Reviews

Scaling of quantum-mechanical molecular force fields

Yu. N. Panchenko

Department of Chemistry, M. V. Lomonosov Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: panchenk@physch.chem.msu.su

Comparative analysis of various methods of empirical scaling of quantum-mechanical harmonic molecular force fields has been performed. The efficiency of using each particular scaling technique was shown to depend on the theoretical level of the quantum-mechanical calculation. The Pulay method of scaling (congruent transformation of the force constant matrix) is applicable in the case where the relative accuracies of determination of diagonal and off-diagonal quantum-mechanical force constants are approximately equal. This requirement is satisfied for a quantum-mechanical force field determined close to the Hartree—Fock limit. This makes it possible to carry out its correction with maximum retention of the peculiarities inherent in the molecule under investigation.

Key words: molecular vibrations, quantum-mechanical calculation, force field.

1. Introduction

The philosophy of computational methods of vibrational spectroscopy[1—4] changed appreciably when quantum-mechanical programs for optimization of the geometry of a molecule and for analytical determination of its force field appeared. It is quantum-mechanical harmonic force fields that are widely used at present for the calculation of frequencies and modes of normal vibrations. However, they require a certain empirical correction. This is due to the more or less systematic overestimation of the force constants in the Hartree—Fock method, which depends on the basis set employed (see, for example, Ref. 5), and to the not so regular discrepancies in the Møller—Plesset theory.[6]

The necessity of the empirical correction is also quite obvious when the approximate density functional theory[7] is used in the computational vibrational spectroscopy. The calculations of the vibrational frequencies of benzene[8] and formamide[9] based on the theory of local density functional are quite illustrative in this respect.[7] In fact, the deviations of the calculated data from the well-known $\nu_{14}(B_{2u})$ experimental (anharmonic) frequencies for the C_6H_6 and C_6D_6 molecules are ~100 cm^{-1} (Ref. 8), and those for the $\nu_8(A')$ and $\nu_{12}(A'')$ frequencies for the $HCONH_2$ molecule are much greater than 100 cm^{-1} (Ref. 9). However, most of the other frequencies are reproduced with a normally accepted accuracy.[8,9] Abandonment of the correction of quantum-mechanical force field, especially in the case of these great deviations from the experimental results, can substantially complicate the theoretical analysis of the vibrational spectrum of a molecule and lead to mistakes in the assignment of the experimental frequencies.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 800—807, April, 1996.

2. Scaling methods

In order to retain the characteristic features of quantum-mechanical force fields, for example, a particular distribution of the signs of off-diagonal elements and an approximate ratio between the force constants, a smaller number of adjusting parameters is used in the empirical correction than the number of parameters in the traditional solution of the inverse vibrational problem in which the role of the latter was played by the variable force constants themselves. Therefore, several procedures for *scaling* the quantum-mechanical force fields presented below have been suggested.

A. Only diagonal force constants are scaled by fixed factors.[10]

B. Diagonal force constants are corrected with scaling factors that are found from experimental vibrational frequencies, the off-diagonal force constants not participating in the adjustment procedure.[11] This variant, like the previous one, is based on the assumption that the off-diagonal force constants are predicted properly by quantum-mechanical calculations of any level.

C. Diagonal force constants are divided into several sets, while all the off-diagonal constants are combined into one set. Each of these sets should possess its own scaling factor determined from experimental frequencies.[12] Thus, scaling of the off-diagonal force constants is also recognized as necessary.

D. The scaling factors for the off-diagonal force constants are determined as the arithmetic mean of the corresponding diagonal force constants.[13]

E. The matrix of the quantum-mechanical force constants is transformed congruently in internal coordinates (the modern Pulay method, see reviews[14,15]). This procedure consists in the transformation

$$F = D_{ii}^{1/2}\,\mathcal{F}\,D_{ii}^{1/2}, \qquad (1)$$

where $\mathcal{F}$ is the matrix of force constants, calculated, for example, in the Hartree—Fock approximation, and D is the diagonal matrix of the scaling factors. It has been shown[16] that the simultaneous scaling of the matrix of kinematic coefficients and matrix $\mathcal{F}$ is equivalent to the scaling of only the matrix of force constants.

