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▶ **To cite this version:**

Romain Garnier, Vincent Le Bris, Marc Odunlami, Didier Bégué, Isabelle Baraille, et al.. Efficient basis selection for the computation of vibrational spectrum. 10th European Conference on Computational Chemistry, Aug 2015, Fulda, Germany. hal-01200748

HAL Id: hal-01200748
https://hal.archives-ouvertes.fr/hal-01200748

Submitted on 17 Sep 2015

Efficient basis selection for the computation of vibrational spectrum

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We propose here an efficient method to define an approximation subspace to compute the first vibrational frequencies of the molecular Hamiltonian which are those of interest in the experimental results. In the Born approximation the Hamiltonian can be written as the sum of the kinetic energy and the potential energy function in normal coordinates [1] reflecting the relative movements of atoms within the molecule. When we keep the kinetic energy and the terms of order 2 of the potential energy, it brings up what is commonly called the Harmonic part of the Hamiltonian.

The eigen-states of this part are completely described by the multivariable Hermite functions that are the traditional solutions of the quantum harmonic oscillator [2]. These are a relevant choice to provide a basis for the calculation of the eigen-states of the Hamiltonian by the variational method. However the curse of dimensionality appears when processing of large molecules. For example, for a molecule to 8 atoms we have 18 normal coordinates and if we vary the degree of the basis functions from 0 to 6 in each direction the total number of basis functions is 7^{18}. Select a minimal basis to solve the eigen system is an important issue. Many current means such that the variation-perturbation theory [2] can target a relevant subspace for calculating a given number of vibrational frequencies of the Hamiltonian, but generally results are not as good as those we obtain with classical full Vibrational Configuration Interaction method [3]. Based on the same approach, we propose a new method to obtain comparable results to the full VCI method [3] with a much smaller number of basis vectors. For example we were able to divide by two the number of basis vectors needed to calculate the first 40 vibrational frequencies of the molecule H_2CO. Results on larger molecules that have unstable behavior will be presented.

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