

# **Overcoming the Overestimation of Harmonic Vibrational Frequencies: The Development of Frequency Scaling Factors for DFT Functionals in Combination with the Correlation Consistent Basis Sets**

Density functional theory (DFT) has a tendency to overestimate fundamental frequencies obtained from experiment due to: (1) a general neglect of anharmonicity in the calculated frequencies, (2) an incomplete description of electron correlation due to the use of an incomplete basis set, and (3) an approximate method used to approximate the Schrödinger equation. Because this overestimation is relatively uniform, global scale factors are often used to enable improved comparison with experiment. Though scaling factors are available for many combinations of DFT and basis sets, such factors have yet to be determined for DFT in combination with the widely used correlation consistent basis sets. In this aspect of our development, scaling factors have been determined for a series of density functionals including B3P86, BP86, BPW91, and BH&HLYP used in combination with the cc-pV $x$ Z and aug-cc-pV $x$ Z ( $x = D, T, Q$ ) basis sets on calculations for frequencies, zero point energies, enthalpies, and entropies.

# **Overcoming the Overestimation of Harmonic Vibrational Frequencies: The Development of Frequency Scaling Factors for DFT Functionals in Combination with the Correlation Consistent Basis Sets**

## **1. Introduction**

For quantum chemists, the Schrödinger equation is fundamental in describing quantum mechanical behavior. Because atomic particles are wavelike in nature, it was correctly assumed that a wave equation could describe these particles' behavior. Schrödinger was one of the first to create a wave equation for this. By solving his equation, quantum mechanical aspects can be found, such as the energy of the system and the probability of finding particles at a certain position.

However, the Schrödinger equation is very difficult to solve exactly. Even the world's most powerful supercomputers and Beowulf clusters must approximate the solution to this equation. So generally, an approximate method must be chosen to solve for the estimated solution. Additionally, solving the equation relies on a description of molecular orbitals, which are described through a combination of atomic orbitals. These atomic orbitals are described mathematically through functions called basis functions, which, in a set together, are called a basis set. Because the solution relies these basis sets, an incomplete basis set (that is, one that is non-infinite) is also a cause of computational error. As more exact methods and larger basis sets both generally require higher computational cost, the selection of these combinations depends on many factors including available processing power, memory, disk space, and time. Therefore, calculations with a lower cost but with less approximation are obviously the most preferred. That is the reason that both Density Functional Theory and the correlation consistent basis sets have become popular choices when solving for quantum mechanical properties.

The correlation consistent basis sets were designed with the idea in mind that as the basis set size increases, the property's value should approach a limit.<sup>1-6</sup> Therefore, it is possible to extrapolate a property to an infinitely large basis set, known as the complete basis set (CBS) limit, at which point it would be impossible for there to be any improvement to the basis set by adding additional basis functions.<sup>7</sup> Therefore, the only remaining error in calculation should be intrinsic to the method used to approximate the solution to the Schrödinger equation. For this reason, the correlation consistent basis sets have become the most widely used throughout the field of computational chemistry.

Density Functional Theory (DFT) has grown in popularity in recent years as an alternative to using *ab initio* methods. Density Functional Theory is mathematically equivalent to solving the Schrödinger equation for electronic structure and other chemical properties. The fact that electron density has only three spatial coordinates despite any number of electrons generally allows for lower computational cost than with *ab initio* when used for calculations on systems of greater size. For this reason, DFT has also become a very common tool for computational chemists.

Several estimations are responsible for the apparent overestimation in calculated vibrational frequencies when compared to those experimentally determined. Firstly, as previously described, both DFT and *ab initio* methods approximate the solution to the Schrödinger equation in an effort to save in computational cost. An incomplete basis set causes an incomplete description of electron correlation, resulting in further error. Finally, there is a general neglect for anharmonicity, which usually results in an overestimation in calculated vibrational frequencies.

However, the difference between experimental and theoretical values tends to be fairly uniform, and for this reason, it is possible to create multiplicative scale factors for theoretical harmonic vibrational frequencies. This should also reduce the intrinsic error in the method located at the CBS limit when using the correlation consistent basis sets. Pople *et al.*<sup>8</sup> created some of the

first scale factors, using the Hartree-Fock method in combination with the 3-21G basis set. Hehre *et al.*<sup>9</sup> worked with the same method and the 6-31G(d) basis set, which resulted in scale factors close to those found by Pople *et al.*<sup>8</sup> Rauhut and Pulay determined scaling factors for the popular DFT functional B3LYP in conjunction with the 6-31G(d) basis set.<sup>10</sup> Scott and Radom<sup>11</sup> performed an extensive study of semi-empirical, *ab initio*, and DFT methods, again with several types of Pople-type basis sets. In their study, BLYP/6-311G(df,p) proved to have the most accurate calculations. Finally, in 2001, Schlegel *et al.* found scaling factors for DFT and *ab initio* methods with the Sadlej pVTZ basis set.<sup>12</sup>

Until now, no scale factors have been created for these DFT functionals in combination with the correlation consistent basis sets. This study was designed to accomplish this task. To do this, two different groups of molecules were studied. The first set contains forty-one molecules from an earlier work by Healy and Holder to create scaling factors for AM1.<sup>13</sup> This set was chosen as they have well established, accepted experimental vibrational frequencies. These molecules were then used to create scaling factors for the vibrational frequencies, enthalpies, and entropies.

