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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:

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

\[
\phi_0^n(x) = \prod_{i=1}^{N} \psi_{n_i}(x_i), \text{ for all } n = (n_1, \ldots, n_N), \psi_{n_i}(x_i) \text{ Hermite function of degree } n_i. \] (2)

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

\[
E_0^n = \sum_{i=1}^{N} (n_i + \frac{1}{2}) \omega_i \hbar.
\] (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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The eigenfunctions of $H_0$ constitute a well-suited approximation space. Indeed, when looking at the form of the operator $H$, we see that $H_0$ 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, $H_0$ is the zero order approximation of $H$.

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.

This technique is in the context of vibrational configuration interaction with perturbation selected interactions.

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

$$\|V\|_2 = \epsilon \cdot \|H_0\|_2, \quad \epsilon < 1.$$  \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 $H$.

References


