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Scaling factors for vibrational frequencies and zero-point vibrational energies of some recently developed exchange-correlation functionals

Yuthana Tantirungrotechai [a],*, Ketthip Phanasant [a], Supacharee Roddecha [a],
Panida Surawatanawong [a], Vallaya Sutthikhum [b], Jumras Limtrakul [c]

[a] Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand
[b] Department of Chemistry, Faculty of Science, Mahasarakham University, Kamrieng Campus, Kantarawichai, Mahasarakham 44150, Thailand
[c] Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

Abstract

The scaling factors for the vibrational frequencies and zero-point vibrational energies evaluated at various combinations of recently developed exchange-correlation functionals and various basis sets are reported. The exchange-correlation functionals considered are B972, B98, HCTH, OLYP, O3LYP, G96LYP, PBE0 and VSXC functionals; the basis sets employed are 3-21G, 6-31G*, 6-31G**, 6-31+G, 6-311G*, 6-311G**, 6-311G(df,p), 6-311+G(df,p), cc-pVDZ and aug-cc-pVDZ. The experimental harmonic frequencies of 122 small molecules and the zero-point vibrational energies of 39 small molecules are used to determine the scaling factors through the least-square fitting procedure. It was found that the scaling factors do not depend significantly on the basis sets considered. The vibrational frequency scaling factors evaluated by using the B98 and PBE0 functionals are recommended on the basis of smallest root mean square error. The zero-point vibrational energy scaling factors evaluated from the B972 functional with Pople's double-zeta basis set and the HCTH functional with Pople's triple-zeta basis set are recommended on the basis of smallest root mean square error.
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1. Introduction

Nowadays, the density functional theory (DFT) establishes itself as one of the most widely used quantum mechanical methodology in the scientific community. The increasing use of DFT can be understood when considering its accuracy and its computational speed [1,2]. Unfortunately, the exchange-correlation functional, the key component in the DFT formalism, is known to us in an approximate form and there is no systematic way to improve its accuracy as in the conventional ab initio methodology. So far, the most commonly used functional by chemists is the B3LYP hybrid functional introduced by the late John Pople and co-workers [3]. Several research groups are continually developing the approximate exchange-correlation functionals and have been introducing these functionals to the scientific community since the past decade. However, systematic comparison of the performance of these new functionals on experimental observables, with the exception of the thermochemistry, remains less common [1,2].

It is known that there is a systematic error in the calculated harmonic vibrational frequency when it is compared to the experimental fundamental vibrational frequency [4]. This is attributed to the inaccurate description of the electron–electron interaction and the neglect of anharmonicity. The scaling factor is commonly used by the experimentalists in order to correct the calculated value to match the experimental observable such as the vibrational frequencies and the thermal contributions to the enthalpy and entropy [5]. The scaling factor for the zero-point vibrational energies (ZPVEs) is used in the theoretical calculation at the high level composite methods such as G2 and G3 [6]. The early set of the vibrational frequency scaling factors was evaluated by Pople et al.; it was obtained at the Hartree–Fock (HF) and the second-order Møller–Plesset Perturbation theory (MP2) level [7,8]. Scott and Radom extended the investigation to the scaling factors for the vibrational frequencies, low-frequency vibrational modes, ZPVE and thermal contributions to enthalpy and entropy of

* Corresponding author.
E-mail addresses: scytt@mahidol.ac.th (Y. Tantirungrotechai), yt203y@yahoo.de (Y. Tantirungrotechai).

the early generation of exchange-correlation functionals, such as BLYP, BP86, B3LYP and B3PW91 [4]. Similarly, Halls and Schlegel evaluated the scaling factors for the vibrational frequencies of exchange-correlation functionals considered by Scott and Radom with the Sadlej basis set which was designed for the calculation of the electric properties of the molecule [9]. Recently, Truhlar and co-workers reported the scaling factors for zero-point vibrational energies of the exchange-correlation functionals, which they have been developing to obtain better prediction of thermochemical and kinetic quantities [10,11].

Although the collection of vibrational frequency scaling factors exists, the functionals covered are mostly those considered by Scott and Radom [12]. In this work, we report the scaling factors for the vibrational frequencies and zero-point vibrational energies of some recent exchange-correlation functionals calculated with various basis sets. These functionals, B972 [13,14], B98 [15], G96LYP [16], HCTH [17], OLYP [18], O3LYP [19], VSXC [20] and PBE0 [21], were considered as they were implemented in the GAUSSIAN 03 program [22].

