



A new, reduced set of scaling factors for both SQM and ESFF calculations

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ABSTRACT

Scaling methods are often used to facilitate the computational prediction and interpretation of vibrational spectra calculated on the basis of quadratic force fields. In this work, a new, reduced set of scaling factors is proposed for both scaled quantum mechanical (SQM) force fields and the recently proposed effective scaling frequency factor (ESFF) method. The calculations are based on a training set of 30 molecules (660 experimental frequencies). By an appropriate regrouping of internal coordinates we were able to reduce the number of scaling factors from 11 down to 9 without loss of quality in the scaled frequencies. The main difference between the new and previously used set of scaling factors is the splitting of the general non-hydrogen XX stretch into two subgroups that differ in their scaling factors by nearly 0.02. This increases flexibility in the 1000–2500 cm⁻¹ region.

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1. Introduction

It is well known that harmonic frequencies of a molecule obtained from a quadratic force field computed at *ab initio* or DFT levels of theory with the aid of a GF matrix method (see e.g. [1,2]) are often too high compared with the fundamentals observed in the experimental spectra. Much better agreement between the calculated and experimental frequencies is obtained using a wide variety of scaling methods, where scaling factors are applied either to force constants or to frequencies. Obviously, an extension of a set of scaling factors within a given method should give rise to better results, in that the root mean square (RMS) deviation between scaled and experimental vibrational frequencies becomes lower. However, the set of scaling factors should be kept as small as possible because of two main reasons. First, scaling factors should be given a strong physical meaning. Thus, we are faced with the problem of finding as many common features for the elements they are attributed to as possible. These features could be similar anharmonicities of some bonds, similar sensitivities to the neglect of a part of correlation effects and so on. Second, in the case of having as many scaling factors in the optimization procedure as the number of assigned vibrational modes, a zero value of the RMS

could be obtained (this is obviously pointless). A review of the recent literature on scaling procedures can be found in Ref. [3].

The well-established scaling approach, the so-called scaled quantum mechanical (SQM) force field approach [4], uses a limited set of scaling factors. They are, in fact, scaling factors for the elements of the force constant matrix, **F**. A set of 12 factors optimized first at DFT/BLYP/6-31G* and DFT/B3LYP/6-31G* levels [5] and reduced to 11 for DFT/B3LYP/6-31G* [6] was designed for an accurate determination of the vibrational spectra of typical organic molecules. Recently, an alternative approach, called effective scaling frequency factor (ESFF) approach [7], has been proposed. It uses effective scaling factors arising from a set of local scaling factors and the normalized diagonal potential energy distribution (PED) coefficients [8]. It was shown [9] that in a general case of molecules with various structural motifs, the ESFF method renders RMS values somewhat lower than SQM. On the other hand, quite significant lowering of RMS compared with SQM (by nearly 30%) was obtained for the set of related molecules appearing in Ref. [10].

Our recent observations [10,11] led to the conclusion that frequencies scaled applying the usual set of 11 factors deviate too much from fundamentals in the middle region of vibrational spectra. The reason is that the differences between harmonic and observed frequencies for modes involving the stretching of the different types of XX bonds (where X denotes a general non-hydrogen atom) are not the same for all bonds. They show a clear trend to increase along with the increase of the bond order. Therefore, regardless the scaling procedure, using the scaling

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factor optimized for XX single or conjugated bonds to describe a stretching of, for example a CO double bond, would lead to too high a scaled frequency. In addition, our initial calculations carried out on triazole compounds reveal that to obtain the correct sequence of scaled frequencies in the region where Ph stretching, PhH rocking as well as the stretching of a CN double bond appear (i.e. 1600–1500 cm^{-1}), different kinds of XX bonds should be given different scaling factors. Note that because the ESFF local factors for XX bonds and XXH valence angles have similar values [9], swapping of harmonic frequencies separated by more than 15 cm^{-1} is not possible with only one XX scaling factor. The present paper deals with this problem. It will also be shown that after appropriate regrouping of internal coordinates, we have been able to reduce the number of scaling factors to 9, and the results preserve their quality.

2. Computational details

The ESFF and SQM calculations presented in this work were based on a training set of 30 molecules proposed by Baker et al. [6]. The geometries of all molecules as well as the force constant matrices were obtained at the DFT (see e.g. [12]) level of theory using B3LYP [13,14] hybrid functional and 6-311G** basis set [15]. The calculations were carried out with the PQS quantum chemistry package [16,17]. A set of 660 assigned experimental frequencies was used [9]. The SQM calculations were carried out using the standard implementation of the method [18]. The ESFF calculations were carried out using our home-made program.