It has previously been established that different scaling factors are needed for zero point vibrational energies (ZPVE). The calculation for ZPVE can be written as the following equation.

$$E(ZPVE) = \frac{1}{2} \sum_i^{\text{all}} h \omega_i^{\text{expt}} \quad (1)$$

While it would follow logic to use the scale factors from vibrational frequencies for the ZPVE, Equation 1 also does not include the effects of anharmonicity. As a result, the ZPVE's from these scaling factors can result in dramatic errors in the determination of both bond energies and atomization energies. Schaefer<sup>14</sup> showed that errors in ZPVE's for systems such as ethane could be so large that they're not even usable. While considering the effects of anharmonicity in the above equation would improve the theoretical ZPVE's, the determination of force fields for large molecules is very difficult to accomplish, both theoretically and experimentally. Therefore, a set of

twenty-four small molecules studied by Schaefer in 1991<sup>14</sup> was used to determine the scale factors for ZPVE. The calculations of force fields for these molecules are believed to be accurate as compared to the previously mentioned set of larger molecules.

## 2. Methodology

All calculations were done using the Gaussian 98 and Gaussian 03 software suites.<sup>15,16</sup> DFT functionals used in this study included the pure functionals BPW91 and BP86, and the hybrid functionals B3P86 and BH&HLYP. The basis sets used were cc-pV $x$ Z and aug-cc-pV $x$ Z where  $x =$  D,T,Q.

A least-squares procedure was used to minimize residual sums. Iterative computer software was used to find the optimal scale factor values in order to create the smallest overall error. The threshold of this software found the scale factors to accuracy greater than the four decimal places reported.

**2.1 Frequency Truncation Point** Scale factors were created for both high and low energy frequencies. Many thermochemical quantity evaluations are more sensitive to low-end vibrational frequencies, high-end frequencies having little effect on the property. For this reason, it is more appropriate to create scale factors for low-end frequencies separately from high-end frequencies.

This study was determined at what wavenumber the distinction between high and low energy should be made. The study was made using truncation points at 1000 cm<sup>-1</sup>, 1200 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, and 1800 cm<sup>-1</sup>. For each functional, scale factors, root mean square errors, and percent error tables were created at each different truncation point.

Additionally, three organic molecules with known vibrational frequencies that were not originally included in the study were used to test the different scaling factors, 2-propenal, furazan, and ethylenimine. The theoretical frequencies for these tests were calculated at the  $x =$  D(2) level

of theory. The reduction in the percent error in the scaled theoretical values at each truncation point was also considered in the determination of the optimal truncation point value.

**2.2 High Energy Vibrational Frequencies.** The least-squares procedure of this study follows from the one previously conducted by Scott and Radom<sup>11</sup>. This procedure seeks to find an optimum scaling factor  $\lambda$  in order to minimize the residual sum  $\Delta$  as given by

$$\Delta = \sum_i^{\text{all}} (\lambda \omega_i^{\text{theor}} - \tilde{\nu}_i^{\text{expt}})^2 \quad (2)$$

where  $\omega_i^{\text{theor}}$  and  $\tilde{\nu}_i^{\text{expt}}$  are the  $i$ th theoretical and  $i$ th experimental frequencies (in  $\text{cm}^{-1}$ ), respectively. Once the optimum scale factor has been found, the root mean square (rms) error is found in order to statistically represent the overall remaining error. This is accomplished through a summation of the squared differences between the experimental values and the scaled theoretical values. That is,

$$\text{rms} = \sqrt{\frac{\sum_i^{n_{\text{all}}} (\omega_i^{\text{scaled}} - \tilde{\nu}_i^{\text{expt}})^2}{n_{\text{all}}}} \quad (3)$$

where  $\omega_i^{\text{scaled}}$  is the  $i$ th scaled theoretical frequency (in  $\text{cm}^{-1}$ ), and  $n_{\text{all}}$  is the total number of modes.

**2.3 Low Energy Vibrational Frequencies.** To minimize the error of low energy frequencies, an inverse least-squares procedure was employed in order to direct greater emphasis on the lowest energy frequencies. Again, an optimum scaling factor  $\lambda$  was found in order to reduce the residual sum  $\Delta$  in the following equation.

$$\Delta = \sum_i^{\text{all}} \left( \frac{1}{\lambda \omega_i^{\text{theor}}} - \frac{1}{\tilde{\nu}_i^{\text{expt}}} \right)^2 \quad (4)$$

The rms values for low energy frequencies were then found analogously to those for the high energy frequencies.

**2.4 Zero Point Vibrational Energy.** The ZPVE's from the second set of molecules were once again subjected to the least-squares procedure, similar to the equation for individual vibrational frequencies.

$$\Delta = \sum_i^{\text{all}} (\lambda \text{ZPVE}_i^{\text{theor}} - \text{ZPVE}_i^{\text{expt}})^2 \quad (5)$$

Again, the rms values were obtained analogously to those of the high energy frequencies.

It should be noted that for the augmented basis sets, only twenty-three molecules were tested for their ZPVE. The aug-cc-pVxZ basis sets do not currently include lithium, so LiF, while included in the cc-pVxZ scale factors, was left out of the augmented ZPVE set calculations.

