

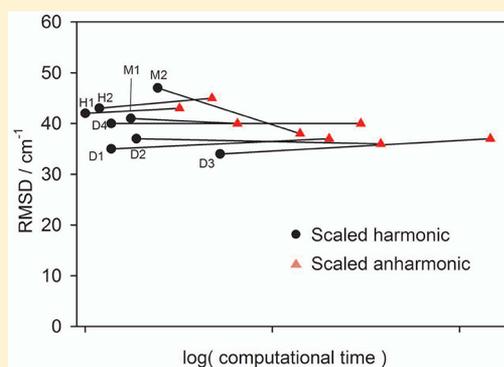
Anharmonic Vibrational Frequency Calculations Are Not Worthwhile for Small Basis Sets

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S Supporting Information

ABSTRACT: Anharmonic calculations using vibrational perturbation theory are known to provide near-spectroscopic accuracy when combined with high-level *ab initio* potential energy functions. However, performance with economical, popular electronic structure methods is less well characterized. We compare the accuracy of harmonic and anharmonic predictions from Hartree–Fock, second-order perturbation, and density functional theories combined with 6-31G(d) and 6-31+G(d,p) basis sets. As expected, anharmonic frequencies are closer than harmonic frequencies to experimental fundamentals. However, common practice is to correct harmonic predictions using multiplicative scaling. The surprising conclusion is that scaled anharmonic calculations are no more accurate than scaled harmonic calculations for the basis sets we used. The data used are from the Computational Chemistry Comparison and Benchmark Database (CCCBDB), maintained by the National Institute of Standards and Technology, which includes more than 3939 independent vibrations for 358 molecules.



1. INTRODUCTION

One of the most popular uses of computational quantum chemistry is to predict (or assign) vibrational spectra. This is usually done in the harmonic approximation, in which the potential energy function (PEF) is taken as a truncated, second-order Taylor series. Neglecting higher-order curvature causes the predictions to deviate from experimental observations of fundamental frequencies. Moreover, the harmonic force constants suffer quantitative deficiencies because of the theoretical and numerical approximations inherent in the underlying electronic structure calculation. As an approximate correction for these two sources of error, an empirical scaling factor (that is, a multiplicative correction) is usually applied to the theoretical frequencies. The value for the scaling factor is typically determined by least-squares fitting to a set of experimental vibrational frequencies.

Pople and co-workers¹ were the first to scale theoretical frequencies. Since then, there have been many studies focused on the details of scaling. One of the most extensive studies is the work by Scott and Radom,² which provides scaling factors for 19 quantum chemistry models. More recently, Alecu et al.³ have published scaling factors for 145 models. The CCCBDB⁴ has scaling factors for over 250 models.

It is possible to include higher-order terms in the Taylor series expansion of the PEF, although at significant computational cost. This is theoretically better than the harmonic approximation and is expected to improve the accuracy of the predictions. The anharmonic vibrational problem is usually solved using second-order perturbation theory with a harmonic

reference wave function (VPT2).⁵ Near-degeneracies may result in small-valued energy denominators in the perturbation expressions; such problematic resonances are typically treated by diagonalization.⁶ The other popular alternative is vibrational mean-field theory (VSCF) and its more sophisticated derivatives.^{7–9} Compared with VPT2, VSCF does not require a well-behaved Taylor series expansion for the PEF and is resistant to problems arising from near-degeneracies but is computationally expensive. Besides these popular approaches, specialized techniques are used for high-precision predictions for small molecules.^{10–12}

Recently, VPT2 has been tested using a variety of density functional methods with a set of 88 molecules (655 modes).¹³ The authors concluded that VPT2 failed to provide a significant improvement over the best-case scaled harmonic frequencies. In this paper, we examine a larger set (176 molecules, up to 2738 modes). Our larger set undoubtedly includes more molecules for which the known⁵ problems (near-degeneracies causing unreasonable predictions) of VPT2 occur. When the predictions are grossly in error, such as an anharmonic correction an order of magnitude larger than the harmonic frequency, they are obvious. For example, the ν_7 mode of C_2Cl_4 is problematic with the MP2/6-31+G(d,p) model: calculated harmonic and anharmonic frequencies of 200 cm^{-1} and 2917 cm^{-1} , respectively (the experimental value is 512 cm^{-1}). Errors

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of this magnitude are easy to spot and exclude. However, less obvious errors may be present and undetected.