This method is used either with the optimization of the scaling factors[17] or with their transfer in the series of related molecules without optimization.[17,18] It should be noted that all our calculations with the optimization or with the transfer of the scaling factors were carried out for optimized geometric parameters.[5,17,19–33]

Procedures ***D*** and ***E*** are based on the assumption that the relative accuracy of the determination of the diagonal and off-diagonal force constants by *ab initio* methods at any level is approximately the same.

F. The vibrational frequencies calculated directly are corrected without any modification of the theoretical harmonic force field.[34,35] This method for the force field scaling can be realized as mere multiplication of the calculated frequencies by the same factor (see, for example, Ref. 36), which is equivalent to procedure ***E*** with only one scaling factor being used (so-called *homogeneous* scaling[9]). This is the simplest limiting minimum case of scaling.

G. Solution of the inverse vibrational problem[4] with the use of actually the greatest number of scaling factors may be considered to be the maximum limiting case of scaling, because all the elements of the force field matrix vary, excluding, perhaps, a certain number of fixed elements, *i.e.*, those having scaling factors of 1 or 0 (the latter is applied to the off-diagonal elements set equal to zero). Besides, for some of the force constants, identical values, *i.e.*, identical scaling factors, other than 0 and 1, are normally used. The fact that the scaling factors themselves are not calculated at each iteration step of the solution of the inverse vibrational problem does not change the main point. The set of scaling factors can be obtained by dividing each element of the matrix of force constants, found at the last iteration step, by the corresponding matrix element of the initial quantum-mechanical force field.

Unlike the Pulay method[14,15] in which all the scaling factors in the case of a force field determined close to the Hartree—Fock limit are positive, approximately identical, and less than unity,[37] the set of factors obtained here does not obey in the general case anywhere near obvious regularities, regarding the sign of the factors for the off-diagonal force constants or their absolute values for all the force constants (except for the fixed ones). This is true, in particular, for a "regularized force field",[38] since the search for the solution nearest to $\mathcal{F}$ in the Euclidean norm ensures[39] the retention of the signs of the force constants and of the approximate ratio between their absolute values only in the ideal case, *i.e.*, in the case where the desired matrix is close to $\mathcal{F}$. However, in practical calculations, the norm of the difference between these matrices is large, because the calculated frequencies deviate from the experimental values by 10—20 % on the average. Therefore, substantial changes in the force matrix and, consequently, in the vibrational modes, may arise during the iteration procedure (see, for example, Ref. 38). Then the formal solution may be inconsistent with the physical requirements to the assignment of the vibrational frequencies that follow from the quantum-mechanical calculation. The introduction of the corresponding limitations on the assignment into the functional being minimized (see Ref. 38) is rather difficult, which dramatically restricts the possibilities of the regularization method.

Note that the required use of a great number of different scaling factors for the diagonal and off-diagonal elements of matrix $\mathcal{F}$ at a low level of the quantum-mechanical evaluation of $\mathcal{F}$ (actually, degeneration of scaling into the solution of the inverse vibrational problem) may also lead, in principle, to a change in the assignment. However, the use of sufficiently complete basis sets with an adequate account of the electron correlation affords scaling factors that are close to one another and do not differ substantially from unity,[5] which excludes the change in the assignment of the vibrational frequencies being calculated.

