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# Optimisation of the variational method for vibrational Hamiltonian eigenvalues computation

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## 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],  $\omega_i$  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

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

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.

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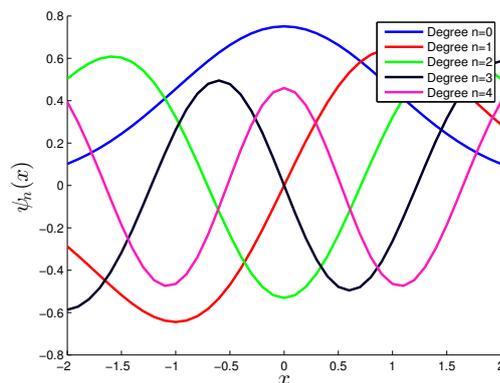


Figure 1: First hermite functions from degree 0 to 4

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  $\mathcal{H}$ .

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  $\epsilon$  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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