**2.5 Enthalpies and Entropy.** Enthalpic and entropic contributions to thermochemical properties rely on vibrational frequencies, with the largest contributions coming from low energy frequencies. However, instead of using the low energy scaling factors, it would be more effective to give these values their own scale factors. Thus, a least squares method was once again employed. The following equation was used to minimize the overall residual sum  $\Delta$ .

$$\Delta = \sum_i^{\text{all}} [\Delta H_{\text{vib}}^{\text{theor}}(T)_i - \Delta H_{\text{vib}}^{\text{expt}}(T)_i]^2 \quad (6)$$

The formulas for determining the values of enthalpy for each mode are determined with the following equations.

$$\Delta H_{\text{vib}}^{\text{theor}}(T)_i = \frac{\lambda \omega_i^{\text{theor}}}{e^{\mu_i^{\text{theor}}} - 1} \quad (7)$$

$$\mu_i^{\text{theor}} = \frac{hc \lambda \omega_i^{\text{theor}}}{kT}$$

where  $\omega_i^{\text{theor}}$  is the  $i$ th theoretical frequency in  $\text{cm}^{-1}$ . The value for  $\Delta H_{\text{vib}}^{\text{expt}}(T)_i$  is obtained using the same approach with the  $i$ th experimental frequency and without  $\lambda$ . The rms value for enthalpy calculations is then determined similarly to the others as follows.

$$\text{rms} = Nhc \sqrt{\frac{\sum_i^{n_{\text{all}}} [\Delta H_{\text{vib}}^{\text{scaled}}(T)_i - \Delta H_{\text{vib}}^{\text{expt}}(T)_i]^2}{n_{\text{all}}}} \quad (8)$$

In this equation,  $\Delta H_{\text{vib}}^{\text{scaled}}(T)_i$  is the enthalpy contribution from the  $i$ th scaled theoretical mode.

The method for determining entropy scale factors again used the least-squares method.

$$\Delta = \sum_i^{\text{all}} [S_{\text{vib}}^{\text{theor}}(T)_i - S_{\text{vib}}^{\text{expt}}(T)_i]^2 \quad (9)$$

Each mode's contribution is calculated by

$$S_{\text{vib}}^{\text{theor}} = \frac{\mu_i^{\text{theor}}}{e^{\mu_i^{\text{theor}}} - 1} - \ln(1 - e^{-\mu_i^{\text{theor}}}) \quad (10)$$

where  $\mu_i^{\text{theor}}$  is obtained the same as in Equation 7, and  $S_{\text{vib}}^{\text{expt}}(T)_i$  is obtained analogously. The rms error is determined analogously to that of enthalpy by

$$\text{rms} = R \sqrt{\frac{\sum_i^{n_{\text{all}}} [S_{\text{vib}}^{\text{scaled}}(T)_i - S_{\text{vib}}^{\text{expt}}(T)_i]^2}{n_{\text{all}}}} \quad (11)$$

where  $S_{\text{vib}}^{\text{scaled}}(T)_i$  is the entropy contribution from the  $i$ th scaled theoretical mode.

### 3. Results and Discussion

In the study of the frequency truncation points, it was determined for all functionals that 1500  $\text{cm}^{-1}$  was the best distinction between high and low energy. Observing the percent error tables and rms values for both high and low frequencies at each point, it can be seen that 1500  $\text{cm}^{-1}$  generally

has the lowest rms values and lowest percent errors. This can be seen in Tables 6, 8, 10, and 12. Additionally, with the testing of the three other organic molecules not included in the creation of these scale factors,  $1500\text{ cm}^{-1}$  also showed the strongest overall reduction in percent error after scaling, as seen in Tables 7, 9, 11, and 13.

The high energy scale factors showed the most overestimation, with scale factors ranging from 0.93 to 0.96 in the hybrid functionals, and scale factors from 0.98 to 0.99 in the pure functionals, as shown in Table 1. Low energy vibrations showed less overestimation in the hybrid functionals, with scale factors from 0.94 to 0.99, and underestimation in the pure functionals, with scale factors from 1.02 to 1.04, as shown in Table 2.

It can be seen that values of ZPVE, enthalpy, and entropy, seen in Tables 3, 4, and 5 respectively, are all actually underestimated with the pure functionals as well. Even the high-energy vibrations for the pure functionals were only slightly overestimated as shown by the scaling factors of 0.99 and 0.98.

In many of the properties, the rms values decreased with each larger sized basis set and the scale factors approached 1.00. However, the trend in scaling factors and rms values was not always true. As the basis sets increased in size, the overestimation is seen to sometimes get even worse, causing a larger rms value and scaling factors that move away from 1.00. So while the correlation consistent sets did generally show convergence, it was occasionally converging away from the experimental values.

The percent errors in Tables 7, 9, 11, and 13 show results indicative of how these scale factors may be applied. While occasionally causing an increase in percent error due to originally accurate calculations or already underestimated frequencies, there is an overall significant decrease in percent error. When observing the  $1500\text{ cm}^{-1}$  columns specifically, almost all vibrations have less

than 3% remaining error. The only vibrations not meeting this qualification were almost always significantly overestimated to begin with.

#### 4. Conclusions

Multiplicative scale factors were created for the BP86, BPW91, B3P86, and BH&HLYP DFT functionals in combination with the cc-pV $x$ Z and aug-cc-pV $x$ Z basis sets where  $x = D, T, Q$ .

In studying the distinction between high and low energy frequencies, it was determined that 1500  $\text{cm}^{-1}$  was the optimal truncation point for all four functionals. It showed the lowest rms errors, highest percentage of frequencies with low percent errors, and the greatest reduction in percent errors from unscaled values.

The values of the scale factors showed that these DFT functionals did not show strong overestimation. Low energy frequencies in the pure functionals were actually underestimated. Percent errors of the scaled vibrations show that most energies were fairly accurate, implying that the rms errors are mostly associated with a few, high percent error frequencies.

Overall, B3P86 had the lowest rms errors, suggesting that out of the four functionals studied, it is the most accurate for predicting vibrational frequencies.