Among the functionals considered, the HTCH, G96LYP and OLYP functionals are the generalized gradient approximation (GGA) functionals. The B972, O3LYP and PBE0 functionals are the hybrid functionals. The VSXC functional is the meta-GGA functionals, which depend on the kinetic energy density term. This functional is based on the density matrix expansion for the exchange-correlation functional up to the fourth order [20]. The B98 functional is the hybrid meta-GGA functional incorporating 21.98% HF exchange. The O3LYP functionals are the new functionals derived from the Lee–Yang–Parr correlation functional, the Handy's OPTX exchange functional which reparameterized the popular Becke88 exchange functional with a flexible formula, and the HF exact exchange [18]. The use of the OPTX functional reduces the weight of the HF exact exchange in O3LYP comparing to that in B3LYP [19]. While the Hartree–Fock exact exchange term in the O3LYP is obtained via the fitting procedure, the Hartree–Fock exact exchange term in the PBE0 functional is determined from the exact theory to be 0.25 [23,24]. The PBE0 or PBE1PBE hybrid functional performed well in many aspects including the excitation energy [25]. The B972, B98, HCTH and VSXC functionals contain large number of fitting parameters in the functional form, which are obtained through statistical fitting to molecular systems. The G96LYP contains the Gill96 exchange functional, which has a rather simple form and has only one parameter [16].

2. Computational details

The evaluation of the scaling factors in this work follows the methodology outlined by Scott and Radom [4]. The F1 set of molecules, consisting of 122 small molecules with the maximum of 10 atoms and the maximum of four heavy atoms in the first and the second rows, was considered for the vibrational frequency calculations [4]. This set comprises of 1066 frequencies. The smaller set of mostly diatomic molecules, denoted Z1, of 39 molecules was considered for

the zero-point vibrational energies [4]. The exchange-correlation functionals employed in this study were the B972, B98, G96LYP, HCTH, OLYP, O3LYP, VSXC and PBE0 functionals. The basis sets used were the 3-21G, 6-31G(d), 6-31+G(d), 6-31G(d,p), 6-311G(d,p), 6-311G(df,p), 6-311+G(df,p), cc-pVDZ and aug-cc-pVDZ. The molecules were firstly optimized at given methodologies, then the analytic harmonic vibrational frequencies were evaluated. The scaling factors λ for vibrational frequencies and zero-point vibrational energies were evaluated by minimizing the square error between the calculated and the experimental values

$$\Delta_{\text{vib}} = \sum_i^{\text{all}} (\lambda\omega_i - \tilde{v}_i)^2 \tag{1}$$

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

where ω_i and $\tilde{v}_i$ are the ith calculated harmonic and ith experimental fundamental frequencies (in cm^{-1}), respectively. The $\text{ZPVE}_i^{\text{theor}}$ and $\text{ZPVE}_i^{\text{expt}}$ are the ith calculated harmonic and ith experimental ZPVEs, respectively. The experimental ZPVEs are obtained by using the experimental harmonic frequencies and their associated anharmonic corrections [26]. The sum in both equations is overall vibrational modes considered.

The experimental values for the vibrational frequencies and the ZPVEs were the same set as used by Scott and Radom [26–32]. The fine numerical grid option tight SCF convergence criteria were used throughout. All the calculations were performed by using the GAUSSIAN 03 rev. B7 program running on PCs running the Linux operating system [22].

3. Results and discussion

Tables 1 and 2 report the scaling factors for the vibrational frequencies and ZPVEs, respectively. In each table, the root mean square errors of vibrational frequencies and zero-point vibrational energies are tabulated in parenthesis. The scaling factors for two quantities are not the same. The scaling factor for ZPVE is slightly greater than that for vibrational frequency among a given combination of functional and basis set. Scott and Radom discussed the reason why the scaling factors for the vibrational frequency and the ZPVE are different [4]. As one would expect, a smaller and incomplete basis set like the 3-21G set gives the scaling factors with the greatest root mean square error. For any given functional, improving the basis set quality generally results in a better correlation of the calculated vibrational frequencies and the ZPVEs with the experimental values. By comparing the Pople's double-zeta basis set with the Dunning's double-zeta correlation-consistent basis set, the 6-31G(d) and 6-31+G(d) sets seem to perform better than the cc-pVDZ and aug-cc-pVDZ sets, judging from smaller root mean square error. It is observed that the addition of diffuse function to the cc-pVDZ set increases the root mean square error of the vibrational frequency scaling factors.

