Abstract

It is said that for a civilization to thrive, three essential pillars must develop independently while also complementing each other: ethics or moral philosophy, science, and politics. If any of these pillars falters, the civilization may be deemed stagnant or at risk of collapse. In an analogous manner, science, containing physics, consists of the two foundational pillars of theory and experiment, shaping our comprehension of the world for centuries. Their ongoing interplay has been vital for explaining and predicting physical phenomena and properties of a plethora of materials.

In our technologically ever-growing and fast-paced era, computing has quickly evolved to become the *third pillar* of science, bridging the gap between theory and experiment. Although, the affordability in computational power and memory has increased unimaginably over the decades, certain computationally-based theories still fail to accurately describe or predict physical properties for some classes of materials. For instance, the state-of-the-art Density Functional Theory, for the last 60 years, provides a decent trade-off between accuracy and computational cost, but exhibits limitations when applied to specific systems owing to approximations in the existing exchange-correlation functionals. Hence, the development of wavefunction methods, such as coupled-cluster theory, that offer a systematically improvable treatment of correlation effects, is of paramount significance.

This work is divided into two major parts. In Chapter 3, we focus on CCSD and CCSD(T) methods applied to the Uniform Electron Gas in the thermodynamic limit. We blend existing analytical proofs with our own analytical and numerical findings to provide a clear understanding of the infrared divergences in zero-gap systems. This lays the theoretical foundation of our new method, CCSD(cT). When applied to metallic lithium, this method exhibits remarkable agreement with experimental estimates. It maintains the advantages of the widely used CCSD(T), such as being accurate for insu-

lating systems and computationally more efficient than including all triple excitations. In Chapter 4, we present a detailed analysis that emphasizes the convergence of correlation energies, along with associated quantities, with respect to the size of the employed basis set of coupled-cluster theories, such as CCSD, CCSD(T), and CCSD(cT). The truncation of these basis functions introduces a basis set incompleteness error (BSIE), altering the electronic wavefunction and pair correlation at short interelectronic distances. A comprehensive exploration of coupled-cluster theories in this context provides valuable corrections to the BSIE, not only saving substantial computational resources but also enhancing our understanding of short-range correlation effects.