#### 5. Data and Tables

##### 5.1 Scale Factors

Table 1: High Energy Frequencies (rms in units of  $\text{cm}^{-1}$ )

Functional	Basis Set (cc-pV $x$ Z)	Scale Factor*	rms
B3P86	D	0.9568	26.6
	T	0.9586	24.4
	Q	0.9590	25.4
	aug, D	0.9564	24.9
	aug, T	0.9588	25.5
	aug, Q	0.9591	25.2
BP86	D	0.9894	33.0
	T	0.9891	26.6

	Q	0.9897	26.5
	aug, D	0.9875	28.9
	aug, T	0.9894	26.5
	aug, Q	0.9898	26.3
BPW91	D	0.9841	32.9
	T	0.9846	26.9
	Q	0.9854	27.0
	aug, D	0.9826	29.5
	aug, T	0.9849	26.9
	aug, Q	0.9854	26.7
BH&HLYP	D	0.9311	29.6
	T	0.9336	30.9

	Q	0.9339	30.9
	aug, D	0.9309	27.9
	aug, T	0.9336	29.8
	aug, Q	0.9340	30.7

\*Though it has become common to report frequency scaling factors to four places past the decimal, due to the accuracy of frequencies, practical use of scaling factors should include three places past the decimal, at most.

Table 2: Low Energy Frequencies (rms in units of  $\text{cm} \cdot 10^5$ )

Functional	Basis Set (cc-pVxZ)	Scale Factor	rms
B3P86	D	0.9778	8.2
	T	0.9802	7.0
	Q	0.9810	6.9
	aug, D	0.9945	6.4
	aug, T	0.9838	6.6
	aug, Q	0.9816	6.9
BP86	D	1.0219	10.1
	T	1.0246	7.4
	Q	1.0247	7.1
	aug, D	1.0433	8.0
	aug, T	1.0272	6.9
	aug, Q	1.0235	6.8
BPW91	D	1.0181	9.8
	T	1.0223	7.3
	Q	1.0208	7.5
	aug, D	1.0390	7.7
	aug, T	1.0261	6.8
	aug, Q	1.0204	7.1
BH&HLYP	D	0.9423	8.3
	T	0.9441	7.7
	Q	0.9438	7.7
	aug, D	0.9558	7.1
	aug, T	0.9461	7.6
	aug, Q	0.9436	7.7

Table 3: ZPVE (rms in units of kJ/mol)

Functional	Basis Set (cc-pVxZ)	Scale Factor	rms
B3P86	D	0.9874	0.50
	T	0.9844	0.43
	Q	0.9847	0.42
	aug, D	0.9898	0.40

	aug, T	0.9849	0.44
	aug, Q	0.9847	0.43
BP86	D	1.0220	0.56
	T	1.0173	0.43
	Q	1.0178	0.41
	aug, D	1.0240	0.44
	aug, T	1.0181	0.44
	aug, Q	1.0176	0.43
BPW91	D	1.0165	0.57
	T	1.0128	0.42
	Q	1.0134	0.40
	aug, D	1.0186	0.44
	aug, T	1.0136	0.43
	aug, Q	1.0131	0.42
BH&HLYP	D	0.9565	0.63
	T	0.9541	0.58
	Q	0.9542	0.57
	aug, D	0.9589	0.55
	aug, T	0.9544	0.60
	aug, Q	0.9542	0.59

Table 4: Enthalpy (rms in units of kJ/mol)

Functional	Basis Set (cc-pVxZ)	Scale Factor	rms
B3P86	D	0.9827	0.022
	T	0.9795	0.020
	Q	0.9797	0.019
	aug, D	0.9956	0.017
	aug, T	0.9818	0.019
	aug, Q	0.9797	0.019
BP86	D	1.0320	0.027
	T	1.0300	0.020
	Q	1.0292	0.019
	aug, D	1.0498	0.022
	aug, T	1.0314	0.018
	aug, Q	1.0285	0.018
BPW91	D	1.0272	0.027
	T	1.0260	0.020
	Q	1.0253	0.019
	aug, D	1.0448	0.022
	aug, T	1.0284	0.019
	aug, Q	1.0247	0.018
BH&HLYP	D	0.9415	0.025
	T	0.9380	0.025
	Q	0.9378	0.025
	aug, D	0.9516	0.021

	aug, T	0.9394	0.024
	aug, Q	0.9373	0.024

Table 5: Entropy (rms in units of J/mol K)

Functional	Basis Set (cc-pVxZ)	Scale Factor	rms
B3P86	D	0.9791	0.14
	T	0.9795	0.12
	Q	0.9801	0.12
	aug, D	0.9952	0.10
	aug, T	0.9826	0.11
	aug, Q	0.9804	0.11
BP86	D	1.0271	0.17
	T	1.0280	0.12
	Q	1.0275	0.11

	aug, D	1.0488	0.14
	aug, T	1.0301	0.11
	aug, Q	1.0266	0.11
BPW91	D	1.0228	0.17
	T	1.0250	0.12
	Q	1.0237	0.12
	aug, D	1.0440	0.13
	aug, T	1.0282	0.11
	aug, Q	1.0233	0.11
BH&HLYP	D	0.9406	0.15
	T	0.9406	0.14
	Q	0.9404	0.14
	aug, D	0.9531	0.12
	aug, T	0.9425	0.14
	aug, Q	0.9400	0.14

