertical red lines represent oscillator strength) and for different time delays after photoexcitation. The S L and K edge spectra are shifted by -10 and -21.4 eV, respectively, based on the analysis reported in the ESI.
IV. CONCLUSION

With respect to the necessity of a deeper understanding of photophysical properties of conjugated oligomers/polymers for a successful design of new photovoltaic materials and architectures, we have systematically investigated the excited-state dynamics of the 4-(2-Thienyl)-2,1,3-benzothiadiazole (BT-1T) molecule. We have verified that the employed level of electronic-structure modelling, CIS, is able to reproduce low-lying absorption-band features reasonably well compared to experiments. For the energy window around and a few eV below the low-lying absorption bands, we have performed time-resolved X-ray absorption spectroscopy simulations to investigate excited-state ($S_1 \rightarrow S_0$) relaxation processes occurring on an ultrafast timescale for BT-1T in gas phase. We found, through the sensitivity of the XAS spectrum to the electronic-structure changes, that nonadiabatic transition from the excited to the ground state is associated with charge transfer from the benzothiadiazole unit to the thiophene unit occurring mostly after $\sim$200 fs. Moreover, excited-state relaxation processes are driven by fast structural motions, notably for time delays $<$ 200 fs. At these short times, we observe sharp changes in the bond lengths connecting the two units as well as the angles including the sulfur atom in the thiophene ring with a significant fingerprint in the C $K$ edge and S $L$ edge XAS spectra. At time delays larger than 200 fs, elongation of the S$_{BT}$ – N bond in the benzothiadiazole ring, shortening of the central C – C bond, and decrease of the S$_T$ angle play the main role. Dynamical changes in $\delta_{C_6-S_T-C_9-H_4}$ also indicate that the thiophene ring undergoes puckering deformations. We demonstrated that not only the structural features, but also the charge transfer (following the changes in the electronic-structure), can be inspected by X-ray absorption spectroscopy unlike nonresonant X-ray scattering, which is only sensitive to the molecular structure.

Knowledge of the excited-state relaxation pathways and timescales in photoexcited organic materials is essential for an overview of the charge-carrier localization and the dynamics having a strong effect on the efficiency of optoelectronic devices based on such materials. Such information clarifies whether charge-transfer relaxation competes with the functional processes on the same timescales in an organic solar cell. Here, we have offered a theoretical methodology addressing time-resolved X-ray absorption experiments to gain the essential information, which can be used, for instance, when designing a new synthetic route or new conjugated materials for high efficiency OPVs.
V. SUPPLEMENTARY MATERIAL

See the electronic supporting information (ESI) for a systematic analysis supporting the CIS XAS spectrum results, as mentioned in the text.

VI. ACKNOWLEDGMENTS

This work received funding from the European Research Council (ERC) under the European Unions Horizon 2020 research and innovation programme (Grant Agreement No. 681881) and was funded in part by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant No. DE-SC0019451, and by the Cluster of Excellence ‘CUI: Advanced Imaging of Matter’ of the Deutsche Forschungsgemeinschaft (DFG) - EXC 2056 - project ID 390715994. K.K. thanks Dr. Christian Rein for valuable and constructive discussions during the preparation of this manuscript. B.L.H. and K.F.N. thank Asmus Ougaard Dohn for providing part of the code used to transform the RDF to a scattering signal as well as Prof. Martin Meedom Nielsen and Dr. Kristoffer Haldrup for the code to calculate the scattering signal from form factors. The authors declare no competing financial interest.

Appendix A: Simulated time-resolved X-ray scattering signal of BT-1T in toluene

Molecular dynamics (MD) and quantum mechanical (QM) calculations are combined to provide a time-resolved X-ray scattering signal of BT-1T in a solvent, toluene, following photo-excitation. The difference scattering signal, $\Delta S$, between the time-zero excited state and the subsequent excited states provides information about the dynamics of the molecular structure.

1. Computational details

The total difference scattering signal is a sum of the three separate contributing terms:

- $\Delta S_u(Q)$ the solute-solute term
• \( \Delta S_c(Q) \) the solute-solvent term

• \( \Delta S_v(Q) \) the solvent-solvent term.

where \( Q \) is the magnitude of the scattering vector. \( \Delta S_u(Q) \) has been calculated using an ensemble of the trajectories used for the XAS calculations. \( \Delta S_c(Q) \) and \( \Delta S_v(Q) \) has been calculated from radial distribution functions (RDFs) derived from the MD trajectories. The RDFs provide information about the solvation structure surrounding the solute as well as the solvent-solvent correlations.

