

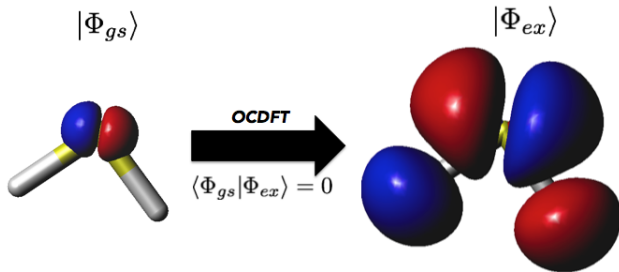
Calculation of X-Ray Absorption Near Edge Structure using Orthogonality Constrained Density Functional Theory

Wallace D. Derricotte, Francesco A. Evangelista

Department of Chemistry, Emory University, Atlanta, GA 30322, USA

Abstract

The advent of synchrotron light sources created a strong resurgence of spectroscopy in the X-ray region. Near-edge X-ray absorption spectroscopy (NEXAS) has proven itself to be a robust technique to probe molecular electronic structure. Theoretical computations are often necessary to glean relevant information from the spectra. Here we report an investigation into the accuracy of orthogonality constrained density functional theory (OCDFT) when applied to the calculation of X-ray absorption near-edge structure. The most dominant feature of this structure, the “edge”, is composed of the excitations of core-electrons from their tightly bound occupied orbitals to the unoccupied virtual space. In order for a method to properly replicate and analyze NEXAS spectra, it must demonstrate accuracy in describing core-electron excitations. OCDFT is assessed over a test set that includes 10 molecules with 43 unique core-electron excitations. The accuracy of the method is tested further by computing the near-edge spectra of Adenine.



1 Introduction

Near edge X-ray absorption spectroscopy (NEXAS) is a useful experimental technique to probe the local electronic and geometrical structure in a variety of scenarios. It has been useful in application to large biological systems [1], small gas phase molecules [2], organic thin-films [3], and semiconducting materials [4]. It’s effectiveness expanded thanks to the application of high-powered synchrotron radiation light sources that produce spectra of superb resolution, quality, and clarity. As these experiments were becoming more advanced, the theory wasn’t developing at the same pace, leaving a plethora of spectra that needed theoretical analysis. Calculations of these spectra are challenging, and require extensive computational methods that explicitly account for the excitations of core-level electrons and treats the subsequent electronic environment these unique excitations create. Several approaches have shown promise in this area including: scaled-opposite-spin CIS(D) [5], multiple scattering X_α methods [6], a maximum overlap Δ SCF approach [7], transition potential theory [8], and time-dependent density functional theory (TDDFT) [9]. DFT is a very attractive option amongst these different approaches because of its cheap computational cost and ability to calculate multiple excited states easily.

Within the density functional theory framework, TDDFT is a rigorous extension of the formalism and is regarded as the method of choice to treat electronic excited states due to it’s relatively cheap computational cost. The method is exact, and incredibly accurate when calculating low lying valence states. However when applied to higher energy core-excitations, conventional exchange-correlation functionals (B3LYP,BLYP,and PBE) decay far too rapidly and fail to accurately convey the asymptotic, $-\frac{1}{r}$ potential these high-energy states truly exhibit. In recent studies it has been shown that by imposing a constraint that prevents valence excitations and only considers electrons promoted from core orbitals, it is possible to avoid the variational collapse and reproduce the NEXAS spectra with sufficient qualitative accuracy. [9] This qualitative agreement

is useful, however, excitation energies computed with TDDFT in tandem with standard density functionals are grossly underestimated when compared to experiment. Any reasonable experimental agreement is only attained when using novel hybrid functionals [10], employing the core-valence partition function [11], or using uncontracted basis functions [12]. At this time, there are no computational methods in the DFT framework that have been proven to accurately treat core-excitations with standard density functionals and conventional contracted basis sets. A method that can produce accurate core-excitation energies with standard density functionals and basis functions is ideal, since these are among the most widely accessible and rigorously studied. [13]

Orthogonality constrained density functional theory (OCDFT) is a variational, time-independent formulation of DFT [14] that maintains the favorable accuracy/cost ratio that makes DFT attractive, without suffering from the same inability to accurately compute charge transfer excitation energies. Previous work in our research group proved OCDFT in conjunction with standard density functionals could accurately handle charge transfer phenomena in H_2 and $[\text{HeH}]^+$ molecules with comparable accuracy to a full configuration interaction (CI) calculation. This success in computing charge-transfer excitation energies, makes it a viable candidate to treat the promotion of electrons from tightly bound core orbitals to unbounded states. In its original formulation, OCDFT was unable to calculate multiple excited states [14], a feature that is routinely employed in standard TDDFT and CIS algorithms. Our goal here is to extend the formulation and allow for the calculation of multiple excited states, then apply OCDFT in tandem with the standard and popular Becke three-parameter Lee-Yang-Parr (B3LYP) functional to a diverse test set of core-excitations to assess its accuracy.

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