3. Results and discussion

In typical applications of the SQM approach, the grouping of *primitive* internal coordinates into 11 types, describing (i) XX stretching, (ii) CCl stretching, (iii) CH stretching, (iv) NH stretching, (v) OH stretching, (vi) XXX in-plane deformation, (vii) XXH in-plane deformation, (viii) HCH in-plane deformation, (ix) HNH in-plane deformation, (x) linear deformation, and (xi) all torsions, was

proposed [6]. Similar grouping of *natural* internal coordinates for scaling of the frequencies within the ESFF approach can also be made [9]. Note that the considerations based on the joint treatment of the SQM and ESFF scaling factors are possible only for the groups involving the bond stretching coordinates. Factors attributed to the bending coordinates are not so straightforward to compare because natural bending coordinates are linear combinations of primitive ones. However, in most cases the classification of a given natural coordinate to one of the above-mentioned types is obvious, as the linear combinations involve primitive coordinates of the same type (or there is a larger contribution coming from one type, e.g., a methylene group HCH scissoring coordinate reads $5\alpha_{\text{HCH}} + \alpha_{\text{XCY}}$ [19], so it can be classified as HXH). It should be noted, however, that there are natural coordinates that involve different types of equally weighted primitive coordinates (e.g., a methyl group symmetric deformation coordinate, which is a linear combination of primitive coordinates of XXH and HXH types).

The inspection of harmonic frequencies demonstrates that ESFF local scaling factors describing all different XH stretching modes should have similar values and, as in the original work [5], they should be included into one group (type). On the other hand, different types of XX bonds behave differently. For example, stronger anharmonicity of the XX double bond compared with the single bond is observed, and for this reason, these two should not be put into the same group. This is to be contrasted with the previous recommendations [5,6], where they were given the same scaling factor. In addition, a verification whether, for example, different types of XXX bending coordinates (and similarly XXH and HXH bending coordinates, *vide infra*) can be combined into one type, is also desirable.

To investigate the fact whether an alternative and more appropriate set of scaling factors exists, the initial, 25-parameter ESFF calculations for 30 molecules of a training set proposed by Baker et al. [6] based on all 660 frequencies [9] were first carried out. Table 1 shows all 25 scaling factors. The notation we adopted is as follows: X denotes a general non-hydrogen atom, and symbols (s), (c), (d), and (t) next to the bond denote a single, conjugated,

Table 1

Twenty-five ESFF local scaling factors and their standard deviations (SD) optimized for 660 frequencies of 30 molecules of a training set. X denotes a general non-hydrogen atom, and s, c, d, and t denote single, conjugated, double, and triple bonds, respectively. The theoretical spectra were obtained at the DFT/B3LYP/6-311G** level of theory. In addition, the number of modes with contribution from a given type of internal coordinate greater than 10, 20, 35 and 50% is also reported.

No.	Type of coordinate	Local factor		Number of frequencies			
		Value	SD	10%	20%	35%	50%
1	CC(s) str.	0.9868	0.0369	71	47	18	13
2	CC(c) str.	0.9753	0.0212	98	80	54	36
3	CC(d) str.	0.9653	0.0270	35	23	16	16
4	CN(s) str.	0.9883	0.0528	31	20	10	5
5	CN(c) str.	0.9524	0.1347	8	5	1	0
6	CN(t) str.	0.9520	0.0403	3	2	2	2
7	CO(s) str.	0.9873	0.0411	35	26	17	11
8	CO(d) str.	0.9608	0.0255	11	10	10	10
9	CCl str.	1.0237	0.1002	19	11	7	6
10	CH str.	0.9643	0.0035	118	118	118	118
11	OH str.	0.9552	0.0156	4	4	4	4
12	NH str.	0.9583	0.0117	8	8	8	8
13	XXX def. (chain)	0.9949	0.0520	65	49	42	32
14	XXX def. (4-membered ring)	0.9933	0.2772	2	2	1	0
15	XXX def. (5-membered ring)	0.9807	0.0657	11	7	5	5
16	XXX def. (6-membered ring)	0.9874	0.0373	61	45	35	27
17	XXH def. (chain)	0.9812	0.0198	79	60	49	39
18	XXH def. (ring)	0.9807	0.0153	166	128	92	71
19	HCH def. (chain)	0.9770	0.0181	41	32	29	28
20	HCH def. (ring)	0.9708	0.0312	9	8	8	7
21	Methyl sym. def.	0.9790	0.0304	15	13	11	10
22	HNH def.	0.9696	0.0607	3	3	2	2
23	Torsions (all)	0.9654	0.0384	101	78	64	58
24	Linear def.	0.9321	0.2043	7	6	4	2
25	Out-of-plane (all)	0.9800	0.0176	140	124	97	87

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