All classical MD simulations are carried out using GROMACS [53]. The procedure considers a frozen solute, BT-1T, surrounded by freely moving solvent molecules, toluene, inside a cubic box. This methodology of having a frozen solute surrounded by freely moving solvent molecules has also been applied in other studies [54]. In this context, frozen means that the solute molecule is fully constrained to not move in space by retaining bond lengths and angles. The cubic box is subjected to periodic boundary conditions and has a side length of 50 containing 638 toluene molecules. This is equal to a concentration of 13.3 mM BT-1T in toluene.

The MD simulation utilizes optimized structures and partial atomic charges (PACs) obtained from density functional theory (DFT) calculations of BT-1T using the B3LYP/6-311++G(d,p) level of theory in Gaussian 16 [55]. The PACs are derived by numerically fitting these through a grid-based scheme (ChelpG) to reproduce the molecular electrostatic potential. This is done for the ground state of BT-1T using time-independent DFT and for the optimized, first excited state of BT-1T using time-dependent DFT, providing the necessary parameters for a force-field utilizing standard OPLS-AA parameters [56] for non-bonded interactions.

According to [57], the RDF can be converted to a scattering signal as:

\[
S(Q) = \sum_i N_i f_i(Q)^2 + \sum_{l,m} f_l(Q) f_m(Q) \frac{N_l(N_m - \delta_{l,m})}{V} 4\pi \int_0^{R_{box}} r^2 [g_{l,m}(r) - 1] \frac{\sin(Qr)}{Qr} dr, \tag{A1}
\]

where \( R_{box} \) denotes half of the length of the simulated box corresponding to the radius of the box, \( N_i \) and \( N_m \) are the total number of atoms of type \( l \) and \( m \), respectively. \( f_i(Q) \) and \( f_m(Q) \) are the atomic form factors for atom \( l \) and \( m \). \( V \) is the volume of the simulated box,
$Q$ is the scattering vector and $g_{l,m}$ is the RDF for atom $l$ and $m$. $\delta_{l,m}$ is the Kronecker delta, where $\delta_{l,m} = 1$ when $l$ is equal to $m$, while $\delta_{l,m} = 0$ when $l \neq m$.

This signal can further be divided into 3 groups namely the solvent-solvent correlation term $S_v(Q)$, the solute-solvent (cross) correlation term $S_c(Q)$, and the solute-solute correlation term $S_u(Q)$. However, the solute-solute term has been calculated on the CIS trajectories. In the scattering signal, $S_c(Q)$ and $S_v(Q)$ all atom-atom pair correlations are considered. This means that the RDFs are made with a reference atom type in the solute (i.e. S, N, C, H) or solvent (i.e. C, H) to another atom type in the solute (i.e. S, N, C, H) or solvent (i.e. C, H).

2. Results

Fig. 10 shows the relative magnitude of the difference scattering signal, $\Delta S/S_{tot}$, for BT-1T in toluene, as function of $Q$ at different times after the excitation. The total signal is

$$S_{tot} = S_{ES,u} + S_{ES,c} + S_{ES,v}$$

where ES denotes the excited state. In Fig. 10(a), the estimated strength of $\Delta S_u/S_{tot}$ appears largest at $Q = 0.5^{-1}$ with a relative magnitude of 0.18%, by assuming that the contribution from solvent response is negligible. The time-dependent signal indicates a largest amplitude at 20 fs after excitation. The order of magnitude is similar for the signal in Fig. 10(b), where the solvent response is included. In Fig. 10(b), the signal shows less time dependence, as the scattering signal of the solvent is significantly stronger than the solute. In Ref. [58] it has been proven possible to detect a similar signal with a relative magnitude of $\frac{\Delta S}{S} = 1 \cdot 10^{-4}$ from a low-noise detector, where $\Delta S = \Delta S_u + \Delta S_c + \Delta S_v$. Since the relative magnitude in Fig. 10(b) is larger than $1 \cdot 10^{-4}$, it can be assumed that it would be possible to measure the difference scattering signal of BT-1T in a 13.3 mM concentration of BT-1T in toluene.
FIG. 10: Estimation of relative magnitude in the difference scattering signal compared to the total scattering signal $\Delta S / S_{\text{tot}}$ for the solute-solvent system (BT-1T subjected in Toluene) shown for different times after photo-excitation. (a) Solvent response neglected and only solute response, $\Delta S = \Delta S_u$. (b) Both solute and solvent response included, $\Delta S = \Delta S_u + \Delta S_v$. 


