On the choice of modals basis set to describe vibrational wave functions

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The Vibrational Mean Field Configuration Interaction (VMFCI) method, developed by Cassam–Chenaï and Liévin [1], proved extremely powerful and flexible to solve the molecular, vibrational, stationary Schrödinger equation [2,3]. It consists in performing vibrational configuration interaction of some contracted degrees of freedom (as in traditional contraction method) in the mean field of the others. The method is implemented in the computer code CONVIV [4] (CON traction VI brations V ariationally).

Before each calculation, one have to choose a “modal” (in analogy with “orbital”) basis set for each mode (including degenerate ones). This choice, irrelevant in the case of complete basis set, is often crucial in the case of finite basis set. The Code CONVIV offers to users a large choice of basis sets : Chebychev orthogonal polynomials, eigenfunctions of one dimensional Schrödinger equation for different potentials : Morse potential, trigonometric Pösch–Teller potential, Kratzer potential, Harmonic potential (possibly shifted). Besides the type of the basis set, one has to determine the parameters defining the potential.

In this poster, we'll give different criteria to optimize the choice of modals for bound or unbound approximate potentials of polyatomic molecules. In particular, we'll show that it exists an optimal number, Nbf, of basis funtions to converge a given number, Nvp, of bound states of an unbound potential, Nbf depending on Nvp [5]. For bounded potentials, a new criteria based on the maximum overlap with the eigenfunctions of 1-D sections of the potential, improves the assignement of vibrational egeinfunctions.

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