Here it is pertinent to mention the results of calculations[30] of the scaled force fields for $CH_2{=}NH$. The scaled field forces calculated for this molecule in the Hartree—Fock and Møller—Plesset approximations with basis sets of various qualities were compared to one another. The maximum deviation from the least value for the diagonal force constants on going from one level of the quantum-mechanical calculations to the other level did not exceed 3 %. For the off-diagonal matrix elements, whose values are greater than several hundredths, this deviation was 21 %, while for smaller elements, it reached 73 %. The increase in the scattering in the case of small off-diagonal elements is apparently due to the difference in the accuracy of the prediction of the diagonal and off-diagonal elements of matrix $\mathcal{F}$ made using quantum-mechanical calculations at various levels. Thus, even at a low accuracy of the estimation of matrix $\mathcal{F}$, the Pulay method[14,15] makes it possible in some cases to obtain scaled quantum-mechanical force fields that do not differ too much from those found using a relatively good approximation.

The search for the matrix of force constants, least deviating in its norm from matrix $\mathcal{F}$, by the regularization method[38] results in this matrix depending entirely on the level of the quantum-mechanical calculation, which gives substantially greater maximum deviations from the least values for diagonal and off-diagonal elements of the corrected force matrices, for example, in the case of the C_2F_6 molecule.[38] The corresponding deviations of the diagonal, medium off-diagonal, and small off-diagonal elements (see above) are 12, 98, and 200 % (see Ref. 40).

Hence, in the Pulay method,[14,15] attention is concentrated on *the manner* in which the correction of the quantum-mechanical force field $\mathcal{F}$ should be carried out with account for the physical requirements (retention of the modes of normal vibrations, *i.e.*, the distribution of signs and the ratio of the force constants), whereas in the regularization method,[38] attention is focused on *how much* $\mathcal{F}$ should be minimally modified from the viewpoint of the matrix norm, in order to achieve the best fit with the experiment. In the former case, qualitative agreement with $\mathcal{F}$ is attained (the modes of vibrations are retained), while in the latter case, formal quantitative agreement, corresponding to the least deviation of the resulting matrix from the initial matrix $\mathcal{F}$ in the matrix norm, is obtained.

This situation can be illustrated by Fig. 1 in which curve *1* conventionally describes the initial quantum-mechanical force field $\mathcal{F}$, and curves *2* and *3* describe the final force fields, *i.e.*, the scaled field F (see Eq. (1) and Refs. 14 and 15) and the "regularized" field F_r,[38] respectively. The points denote the experimental parameters (for example, vibrational frequencies) that have been used for the correction of the force field $\mathcal{F}$. The correction of curve *1* is conventionally reduced to its displacement and a variation of its form. When the scaling is carried out according to Pulay[14,15] using only one factor (homogeneous scaling), curve *1* is transformed unchanged into curve *2*. In some cases, this scaling makes it possible to assign experimental vibrational frequencies even of rotational isomers (see, for example, Ref. 21). If several similar scaling factors are used, curve *2* corresponds to a displaced and somewhat distorted curve *1*, and the deviation of the calculated vibrational frequencies from the experimental values does not exceed the generally admissible limit. An example is provided by the correction of the quantum-mechanical force fields of *trans*-1,3-butadiene,[5] in which the scattering of the scaling factors for the force field in the MP2/6-31 G*//MP2/6-31 G* approximation was 0.07 (the minimum value was 0.88 and the maximum value was 0.95). It is clear that with the scaling factors being so similar, the ratios between the elements of a force matrix virtually do not change, and the modes of vibrations for the frequencies calculated from $\mathcal{F}$ (see Eq. (1)), are retained almost completely.