Table 1
The vibrational frequency scaling factors evaluated at several combinations of exchange-correlation functionals and basis sets

	B972	B98	G96LYP	HCTH	OLYP	O3LYP	PBE0	VSXC
3-21G	0.9621 (82)	0.9712 (82)	1.0020 (95)	0.9803 (89)	0.9893 (90)	0.9704 (82)	0.9627 (79)	0.9772 (98)
6-31G(d)	0.9520 (41)	0.9608 (36)	0.9929 (46)	0.9704 (44)	0.9782 (43)	0.9602 (42)	0.9519 (38)	0.9688 (44)
6-31+G(d)	0.9538 (41)	0.9630 (38)	0.9947 (47)	0.9728 (49)	0.9801 (46)	0.9625 (41)	0.9540 (39)	0.9712 (48)
6-31G(d,p)	0.9532 (38)	0.9625 (37)	0.9936 (45)	0.9713 (44)	0.9788 (43)	0.9615 (43)	0.9536 (39)	0.9686 (47)
6-311G(d,p)	0.9587 (38)	0.9675 (36)	0.9980 (45)	0.9762 (45)	0.9839 (44)	0.9671 (42)	0.9593 (39)	0.9736 (45)
6-311G(df,p)	0.9587 (43)	0.9666 (39)	0.9975 (42)	0.9767 (48)	0.9840 (42)	0.9671 (42)	0.9593 (40)	0.9734 (46)
6-311+G(df,p)	0.9593 (41)	0.9679 (36)	0.9978 (44)	0.9772 (46)	0.9849 (43)	0.9678 (42)	0.9601 (40)	0.9740 (46)
cc-pVDZ	0.9618 (45)	0.9710 (40)	1.0013 (47)	0.9791 (52)	0.9875 (49)	0.9696 (49)	0.9622 (45)	0.9770 (53)
aug-cc-pVDZ	0.9606 (48)	0.9707 (50)	1.0029 (55)	0.9790 (58)	0.9873 (56)	0.9701 (52)	0.9610 (49)	0.9758 (58)

The root mean square errors in cm^{-1} are quoted in parenthesis. The F1 set of molecules consisting of 1066 frequencies is used to determine the scaling factor [4].

Table 2
The ZPVE scaling factors evaluated at several combinations of exchange-correlation functionals and basis sets

	B972	B98	G96LYP	HCTH	OLYP	O3LYP	PBE0	VSXC
3-21G	0.9758 (0.34)	0.9850 (0.35)	1.0146 (0.41)	0.9935 (0.37)	1.0024 (0.38)	0.9852 (0.35)	0.9773 (0.34)	0.9870 (0.40)
6-31G(d)	0.9720 (0.08)	0.9809 (0.08)	1.0120 (0.13)	0.9911 (0.11)	0.9985 (0.12)	0.9817 (0.09)	0.9727 (0.08)	0.9879 (0.11)
6-31+G(d)	0.9739 (0.08)	0.9830 (0.08)	1.0139 (0.12)	0.9933 (0.10)	1.0007 (0.10)	0.9841 (0.08)	0.9748 (0.08)	0.9900 (0.10)
6-31G(d,p)	0.9740 (0.07)	0.9828 (0.08)	1.0126 (0.11)	0.9924 (0.08)	0.9997 (0.09)	0.9835 (0.08)	0.9750 (0.08)	0.9882 (0.09)
6-311G(d,p)	0.9793 (0.08)	0.9877 (0.09)	1.0165 (0.10)	0.9973 (0.08)	1.0045 (0.08)	0.9889 (0.08)	0.9807 (0.09)	0.9930 (0.09)
6-311G(df,p)	0.9793 (0.09)	0.9875 (0.09)	1.0159 (0.10)	0.9972 (0.08)	1.0046 (0.08)	0.9889 (0.09)	0.9807 (0.10)	0.9928 (0.09)
6-311+G(df,p)	0.9800 (0.08)	0.9882 (0.08)	1.0164 (0.09)	0.9981 (0.07)	1.0057 (0.07)	0.9898 (0.08)	0.9815 (0.09)	0.9938 (0.09)
cc-pVDZ	0.9824 (0.10)	0.9922 (0.10)	1.0227 (0.12)	1.0013 (0.10)	1.0092 (0.10)	0.9931 (0.10)	0.9838 (0.11)	0.9966 (0.11)
aug-cc-pVDZ	0.9854 (0.08)	0.9945 (0.08)	1.0237 (0.10)	0.9972 (0.10)	1.0046 (0.11)	0.9955 (0.08)	0.9807 (0.10)	0.9996 (0.08)

