

A Neural Network Based Method for Calculation of Vibrational Spectra

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We address the problem of computing a vibrational spectrum using a small number of basis functions in the expansion of the wavefunction and a small number of samples of the potential energy surface (PES). While it is possible today to solve for hundreds of ν -levels of a 5-6 atomic molecule (in vacuum) with high accuracy, the task is formidable due to the size of the Hamiltonian matrix. The most difficult calculations to date implicate matrices with as many as hundreds of millions of rows. This also requires the knowledge of the PES at millions of locations, so a PES function is necessary, the construction of which is also problematic.

In many applications, however, only several ν -levels are desired, and the accuracy $< 0.1 \text{ cm}^{-1}$ is not required. For example, in applications ranging from heterogeneous catalysis to selective uptake of molecules by nanotubes, it is important to identify species and adsorbate complex geometries. This can be done using IR spectra, as they are very sensitive to geometry and can be used to identify species and understand structure when it cannot be assigned based on energy alone. Spectra can serve as proxy to catalytic activity. Spectra can also be used for nanotube quality assessment (Figure 1). A complex with an adsorbed molecule has a much higher dimensionality than the molecule in vacuum, which is why today, only normal mode, harmonic analysis of frequencies is practical. However, the PES of adsorbate-containing systems deviates strongly from a (uncoupled) harmonic well. A method is desired to compute spectral signatures of molecule-surface/particle complexes taking into account the real shape of the PES.

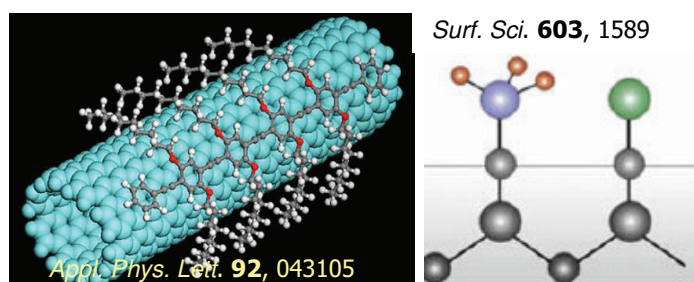


Figure 1. Adsorbate complexes are one example where computing IR frequencies is important for species identification. However, only DFT's harmonic analysis is practical today.

We present a method that calculates several vibrational levels from a very small, flexible basis of neurons of a neural network (NN). It simplifies the solution of the Schrödinger equation in many dimensions, where basis size explosion (due mainly to the use of direct product bases) is the principal impediment to studying larger molecular and reactive systems. The wavefunction is represented in the form of a radial-basis NN

$$\psi_k(\mathbf{y}) = \sum_{i=1}^N \sum_{s=1}^{\zeta} c_{isk} \left(\frac{b_{isk}}{\sqrt{\pi}} \right)^d \exp \left(-b_{isk}^2 \sum_{j=1}^d (w_{ij} - y_j)^2 \right) \quad (1)$$

It is an expansion over N parameterized (flexible) basis functions each consisting of ζ Gaussian terms with the same center but different and adjustable widths. This allows a wide range of shapes of the basis functions with few additional parameters, see Figure 2.

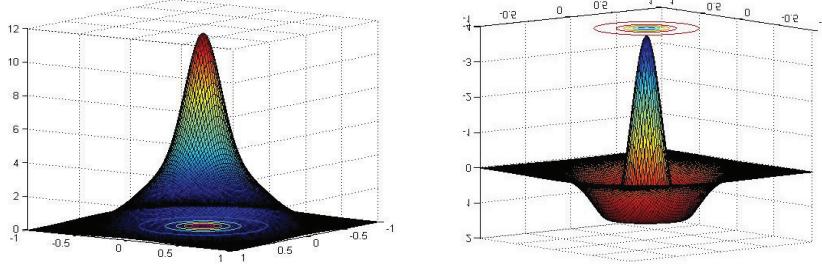


Figure 2. Various shapes of the basis functions are possible with multi- ζ Gaussian basis.

Expansion (1) automatically satisfies boundary conditions. In contrast to previous attempts at NN-eigensolvers, our approach combines non-linear optimization of parameters of the basis of neurons (blue in Eq. (1)) with a method to solve a rectangular matrix problem for linear parameters (red in Eq. (1)), which improves dimensionality scaling and allows for the output of many levels at the same time. Requiring that Eq. (1) satisfy the Schrödinger equation at a set of M points in the configuration space leads to a rectangular matrix problem

$$(\mathbf{M}_{M \times \zeta N} - E_k \mathbf{S}_{M \times \zeta N}) \mathbf{c}_k = 0 \quad (2)$$

where \mathbf{S} is the overlap matrix and \mathbf{M} depends on the Hamiltonian (problem-dependent). Eq. (2) is solved for the linear parameters \mathbf{c} while the non-linear basis parameters \mathbf{b} and \mathbf{w} are fitted.

The algorithm [*Can. J. Chem.* **87**, 864 (2009), *Chem. Phys. Lett.*, **474**, 217 (2009)] avoids the calculation of integrals and of the potential energy function. We demonstrate its application to a model problem in up to 6 dimensions and to the spectrum of water. Only a few dozens of neurons are needed to compute five levels of water from a small set of samples of the potential surface (Figure 3).

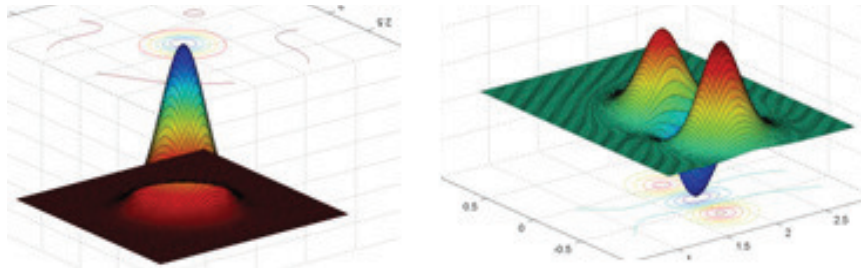


Figure 3. Example: 2D cuts of the third vibrational level of H_2O . In this calculation, 5 v -levels were obtained from only 15 flexible ($\zeta=3$) basis functions and 3000 samples of the potential surface.