Journal of Molecular Spectroscopy 264 (2010) 66–74

Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

An effective scaling frequency factor method for scaling of harmonic vibrational frequencies: The use of redundant primitive coordinates

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ARTICLE INFO

Article history:
Received 11 August 2010
In revised form 10 September 2010
Available online 16 September 2010

Keywords:
Scaling procedures
Harmonic approximation
ESFF
SQM
Redundant primitive coordinates
Transferability

ABSTRACT

A modified effective scaling frequency factor (ESFF) method that takes advantage of the potential energy distribution (PED) coefficients calculated in the basis of redundant primitive internal coordinates is presented. This approach is simpler and more flexible than that based on the natural internal coordinates. The sets of optimal scaling factors for routine 9- and 11-parameter ESFF calculations based on B3LYP/6-311G** force fields are derived from Baker's training set of 30 molecules (660 frequencies). The calculated root-mean-square (RMS) deviations for all frequencies are 11.42 and 11.44 cm^{-1} for 9- and 11-parameter scaling, respectively. They are somewhat lower than in the case of ordinary ESFF calculations. The new sets of factors seem to be particularly well suited for scaling of frequencies in the middle region of the vibrational spectra (1000–2500 cm^{-1}) – the RMS values in this range are 8.37 for 9-, and 9.56 cm^{-1} for 11-parameter scaling. These values are to be compared with 9.20 and 10.29 cm^{-1}, respectively, calculated within the natural coordinates based ESFF formalism.

1. Introduction

Quadratic potential energy surface (PES) of a molecule is a reasonable approximation of the real PES assuming that small atomic displacements from the expansion point in the Taylor series (typically, an equilibrium geometry) are considered. When calculated at high theoretical level it is capable of providing harmonic frequencies and normal modes that can be attributed to fundamentals observed in a variety of vibrational spectra (IR, Raman, etc.). This can be accomplished my means of the GF matrix method [1,2]. Harmonic frequencies often remain in large error compared to fundamentals – thus, they have to be corrected. One way is to use the cubic and possibly higher-order terms in the expansion of PES (see e.g. [3–5] and references therein). However, any extension of PES beyond the quadratic form is extremely demanding from the computational point of view, and therefore such applications are not practical for large systems. Empirical scaling of the quadratic force constants or harmonic frequencies of a molecule is an alternative and efficient method of obtaining accurate theoretical vibrational spectra. The computational cost of calculating the corrected frequencies is practically the same as in the case of ordinary harmonic frequency calculations. Scaling methods are also known to provide corrections for the deficiencies of the approximations used in order to obtain the force constant matrix (the neglect of a part of correlation effects in the wave function, the incompleteness of a basis set etc.).

The leading method in the field of scaling is the scaled quantum mechanical (SQM) force field method [6]. The method was first implemented for the force fields expressed in terms of the non-redundant linearly independent natural internal coordinates [7]. Such coordinates, often referred to as local-symmetry coordinates, are linear combinations of primitive coordinates [8]. The basis for the SQM method was then reformulated [9], and now the standard, commercial implementation of the method [10] scales directly the primitive valence force constants. In both formalisms the coordinates are classified into chemically similar groups; the scaling factor for all coordinates within a given group is the same.

Recently, an alternative multi-parameter scaling method, called an effective scaling frequency factor (ESFF) method, was proposed [11]. The idea of classification of coordinates is retained in ESFF. However, in contrast to SQM, it is a frequency scaling procedure. Each harmonic frequency is scaled by its own, effective scaling factor (ESF). ESFs are constructed from the limited set of the so-called local scaling factors (LSFs), as their sums weighted by the contributions of local modes to the given normal mode. The contributions can be determined from the normalized diagonal potential energy distribution (PED) coefficients [12] after solving the vibrational problem. The original implementation of the ESFF procedure is based on the transformation of the Cartesian force constants into the set of linearly independent natural internal coordinates. Thus, the calculated PED coefficients correspond to the contributions of the local-symmetry motions that participate in the given overall

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doi:10.1016/j.jms.2010.09.004