It is important to emphasize that we are characterizing the performance of VPT2 when used with moderately reliable PEFs. When used with high-level PEFs, the VPT2 method can be quite accurate. For example, Rauhut and co-workers have predicted the fundamental frequencies of the CHFClBr molecule to within 12 cm^{-1} by adding VPT2 anharmonic corrections to CCSD(T) harmonic frequencies.¹⁴ In contrast, more modest anharmonic calculations often benefit from empirical scaling, just as harmonic frequencies do.¹⁵

Anharmonic computations are not yet routine because they are expensive. A VPT2 anharmonic computation requires cubic and some quartic derivatives of the PEF, which are usually evaluated by numerical differences of analytically computed second derivatives. This consumes much more computer time than a harmonic calculation, which requires only second derivatives. To illustrate the costs, the horizontal axis of Figure 1 shows the relative computation times for formaldehyde

(CH_2O) at various levels of theory. For this small molecule, the cost of a VPT2 anharmonic calculation is about 10 times the cost of the corresponding harmonic calculation. The difference will be larger for bigger molecules, since there are more cubic and quartic derivatives to evaluate.

This work continues our studies of quantum chemical calculations as “virtual measurements,”¹⁵ where the experimental data are taken from the Computational Chemistry Comparison and Benchmark Database (CCCBDB).⁴ We calculate harmonic and anharmonic frequencies for a set of fundamental molecular vibrations using a variety of low-level *ab initio* models: combinations of Hartree–Fock (HF), second-order perturbation (MP2), and hybrid density functional (B3LYP) theories with the 6-31G(d) and 6-31+G(d,p) basis sets. In addition, we use PBEPBE/6-31G(d) and B3LYP/cc-pVTZ. We use VPT2, as implemented in a popular quantum chemistry package, to obtain the anharmonic corrections. We compare the resulting frequencies with experimental, fundamental frequencies to determine the relative performance of the harmonic and anharmonic methods. The experimental and harmonic modes have already been aligned in the CCCBDB, using the frequencies, symmetries (irreducible representations), and, when available, intensities. We use empirical factors to scale the anharmonic and harmonic predictions and compare the accuracies of the scaled harmonic and scaled anharmonic methods. In this work, a set of calculated frequencies is considered accurate if it has a low root-mean-square deviation (RMSD) with respect to the experimental frequencies. Our results show that scaled harmonic and scaled anharmonic calculations are usually equally accurate. This is a disappointing result, since the anharmonic calculations are much more expensive.

2. METHODOLOGY

2.1. Calculations. Anharmonic vibrational frequencies were computed using a partial quartic force field computed by using finite differences of analytical second derivatives.⁵ Near-degeneracies were treated by diagonalization according to the software defaults. Note that some results are sensitive to those defaults.¹⁵ All open-shell calculations were spin-unrestricted. Core orbitals were frozen, i.e., uncorrelated, in all MP2 calculations, including those involving group 1 (alkali) and group 2 (alkaline-earth) metals. All calculations were done using “tight” geometry convergence criteria, and DFT calculations were done using the “ultrafine” grid (99 radial and 590 angular points) as recommended.¹⁶ All computations were performed using the Gaussian 09 software package.^{17,18} The molecules, taken from the CCCBDB, range from 3 to 18 atoms, with an atomic number up to 35 (Br). Most are organic compounds. Diatomic molecules were excluded because they are not representative of molecules in general and because VPT2 is seldom used for diatomic molecules (superior variational methods are convenient). Certain molecules in the CCCBDB were not included in the present study because of apparent problems with MP2 harmonic frequencies. (See section XIII.F.1 of the CCCBDB.⁴) Because of software limitations, we excluded molecules that possess a 3-fold or higher symmetry axis. The complete list of molecules, along with all data, is included in the Supporting Information.

2.2. Choice of Scaling Factors. Some publications have noted slightly different biases for low and high harmonic frequencies.^{2,19–22} A few have recommended scaling low and high harmonic frequencies separately.^{19,20,22,23} However, as

