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Frequency Scaling Factors for DFT Functionals Paired with the Correlation Consistent Basis Sets

Ian R. Haken¹, Pankaj Sinha¹, Scott E. Boesch²,
Changming Gu², Ralph A. Wheeler², Angela K. Wilson¹

¹*Department of Chemistry, University of North Texas, Denton, Texas, 76203*

²*Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73019-3051*



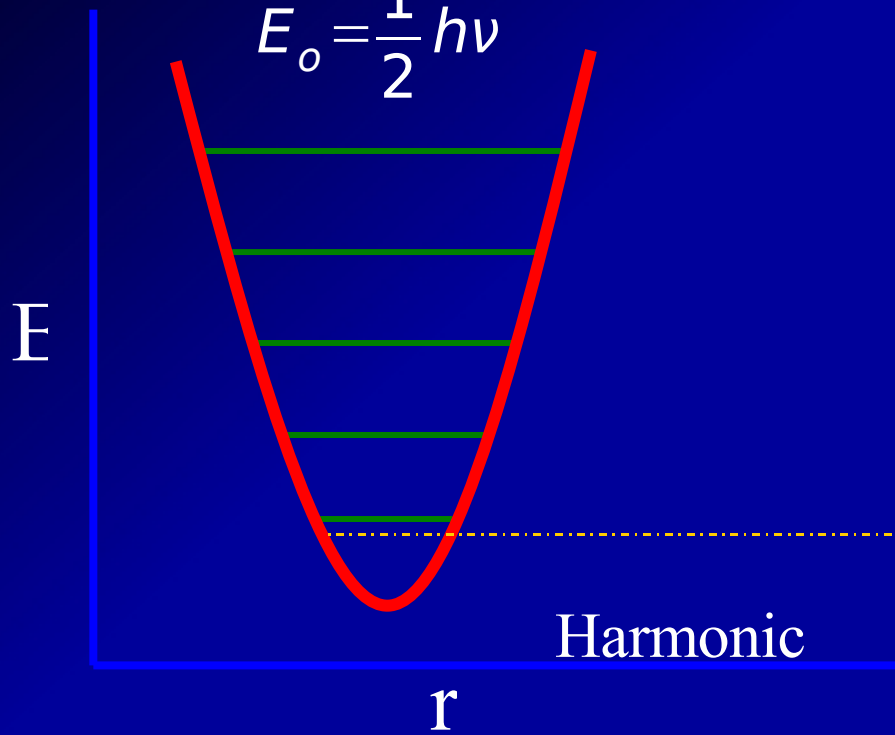
Outline

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 - Molecules and Functionals
- **Vibrational Frequencies**
- **Enthalpy and Entropy**
- **Zero Point Vibrational Energies**
- **Results and Conclusions**

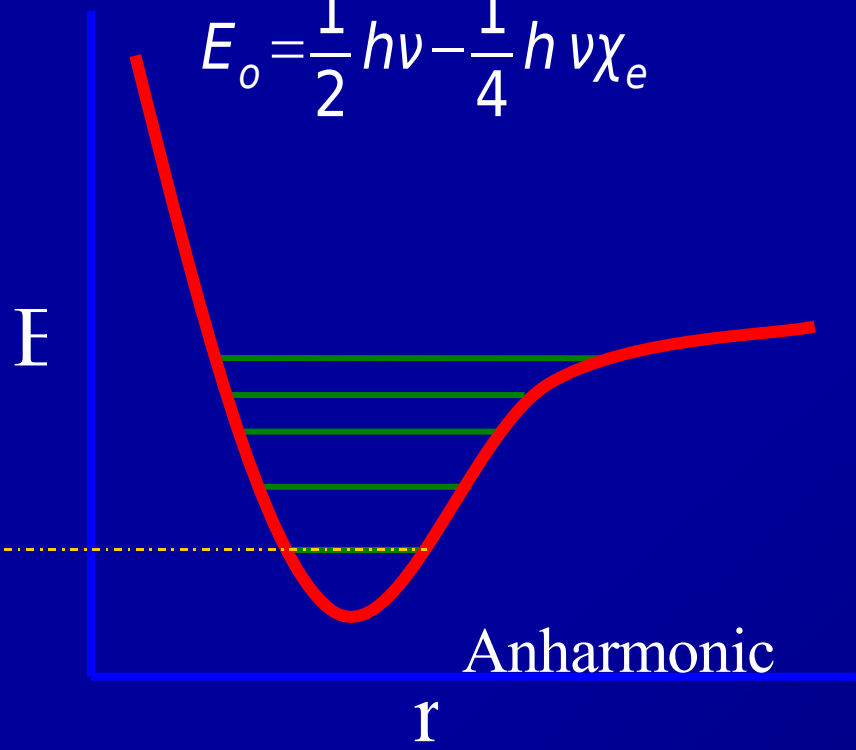


Vibrational Anharmonicity

$$E_0 = \frac{1}{2} h\nu$$



$$E_0 = \frac{1}{2} h\nu - \frac{1}{4} h\nu\chi_e$$



Calculated harmonic frequencies are usually overestimated.
Common computational methods neglect **ANHARMONICITY**.