Rev. 109, 897 (2009).


Supplementary Material:
Simulation of Time-Resolved X-ray Absorption Spectroscopy of Ultrafast Dynamics in Particle-Hole-Excited 4-(2-Thienyl)-2,1,3-benzothiadiazole
Khadijeh Khalili,1 Ludger Inhester,2,3 Anders Skovbo Gertsen,1 Bianca Laura Hansen,4 Kristian Frellesen Nielsen,4 Jens Wenzel Andreasen,1, a) and Robin Santra2,3,5
1)Department of Energy Conversion and Storage, Technical University of Denmark, Anker Engelunds Vej, 2800 Kgs. Lyngby, Denmark
2)Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany
3)The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany
4)Department of Physics, Technical University of Denmark, Fysikvej, 2800 Kgs. Lyngby, Denmark
5)Department of Physics, Universität Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany

a)jewa@dtu.dk
Here we aim to estimate the accuracy of the calculated X-ray absorption spectroscopy (XAS) results at the CIS level of theory and considering different basis sets. For this purpose, in the first section (after analysis the effects of the basis sets on the excitation energies) we chose a small molecule, formaldehyde, not only because of the feasibility of doing higher-level calculations but also because of the availability of an experimental XAS spectrum. We compare the spectra based on the ionization energy estimated from Koopmans’ theorem (negative orbital energy) with the experimental ionization potential. As the next step, the positions of the lowest absorption resonances will be compared. In the second section, we calibrate calculated core absorption spectra based on comparison with experimental data. To this end and since there is no experimental XAS spectrum for the BT-1T molecule considered in the study, we chose molecules similar to it, as explained later.

The last section provides an analysis for a better understanding of the time-resolved spectra in the main text.

Contents

I. Basis set analysis

II. Calibration of XAS spectra
   A. Carbon K-edge
   B. Sulfur K-edge
   C. Nitrogen K-edge
   D. Sulfur L-edge

III. Conclusion

IV. Excited-state XAS spectrum

I. Basis set analysis

In this section, we first analysis the effect of the considered geometry on the CIS excitation energies. The values presented for the lowest-excited-state transition energies in Table I in the main text are overestimated relative to the experimental value. We therefore repeat the CIS calculation
using the 6-31+G(d)-optimized geometry. Figure S1 shows an improvement in the CIS transition energy relative to Table I in the main text. Such that the considered 6-31G basis set gives 3.77 eV, which is lower than 4.08 eV in Table I. Moreover, it shows a distance of ~0.06 eV in the transition energy from the results from the available largest basis set here. The remaining discrepancy in the transition energies (the lowest value of ~3.70 eV) compared to the experimental value can be related to the charge-transfer nature of this excitation, which is known to cause overestimated results from CIS method\textsuperscript{1}.

![Figure S1: Comparison of the CIS transition energies for the first excited-state calculated using different basis sets. The horizontal red line indicates the reference 6-31++G(d) results as the possible largest basis set, whereas the green line gives the reference for 6-31G as the border for the error.](image)

Further, the accuracy of the calculated XAS spectra of formaldehyde, CH\textsubscript{2}O (Fig. S2), at the CIS level of theory is estimated by comparing them with experimental data. Figure S3 compares calculated oscillator strengths for formaldehyde in the region of oxygen K-shell absorption thresholds from calculations employing three different basis sets. The experimental data are represented

