Calculation of Photoionization Cross-Section Using Square Integrable Basis Sets for Atoms and Molecules

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INTRODUCTION

Photoionization cross-section and dynamic polarizabilities are very important to understand a large number of phenomena, such as optical refractivity and for interpreting the photoelectron spectra of free and adsorbed species. The main difficulty in determining the photoionization cross-section resides in the calculation of continuum wave functions. Langhoff[1] proposed a procedure for constructing the photoionization cross-section from an approximate spectral representation of the dynamic polarizability using L^2 basis functions. The complex dynamic polarizability contains both the absorptive and dispersive information about the system. Thus, photoionization cross-section and 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. This discrete representation of the continuum is used to construct an approximation to the complex dynamic polarizability, $\alpha(z) = \sum_{n\neq 0} \frac{f_{on}}{w_{on}^2 - z^2}$ (eq.1) which is used in an analytical continuation using Padé approximants[2].

METHODS

Ab initio wave functions of Li and Na were constructed at CASCCF/MRCI level with the basis set cc-pv5z augmented with diffuse primitives according to Kauffman procedure[3] in order to correctly represent the region of the continuum. In both systems, transitions of the type $^1P \leftarrow {}^1S$ were studied. The spectra of the discrete distribution of oscillator strengths and transition energies are used to construct an approximation to (eq.1) from which the photoionization cross-section is obtained.

RESULTS AND DISCUSSION

One way of verifying if the discrete distribution of oscillator strengths, obtained with L^2 basis set, furnishes a good representation for $\alpha(z)$ (eq.1) is to determine whether it is able to reproduce the sum rules[2] and our results have revealed to be very accurate in this respect. Figure 1 shows our results for the photoionization cross-section of Li compared to the experimental curve[4].

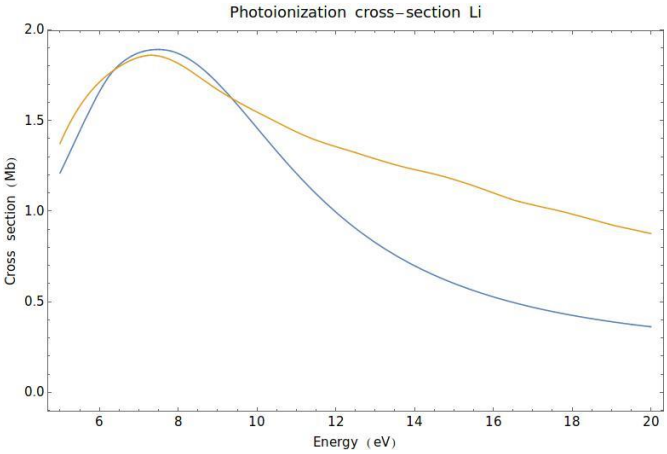

Figure 1. Photoionization cross-section of Li. In blue: our results. In yellow: experimental curve[4].

CONCLUSIONS

The results obtained with the present method show a reasonable agreement with experiments from the onset up to 10 ev. The less pronounced decay of the experimental curve can be attributed to the presence of vapor of Li_2 in the experiment. Our method uses L^2 basis set and correlated wave function what makes it potentially applicable for molecules.

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