Combining quantum mechanics and machine-learning calculations for anharmonic corrections to vibrational frequencies

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Several methods are available to compute the anharmonicity in semi-rigid molecules. However, such methods are not routinely employed yet because of their large computational cost, especially for large molecules. The potential energy surface is required and generally approximated by a quartic force field potential based on \textit{ab initio} calculation, thus limiting this approach to medium-sized molecules. We developed a new, fast and accurate hybrid Quantum Mechanics/Machine Learning (QM/ML) approach to reduce the computational time for large systems. With this novel approach, we evaluated anharmonic frequencies of 37 molecules thus covering a broad range of vibrational modes and chemical environments. The obtained fundamental frequencies reproduce results obtained using B2PLYP/def2tzvpp with a root-mean-square deviation (RMSD) of 21 cm$^{-1}$ and experimental results with a RMSD of 23 cm$^{-1}$. Along with this very good accuracy, the computational time with our hybrid QM/ML approach scales linearly with $N$ while the traditional full \textit{ab initio} method scales as $N^2$, where $N$ is the number of atoms.

I. INTRODUCTION

Recent advances in vibrational spectroscopy originate from progress at both experimental and theoretical levels. On the one hand, the development of ultrafast lasers has allowed for probing molecular dynamics on extremely short time scales[1, 2]. On the other hand, computational spectroscopy has benefited from novel quantum mechanics calculations whose accuracy is comparable to experimental measurements[3–8]. In this research field, the combining role of experiments and simulations is two-fold: Experiments help to assess the accuracy of the numerical calculations, which in turn, enable for disentangling the complexity of the experimental measurements[9][13]. To obtain additional progress in computational spectroscopy, the current challenge is to carry out calculations for large molecules while maintaining the accuracy obtained for the smaller ones[14][19]. Such glass ceiling proves to be even more difficult to break when it comes to computing the anharmonic corrections to vibrational frequencies[14][19].

Indeed, anharmonicity of the electronic potential is often neglected and taken into account a posteriori using corrective factors that are empirically determined to match experimental measurements. More rigorously, explicit modeling of anharmonicity is also carried out using several methods including VSCF[22], VSCF-PT[23][25], VT2[26], GVPT2[27][31]. Because of the required high-level of \textit{ab initio} calculations, the current calculations are computationally demanding which hinders studying molecules of more than tens of atoms.

Alternatively, instead of such a full \textit{ab initio} calculation, several studies have been suggested. For solvated molecules, the computing time can be reduced using a hybrid QM/MM potential[18]. Other methods limit the maximum number of modes to be coupled to 2[19], but the most used approach is a hybrid one where the geometric structure optimization and harmonic calculations are computed at a high level of theory as the DFT theory and anharmonic corrections are obtained with semi-empirical methods[17].

More recently, we proposed to use molecular mechanic (MM) potential and in particular, the MMFF94[32] method which represents an even lower level of theory[16]. The success of such a hybrid approach is two-fold. On the one hand, the accuracy is comparable to full \textit{ab initio} calculations, and on the other hand, it allows for a considerable reduction of computational costs. However, MMFF94 method can only be employed for organic molecules and an alternative approach must be derived.

Machine-learning methods have been recently employed to bridge the gap between molecular mechanic potentials and \textit{ab initio} calculations by providing a framework to reach the accuracy of the latter while maintaining a low computational cost[33][55]. Four classes of methods are usually considered: (1) Gaussian approximation potentials[30][37], (2) Kernel Ridge Regression[38][40], (3) Sparse Linear Regression[41][44] and (4) Artifi-
cional Neural Network (ANN)\textsuperscript{[15, 17]. Recent comparisons between these different methods have also been carried out\textsuperscript{[18–19].}

In this context, we propose the use of machine-learning techniques and in particular ANN potential. This way, our novel approach overcomes the limitations of the previous one and is now versatile enough to compute anharmonic corrections to vibrational frequencies in organic, as well as inorganic molecules. In this article, we will first describe the methodology with particular details on the choices that were made for the ANN parameters and the benchmarking molecules. Then, we will compare the obtained results with experiments and also more advanced \textit{ab initio} calculations.