## 5.2 Frequency Truncation Point Analysis

### 5.2.1 B3P86

Table 6: Scale factors and rms values for high and low energy frequencies

Truncation Point (cm <sup>-1</sup> )	Basis Set (cc-pVxZ)	Scale Factor High Energy	Rms (cm <sup>-1</sup> ) High Energy	Scale Factor Low Energy	rms (cm*10 <sup>-5</sup> ) Low Energy
1000	D	0.9625	43.6	0.9756	11.1
	T	0.9627	45.8	0.9803	9.4
	Q	0.9627	37.6	0.9810	9.3
	aug, D	0.9628	38.1	0.9945	8.6
	aug, T	0.9632	37.7	0.9839	8.9
	aug, Q	0.9633	37.7	0.9814	9.3
1200	D	0.9612	40.5	0.9767	9.6
	T	0.9617	33.1	0.9803	8.2
	Q	0.9622	33.2	0.9810	8.0
	aug, D	0.9612	42.3	0.9945	7.5
	aug, T	0.9621	33.6	0.9839	7.8
	aug, Q	0.9622	33.2	0.9814	8.0
1500	D	0.9568	26.6	0.9778	8.2
	T	0.9586	24.4	0.9802	7.0
	Q	0.9590	25.4	0.9810	6.9
	aug, D	0.9564	24.9	0.9945	6.4
	aug, T	0.9588	25.5	0.9838	6.6
	aug, Q	0.9591	25.2	0.9816	6.9
1800	D	0.9567	26.2	0.9741	8.0
	T	0.9584	25.8	0.9722	6.9
	Q	0.9589	25.8	0.9719	6.8
	aug, D	0.9557	22.9	0.9907	6.3
	aug, T	0.9585	24.9	0.9754	6.6
	aug, Q	0.9588	25.6	0.9720	6.8

Table 7: Percent errors for three organic molecules using B3P86/cc-pVDZ

	%Error (No Scale)	%Error (1000)	%Error (1200)	%Error (1500)	%Error (1800)
2-Propenal					
CC torsion	11.108	8.397	8.519	8.641	8.230
CCC bend	4.553	6.882	6.777	6.672	7.025
CCO deform	1.346	1.127	1.015	0.904	1.279
CH2 Twist	2.796	0.288	0.401	0.514	0.134
CH2 rock	0.663	1.793	1.682	1.571	1.944
CH2 Wag	2.747	0.240	0.353	0.466	0.086
CH(alpha) Bend (OOP)	4.278	1.733	1.848	1.963	1.577
CH(beta) Bend (OOP)	4.372	1.825	1.940	2.055	1.668
C-C stretch	0.524	3.246	1.818	1.708	2.080
CH(beta) Bend (IP)	0.319	3.443	3.573	1.908	2.279
CH(alpha) Bend (IP)	0.791	2.989	3.120	1.447	1.820
CH2 Scissors	0.747	3.031	3.162	1.489	1.862
C=C stretch	4.512	0.593	0.457	0.003	1.805
CO stretch	5.402	1.449	1.312	0.849	2.672
CH(alpha) stretch	2.905	0.954	1.087	1.540	1.550
CH2 symmetric stretch	5.063	1.123	0.987	0.524	0.514
CH(beta) stretch	5.645	1.683	1.546	1.081	1.071
CH2 asymmetric stretch	4.994	1.056	0.920	0.458	0.447
Furazan					
Ring Deformation (OOP)	5.179	2.613	2.729	2.844	2.455
Ring Deformation (OOP)	4.726	2.170	2.285	2.401	2.013
CH Bend (OOP)	3.953	1.417	1.531	1.645	1.261
CH Bend (OOP)	7.887	5.255	5.373	5.492	5.093
Ring Deformation (IP)	4.482	1.933	2.048	2.163	1.776
Ring Deformation (IP)	4.108	1.568	1.682	1.797	1.411
Ring Deformation (IP)	2.173	0.320	0.208	0.095	0.473
Ring Deformation (IP)	5.032	1.093	2.585	2.700	2.312
CH Bend (IP)	2.910	0.949	0.512	0.626	0.245
CH Bend (IP)	0.611	3.162	1.733	1.623	1.995
Ring Deformation (IP)	3.074	0.792	0.926	0.785	0.404
Ring Deformation (IP)	4.396	0.481	0.345	2.078	1.692
Ring Deformation (IP)	3.409	0.469	0.604	1.059	0.730
CH stretch	4.809	0.879	0.743	0.282	0.271
CH stretch	5.051	1.111	0.975	0.512	0.502
Ethylenimine					
CH2 Rock	0.573	2.999	2.890	2.781	3.148
CH2 rock	9.487	6.816	6.936	7.057	6.651
Ring Deformation	4.822	2.265	2.380	2.495	2.107
Ring Deformation	0.317	2.131	2.021	1.911	2.282
NH bend	0.255	2.689	2.579	2.469	2.838
CH2 Wag	0.074	3.821	2.402	2.292	2.662
CH2 Twist	1.239	2.557	1.120	1.008	1.383

CH2 Wag	0.389	3.376	1.950	1.840	2.211
Ring stretch	3.393	0.484	0.619	1.098	0.715
NH Bend	5.250	1.303	1.166	2.913	2.524
CH2 twist	0.683	4.408	4.537	2.888	3.256
CH2 sciccors	0.144	3.612	3.742	2.079	2.450
CH2 sciccors	1.808	2.010	2.142	0.452	0.829
CH2 symmetric stretch	3.209	0.661	0.795	1.249	1.260
CH2 symmetric stretch	3.441	0.438	0.572	1.027	1.038
CH2 asymmetric stretch	3.942	0.044	0.091	0.548	0.559
CH2 asymmetric stretch	4.373	0.459	0.323	0.136	0.147
NH stretch	4.986	1.049	0.912	0.451	0.440

