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Optimisation of the variational method for vibrational Hamiltonian eigenvalues computation

Romain Garnier *

abstract

We propose here an efficient method to define a representative approximation subspace to compute the first eigenvalues of the vibrational Hamiltonian which are those of interest in the experimental results. In the Born Oppenheimer approximation, calling by $\mathbf{x} = (x_1, \dots, x_N)$ the dimensionless normal coordinates [4], ω_i the angular frequency associated with the coordinate x_i and \hbar the reduced Planck constant, the vibrational Hamiltonian \mathcal{H} writes as a sum of the nuclear kinetic and potential energies:

$$\begin{aligned} \mathcal{H}(\mathbf{x}) &= \mathcal{H}_0 + \mathcal{V} \\ &= \sum_{i=1}^N \frac{\hbar\omega_i}{2} \left(-\frac{\partial^2}{\partial x_i^2} + x_i^2 \right) + \sum_{S_V \geq \|\mathbf{s}\|_1 \geq 3} K_{\mathbf{s}} \prod_{i=1}^N x_i^{s_i}, \quad \mathbf{s} = (s_1, \dots, s_N). \end{aligned} \quad (1)$$

In (1) each monomial have a total degree $\|\mathbf{s}\|_1 \leq S_V$. The polynomial approximation of the potential energy is constituted by \mathcal{V} and the second order monomials included in \mathcal{H}_0 .

The eigenfunctions of \mathcal{H}_0 are pseudo-periodic signals vibrating at multiple level of fundamentals Harmonic frequencies. They write as

$$\phi_{\mathbf{n}}^0(\mathbf{x}) = \prod_{i=1}^N \psi_{n_i}(x_i), \quad \text{for all } \mathbf{n} = (n_1, \dots, n_N), \psi_{n_i}(x_i) \text{ Hermite function of degree } n_i. \quad (2)$$

And the harmonic corresponding eigenvalues of \mathcal{H}_0 are

$$E_{\mathbf{n}}^0 = \sum_{i=1}^N \left(n_i + \frac{1}{2} \right) \omega_i \hbar. \quad (3)$$

Variational method in quantum mechanic is used to design a method that uses an adapted set of trial wave functions defining a subspace where the eigen-pairs of \mathcal{H} are computed.

The eigenfunctions of \mathcal{H}_0 (2) constitute a well-suited approximation space. Indeed, when looking at the form of the operator \mathcal{H} (1) we see that \mathcal{H}_0 already contains Kinetic energy and the quadratic terms of the potential energy faithfully representing its behaviour in a localized area around equilibrium. In other words, \mathcal{H}_0 is the zero order approximation of \mathcal{H} .

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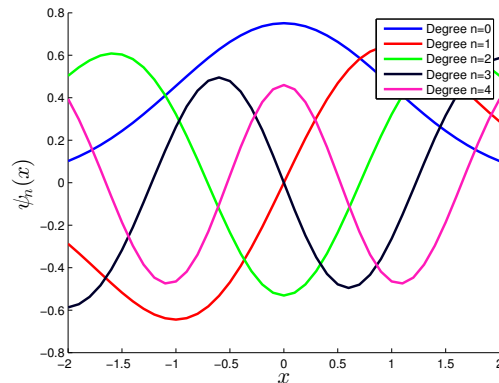


Figure 1: First hermite functions from degree 0 to 4

In order to deal with the curse of dimensionality that rapidly Happens because of the product space structure of the approximation space, we propose a basis selection technique based on perturbational theory [3].

This technique is in the context of vibrational configuration interaction with perturbation selected interactions [2, 1].

Calling by $\|\mathcal{V}\|_2$ the spectral norm of the operator \mathcal{V} , the first eigenvalues of \mathcal{H} are considered perturbation of the first harmonic eigenvalues because

$$\|\mathcal{V}\|_2 = \epsilon * \|\mathcal{H}_0\|_2, \quad \epsilon < 1. \quad (4)$$

Actually, the value of ϵ depends on the distance with the ground state and then constitute relevant information for the selection of the minimal required sub basis for the computation of the eigen-pairs of \mathcal{H} .

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