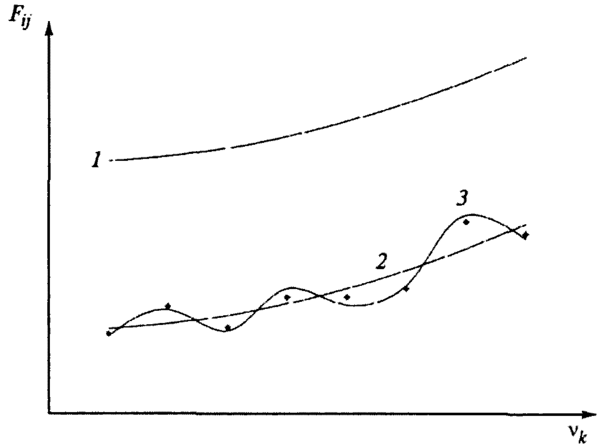

Fig. 1. Conventional graphical explanation of the scaling of the quantum-mechanical force field and its correction by solving the inverse vibrational problem (including the solution by regularization method). Presented fields: initial field (*1*); field corrected using one (common for all coordinates) scaling factor (*2*); field corrected by the least-squares method (*3*). The points denote arbitrary experimental parameters (for example, vibrational frequencies) used for the correction of the initial quantum-mechanical force field.

In the case where the inverse vibrational problem is solved by the least-squares method or by the regularization method,[38] when the disturbance of the distribution of signs of the off-diagonal elements and of the ratio between the diagonal and off-diagonal elements of the final force matrix F_r with respect to the initial matrix $\mathcal{F}$ in the practical calculations is admissible, curve *1* is transformed into a type *3* curve. This is caused by the fact that in the regularization method, the $\|AF_r - \Lambda\|^2 +$

$\alpha\|F_r - \mathcal{F}\|^2$ minimum condition is used (A is a nonlinear operator that assigns a set of computable Λ values to each matrix of force constants and α is an additional variable parameter, which is selected by a special procedure), with the calculated vibrational frequencies being 10—20 % higher than the experimental values. In fact, this leads to an inevitable considerable decrease in the diagonal force constants and to the compensation of this decrease by a variation of the absolute values and the signs of the off-diagonal elements of the force matrix. The resulting agreement of the calculated vibrational frequencies with their experimental analogs, due to the large number of fitting parameters, must be better than that in the case of curve *2*. However, the significant properties of the *ab initio* force matrix, which correspond to curve *1*, are lost. The latter indicates that the statement of the problem in the regularization method is obviously incorrect from the viewpoint of molecular vibrational physics.

This problem has been considered in more detail previously.[40—42] The software for scaling the quantum-mechanical force fields has been published.[43] The difference between the philosophies of scaling and solution of the inverse vibrational problem has been noted in a review.[44] A procedure similar to that reported recently[38] has been used previously[45] with the involvement of weighting factors.

3. Pulay method[14,15]

A comparison of the Pulay approach with other versions of scaling shows a number of advantages. The first is its invariance upon certain transformations of valence coordinates (for example, in method ***D***, this invariance is not fulfilled). The second advantage is that a small number of scaling factors, not exceeding the number of different quasi-equivalent coordinates, is used, *i.e.*, this number is smaller than the dimensionality of the square matrix $\mathcal{F}$. Furthermore, it has been shown that the application of this method to, for example, the force fields of the 1,3-butadiene molecule calculated with systematically increasing quality of the basis set and with subsequent account of the electron correlation in the second order of the Møller—Plesset perturbation theory leads to a consecutively decreasing number of different scaling factors and to a decrease in their scattering.[5] In addition, in relation to the $HCONH_2$ molecule it has been shown[9] that calculations with low-quality basis sets require separate scaling of the diagonal and off-diagonal force constants, *i.e.*, the number of scaling factors needed is greater than that in the Pulay method, while the latter could be applied only to the force fields found with high-quality basis sets. These calculations[5,9] indicate that the Pulay method is used most successfully in those cases where the relative accuracy of the determination of diagonal and off-diagonal elements of the force matrix is approximately the same. The experience of these calculations shows that this requirement is best fulfilled in the SCF approximation for the force constants determined close to the Hartree—Fock limit (see, for example, the results obtained for the rotational isomers of glyoxal[46]).