![Figure S2: Molecular schematic of formaldehyde.](image)
by the vertical black lines. The CIS ionization edges of the calculations based on the 6-31G, 6-31+G, and 6-311++G(d,p) are located, respectively, at 21.07, 21.32, and 20.68 eV higher than the experimental value of 539.30 eV. Therefore, the calculated spectra are shifted by -21.07, -21.32, and -20.68 eV for the three calculations such that the ionization edges match the experimental value. The experimental photoionization spectrum of formaldehyde at the O K-edge has an intense resonance at 530.82 eV (8.48 eV below the edge) and some other weaker Rydberg states at higher energies. The CIS calculations, however, give the first resonance at $\sim$15 eV below the calculated edge. Thus, CIS tends to overestimate the distance between ionization edge and first resonance by $\sim$5-6 eV. Moreover, the position of the first resonance in the CIS calculations shows a rather low sensitivity to the basis set, indicating that a relatively modest basis set is sufficient to reveal a qualitatively correct spectrum in the range of the low-lying absorption resonances that we are considering in our study. Figure S3 also shows that a few eV below the ionization edge the Rydberg series arise, in which the results are highly sensitive to basis set as also reported by other theoretical studies. This energy region is out of the scope of the current study and the choice of basis set does not affect our reported results.

Apart from the offset, we conclude that the CIS results qualitatively reproduce the experimental spectra for the lower absorption energies if one considers that the ionization potential as well as the relative position of the lowest resonances are considerably shifted (here $\sim$21 eV and 5-6 eV, respectively).

II. Calibration of XAS spectra

In this section, we calibrate the core XAS spectra of the BT-1T molecule. Since there are no experimental L- and K-shell photoabsorption spectra of BT-1T, we calibrate our computational results with available experimental data for thiophene and 2-mercaptobenzothiazole.

A. Carbon K-edge

In section I of this electronic supporting information (ESI), we calibrated the XAS spectrum of formaldehyde by matching the experimental and theoretical ionization potentials. We found that after a shift of $\sim$21 eV towards lower energies, the CIS first absorption band is located 5-6 eV lower than the experimental one. Since in the current study we are concentrating only on the
FIG. S3: The normalized oscillator strengths of formaldehyde, CH$_2$O, in the region of the O K-shell absorption thresholds calculated at the CIS level of theory (shifted by $\sim$-21 eV). The vertical black lines represent the positions of the experimental absorption bands.

To calibrate the calculated XAS spectra based on the shift of the first resonance in the spectrum compared to the experimental data, we consider CIS/6-31G level of theory as a compromise between cost and accuracy. We then calibrate calculated C K-edge spectra of three different molecules based on available experimental data in a region of $\sim$5 eV including the first absorption band. As shown in Fig. S4(a), the experimental C 1s $\rightarrow$ $\pi^*$ resonance peak of formaldehyde$^2$ between 285 and 287 eV is reproduced in the calculated spectrum after -8.9 eV shift in transition energy. Moreover, both experimental$^4$ and calculated (shifted by -11 eV) C K-edge spectra of thiophene (Fig. S5) in gas phase are characterized by a sharp peak (A) which corresponds to two transitions followed by a weaker peak, B, as shown in Fig. S4(b). Table I represents the comparison between experimental and theoretical transition energies. Fig. S4(c) shows that the calculated C K-edge XAS spectrum of 2-mercaptobenzothiazole (shown schematically in Fig. S6) requires a shift of -10.3 eV to have almost the same transition energy for the first absorption band compared to the experimental spectrum$^5$. Transition energies of the observed resonances are listed in Table II. We therefore conclude that the features of the calculated XAS spectra are reproduced compared to experimental spectrum. However, the energy difference between the peaks is overestimated. Moreover, we observe that for larger molecules, the shifts in the spectra change slightly, from -11 eV for thiophene to -10.3 eV for 2-mercaptobenzothiazole.
Therefore, we consider a shift of -11 eV to calibrate the CIS C K-edge spectrum of BT-1T in the manuscript.

![Graphs showing XAS spectra of formaldehyde, thiophene, and 2-mercaptobenzothiazole](image)

(a) Formaldehyde  
(b) Thiophene  
(c) 2-Mercaptobenzothiazole

FIG. S4: Comparison of the pre-edge features of the experimental gas-phase carbon 1s XAS spectra of formaldehyde (a), thiophene (b), and 2-mercaptobenzothiazole (c) with the relevant calculated spectra at the CIS level of theory using the 6-31G basis set (this work). The arrows are guides to the eye for specific features.