(normal) molecular motion. Clearly, the constraints imposed on the weights of primitive coordinates in the given natural coordinate [8] may not fully account for the contributions of primitive internals in a given mode in some cases. This will be shown in Section 4.1 where the comparison of two different sets of PED coefficients (i.e. these calculated in the basis of non-redundant natural and redundant primitive internal coordinates) is reported. In view of the assumptions of the ESFF method this may constitute a disadvantage; a full set of the redundant primitive internal coordinates seems to be more flexible in this respect. In spite of that, the ESFF procedure turned out to be well suited for the calculations of the vibrational spectra. The LSFs were carefully checked for transferability [13]. The training set of molecules proposed by Baker et al. [9] was used, and the set of 660 experimental bands found by us previously was considered. The calculations revealed that the LSFs are at least as well transferable as the force constant factors of the SQM procedure. A slight reduction of the overall root-mean-square deviation (RMS) was even obtained. This enabled us to conclude that ESFF may be an alternative to SQM – it is simpler and performs equally well as far as frequencies are concerned. The high quality of the vibrational spectra predicted by the ESFF method was confirmed in the paper devoted to reducing of the number of types of internal coordinates the scaling factors are attributed to [14], as well as by other applications [15,16].

In this paper a new formalism of the ESFF method based on the transformation of the Cartesian force constants into a redundant set of primitive internal coordinates is presented. Apart from the (expected) above-mentioned higher flexibility of this set the obvious advantage of the new formalism consists in simplification of the ESFF calculations. All primitive coordinates were easily and automatically generated on the basis of the atomic connectivities. Thus, the tedious manual generation of the natural internal coordinates we were carrying out so far was avoided. In a view of the applications of the ESFF procedure to really large systems (we are currently working with the series of silicon-containing compounds and the representative fragments of macromolecules obtained in the processes of their polycondensation; other applications are also planned) this reformulation is absolutely necessary.

2. Modified ESFF method

The solution of the vibrational problem within the GF matrix formalism in the non-redundant internal coordinate representation $\mathbf{s}^T = (s_1, s_2, \ldots, s_{3N-6})$ [1,2],

$$\mathbf{F}_s \boldsymbol{\alpha}_s = \mathbf{G}_s^{-1} \boldsymbol{\alpha}_s \boldsymbol{\omega}^2, \tag{1}$$

provides, in addition to the harmonic frequencies ω_i, $i = 1,2,\ldots,3N-6$, an $\boldsymbol{\alpha}_s$ transformation matrix defining the relation between the internal coordinates $\mathbf{s}$ and the normal coordinates $\mathbf{Q}$, $\mathbf{Q}^T = (Q_1, Q_2, \ldots, Q_{3N-6})$, i.e.

$$\mathbf{s} = \boldsymbol{\alpha}_s \mathbf{Q}. \tag{2}$$

This matrix can be used to obtain the so-called PED coefficients [12]

$$p_{ii,k} = \frac{\alpha_{s,ik}^2 F_{s,ii}}{\sum_j \alpha_{s,jk}^2 F_{s,jj}} \tag{3}$$

which are the basic quantities in the ESFF procedure. The above-mentioned, diagonal PED coefficients determine the contributions of a given local motion (index i) to the kth normal mode. The reformulation of the ESFF procedure in terms of the redundant primitive coordinates $\mathbf{r}^T = (r_1, r_2, \ldots, r_K)$, where $K > 3N-6$, has to be based on the uniquely defined set of PED coefficients for a given set of $\mathbf{r}$. Thus the α_r matrix ($\mathbf{r} = \boldsymbol{\alpha}_r \mathbf{Q}$) as well as the $\mathbf{F}_r$ matrix have to be found. Since the force field of a molecule in the redundant set of internal coordinates is not uniquely defined we decided to use the canonical force constant matrix (see e.g. Refs. [17–23]).

