Development of a new tool for electronic resonances using multireference algebraic diagrammatic construction (MR-ADC) theory within non-Hermitian quantum mechanics

Electronic resonance states are metastable continuum states that atoms or molecules can occupy during interactions with external factors, such as electrons or photons. These states are pervasive in nature and play crucial roles across various physical, biological, and chemical phenomena. For instance, they contribute to radiation-induced damage in biological systems, including DNA and RNA degradation via electron interactions, and tissue damage during radiotherapy. Additionally, resonances facilitate molecular formation in interstellar space and drive chemical reactions in plasmas.

Describing electronic resonance states theoretically is particularly challenging, even for simple systems like atoms or small molecules. This difficulty arises from their metastable nature, embedded in the continuum, which leads to their eventual decay. Unlike bound states, resonances cannot be directly associated with discrete energy levels. Moreover, computational methods capable of predicting resonance properties with the same precision as bound states remain underdeveloped.

The primary objective of this research is to develop innovative computational techniques to model resonance states in strongly correlated systems. Specifically, the focus is on constructing tools for the efficient computation of complex potential energy surfaces (CPES)—multidimensional representations that describe how the energy and lifetime of resonance states vary with molecular geometry. Developing CPES for systems undergoing autoionization is particularly complex due to the presence of numerous nearly degenerate states. However, these surfaces are essential for accurately predicting chemical dynamics and measurable quantities, such as reaction rates and scattering cross-sections.

To address these challenges, the proposed approach integrates non-Hermitian quantum mechanics (NHQM) techniques with the multireference algebraic diagrammatic construction (MR-ADC) method. Unlike traditional Hermitian quantum mechanics, NHQM associates resonances with discrete states represented by complex-valued energies, where the imaginary component corresponds to the decay rate. Meanwhile, the MR-ADC method, a state-of-the-art tool in electronic structure theory, is highly effective for computing multiple excited states with diverse electronic configurations in strongly correlated systems.

While existing single-reference methods are suitable for modeling one-electron decay processes like shape resonances, they often struggle with two-electron decay mechanisms, such as Auger decay, Interatomic Coulombic Decay (ICD), and Feshbach resonances. These processes require advanced treatment of dynamic electron correlation and multielectronic configurations. The MR-ADC method is particularly adept at addressing these challenges. Additionally, MR-ADC offers direct access to the spectroscopic properties of excited states with computational costs significantly lower than those of other multireference methods.

In the second phase of the project, the developed theoretical tools will be applied to study one-electron decay processes, such as shape resonances, in various molecular systems through the calculation of complex potential energy surfaces. The subsequent focus will shift to two-electron decay mechanisms, including Auger decay and ICD.

The proposed tools are expected to provide several key advantages: (i) the ability to describe various classes of resonances, such as Auger, ICD, Feshbach resonances, or core-excited shape resonances; (ii) deeper insights into the spectroscopic properties of electronic resonances; (iii) a straightforward and universal computational protocol; (iv) relatively low computational costs compared to other multireference methods;

Ultimately, this research aims to overcome computational limitations and improve our understanding of electronic resonances in strongly correlated systems, with a versatile framework compatible with quantum-chemical software, enabling new applications in spectroscopy, quantum dynamics, and theoretical chemistry.