B. Sulfur K-edge

Figure S7 compares the experimental XAS spectrum of thiophene\(^3\) with the calculated spectrum at the CIS level of theory using the 6-31G basis set (this work). Table S3 lists the energies for transitions observed in the experimental and theoretical spectra. In the range of low-energy
TABLE I: Transition energies (in eV) of the lowest absorption bands (below the core ionization threshold) in the carbon 1s XAS spectra of thiophene from experiment and theory.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experiment</th>
<th>CIS (shifted by -11 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>285.15</td>
<td>285.17</td>
</tr>
<tr>
<td></td>
<td>285.30</td>
<td>285.28</td>
</tr>
<tr>
<td>B</td>
<td>286.68</td>
<td>287.56</td>
</tr>
<tr>
<td></td>
<td>286.70</td>
<td>287.57</td>
</tr>
</tbody>
</table>

FIG. S6: Molecular schematic of 2-mercaptobenzothiazole (thione form).

transitions, CIS (shifted by -21.4 eV, energy difference between experimental 2473.1 and theoretical 2494.4 eV) approximately reproduces the experimental spectrum giving an intense peak (A) followed by a weaker feature (B) corresponding to two transitions at higher energies. This energy shift is considered to calibrate the CIS S K-edge XAS spectrum of BT-1T.

C. Nitrogen K-edge

2-Mercaptobenzothiazole has been chosen to calibrate the CIS N K-edge spectrum of BT-1T. Figure S8 presents the experimental and calculated XAS spectra of 2-mercaptobenzothiazole below the N K-edge ionization threshold (calculated value of 426.1 eV). The experimental spectrum
TABLE II: Transition energies (in eV) of the lowest absorption bands (below the core ionization threshold) in the carbon 1s XAS spectra of 2-mercaptobenzothiazole from experiment and theory.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experiment</th>
<th>CIS (shifted by -10.3 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>285.43</td>
<td>285.44</td>
</tr>
<tr>
<td></td>
<td>285.58</td>
<td>285.60</td>
</tr>
<tr>
<td></td>
<td>285.86</td>
<td>285.68</td>
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<tr>
<td>B</td>
<td>286.24</td>
<td>287.01</td>
</tr>
<tr>
<td>C</td>
<td>287.02</td>
<td>288.13</td>
</tr>
</tbody>
</table>

FIG. S7: Comparison of the pre-edge features of the experimental gas-phase sulfur 1s XAS spectrum of thiophene with the calculated spectrum.

shows two main peaks at 401.4 and 402.9 eV. The calculated spectrum preserves the first two peaks. Referring to Table S4, we consider a 16 eV shift towards lower energies to calibrate the CIS N K-edge XAS spectra of BT-1T in the main manuscript.

D. Sulfur L-edge

Apart from weak absorption bands in the low-energy region of the experimental sulfur L-edge spectrum of 2-mercaptobenzothiazole (in Fig. S9), four main resonances at 163.33, 164.59,
Table S3: Transition energies (in eV) of the lowest absorption bands (below the core ionization threshold) in the sulfur 1s XAS spectra of thiophene from experiment and theory (this work).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experiment</th>
<th>CIS (shifted by -21.4 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2473.1</td>
<td>2473.0</td>
</tr>
<tr>
<td>B</td>
<td>2474.6</td>
<td>2475.3</td>
</tr>
<tr>
<td></td>
<td>2475.2</td>
<td>2475.9</td>
</tr>
</tbody>
</table>

FIG. S8: Comparison of the pre-edge features of the experimental gas-phase nitrogen 1s XAS spectrum of 2-mercaptobenzothiazole with the calculated spectrum. The arrows are guides to the eye for specific features.

Table S4: Transition energies (in eV) of the lowest absorption bands (below the core ionization threshold) in the nitrogen 1s XAS spectra of 2-mercaptobenzothiazole from experiment and theory.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experiment</th>
<th>CIS (shifted by -16 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>401.4</td>
<td>401.2</td>
</tr>
<tr>
<td>B</td>
<td>402.9</td>
<td>403.1</td>
</tr>
</tbody>
</table>

165.31, and 166.35 eV are observed. Adjusting the first intense CIS absorption band by a shift of
-10 eV, a second theoretical peak is observed corresponding to resonances at 165.81, 165.93, and 166.43 eV as reported in Table S5. We therefore apply a -10 eV shift in the CIS S L-edge spectra of BT-1T.