Other Sources of Error

- Incomplete basis set
 - Incomplete electron correlation
- Approximate methods
 - Approximate solution to the Schrödinger Equation



The Solution: Scale Factors

- With the use of scale factors, a molecule's calculated vibrational energies can be better correlated with experimental values.
- Scale factors have been determined for a wide range of method and basis set combinations (each unique).
- Until now no global set of scale factors have been determined for the functionals in this study in combination with the correlation-consistent basis sets.



Methods and Basis Sets Studied

- Methods
 - B3P86, BP86, BPW91, BH&HLYP
- Basis sets
 - cc-pVnZ and aug-cc-pVnZ where $n = D, T, Q$



Molecules Studied

- A set of 41 organic molecules with experimental vibrational energies were chosen to create these scale factors



Least-Squares Method

- Least-squares approach was used to determine the optimal scale factors
 - Following the example of a previous study by Scott and Radom¹
- Each different property, i.e. frequencies, ZPVEs, enthalpies, and entropies, requires its own version of this method

¹Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.



Low vs. High Energy

- Thermochemical property evaluations are often dominated by low-end vibrational frequencies
- Scale factors are created for both high and low energy frequencies separately



Truncation Study

- A separate study was undertaken to determine optimal truncation points for each functional
- Chosen truncation points were 1000 cm^{-1} , 1200 cm^{-1} , 1500 cm^{-1} , and 1800 cm^{-1}
- Root mean square errors and percent error tables were considered in selection
- The best result was 1500 cm^{-1}



Least-Squares Method: High Energy Frequencies

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

Root Mean Square Error

$$\Delta_{\min} = (\lambda \omega_i^{\text{theor}} - \tilde{\nu}_i^{\text{expt}})^2$$

$$\text{rms} = \left(\sum_i^{n_{\text{all}}} \Delta_{\min} / n_{\text{all}} \right)^{0.5}$$



Least-Squares Method: Low Energy Frequencies

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

Root mean square error determined analogously to high energy frequencies



Results: High Energy

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (cm ⁻¹)
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

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (cm ⁻¹)
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



Results: Low Energy

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (cm*10 ⁵)
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

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (cm*10 ⁵)
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



Enthalpies

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

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

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

Root mean square error, minimized residuals determined analogously

$$\text{rms} = Nhc \left(\sum_i^{n_{\text{all}}} \Delta_{\text{min}} / n_{\text{all}} \right)^{0.5}$$



Results: Enthalpy

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (kJ/mol)
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

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (kJ/mol)
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



Entropies

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

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

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

Root mean square error, minimized residuals determined analogously

$$\text{rms} = R \left(\sum_i^{n_{\text{all}}} \Delta_{\text{min}} / n_{\text{all}} \right)^{0.5}$$



Results: Entropy

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (J/mol K)
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

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (J/mol K)
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



Zero Point Vibrational Energies

- Previously established that ZPVEs require different scaling factors

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

- This equation disregards anharmonicity which can cause large errors in the determination of bond energies and atomization energies



Zero Point Vibrational Energies

- Errors in ZPVEs for systems such as ethane can be as large as the target accuracy
- Set of 24 small molecules studied by Schaefer² in 1991 chosen for ZPVE scale factors
- Set of 24 ZPVEs used for cc-pVnZ ($n = D, T, Q$)
- Set of 23 ZPVEs, without LiF, used for aug-cc-pVnZ ($n = D, T, Q$)

²Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128.



Zero Point Vibrational Energies

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

Root mean square error determined analogously to high energy frequencies



Results: ZPVE

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (kJ/mol)
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

Functional	Basis Set (cc-pVnZ)	Scale Factor	rms (kJ/mol)
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



Conclusions

- Scale factors were created for the B3P86, BP86, BPW91, and BH&HLYP functionals with the cc-pVnZ and aug-cc-pVnZ ($n = D, T, Q$) basis sets
- For all functionals, all high energy frequencies had less than 5% remaining percent error



Future Study

- Continue creation of scale factors for a wider range of DFT functionals, such as HCTH and MPW1K



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