The root mean square errors in kilocalorie per mole are shown in parenthesis. The Z1 set of molecules containing 39 molecules is used to determine the scaling factor [4].

The scaling factors for the vibrational frequency are reported in Table 1. The tabulated scaling factors have the value in range of 0.95–1.00. For any given functional, changing the basis set causes only a slight change in the scaling factor. The scaling factor depends more on the exchange-correlation functional than on the basis set. For the 6-31G(d) basis set frequently used for the geometry optimization, the scaling factors in the order of increasing root mean square error are B98 (0.9608) < PBE0 (0.9519) < B972 (0.9520) < O3LYP (0.9602) < OLYP(0.9782) < HCTH (0.9704) < VSXC (0.9688) < G96LYP (0.9929). The G96LYP functional produces the scaling factor closest to 1, although the root mean square error is not the smallest among the functionals studied. This implies that the G96LYP functional predicts the harmonic vibrational frequency closest to the experimental fundamental frequency. The PBE0 and B98 functionals yield the scaling factors with the lowest root mean square error. The B98 and PBE0 functionals correlate well with the experiments and are recommended for the vibrational frequency calculation when the scaling factors are known.

Table 2 reports the ZPVE scaling factors. The ZPVE scaling factors are generally greater than the vibrational frequency scaling factors and are in the range of 0.97–1.02. As we improve the basis set quality, the root mean square errors generally decrease, as shown in Table 1. For the 6-31G(d) basis set which is frequently used for the geometry optimization, the scaling factors in the order of increasing root mean square error are B972 (0.9720) < PBE0 (0.9727) ≈ B98 (0.9809) < O3LYP (0.9817) < HCTH (0.9911) < VSXC (0.9879) < OLYP(0.9985) < G96LYP (1.0120). Generally, the HCTH and OLYP functionals give ZPVE scaling factors close to 1. The scaling factors from the G96LYP functional are

greatest with values around 1.01. The scaling factors from the B972 functional have the lowest root mean square error for the Pople's double-zeta basis sets while the HCTH functional performs best for the Pople's triple-zeta basis sets. The B972 functional with the Pople's double-zeta basis set and the HCTH functional with the Pople's triple-zeta basis set are, therefore, recommended for the ZPVE calculations on the basis of lowest root mean square error.

Tables 1 and 2 provide the information of the scaling factors that minimize the root mean square error at various functionals and basis sets. For overall data, the B98/6-31G(d) and B98/6-311+G(df,p) methods produce the vibrational frequency scaling factors with the smallest root mean square error of 36 cm^{-1} and the HCTH/6-311+G(df,p) and OLYP/6-311+G(df,p) methods result in the ZPVE scaling factors with the smallest root mean square error of 0.07 kcal/mol.

4. Conclusions

The scaling factors for the vibrational frequencies and the zero-point vibrational energies were evaluated with various combinations of the exchange-correlation functionals and basis sets. The scaling factor is less affected by the basis set than by the exchange-correlation functional. For the vibrational frequency, the PBE0 and B98 functionals are recommended as resulting in the scaling factor with the smallest root mean square error for all basis sets considered. The G96LYP functional predict the harmonic frequencies closest in value to the experimental fundamental frequencies. The ZPVE scaling factor is generally greater than the vibrational

frequency scaling factor for a given functional and basis set. The B972 functional with Pople's double-zeta basis set and the HCTH functional with Pople's triple-zeta basis set are recommended for the ZPVE calculation.

Acknowledgements

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