The theoretical justification of the Pulay method has been presented previously.[37] An idealized molecular model was considered; it was based on the following assumptions: realizability of the Born—Oppenheimer approximation, possibility of using the harmonic approximation for the force constants, accessibility of experimental harmonic frequencies, marginal magnitudes of the relativistic contributions to the force constants, and possibility of determining the theoretical force constants corresponding to the Hartree—Fock limit. Using the variational formalism for the first and second analytical derivatives of energy, it has been shown that for scaling to be successfully accomplished, the following conditions should be fulfilled: (1) relatively large differences between the energies of the ground and excited electronic states of the molecule; (2) singlet stability of the solution of the problem in the SCF approximation for the ground state[47]; (3) good localizability of the set of occupied molecular orbitals of the ground electronic state.

Taking into account these conditions, an *approximate* relationship between the exact (non-relativistic) square force constants and those close to the Hartree—Fock limit has been found.[37] Near the "exact" equilibrium nuclear configuration of the molecule, these values differ by a factor that is equal to the squared C_0 coefficient at the Hartree—Fock determinant in the configurational expansion of the exact electronic wave function:

$$\frac{d^2E}{dq^2} \approx C_0^2 \frac{d^2E_{HF}}{dq^2} \quad \text{or} \quad F_{ij} \approx C_0^2 \mathcal{F}_{ij}. \qquad (2)$$

Here E is the total energy of the molecule, and E_{HF} is its Hartree—Fock estimation. Equation (2) indicates that, generally speaking, the scaling factors should be identical. This equation is equivalent to the simplest scaling procedure ***E*** in which one common scaling factor $D_{ii} \approx C_0^2$ is used for all the internal coordinates (see Eq. (1)). Since the wave function is normalized, $C_0^2 \leq 1$. Thus, it was actually shown[37] that the force constants found by the SCF method close to the Hartree—Fock limit are approximately *linearly* related to the exact force constants (the CI scheme), *i.e.*, scaling efficiently takes into consideration the dynamic electron correlation.

It should be noted that separate scaling of some off-diagonal force constants by the Pulay method has been carried out[48] to reproduce the splitting of the frequency of the C=C stretching vibration in 1,3,5-hexatriene. However, this calculation cannot be regarded as an example of different accuracies of the determination of the diagonal and off-diagonal elements of the quantum-mechanical force field matrix, since the splitting mentioned above can probably be accounted for by perturbation caused by vibronic coupling (see Refs. 24, 26, 27 and references cited therein).

The Pulay method for the determination of the scaling factors could also be used in the case of Hartree—Fock force fields found with a basis set of rather low quality, when different relative errors may arise for the diagonal and off-diagonal force constants. This required invoking experimental geometry, instead of the optimized structural parameters, in the determination of the second derivatives of energy (*i.e.*, force constants). In some cases this approach gave plausible results (see reviews[14,15]). It is likely that the use of experimental geometry for determining quantum-mechanical force constants is similar, to a certain degree, to an increase in the level of the quantum-mechanical calculation, which usually leads to a better agreement of the series of geometrical parameters and the experimental structure.

In the Pulay method, the effects of anharmonicity are implicitly incorporated in the scaling factors. In relation to ethylene it has been shown[28] that allowance for the anharmonicity of the experimental vibrational frequencies gives a relatively small contribution to the values of scaling factors. The anharmonicity constants are known to possess the same signs and to substantially decrease with a decrease in the frequency of the fundamental vibration. However, since for various types of vibrations involving various atoms, they are quite different, anharmonicity can manifest itself as a certain scattering of the scaling factors even at a substantial increase in the quality of the calculations of the quantum-mechanical force field.

The Pulay method, like the majority of other scaling procedures, makes it possible to retain the distribution of the signs of all the elements of the quantum-mechanical matrix $\mathcal{F}$. However, the main distinction of this method from methods ***A—D*** and ***G*** presented above is the possibility of maintaining the approximate ratio between the absolute values of the elements in each row or each column of force matrix $\mathcal{F}$. Thus, the Pulay scaling makes it possible to carry out the correction of quantum-mechanical force field in a *regular* manner. Of course, the best result is achieved by virtue of scaling method *F*. However, it has been shown previously[5] that as the quality of the calculation in the SCF approximation increases, scattering of the scaling factors substantially decreases, which reflects the approach to variant ***F*** in which only one scaling factor is used, and the modes of vibrations do not change after the scaling.