The present version of our home-made ESFF program that takes advantage of the non-redundant set of natural internal coordinates was modified in the following way. The $\mathbf{B}_r$ matrix ($\mathbf{r} = \mathbf{B}_r \boldsymbol{\rho}$, where $\boldsymbol{\rho}$ is a column vector containing the Cartesian atomic displacements) can be easily found for any $\mathbf{r}$, and its Moore–Penrose generalized inverse $\mathbf{B}_r^-$ [24–26] (see also Ref. [27] for a summary of the formulas) fulfilling the Eckart conditions, can be determined. We use all primitive internal coordinates that follow from the atomic connectivities. The force constant matrix in the redundant coordinates representation

$$\mathbf{F}_r = (\mathbf{B}_r^-)^T \mathbf{f}^x \mathbf{B}_r^-, \tag{4}$$

where $\mathbf{f}^x$ denotes the Cartesian force constant matrix, was transformed to represent the canonical force field (Eq. (30) of Ref. [19]). The solution of the vibrational problem

$$\mathbf{F}_r \boldsymbol{\alpha}_r = \mathbf{G}_r^{-1} \boldsymbol{\alpha}_r \boldsymbol{\omega}^2, \tag{5}$$

in which the $\mathbf{G}_r^{-1}$ matrix is singular, was then carried out in the following way. First, the (rectangular) $\mathbf{A}$ transformation matrix to (some) non-redundant internal coordinate set $\mathbf{s}$ ($\mathbf{s} = \mathbf{A}\mathbf{r}$) was determined. We actually used $\mathbf{A} = \mathbf{O}^T$; $\mathbf{O}$ contains the eigenvectors that diagonalize $\mathbf{B}_r \mathbf{B}_r^T$ corresponding to non-zero eigenvalues. Then the Moore–Penrose inverse $\mathbf{B}_s^-$ of the $\mathbf{B}_s$ matrix ($\mathbf{B}_s = \mathbf{A}\mathbf{B}_r$) was found, the $\mathbf{F}_s$ matrix

$$\mathbf{F}_s = (\mathbf{B}_s^-)^T \mathbf{f}^x \mathbf{B}_s^- \tag{6}$$

was constructed, and the vibrational problem (1) was solved. The calculated frequencies were identical as these obtained on the basis of the Cartesian force fields using the PQS quantum chemistry package [28,29]. Since $\boldsymbol{\rho} = \mathbf{B}_s^- \mathbf{s} = \mathbf{B}_s^- \boldsymbol{\alpha}_s \mathbf{Q}$ and $\mathbf{r} = \mathbf{B}_r \boldsymbol{\rho} = \boldsymbol{\alpha}_r \mathbf{Q}$ we conclude that

$$\boldsymbol{\alpha}_r = \mathbf{B}_r \mathbf{B}_s^- \boldsymbol{\alpha}_s. \tag{7}$$

Having defined the $\boldsymbol{\alpha}_r$ and the canonical $\mathbf{F}_r$ matrices the PED coefficients can be uniquely defined according to Eq. (2), in which subscript "s" is to be replaced by "r". Then, the ESFF scaling procedure can be carried out in the usual way.

When working with the redundant internal coordinates the use of the canonical force constants appears to be a natural choice. As will be demonstrated the frequencies scaled within this new formalism are by no means inferior compared to these, based on the original, natural internal coordinates based formalism. However, we also implemented the modified scheme, in which the contributions of local modes to the given normal mode were calculated on the basis of the amplitudes $\boldsymbol{\alpha}$ only, i.e. we redefined $p_{ii,k}$ (note that they will no longer be called PEDs; the word "contributions" will be used instead) according to

$$p_{ii,k} = \frac{\alpha_{ik}^2}{\sum_j \alpha_{jk}^2}. \tag{8}$$

With this definition the ESFF scaling procedure will be referred to as ESFF2. To justify to some extent this modification we mention at this point that the deviations from the parabolic shape of PES (which are expected to be accounted for by the scaling procedures) increase along with an increase of the displacement of the internal coordinates from their equilibrium values regardless the value of the diagonal force constant. It should be remembered, however, that the anharmonicity of PES is also a function of force constants. Note that the proposed modification can be used in both formalisms of the ESFF method (i.e. based on the non-redundant natural and redundant primitive internal coordinates), and for this reason the subscripts "s" and "r" are missing in Eq. (8). In the following the ESFF2 results will also be reported.