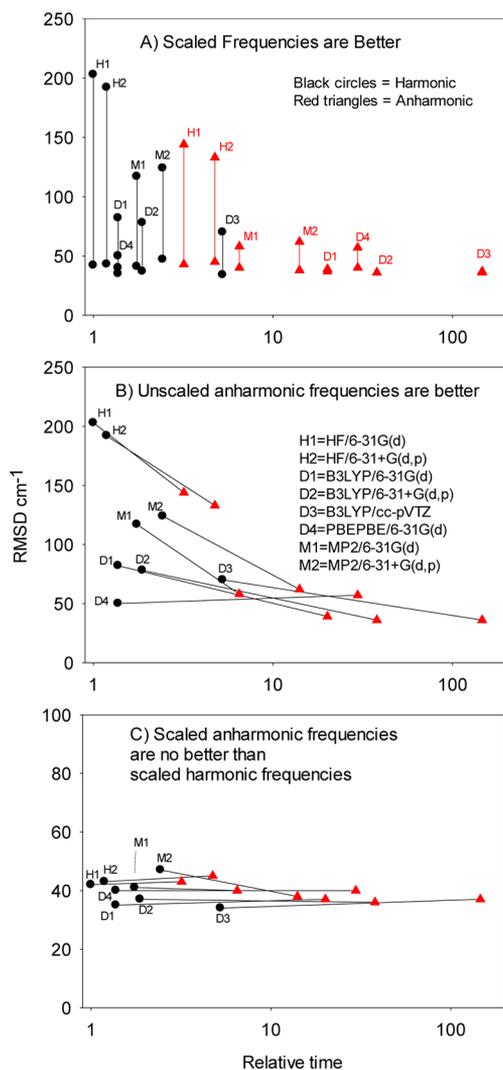


Figure 1. Root-mean-square deviations (RMSDs) for unscaled and scaled harmonic and anharmonic calculations plotted against relative computational time for CH_2O . (A) Scaled frequencies compared with unscaled. (B) Unscaled anharmonic frequencies compared with unscaled harmonic. (C) Scaled anharmonic frequencies compared with scaled harmonic (note expanded vertical scale).

noted in the Introduction, common practice is still to use one empirical factor to scale all frequencies. Here, we scale harmonic frequencies with a single factor in order to conform to common practice. Moreover, scaling harmonic frequencies using two parameters will improve the harmonic results and cannot change our overall conclusion. We use the harmonic scaling factors previously reported.²⁴ In contrast, for anharmonic frequencies, we use two scaling factors, as recommended elsewhere.¹⁵ We have derived new scaling factors for the models not previously reported. The scaling factors are collected in Table 1.

Table 1. Vibrational Scaling Factors Used in This Study

	HF ^a	MP2 ^b	B3LYP ^c	PBEPBE ^c
6-31G(d)				
harmonic	0.8982	0.9411	0.9594	0.984
anharmonic high	0.9398	0.9797	1.0015	1.026 ^d
anharmonic low	0.9047	0.9675	0.9863	1.022 ^d
6-31+G(d,p)				
harmonic	0.9039	0.9398	0.9632	
anharmonic high	0.9438	0.9698	1.0005	
anharmonic low	0.9117	0.9822	0.9988	
cc-pVTZ				
harmonic			0.965	
anharmonic high			1.000 ^d	
anharmonic low			1.010 ^d	

^aHigh/low boundary at 2700 cm⁻¹. ^bHigh/low boundary at 2600 cm⁻¹. ^cHigh/low boundary at 2500 cm⁻¹. ^dDetermined in the present work.

2.3. Analysis. As recommended by Pernot and Cailliez,²⁵ we compare the root-mean-square deviations (RMSDs) from experimental values to estimate the relative accuracies of the frequencies predicted using each theoretical model. The RMSD for a set of frequencies is defined in the usual way as

$$\text{RMSD} = \sqrt{\frac{1}{m} \sum_{i=1}^m (x_{i,\text{calc}} - \nu_{i,\text{expt}})^2} \quad (1)$$

where m is the number of frequencies in the set and the $x_{i,\text{calc}}$ are the calculated frequencies (harmonic or anharmonic, scaled or unscaled). The RMSDs are listed in Table 2 and compared in Figure 1.

In Figure 1A, each vertical line shows how the RMSD decreases from a set of unscaled frequencies to the corresponding scaled frequencies. The improvement is

substantial for all sets of harmonic frequencies, which is the reason that scaling factors are popular. For the anharmonic frequencies, the B3LYP results are not significantly improved by scaling, which is consistent with the values of the scaling factors in Table 1 (near unity). Even with scaling, RMSD values for all methods are far from zero.

In Figure 1B, results are shown only for unscaled frequencies. For each line, a negative slope corresponds to improvement due to anharmonic VPT2 theory. The only line with a positive slope is that for the PBEPBE/6-31G(d) method; we speculate that this is caused by a few undetected resonance-related problems in the VPT2 calculations. In general, VPT2 results are markedly better than the harmonic predictions. The horizontal axis, relative computational time, shows the roughly 10-fold increase in computational time (for the CH₂O molecule) required for including anharmonicity.

Figure 1C is the basis for the conclusion summarized by the title of this report. It is analogous to Figure 1B, except that results are shown only for scaled frequencies. A negative slope indicates that the scaled anharmonic frequencies are better than the scaled harmonic frequencies. This is most evident for the MP2/6-31+G(d,p) model (when the C₂Cl₄ molecule is excluded). A positive slope indicates that the scaled anharmonic frequencies are worse than the scaled harmonic frequencies. A horizontal line corresponds to no change in RMSD upon adding explicit anharmonic effects. Most of the lines are essentially horizontal, indicating that there is no meaningful benefit from the anharmonic theory.

For B3LYP, the larger cc-pVTZ basis set makes little difference. Post-Hartree–Fock methods, which make heavy use of the virtual orbitals, should show a larger effect from a bigger basis set but are not yet available to us because of their high computational cost. As suggested by a reviewer, this is an opportunity for further study, perhaps using a smaller set of molecules to reduce the computational expense.