The geometrical interpretation of scaling methods ***E*** and ***F*** has been reported previously.[39] The smallest variations of the modes of vibrations due to the Pulay scaling is observed in the case of vibrations that are most characteristic in the mode. It is of prime importance that these slight variations are determined by the inhomogeneity of the scaling factors, *i.e.*, by their deviations from the average value, rather than by their absolute values. It is obvious that for quantum-mechanical calculations that lead to irregular and greater deviations of the resulting frequencies from the experiment than those obtained for the force constants calculated close to the Hartree—Fock limit, scaling would most likely alter to a greater extent the modes of the vibrations that are least characteristic in mode and most close in frequency and that belong to the same type of symmetry.[16] Therefore, it seems more expedient to determine the quantum-mechanical force field in the SCF approximation close to the Hartree—Fock limit.

The use of the Møller—Plesset method with low-quality basis sets (see, for example, Ref. 38) normally leads to somewhat better agreement of some geometrical parameters with the experimental values, but decreases the accuracy of determination of the off-diagonal force constants. In this case, a larger number of scaling factors is needed than in the case of the matrix of force constants found close to the Hartree—Fock limit. As regards the agreement between the calculated and experimentally found geometric parameters, it should be noted that average, rather than equilibrium, values for the latter are usually reported. In addition, the relationship between the geometry found with various basis sets in the Hartree—Fock approximation and the corresponding experimental geometry has been analyzed.[49]

A further principal assumption made in scaling method ***E*** (apart from the assumed identical accuracies of the quantum-mechanical determination of the diagonal and off-diagonal force constants) is that the relative errors of the SCF approach in the calculation of force constants in the series of related compounds are approximately equal. This provides the basis for the transferability of the scaling factors in these series (for example, in the series of hydrocarbons with conjugated double bonds[24,26,27] or of rotational isomers[17,19–23,25–27,31–33]). In this case, a classification in terms of the pairs of bound atoms[50–52] or its simplified versions are used.

The possibility of transferring the scaling factors over the series of related molecules has been considered.[53] In fact, taking into account the localizability of MO, the C_0 coefficients can be referred to particular internal coordinates. For the q_i and q_j internal coordinates of molecule M, the *exact* relationship $F_{ij}{}^{\mathrm{M}} = C_0{}^2\mathcal{F}_{ij}{}^{\mathrm{M}} + W_{ij}{}^{\mathrm{M}}$ can be given, where $W_{ij}{}^{\mathrm{M}}$ is the minor compensating term, which has a local character for all the molecules M′ that incorporate the same structural fragments and have the same q_i and q_j nuclear coordinates as the molecule M.[37] This statement is based on the fact that the variations of the localized MO for related compounds are small. The compensating contributions for the pairs of coordinates of substantially distant groups of atoms are obviously equal to zero. Therefore, the $\gamma_{ij} = W_{ij}{}^{\mathrm{M}'}/\mathcal{F}_{ij}{}^{\mathrm{M}'}$ expression may be regarded as a characteristic of the q_i and q_j pair of coordinates rather than a characteristic of the M or M′ molecule as a whole. This follows from the local character of $W_{ij}{}^{\mathrm{M}'}$ and $\mathcal{F}_{ij}{}^{\mathrm{M}'}$ and from the small magnitude of $W_{ij}{}^{\mathrm{M}'}$ compared to $\mathcal{F}_{ij}{}^{\mathrm{M}'}$. If γ_{ij} still depends slightly on M′, the variations of γ_{ij} on going from M to M′ are small. Then

$$F^{\mathrm{M}}{}_{ij} = C_0{}^2\mathcal{F}_{ij}{}^{\mathrm{M}} + \gamma_{ij}\mathcal{F}_{ij}{}^{\mathrm{M}} = (C_0{}^2 + \gamma_{ij})\mathcal{F}_{ij}{}^{\mathrm{M}}.$$