### 5.2.2 BP86

Table 8: Scale factors and rms values for high and low energy frequencies

Truncation Point (cm <sup>-1</sup> )	Basis Set (cc-pVxZ)	Scale Factor High Energy	rms (cm <sup>-1</sup> ) High Energy	Scale Factor Low Energy	rms (cm*10 <sup>-5</sup> ) Low Energy
1000	D	0.9558	46.1	1.0207	14.0
	T	0.9942	40.0	1.0249	10.1
	Q	0.9948	40.5	1.0247	9.6
	aug, D	0.9951	49.8	1.0444	10.9
	aug, T	0.9948	41.4	1.0274	9.3
	aug, Q	0.9950	40.7	1.0233	9.2
1200	D	0.9942	44.4	1.0213	11.9
	T	0.9928	37.3	1.0248	8.7
	Q	0.9934	36.6	1.0247	8.2
	aug, D	0.9929	46.2	1.0438	9.3
	aug, T	0.9933	37.4	1.0274	8.0
	aug, Q	0.9935	36.6	1.0235	7.9
1500	D	0.9894	33.0	1.0219	10.1
	T	0.9891	26.6	1.0246	7.4
	Q	0.9897	26.5	1.0247	7.1
	aug, D	0.9875	28.9	1.0433	8.0
	aug, T	0.9894	26.5	1.0272	6.9
	aug, Q	0.9898	26.3	1.0235	6.8
1800	D	0.9890	33.8	1.0217	9.8
	T	0.9886	27.0	1.0244	7.2
	Q	0.9891	26.6	1.0245	6.9
	aug, D	0.9866	27.1	1.0430	7.8
	aug, T	0.9888	26.3	1.0270	6.7
	aug, Q	0.9892	26.3	1.0233	6.6

Table 9: Percent errors for three organic molecules using BP86/cc-pVDZ

	%Error (No Scale)	%Error (1000)	%Error (1200)	%Error (1500)	%Error (1800)
2-Propenal					
CC torsion	8.735	10.985	11.051	11.116	11.094

CCC bend	7.524	5.610	5.555	5.499	5.518
CCO deform	1.962	0.068	0.126	0.185	0.166
CH2 Twist	0.560	1.499	1.559	1.618	1.598
CH2 rock	2.644	0.629	0.571	0.512	0.532
CH2 Wag	1.787	0.246	0.305	0.364	0.344
CH(alpha) Bend (OOP)	0.116	2.188	2.248	2.308	2.288
CH(beta) Bend (OOP)	0.894	2.983	3.043	3.104	3.084
C-C stretch	2.907	3.315	0.839	0.781	0.800
CH(beta) Bend (IP)	2.857	3.265	3.421	0.730	0.749
CH(alpha) Bend (IP)	2.531	2.941	3.097	0.397	0.416
CH2 Scissors	2.550	2.959	3.115	0.416	0.435
C=C stretch	0.205	0.216	0.376	0.857	2.380
CO stretch	0.096	0.324	0.484	0.965	2.269
CH(alpha) stretch	1.878	2.290	2.447	2.918	2.957
CH2 symmetric stretch	1.922	1.494	1.331	0.842	0.801
CH(beta) stretch	2.376	1.946	1.782	1.291	1.250
CH2 asymmetric stretch	1.888	1.460	1.297	0.808	0.767
Furazan					
Ring Deformation (OOP)	0.627	2.710	2.771	2.831	2.811
Ring Deformation (OOP)	0.116	2.188	2.248	2.308	2.288
CH Bend (OOP)	8.444	6.549	6.494	6.439	6.458
CH Bend (OOP)	2.793	0.781	0.722	0.664	0.683
Ring Deformation (IP)	1.675	0.360	0.419	0.478	0.458
Ring Deformation (IP)	2.791	0.779	0.721	0.662	0.682
Ring Deformation (IP)	2.064	0.037	0.022	0.080	0.061
Ring Deformation (IP)	0.964	1.380	1.146	1.205	1.185
CH Bend (IP)	1.136	1.551	0.970	1.029	1.009
CH Bend (IP)	3.781	4.185	1.732	1.674	1.693
Ring Deformation (IP)	1.838	2.250	2.407	0.312	0.292
Ring Deformation (IP)	0.766	1.183	1.342	1.407	1.387
Ring Deformation (IP)	2.218	2.629	2.785	3.254	0.096
CH stretch	1.663	1.236	1.073	0.585	0.544
CH stretch	1.930	1.502	1.339	0.850	0.809
Ethylenimine					
CH2 Rock	4.531	2.555	2.498	2.441	2.460
CH2 rock	2.329	4.447	4.509	4.570	4.550
Ring Deformation	0.666	1.390	1.450	1.510	1.490
Ring Deformation	3.658	1.664	1.606	1.548	1.567
NH bend	3.232	1.229	1.171	1.113	1.132
CH2 Wag	4.558	4.959	2.526	2.468	2.487
CH2 Twist	2.962	3.369	0.895	0.836	0.856
CH2 Wag	3.031	3.438	0.966	0.908	0.927
Ring stretch	0.629	1.046	1.205	1.547	1.527
NH Bend	1.594	2.008	2.165	0.561	0.541
CH2 twist	0.459	0.877	1.036	1.721	1.701
CH2 sciccors	2.995	3.402	3.557	0.870	0.890

CH2 sciccors	1.874	2.286	2.443	0.275	0.256
CH2 symmetric stretch	0.047	0.374	0.534	1.014	1.054
CH2 symmetric stretch	0.230	0.190	0.351	0.832	0.872
CH2 asymmetric stretch	0.686	0.263	0.102	0.381	0.422
CH2 asymmetric stretch	1.125	0.701	0.539	0.053	0.013
NH stretch	0.467	0.045	0.115	0.598	0.638

