

## Core-valence stockholder AIM analysis and its connection to non-adiabatic effects in small molecules [1]

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Non-adiabatic corrections to the rovibrational energy levels of light molecules are essential if we wish to make calculations that account to high resolution spectroscopy [2]. They should be added to the energies obtained from potential energy surfaces generated by highly accurate Born-Oppenheimer calculations, after adding Born-Oppenheimer diagonal corrections and relativistic corrections.

The non-adiabatic corrections are hardly obtained from exact calculations. Instead, they are evaluated as the difference between the energies obtained with the nuclear masses and with effective masses in the nuclear equation. We propose here a model to obtain the **R**-dependent percentage of electrons that moves with the atomic nuclei during molecular vibration. For this, we invoke a previous theory of separation of motions of core and valence fractions of electrons in a molecule [3] and the concept of Atoms-in-Molecules (AIM) in the stockholder scheme [4]. We develop one-electron effective potentials which allow the identification of the parts of the AIM which move along with the nuclei. These electrons are called core electrons. In the nuclear equation, the reduced mass of the nuclei is then replaced by a mass that corresponds to the nucleus mass plus the core electron mass. With this recipe, we calculate the most accurate non-adiabatic corrections to vibrational energy levels so far for the apolar (H2<sup>+</sup>, H2) and polar (HeH<sup>+</sup>, LiH) molecules. This achievement can resume the discussion of the AIM being observable or not.

Key-words: Non-adiabatic corrections, AIM, molecular spectroscopy

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