II. METHODS

A. The hybrid Quantum mechanics/Machine learning approach

Anharmonic corrections to vibrational frequencies are computed within the explicit framework of the generalized second-order vibrational perturbation theory (GVPT2)\textsuperscript{[28–29]. We will only briefly outline key features of the approach before describing more thoroughly the choices that were made for our own implementation. For a given molecule of \( N \) atoms, the potential energy surface is a function of the normal coordinates denoted \( \mathbf{Q} \). There are \( f \) normal coordinates with \( f = 3N - 6 \) for a non-linear molecule and \( f = 3N - 5 \) otherwise. Within GVPT2, the potential energy surface (PES) is approximated by a quartic force field using:

\[
V(\mathbf{Q}) = V_0 + V_1(\mathbf{Q}) + V_2(\mathbf{Q}) + V_3(\mathbf{Q})
\]

\[
V_1(\mathbf{Q}) = \sum_{i=1}^{f} \frac{1}{2} h_i Q_i^2 + \frac{1}{6} \sum_{i \neq j} u_{ij} Q_i Q_j
\]

\[
V_2(\mathbf{Q}) = \sum_{i,j,k \neq k} \frac{1}{2} t_{ij,k} Q_i Q_j Q_k + \frac{1}{6} \sum_{i,j,k \neq k} u_{ij,k} Q_i^2 Q_j^2 + \sum_{i,j,k \neq k} \frac{1}{4} u_{ij,k} Q_i^2 Q_j Q_k
\]

\[
V_3(\mathbf{Q}) = \sum_{i,j,k \neq k} t_{ijk} Q_i Q_j Q_k + \sum_{i,j,k \neq k} \frac{1}{2} u_{ijk} Q_i^2 Q_j Q_k
\]

where \( V_0, h_i, t_{ij,k} \) and \( u_{ij,k} \) denote respectively the energy and its second-, third-, and fourth-order derivatives with respect to the normal coordinates at the equilibrium geometry, calculated through numerical differentiations of the energy (see Yagi et al.\textsuperscript{[50]). From there, computing vibrational frequencies requires calculating those derivatives. In our implementation, the second derivatives are obtained directly using harmonic frequencies from high-level DFT calculations. Then, the third and the fourth derivatives are computed using a fitted potential based on a feed-forward neural network. As such, the energy for each atom depends on symmetry functions which measure the local environment. The relationship between these symmetry functions and the atomic energy is described by a neural network which consists of ten neurons and two hidden layers. In particular, the employed descriptors are the radial and the narrow angular symmetry functions put forward by Belher\textsuperscript{[51]} and the three activation functions are two hyperbolic tangents and a logistic function. The parameters for the symmetry functions are given in Table S1 and S2 in supporting information. The parameterization of the neural network components is carried out using the Kalman Filter optimization method\textsuperscript{[52]} on energy and forces obtained with training geometries. The n2p2 Neural Potential Package\textsuperscript{[53]} was used to build the ANN potential\textsuperscript{[52, 54].}

We performed two types of quantum mechanics calculations: (1) geometry optimization to obtain equilibrium positions of the atoms and the harmonic frequencies which is also necessary with any full \textit{ab initio} approach and (2) additional single-point calculations around the equilibrium positions to train the neural network potential. In particular, we take in consideration random displacements of each atom from the equilibrium position in the three Cartesian directions by \( \pm 0.01, \pm 0.05, \pm 0.2 \) and \( \pm 0.3 \)Å which leads to \( 3N \times 8 \) geometries per molecule. With such displacements, we make sure that atoms are sufficiently displaced to sample the anharmonicity of the PES. We used 95\% of the data sets for the training of the neural network and 5\% for the testing, and the root mean squared error is less than 0.5 meV for energy and 30 meV/Å for forces. Altogether, the quantum-mechanics calculations are carried out with the B2PLYP/def2tzvpp method as implemented in the Gaussian09 package\textsuperscript{[55].}

Finally, the anharmonic corrections are performed using our iGVPT2\textsuperscript{[57]} code, linked to the n2p2 library to compute ANN energies. See Figure 1 for an algorithmic representation of the entire hybrid method.