![CIS (-10 eV) vs Exp.](image)

**FIG. S9:** Comparison of the pre-edge features of the experimental gas-phase sulfur $2p$ XAS spectrum of 2-mercaptobenzothiazole et al$^5$ with the calculated spectrum.

Table S5: Transition energies (in eV) of the lowest absorption bands (below the core ionization threshold) in the sulfur $L$-edge XAS spectra of 2-mercaptobenzothiazole from experiment and theory.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experiment</th>
<th>CIS (shifted by -10 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>163.33</td>
<td>163.40</td>
</tr>
<tr>
<td></td>
<td>164.59</td>
<td>165.81</td>
</tr>
<tr>
<td></td>
<td>165.31</td>
<td>165.93</td>
</tr>
<tr>
<td></td>
<td>166.35</td>
<td>166.43</td>
</tr>
</tbody>
</table>

**III. Conclusion**

From our comparison with experimental data in Section I of the ESI, we are confident that the relatively small basis set we have chosen is sufficient to study the first few absorption lines in
the X-ray absorption spectrum. Furthermore, the CIS method reproduces a qualitatively correct spectrum in this energy range, when the spectrum is corrected with an absolute shift. In Section II of the ESI, we found the relevant absolute shifts for different core absorption spectra by matching the first absorption bands with the corresponding experimental data.

IV. Excited-state XAS spectrum

In theory, an excited-state time-resolved XAS spectrum is calculated by probing excitations from a valence-excited state to a core-excited state. The determining factor in calculating the absorption spectrum is the transition dipole moments between CI eigenvectors, which are calculated for the initial and final states and are dependent on both CI eigenvector coefficients and transition dipole moments between molecular orbitals. In order to better investigate the approach, the CIS eigenvectors of the core-excited state (sulfur edge) of BT-1T are compared with the CIS eigenvector of the valence-excited state in Table S6. Table S7 presents the transition dipole moments between the corresponding molecular orbitals. In Tables S6 and S7 orbital numbers 56 and 57 are the HOMO and LUMO, and the core orbitals 1 and 2 are localized on the two sulfur atoms $S_{BT}$ and $S_T$, respectively. The transition $1 \rightarrow 59$ (LUMO+2) has the largest CIS coefficient and the largest value of transition dipole moment and, therefore, is supposed to have the largest oscillator strength as shown with the cyan vertical line shown in Fig. S10.
Table S6: CIS eigenvectors for the valence- and core-excited states (sulfur K-edge). Number of the excited state, its energy, corresponding transitions and coefficients are reported here. Core molecular orbitals 1 and 2 are localized on \(S_{BT}\) and \(S_T\), and orbitals number 56 and 57 are the HOMO and LUMO, respectively.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Nr.</th>
<th>E(eV)</th>
<th>Transition</th>
<th>Coef.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence-excited state</td>
<td>#1</td>
<td>4.34 eV</td>
<td>56→57</td>
<td>0.92</td>
</tr>
<tr>
<td>Core-excited state</td>
<td>#4861</td>
<td>2474.68</td>
<td>Core1→59</td>
<td>-0.89</td>
</tr>
<tr>
<td></td>
<td>#4862</td>
<td>2473.51</td>
<td>Core2→62</td>
<td>-0.83</td>
</tr>
<tr>
<td></td>
<td>#4863</td>
<td>2475.40</td>
<td>Core1→57</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>#4864</td>
<td>2475.51</td>
<td>Core1→63</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>#4865</td>
<td>2497.24</td>
<td>Core2→58</td>
<td>-0.74</td>
</tr>
<tr>
<td></td>
<td>#4866</td>
<td>2497.33</td>
<td>Core2→64</td>
<td>0.47</td>
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<tr>
<td></td>
<td>#4867</td>
<td>2497.33</td>
<td>Core2→67</td>
<td>-0.48</td>
</tr>
</tbody>
</table>

Table S7: Magnitude of selected transition dipole moment of 2 core MOs.

