

Development of anharmonic vibrational structure theory using backflow transformation

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The anharmonic vibrational structure analysis using the first principles calculations has been widely used in molecular spectroscopy to assign peaks/bands in infrared (IR) spectra and to determine molecular geometries. In anharmonic vibrational structure theory, an accurate trial wavefunction is indispensable to describe the molecular vibrational nature. Especially, it is important for generating accurate trial wavefunction to include many-body effect in the vibrational wavefunction.

In this study, we developed new vibrational coordinates using backflow transformation (BF),¹⁾ which is one of the theoretical approaches to take a correlation effect in quantum many-body systems into account, in order to improve the vibrational trial wavefunction. In the BF approach, vibrational normal coordinates $\{Q_m\}$ for each vibrational mode is transformed into a collective coordinate as,

$$Q_m \rightarrow Q_m + \zeta_m(Q_1, Q_2, \dots, Q_{N_v}), \quad \zeta_m = \sum_{n \neq m}^{N_v} \left(\sum_{\alpha=1}^{N_{\text{ex}}} \sum_{\beta=1}^{N_{\text{ex}}} c_{\alpha\beta}^{(mn)} Q_m^\alpha Q_n^\beta \right),$$

where a multivariable function ζ_m is a *backflow displacement*, which determines the transformation into collective coordinates, N_v the number of vibrational modes, N_{ex} the expansion order of the polynomial, and $c_{\alpha\beta}$ the expansion coefficient. The variational Monte Carlo method,²⁾ which is one of the most accurate methods to solve a vibrational Schrödinger equation, was used to analyze the molecular properties of each state. The backflow transformation was applied to vibrational self-consistent field (VSCF) wavefunction. In this study, the theoretical accuracy of BF in quantum vibrational problems has been tested for fundamental tones, overtones, and combination tones of H₂O molecule.

As a result, BF worked very well for improvement of frequencies. The mean absolute percentage error (MAPE) from the corresponding experimental values by BF was 0.8 %, which is around half of the MAPE by VSCF (1.3 %) and reasonably agree with the MAPE by the vibrational configuration interaction (VCI) wavefunction (0.6 %). The vibrational probability density to which the BF transformation was applied is also consistent with the VCI results and showed that the BF transformation appropriately take into account the correlation effects in quantum many-body systems.

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