

Total photoabsorption cross sections with square integrable basis set

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Abstract: Photoionization cross-section and dynamic polarizabilities are important properties in areas such as optical refractivity and photoelectron spectra of free and adsorbed species. On the theoretical side, the main difficulty in determining the photoionization cross-section resides in the calculation of continuum wave functions. This can be done by explicit construction¹, which has the disadvantage, among others, of treating bound electrons at Hartree-Fock level. The other possibility is the discretization of the continuum. In the spirit of the second approach, Langhoff² proposed a procedure for constructing the photoionization cross-section from an approximate spectral representation of the dynamic polarizability by moment-theory techniques with L^2 basis functions. The technique is known as Stieltjes imaging. The complex dynamic polarizability contains both the absorptive and dispersive information about the system. Thus, the photoionization cross-section and the dynamic polarizability can be obtained simultaneously, once a representation is found for the complex polarizability. This can be achieved by using a discrete basis set L^2 to represent both the bound and the continuum states of the system.

Alternatively, the complex dynamic polarizability can be constructed by analytic continuation of the approximated representation^{3,4}, by using Padé approximants or continued fractions⁵. Pseudo-spectra, which are used as input for an approximated form of the complex dynamic polarizability can be obtained by a variety of methods of electronic structure. Recently, our group has shown the suitability of using linear response coupled cluster approximation (LR-CC)⁶ based on the Lanczos diagonalization to obtain pseudo-spectra used in analytic continuation. Lanczos algorithm is able to converge a large number of pseudo-states while diagonalization by Davidson algorithm is efficient only for a few low-lying states. In the present work, we try another possibility, i.e., to use time-dependent density functional theory (TDDFT) to generate pseudo-spectra and, consequently, total photoabsorption cross sections in both valence and inner-shell regions.

In Figure 1, we present our recent results obtained with TDDFT for the furan molecule. On the top panel we have the total photoabsorption cross section and on the bottom one we show the oxygen K-shell cross section. As one can observe from the results presented in Figure 1, there is a good agreement among calculated and experimental cross-section. In the symposium we will show that, in general, results obtained from TDDFT are not as accurate as LR-CC, as could be expected, but they are accurate enough to describe the general trends of the photoabsorption spectra. This has encouraged us to extend the method to larger molecules. (CNPq, FAPERJ, CAPES)

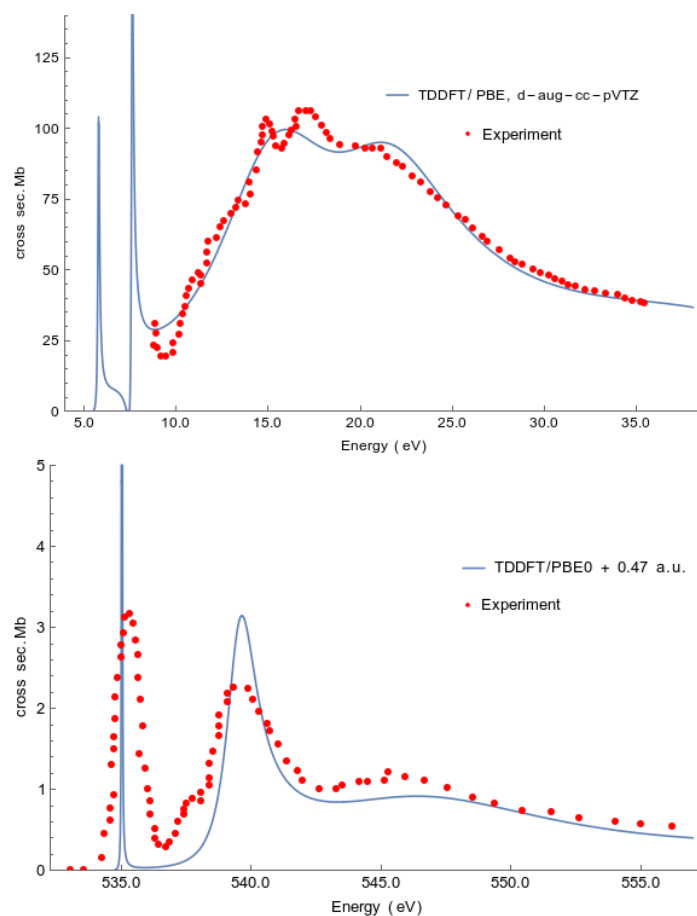


Figure 1: (Top) Furan total photoabsorption cross section obtained with TDDFT where PBE functional has been employed. Experimental values [7]. (Bottom) Oxygen K-shell photoabsorption cross section obtained with TDDFT where PBE0 functional has been used. Experimental values [8].

Key-words: Time-dependent density functional theory, cross-sections, photoabsorption, coupled cluster

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