The results in Table 2 are for overall performance. Performance for individual vibrational frequencies is variable; some do improve with an anharmonic calculation. One way to illustrate this, not involving RMSDs, is shown in Figure 2. For one choice of PEF, we first compile the unsigned errors of the scaled harmonic ($\Delta_{\text{har}} = |\text{scaled harmonic} - \text{experimental}|$) and scaled anharmonic ($\Delta_{\text{anh}} = |\text{scaled anharmonic} - \text{experimental}|$) predictions and then compute the signed difference of these errors, $B = \Delta_{\text{har}} - \Delta_{\text{anh}}$. More concisely,

$$B = |\text{scaled } \omega - \text{expt}| - |\text{scaled } \nu - \text{expt}| \quad (2)$$

Table 2. Root Mean Square Deviations (RMSD) and Largest Unsigned Deviations (MAX) for Unscaled and Scaled Harmonic and Anharmonic Frequencies (cm⁻¹ units)

model	m	harmonic frequencies, unscaled		anharmonic frequencies, unscaled		harmonic frequencies, scaled (one factor)		anharmonic frequencies, scaled (two factors)	
		RMSD	MAX	RMSD	MAX	RMSD	MAX	RMSD	MAX
HF/6-31G(d)	2738	203	579	144	442	42	287	43	265
MP2/6-31G(d)	2715	117	315	58	377	41	258	40	322
B3LYP/6-31G(d)	2706	82	228	39	237	35	247	37	238
HF/6-31+G(d,p)	2673	192	642	134	463	43	255	45	254
MP2/6-31+G(d,p)	2642	124	394	78	2451	47	312	60	2361
excluding C ₂ Cl ₄	2630	124	394	62	335	47	266	39	305
B3LYP/6-31+G(d,p)	1926	78	277	36	284	38	259	36	284
B3LYP/cc-pVTZ	2696	70	264	36	383	34	254	38	382
PBEPBE/6-31G(d)	2684	50	231	57	361	40	246	40	281

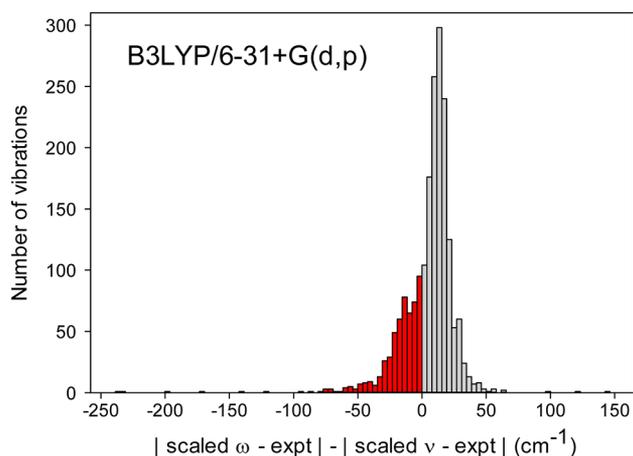


Figure 2. Benefits [eq 2] for anharmonic calculations using the B3LYP/6-31+G(d,p) model PEF. Negative (red) values indicate that anharmonic errors are larger than harmonic errors.

Thus, B represents the benefit from the anharmonic calculation. A positive value means that the anharmonic prediction is better, and a negative value means that the harmonic prediction is better. Figure 2 shows an asymmetrical distribution (mean = 5.3 cm^{-1} , standard deviation = 21.3 cm^{-1}). The long negative tail suggests that it would be beneficial to develop diagnostics for detecting problems in the VPT2 analysis. For the other PEFs, histograms analogous to Figure 2 are provided in the Supporting Information.

Our results indicate that expensive VPT2 calculations are not worthwhile with the PEFs tested here. However, this should not be interpreted to mean that VPT2 is an unsuccessful theory. As stated in the Introduction, VPT2 works well when a high-quality PEF is available. In addition to ample evidence in the literature, representative results for ethylene (C_2H_4), up to CCSD(T)/cc-pVQZ, are provided in the Supporting Information.

3. CONCLUSIONS

Without empirical scaling, anharmonic frequencies are clearly more accurate than harmonic frequencies, as expected. However, the scaled frequencies are all of comparable accuracy; the much greater cost of anharmonic calculations does not provide a benefit for the electronic structure methods tested here. It is necessary to use a PEF from a high-level electronic structure calculation, better than those evaluated here, to obtain a clear benefit from anharmonic VPT2 calculations.

■ ASSOCIATED CONTENT

📄 Supporting Information

Complete citation for ref 17, several computations for C_2H_4 (two tables), analogs of Figure 2 for the other PEFs (seven figures), and Excel spreadsheet containing all data used in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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