Uncertainty quantification in calculations of molecular processes.

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Models of fusion plasma and other important natural and technological processes are becoming increasingly relient on calculated data. Uncertainty quantification (UQ) for processes containing molecules remain unusual; however there are recent recommendations on how to approach this problem [1]. First principles quantum mechanical calculations on molecular structure and collision processes have a number of important characteristics. Firstly the equations of these problems are well known and effectively exact, so the problem is fully and precisely specified. Secondly most solution techniques are relatively free from issues with numerical uncertainties. This means that the uncertainties are dominated by systematic errors associated with the model chosen to represent the problem. Understanding and quantifying these systematic errors can provide important insights and improved UQ for key problems.

The process of UQ in molecular systems will be illustrated by considering the question of how much radiation does one molecule of CO_2 absorb. Recent high-accuracy ab initio calculations of transitions intensities for CO_2 give excellent (< 0.5%) agreement with a few lines measured to high accuracy [2]. However comprehensive lists of transitions generated for atmospheric monitoring [3] give significant (1%) differences with laboratory measurements of spectra performed for the same purpose and other systematic differences as a function of CO_2 rotational state. The talk will describe how detailed interaction between theory and experiment has allowed these studies to be reconciled yielding a consistent, high quality list of transitions which are currently being considered for use by the OCO-2 mission for use their spectral retrievals. The prospects for systematic UQ for molecular processes will be discussed.

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