### 5.2.3 BPW91

Table 10: Scale factors and rms values for high and low energy frequencies

Truncation Point (cm <sup>-1</sup> )	Basis Set (cc-pVxZ)	Scale Factor High Energy	rms (cm <sup>-1</sup> ) High Energy	Scale Factor Low Energy	rms (cm*10 <sup>-5</sup> ) Low Energy
1000	D	0.9907	46.5	1.0170	13.6
	T	0.9897	40.5	1.0228	9.9
	Q	0.9906	40.9	1.0209	10.2
	aug, D	0.9902	50.1	1.0402	10.6
	aug, T	0.9905	42.0	1.0267	9.3
	aug, Q	0.9906	41.3	1.0204	9.6
1200	D	0.9890	44.7	1.0176	11.5
	T	0.9882	37.7	1.0226	8.5
	Q	0.9891	37.0	1.0210	8.8
	aug, D	0.9880	46.4	1.0396	9.1
	aug, T	0.9888	37.9	1.0265	8.0
	aug, Q	0.9891	37.2	1.0206	8.2
1500	D	0.9841	32.9	1.0181	9.8
	T	0.9846	26.9	1.0223	7.3
	Q	0.9854	27.0	1.0208	7.5
	aug, D	0.9826	29.5	1.0390	7.7
	aug, T	0.9849	26.9	1.0261	6.8
	aug, Q	0.9854	26.7	1.0204	7.1
1800	D	0.9837	33.6	1.0179	9.6
	T	0.9841	27.2	1.0221	7.1
	Q	0.9849	27.2	1.0206	7.3
	aug, D	0.9817	27.7	1.0387	7.5
	aug, T	0.9843	26.7	1.0259	6.7
	aug, Q	0.9848	26.6	1.0203	6.9

Table 11: Percent errors for three organic molecules using BPW91/cc-pVDZ

	%Error (No Scale)	%Error (1000)	%Error (1200)	%Error (1500)	%Error (1800)
2-Propenal					
CC torsion	8.095	9.932	9.997	10.051	10.030
CCC bend	7.302	5.726	5.670	5.624	5.643
CCO deform	1.709	0.038	0.021	0.070	0.050
CH2 Twist	0.543	1.148	1.208	1.258	1.238
CH2 rock	2.186	0.524	0.465	0.416	0.436
CH2 Wag	1.234	0.445	0.505	0.554	0.534

CH(alpha) Bend (OOP)	0.645	2.356	2.416	2.466	2.446
CH(beta) Bend (OOP)	1.404	3.128	3.189	3.239	3.219
C-C stretch	2.406	3.314	0.689	0.640	0.659
CH(beta) Bend (IP)	2.369	3.277	3.443	0.602	0.622
CH(alpha) Bend (IP)	1.991	2.902	3.069	0.217	0.237
CH2 Scissors	1.989	2.900	3.067	0.215	0.235
C=C stretch	0.588	0.347	0.518	1.011	2.388
CO stretch	0.365	0.569	0.740	1.231	2.161
CH(alpha) stretch	1.177	2.096	2.264	2.749	2.788
CH2 symmetric stretch	2.489	1.536	1.362	0.860	0.819
CH(beta) stretch	2.896	1.939	1.764	1.260	1.219
CH2 asymmetric stretch	2.426	1.474	1.300	0.798	0.757
Furazan					
Ring Deformation (OOP)	0.975	2.692	2.752	2.803	2.783
Ring Deformation (OOP)	0.432	2.139	2.199	2.250	2.230
CH Bend (OOP)	7.600	6.029	5.973	5.927	5.946
CH Bend (OOP)	2.195	0.532	0.474	0.425	0.444
Ring Deformation (IP)	0.905	0.780	0.839	0.889	0.869
Ring Deformation (IP)	2.318	0.658	0.599	0.550	0.570
Ring Deformation (IP)	1.829	0.160	0.102	0.052	0.072
Ring Deformation (IP)	0.514	1.439	1.237	1.286	1.267
CH Bend (IP)	0.625	1.549	1.124	1.174	1.154
CH Bend (IP)	3.252	4.152	1.549	1.501	1.520
Ring Deformation (IP)	1.393	2.310	2.477	0.392	0.373
Ring Deformation (IP)	0.311	1.239	1.408	1.493	1.473
Ring Deformation (IP)	1.792	2.705	2.872	3.353	0.034
CH stretch	2.187	1.237	1.063	0.563	0.522
CH stretch	2.460	1.507	1.333	0.831	0.790
Ethylenimine					
CH2 Rock	3.861	2.227	2.169	2.121	2.141
CH2 rock	3.364	5.122	5.184	5.235	5.215
Ring Deformation	0.126	1.828	1.888	1.938	1.918
Ring Deformation	3.063	1.415	1.357	1.309	1.328
NH bend	2.802	1.150	1.092	1.043	1.063
CH2 Wag	3.870	4.764	2.178	2.130	2.149
CH2 Twist	2.340	3.248	0.621	0.572	0.592
CH2 Wag	2.603	3.509	0.889	0.840	0.860
Ring stretch	0.148	1.077	1.247	1.659	1.639
NH Bend	1.207	2.126	2.294	0.581	0.561
CH2 twist	0.081	1.011	1.180	1.727	1.707
CH2 sciccors	2.503	3.409	3.575	0.738	0.757
CH2 sciccors	1.353	2.270	2.438	0.433	0.413
CH2 symmetric stretch	0.570	0.365	0.536	1.029	1.069
CH2 symmetric stretch	0.752	0.185	0.356	0.850	0.890
CH2 asymmetric stretch	1.204	0.263	0.091	0.405	0.445
CH2 asymmetric stretch	1.646	0.701	0.528	0.030	0.011

NH stretch	1.094	0.154	0.018	0.513	0.554
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## 5.2.4 BH&HLYP