For simplicity, in the next sections, we refer to:

- Full B2PLYP as a GVPT2 calculation where all the values are calculated using the B2PLYP/def2tzvpp method via Gaussian software.

- Hybrid B2PLYP/ANN as our hybrid method where the B2PLYP/def2tzvpp was used to compute the harmonic modes while the cubic and fourth ones are computed using the ANN potential.

- Full ANN as calculation where all derivatives are calculated using ANN potential via a custom-made interface to n2p2 library. The fundamental frequencies are calculated using GVPT2 method.

B. Reference data

The hybrid Quantum mechanics/Machine learning approach is tested on 37 molecules: Water (H\(_2\)O), Kryp-
1: Set the High level method and the software to be used (here B2PLYP/def2tzvpp using Gaussian)
2: Optimize geometry using the high level method
3: Compute harmonic modes using the high level method
4: Generate \(3N \times 8\) geometries for ANN training potential
5: for each geometry \textbf{do} \\
   \hspace{1cm} This loop can be run in parallel
6: Compute energies and forces
7: Build the ANN potential by training on the energies and forces of geometries generated at previous step
8: Generate all geometries needed to calculate the cubic and quartic derivatives using the ANN potential
9: for each geometry \textbf{do} \\
   \hspace{1cm} This loop can be run in parallel
10: Compute energy
11: Using the calculated energies, compute cubic and quartic energy derivatives
12: Using these derivatives, compute anharmonic frequencies by GVPT2 method

FIG. 1. Hybrid B2PLYP//ANN approach-pseudocode

ton difluoride (KrF₂), Carbonyl selenide (OCSe), Sulfur dioxide (SO₂), selenium dioxide (SeO₂), Carbon diselenide (CSe₂), Titanium dioxide (TiO₂), Ammonia (NH₃), chlorine trifluoride (ClF₃), Formaldehyde (H₂CO), Hydrogen peroxide (H₂O₂), Gallium trichloride (GaCl₃), Aluminum chloride difluoride (AlFCl₂), aluminum dichloride fluoride (AlFCl₂), Zinc methylen (ZnCH₂), Methane (CH₄), Bromoform (CHBr₃), silicon tetrabromide (SiBr₄), Titanium tetrachloride (TiCl₄), Carbon tetrabromide (CBr₄), Formic acid (CH₂O₂), Methanimine (CH₂NH), Methyl Alcohol (CH₃OH), Methane selenol (CH₃SeH), Vinyl bromide (C₂H₅Br), Chlorothene (CH₂CHCl), Selenium hexafluoride (SeF₆), 1,2-Dibromoethane (C₂H₅Br₂), methyl germane (GeH₃CH₃), Ethyl bromide (C₂H₅Br), Cyclopropane (C₃H₆), Propylene oxide (C₃H₆O), pyruvic acid (C₃H₅O₂), benzene (C₆H₆), Thiophene (C₄H₄S), Dimethyl sulfite (C₂H₅O₃S) and Naphthalene (C₁₆H₁₀).

All of these molecules were specially chosen because they span over a large chemical space and because their vibrational frequencies were experimentally measured (taken from NIST Database[28]). Altogether, our benchmarking is made on 407 experimental fundamental frequencies available to the 37 molecules. For molecules where it is possible to compute the full B2LYP/def2tzvpp anharmonic corrections to vibrational frequencies, we used them as a second way to assess the accuracy of our approach. For this second comparison, we worked with 371 frequencies available to the 34 molecules.