<table>
<thead>
<tr>
<th>Core 1</th>
<th>Core 2</th>
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</thead>
<tbody>
<tr>
<td>Transition Magnitude</td>
<td>Transition Magnitude</td>
</tr>
<tr>
<td>1→50</td>
<td>6.61×10^{-5}</td>
</tr>
<tr>
<td>1→51</td>
<td>3.50×10^{-3}</td>
</tr>
<tr>
<td>1→52</td>
<td>2.92×10^{-3}</td>
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<tr>
<td>1→53</td>
<td>3.37×10^{-3}</td>
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<tr>
<td>1→54</td>
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<tr>
<td>1→55</td>
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<td>1→56</td>
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<tr>
<td>1→57</td>
<td>3.21×10^{-3}</td>
</tr>
<tr>
<td>1→58</td>
<td>1.52×10^{-3}</td>
</tr>
</tbody>
</table>

Continued on next page
Table S7 – continued from previous page

<table>
<thead>
<tr>
<th>Transition</th>
<th>Magnitude</th>
<th>Transition</th>
<th>Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→59</td>
<td>5.48×10^{-3}</td>
<td>2→59</td>
<td>3.31×10^{-5}</td>
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<td>1→60</td>
<td>4.34×10^{-4}</td>
<td>2→60</td>
<td>1.65×10^{-4}</td>
</tr>
<tr>
<td>1→61</td>
<td>6.20×10^{-4}</td>
<td>2→61</td>
<td>1.84×10^{-3}</td>
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<tr>
<td>1→62</td>
<td>1.96×10^{-4}</td>
<td>2→62</td>
<td>4.06×10^{-3}</td>
</tr>
<tr>
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<td>2→63</td>
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<tr>
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<td>2→66</td>
<td>1.23×10^{-3}</td>
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<tr>
<td>1→67</td>
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<td>1→68</td>
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<td>2→68</td>
<td>1.15×10^{-3}</td>
</tr>
<tr>
<td>1→69</td>
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<td>2→69</td>
<td>1.21×10^{-3}</td>
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<td>1→70</td>
<td>7.49×10^{-4}</td>
<td>2→70</td>
<td>1.61×10^{-3}</td>
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</tbody>
</table>

Figure S10 shows the calculated static S K-edge XAS for the two electronic states at the GS geometry (shifted by -21.4 eV, as reported in Section II B of the ESI). The ES XAS is unsurprisingly red shifted from the GS spectrum and corresponds to excitations from the S 1s orbitals into the hole in the π orbital. Some of the fundamental factors that can change the ES spectrum, e.g. dynamical correlation, can not be captured by CIS (it would require at least CISD). Both the spectra show the first absorption band characterized by two core transitions (localized on the two sulfur atoms) followed by one peak that is a superposition of four transitions with close energies. The first absorption bands in the two spectra have different shapes because the two electronic states involved in the transition have different charge distributions on the two sulfur atoms. Figure S11 further compares GS and time-zero ES XAS averaged over the initial conditions used for the trajectories. The time-zero ES XAS spectrum appears at the same energy as the ES spectrum in Fig. S10 but with a rather symmetric shape due to the statistics from averaging over sampled initial conditions.
FIG. S10: Calculated ground- and excited-state S K-edge XAS of BT-1T in gas phase. The vertical colored lines are oscillator strengths corresponding to each sulfur inner-shell excitation.

FIG. S11: Comparison of the calculated ground-state and time-zero excited-state S K-edge XAS of BT-1T in gas phase (averaged over initial conditions).
Comparison between the static GS and ES C K-edge XAS of BT-1T is shown in Fig. S12. It shows that the core transitions associated with carbon atoms C_{10}, C_3, and C_5 have the main contribution in the first absorption band in the ES spectrum. This information is used in the main text to explain the behavior of the time-resolved spectra.

FIG. S12: Calculated ground- and excited-state C K-edge XAS of BT-1T in gas phase. The vertical colored lines are oscillator strengths corresponding to inner-shell transitions in specific carbon atoms.
References


[38] The xfel principle, Booklet. [http://photon-science.desy.de/sites/site_photonscience/content/e62/e189219/e187240/e208351/e187350/felbasics_eng.pdf](http://photon-science.desy.de/sites/site_photonscience/content/e62/e189219/e187240/e208351/e187350/felbasics_eng.pdf).