Table 12: Scale factors and rms values for high and low energy frequencies

Truncation Point (cm <sup>-1</sup> )	Basis Set (cc-pVxZ)	Scale Factor High Energy	rms (cm <sup>-1</sup> ) High Energy	Scale Factor Low Energy	rms (cm*10 <sup>-5</sup> ) Low Energy
1000	D	0.9349	38.1	0.9404	11.4
	T	0.9354	34.3	0.9437	10.6
	Q	0.9357	34.3	0.9433	10.5
	aug, D	0.9354	39.2	0.9553	9.6
	aug, T	0.9357	34.1	0.9458	10.4
	aug, Q	0.9359	34.2	0.9430	10.5
1200	D	0.9341	35.9	0.9414	9.7
	T	0.9350	31.2	0.9439	9.1
	Q	0.9353	31.2	0.9436	9.0
	aug, D	0.9343	36.6	0.9555	8.3
	aug, T	0.9352	30.8	0.9460	8.9
	aug, Q	0.9354	31.0	0.9433	9.0
1500	D	0.9311	29.6	0.9423	8.3
	T	0.9336	30.9	0.9441	7.7
	Q	0.9339	30.9	0.9438	7.7
	aug, D	0.9309	27.9	0.9558	7.1
	aug, T	0.9336	29.8	0.9461	7.6
	aug, Q	0.9340	30.7	0.9436	7.7
1800	D	0.9315	28.7	0.9422	8.1
	T	0.9339	31.6	0.9440	7.5
	Q	0.9341	31.8	0.9437	7.5
	aug, D	0.9308	27.7	0.9556	6.9
	aug, T	0.9338	30.7	0.9460	7.4
	aug, Q	0.9341	31.5	0.9435	7.5

Table 13: Percent errors for three organic molecules using BH&HLYP/cc-pVDZ

	%Error (No Scale)	%Error (1000)	%Error (1200)	%Error (1500)	%Error (1800)
2-Propenal					
CC torsion	14.126	7.324	7.439	7.541	7.530
CCC bend	0.654	5.345	5.245	5.154	5.164
CCO deform	4.769	1.475	1.370	1.276	1.286
CH2 Twist	6.997	0.620	0.727	0.824	0.813
CH2 rock	4.336	1.883	1.778	1.685	1.695
CH2 Wag	8.375	1.916	2.024	2.122	2.111
CH(alpha) Bend (OOP)	9.060	2.560	2.669	2.767	2.756
CH(beta) Bend (OOP)	8.810	2.325	2.434	2.532	2.521
C-C stretch	4.167	2.614	1.937	1.843	1.854
CH(beta) Bend (IP)	4.326	2.466	2.549	1.694	1.704
CH(alpha) Bend (IP)	4.929	1.902	1.986	1.125	1.136

CH2 Scissors	4.940	1.892	1.976	1.115	1.126
C=C stretch	8.638	1.566	1.479	1.153	2.359
CO stretch	10.335	3.153	3.064	2.733	3.958
CH(alpha) stretch	7.237	0.256	0.170	0.151	0.108
CH2 symmetric stretch	7.805	0.787	0.701	0.378	0.421
CH(beta) stretch	8.359	1.304	1.218	0.893	0.936
CH2 asymmetric stretch	7.520	0.520	0.434	0.112	0.155
Furazan					
Ring Deformation (OOP)	8.245	1.794	1.902	1.999	1.988
Ring Deformation (OOP)	8.571	2.100	2.209	2.307	2.296
CH Bend (OOP)	9.870	3.322	3.432	3.530	3.519
CH Bend (OOP)	14.418	7.599	7.713	7.816	7.805
Ring Deformation (IP)	10.744	4.144	4.255	4.355	4.343
Ring Deformation (IP)	13.627	6.855	6.968	7.071	7.059
Ring Deformation (IP)	7.451	1.047	1.154	1.251	1.240
Ring Deformation (IP)	10.620	3.419	4.138	4.237	4.226
CH Bend (IP)	4.451	2.349	1.670	1.576	1.586
CH Bend (IP)	5.861	1.031	0.343	0.247	0.258
Ring Deformation (IP)	7.335	0.347	0.262	1.142	1.131
Ring Deformation (IP)	9.576	2.442	2.355	3.253	3.242
Ring Deformation (IP)	9.351	2.232	2.145	1.817	3.030
CH stretch	7.411	0.418	0.332	0.010	0.053
CH stretch	7.625	0.618	0.532	0.209	0.252
Ethylenimine					
CH2 Rock	3.404	2.759	2.656	2.562	2.573
CH2 rock	12.958	6.226	6.339	6.441	6.429
Ring Deformation	8.872	2.383	2.492	2.590	2.579
Ring Deformation	4.176	2.033	1.929	1.835	1.845
NH bend	3.331	2.827	2.724	2.631	2.641
CH2 Wag	5.489	1.379	0.693	0.598	0.609
CH2 Twist	6.044	0.859	0.170	0.074	0.085
CH2 Wag	4.710	2.106	1.426	1.331	1.342
Ring stretch	7.460	0.465	0.379	1.260	1.249
NH Bend	6.016	0.885	0.970	0.101	0.112
CH2 twist	5.687	1.193	1.278	0.411	0.422
CH2 sciccors	4.101	2.676	2.759	1.906	1.916
CH2 sciccors	5.908	0.987	1.072	0.203	0.214
CH2 symmetric stretch	5.896	0.997	1.082	1.400	1.357
CH2 symmetric stretch	6.184	0.728	0.813	1.132	1.089
CH2 asymmetric stretch	6.557	0.380	0.465	0.784	0.742
CH2 asymmetric stretch	7.011	0.045	0.041	0.362	0.319
NH stretch	8.625	1.553	1.466	1.141	1.184

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