III. BENCHMARKS

For each molecule of our data set, after optimization of the geometry using B2PLYP/def2tzvpp method, the

FIG. 2. Distribution of the vibrational frequency deviation between hybrid calculations and full \textit{ab initio} calculations.
cm$^{-1}$ for all the frequencies and it becomes 20 cm$^{-1}$ and 24 cm$^{-1}$ when respectively restricted to only the low and high frequencies. More precisely, fundamental frequencies obtained from our hybrid model are compared to results obtained from the full B2PLYP approach in Figure 3. The correlation coefficient $R^2$ is equal to 0.999588 thus reflecting the very good quality of the agreement between the hybrid and the full B2PLYP approaches.

FIG. 3. Scatter plots for the fundamental frequencies/cm$^{-1}$. Black points are for present data ($R^2 = 0.999588341$) while the red line corresponds to the ideal case.

Following Fig. 3, it appears that our results depend on the considered molecule. In particular, the largest molecules including Cyclopropane(C$_3$H$_6$) and Methyl German GeH$_3$CH$_3$ exhibit the largest error which is due to the higher difficulty in obtaining a good description of anharmonic effect on bend scissor HCH modes. This error is not due to the number of neurons or to the Group Symmetry Function. Indeed, the forces are reproduced with a small RMS (11 meV/Å for C$_3$H$_6$ and 14 meV/Å for GeH$_3$CH$_3$). Despite this specific case, the averaged RMSD on over all modes of all molecules remains very small.

Altogether, our results are consistent with previous precision obtained using MMFF94 [16]. However, the advantage of this novel approach is the large versatility as virtually any molecules can be considered.

### B. Assessment of the hybrid approach by comparison with experiment

Table I. Statistical errors in cm$^{-1}$ using all frequencies, low frequencies ($<2000$ cm$^{-1}$) and High ones (>2000 cm$^{-1}$).

| Method Type | Reference | RMSD | AUE | ASE | UMAX |
|------------|-----------|------|-----|-----|-------|
| Hybrid Fundamental | B2PLYP | 20.54 | 13.11 | 3.22 | 96.74 |
| Hybrid Fundamental | Experiment | 22.93 | 16.19 | 0.56 | 117.91 |
| B2PLYP Fundamental | Experiment | 19.80 | 13.07 | -3.82 | 98.51 |
| ANN Fundamental | B2PLYP | 21.99 | 13.97 | 2.42 | 174.10 |
| ANN Fundamental | Experiment | 23.11 | 16.32 | -1.00 | 86.93 |
| ANN Harmonic | B2PLYP | 18.15 | 11.88 | -2.47 | 98.47 |

Low Frequencies

| Method Type | Reference | RMSD | AUE | ASE | UMAX |
|------------|-----------|------|-----|-----|-------|
| Hybrid Fundamental | B2PLYP | 19.60 | 11.62 | 5.08 | 98.51 |
| Hybrid Fundamental | Experiment | 20.80 | 14.26 | 3.69 | 117.91 |
| B2PLYP Fundamental | Experiment | 16.18 | 10.35 | -1.15 | 85.86 |
| ANN Fundamental | B2PLYP | 23.11 | 14.03 | 3.15 | 174.10 |
| ANN Fundamental | Experiment | 21.79 | 15.16 | 1.27 | 85.55 |
| ANN Harmonic | B2PLYP | 19.10 | 12.21 | -3.72 | 98.47 |

High Frequencies

| Method Type | Reference | RMSD | AUE | ASE | UMAX |
|------------|-----------|------|-----|-----|-------|
| Hybrid Fundamental | B2PLYP | 23.66 | 18.54 | -3.53 | 62.88 |
| Hybrid Fundamental | Experiment | 29.40 | 23.23 | -10.85 | 84.38 |
| B2PLYP Fundamental | Experiment | 28.60 | 21.95 | -12.52 | 96.74 |
| ANN Fundamental | B2PLYP | 17.29 | 13.77 | -0.27 | 47.62 |
| ANN Fundamental | Experiment | 27.40 | 20.55 | -9.25 | 86.93 |
| ANN Harmonic | B2PLYP | 13.82 | 10.60 | 2.38 | 37.14 |

