High-precision theoretical spectroscopy of core-excited and core-ionized electronic states

Electrons in an atom or molecule can be divided into two categories: core and valence. Core electrons are located close to the atomic nucleus, in tightly bound inner shells, and do not participate in the formation of chemical bonds. In contrast, valence electrons are present in the outer shells and are responsible for the formation of chemical bonds and interactions between molecules.

When highly-energetic X-ray photons interact with a molecule, they can excite core electrons, removing them from the inner shells. This process forms the basis of various X-ray spectroscopy techniques, which enable the identification of elements, determination of their oxidation states, and the study of molecular structures. Thus, X-ray spectroscopy is not only an effective tool for investigating the fundamental properties of matter but also finds broad practical applications, such as in chemical analysis or medical diagnostics.

Advances in experimental techniques over the past several years, particularly the development of free-electron lasers, have allowed for the observation of highly detailed phenomena related to core electrons. For example, researchers have measured with great precision how the methyl iodide molecule CH_3I dissociates under intense X-ray radiation. Such studies pave the way for understanding the mechanisms leading to damage in biological materials caused by X-ray radiation. However, to fully harness the potential of such observations, advanced theoretical tools are essential.

The goal of this project is to develop new theoretical methods for the accurate prediction and interpretation of spectra resulting from core-electron excitation or ionization. This will provide a better understanding of what happens to atoms or molecules after one or more core electrons are removed. In particular, we aim to address the following questions:

- How do interactions between valence electrons affect the behavior of molecules after the removal of a core electron?
- How do molecular vibrations influence the shape of X-ray spectra?
- What is the best way to mathematically describe the motion of free electrons emitted after the prior excitation of a core electron?
- What factors determine the relative importance of different relaxation channels (such as molecular dissociation or Auger electron emission)?

Our modeling methods will rely solely on the fundamental principles of quantum mechanics. We plan to use advanced mathematical and computational techniques, such as the equation-of-motion coupled-cluster (EOM-CC) method. The EOM-CC method enables accurate modeling of the properties of molecules in excited states. We aim to extend this method so that it will be fully effective also for studying the properties of molecules after core-electron removal.

Additionally, we will develop optimal methods for describing the motion of electrons emitted during relaxation processes, such as Auger decay. To understand the influence of nuclear motion on Auger decay, we plan to apply modern machine learning techniques. This will allow us to simulate how the molecular vibrations affect spectra resulting from X-ray absorption.

The developed methods will be applied to study simple model molecules, such as water, carbon dioxide, or benzene. This will enable a better understanding of the cascade of molecular processes triggered by the absorption of high-energy radiation. We expect that our research will provide new insights into the behavior of molecules under extreme conditions and will significantly aid the interpretation of experimental results.