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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 \( x = (x_1, \ldots, x_N) \) 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 \( H \) writes as a sum of the nuclear kinetic and potential energies:

\[
H(x) = H_0 + V = \sum_{i=1}^{N} \frac{\hbar \omega_i}{2} \left( -\frac{\partial^2}{\partial x_i^2} + x_i^2 \right) + \sum_{S \geq \|s\|_1 \geq 3} K_s \prod_{i=1}^{N} x_i^{s_i}, \ s = (s_1, \ldots, s_N). \tag{1}
\]

In (1) each monomial have a total degree \( \|s\|_1 \leq S_V \). The polynomial approximation of the potential energy is constituted by \( V \) and the second order monomials included in \( H_0 \).

The eigenfunctions of \( H_0 \) are pseudo-periodic signals vibrating at multiple level of fundamentals Harmonic frequencies. They write as

\[
\phi^0_n(x) = \prod_{i=1}^{N} \psi_{n_i}(x_i), \text{ for all } n = (n_1, \ldots, n_N), \psi_{n_i}(x_i) \text{ Hermite function of degree } n_i. \tag{2}
\]

And the harmonic corresponding eigenvalues of \( H_0 \) are

\[
E^0_n = \sum_{i=1}^{N} (n_i + \frac{1}{2}) \omega_i \hbar. \tag{3}
\]

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 \( H \) are computed.

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Figure 1: First hermite functions from degree 0 to 4

The eigenfunctions of $\mathcal{H}_0$ constitute a well-suited approximation space. Indeed, when looking at the form of the operator $\mathcal{H}$, 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 perturbation 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

$$\|\mathcal{V}\|_2 = \epsilon \times \|\mathcal{H}_0\|_2, \ \epsilon < 1.$$  \hspace{1cm} (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 $\mathcal{H}$.

References