All Frequencies

with a distribution peaked around 0. Averaging through our entire benchmark set, we obtained a root mean squared deviation (RMSD) of 23 cm$^{-1}$ for all the frequencies (Table I) and it becomes 21 cm$^{-1}$ and 29 cm$^{-1}$ when respectively restricted to only the low and high frequencies. The mean absolute errors are 16 cm$^{-1}$, 14 cm$^{-1}$ and 23 cm$^{-1}$ for respectively all the frequencies, only the low and high frequencies. This error can originate from two sources: (1) Dataset used to fit the ANN potential to the ab initio method (B2PLYP) and (2) The method (GVPT2) used to compute the fundamental frequencies. To distinguish between these two, the frequencies obtained with the full B2PLYP approach are compared with experimental ones which leads to a RMSD equal to 20, 16 and 29 cm$^{-1}$ for respectively all, low and high frequencies. The full ab initio calculations lead to an agreement with experiments that is similar to the hybrid approach. Altogether, this demonstrates that the ANN potential does not really provide any additional error.

Fig. 4 shows that the errors depend on the considered molecules. The large error obtained for Cyclopropane is due to the frequency mode discussed in the previous section. In addition, we observe a large error for ZnCH$_3$ due to the frequency mode discussed in the previous section. The CH2 wagging potential does not really provide any additional error. Fig. 4 shows the deviation between our hybrid calculations and experimental measurements. Most frequencies are obtained with a deviation smaller than 10 cm$^{-1}$.
FIG. 4. Error in vibrational frequency obtained by hybrid calculations relative to full \textit{ab initio} calculations for each molecule.

more appropriate to study the anharmonic effect on this molecule. An error in the experimental value cannot be excluded either. Indeed, the 543.8 cm$^{-1}$ of CH2 wagging mode in CH2 seems to be too small compared to the same mode in other molecules.

C. Assessment of full ANN approach

We have seen above that hybrid B2PLYP/ANN approach gave very good results as compared with the full B2PLYP approach. Therefore, we further considered an alternative approach, where equilibrium geometry, second, cubic and quartic derivatives are all calculated using the PES obtained with the ANN potential. When comparing with the full B2PLYP approach, RMSD for fundamental frequencies is equal to 22, 23 and 17 cm$^{-1}$ for respectively all, low and high frequencies, and the RMSD for harmonic frequencies is equal to 18, 19 and 14 cm$^{-1}$ for respectively all, low and high frequencies (Table 1). This shows that our full ANN approach also leads to very good results as compared with B2PLYP(See Figures 7 and 2). The comparison between Figures 7 and 2 shows very similar deviations in the vibrational frequency with slightly better results for Hybrid B2PLYP/ANN approach. Similarly, the comparison of our full ANN approach with the experimental results shows very good agreement. While the RMSD of full ANN approach is similar to that of our hybrid B2PLYP/ANN one, this full ANN approach leads, in general, to slightly less accurate results which arises from the errors already obtained in the ANN calculation of few very-low harmonic frequencies. Such error could be coped with by increasing the number of data in the training set which naturally increases the computational cost. Altogether, the full ANN approach remains a good alternative to hybrid B2PLYP/ANN one, especially for very large molecules where the harmonic B2PLYP calculation can take very large computational time.

D. Timings

Regarding the computational timing, we take C$_4$H$_8$S, relatively one of the large molecules in our benchmark set,
FIG. 6. Error in vibrational frequency obtained by hybrid calculations and experimental measurements for each molecule.

as an example. As illustrated in Figure 6, when using the full B2PLYP treatment, it took 2240 hours in CPU time and 72 hours in real-time on 40 cores. Calculations using the hybrid B2PLYP/ANN was considerably reduced as it took only 400 hours in CPU time and 7 hours in real-time (using 100 cores for Data and only 8 cores for the training part). The main advantage here is that for each molecule, calculations of the distorted structures were run in parallel. It is evident that the computational time should grow with the number of atoms. In the hybrid calculation, the time grows as $3N \times 8$ while it grows as $\approx (3N)^2$ for a full ab initio calculation.[16] Hence, beside its very good accuracy, the hybrid calculation approaches is ten times faster than full ab initio methods. This significant reduction in the computational time enables us to carry out the anharmonic corrections to vibrational frequencies of large molecules, which was not feasible before.

E. Effect of data sets

The main goal in this work was to construct an accurate PES through a fast method. This requires the use of data sets made of ab initio energies and forces. We choose a simple and general method to generate these data, making several small (important for modes with high frequencies) and large (important for modes with low frequencies) displacement of each atom from the equilibrium position in the three Cartesian directions. With a large number of displacements, the PES is well described. However, the computing time increases with the number of displacements. It will therefore be necessary to find a good compromise between precision and number of geometries. So far, our results were obtained with $3N \times 8$ displacements. To study the effect of the number of data points, we calculated the fundamental frequencies using a ANN potential, fitted on $3N \times 6$ displacements ($\pm 0.01, \pm 0.05, \pm 0.2 \text{Å}$), by removing the very large ones. First, for the neural network optimization, we obtained a RMSD about 9.2 meV/Å for forces and 0.11 meV for
FIG. 8. Error in vibrational frequency obtained by full ANN calculations and full ab initio ones. Energies, which is smaller than what was obtained with a larger data set (14.8 meV/Å for forces and 0.21 meV for energies). This is simply because there are fewer data points to fit. Then, the RMSD between the full B2PLYP fundamental frequencies and the Hybrid ones is about 24.5 cm$^{-1}$ to be compared to 21.0 cm$^{-1}$ observed using the 3N × 8 geometries. The result with the smaller data sets is slightly less accurate than that of the larger ones but the effect is not significantly important. By removing geometries with very large displacements (0.3 Å), the error for modes with lowest frequencies grows, especially for CH$_2$NH and C$_3$H$_4$O$_3$ molecules, which explains the increase in the value of RMSD. We note that by removing large displacements, the CPU computing time is reduced by a factor of 8/6, but it does not necessarily reduce the real computing time because the calculations of energies and forces are independent and can be done in parallel.

IV. CONCLUSION

To summarize, anharmonic contributions to vibrational frequencies are usually either computed with empirical correction factors or with a full quantum mechanics calculations. We proposed an alternative approach which combines quantum chemistry calculations with machine-learning potential. In particular, B2PLYP/def2tzvpp is employed to compute equilibrium geometries and harmonic contributions while the anharmonicity is obtained through the GVPT2 framework where derivatives of the PES are computed with a neural network force-field potential. With this approach, we managed to reach a RMSD equal to 23 cm$^{-1}$ when compared to experimental results and to 21 cm$^{-1}$ when compared to full B2PLYP/def2tzvpp calculations. In terms of computational timing, we gained a factor of almost ten with the latter method which allows us to study large molecules. Moreover, the use of a neural network force-field makes our approach transferable to molecules made of any types of atoms. Furthermore, we demonstrate that the PES obtained with machine-learning is accurate enough to compute anharmonic frequencies. We implemented the approach within the GVPT2 framework, but
the obtained PES could also be employed with other vibrational frequency methods such as VSCF, cc-VSCF, VCI-P. Finally, beyond the calculation of vibrational frequencies, our work participates in the common effort to speed up ab initio calculations and is therefore an additional evidence that machine-learning technique is a very effective tool for material science.

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VI. SUPPORTING INFORMATION AVAILABLE

File available free of charge:

- SuppInfo.pdf: List of all calculated frequencies, Group symmetry functions and the statistical parameters of machine learning study.
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