In view of the fact that $C_0^2 \approx 1$ and γ_{ij} is small, the error resulting from the replacement of $(1 + \gamma_{ij})$ by $[(1 + \gamma_{ii})(1 + \gamma_{jj})]^{1/2}$ may also be considered to be small, and for force fields, $F_{ij}^{\mathrm{M}} = D_{ii}^{1/2}D_{jj}^{1/2}\mathcal{F}_{ij}^{\mathrm{M}}$, where D_{ii} and D_{jj} are the scaling factors (see Eq. (1)) depending only on the q_i and q_j coordinates. Generally speaking, this reasoning suggests that the scaling factors can be transferred over the series of related molecules. However, it should be noted that the property of "locality" is possessed, first of all, by valence coordinates[1—4] and their linear combinations, for example, the coordinates of local symmetry.[54]

In a variety of cases, scaling factors are transferable even for the force constants calculated with basis sets of relatively low quality, far removed from the Hartree—Fock limit.[14,15] However, the case of the glyoxal molecule has shown[46] that when rotational isomers exist, the transfer of the scaling factors of the force field of one conformer to the other requires that the quantum-mechanical force constants be obtained in AO basis sets that are sufficiently similar in their properties to the complete ones.

The transferability of scaling factors has been tested with a series of related compounds, namely, ethylene, *trans*-1,3-butadiene, *trans,Trans,trans*-1,3,5-hexatriene, and *trans,Cis,trans*-1,3,5-hexatriene[24] and for all-*trans* 1,3,5,7-octatetraene[27] and 1,3,5,7,9-decapentaene.[55] The scaling factors found[17] for *trans*-1,3-butadiene were used for the above series of molecules. This is due to the fact that the conjugated system of butadiene has a number of features not possessed by ethylene. The assignment of the experimental vibrational frequencies of butadiene was based on the data on its 12 isotopomers. The scaling factors also efficiently took into account the anharmonicity of these frequencies. The calculations in the SCF approximation confirmed completely the transferability of scaling factors in the above series of related compounds.[24,27,55]

It is of interest that this procedure made it possible to demonstrate to a certain extent the significance of the vibronic coupling in oligoenes.[24,27,55] This manifested itself in the overestimation of the calculated frequency of the totally symmetrical C=C vibration, whose experimental value is affected by a contribution of the vibronic coupling, which is not taken into account in the Hartree—Fock approximation. Generally speaking, the first of the three conditions[37] necessary for successful scaling is not actually fulfilled in the case of oligoenes. Therefore, for 1,3,5-hexatriene, a special scaling factor for the coordinate of the C=C bond stretching was introduced; this made it possible to efficiently take into account the vibronic decrease in its stretching frequency[24] and to attain good agreement of the results of calculations with experimental results for the above-mentioned vibrational frequencies of oligoenes.[27,55] It should be noted that *ab initio* calculations of the energies of the ground and excited singlet states of butadiene, hexatriene, and octatetraene have shown[56] that the energy gap in the series of these molecules regularly decreases. While using the scaling factors, one should also bear in mind that the deviations of frequencies calculated by *ab initio* methods from experimental results are mostly due to the fact that these methods are rough and due to the anharmonicity of the experimental vibrational frequencies.[57]

* * *

The use of a particular scaling procedure depends objectively on the level of the quantum-mechanical calculation that allows the use of a greater or smaller number of fitting parameters, since the quality of the force field calculated by an *ab initio* method depends on whether or not the basis set is complete and also on the extent to which the electron correlation effects have been taken into account. If the quantum-mechanical calculation of force constants is carried out in the SCF approximation close to the Hartree—Fock limit, the Pulay method[14,15] in which the geometrical-mean values of the corresponding diagonal scaling factors are used for the off-diagonal elements of the force matrix should correct quite efficiently the drawbacks of the force field associated with the fact that the dynamic electron correlation is not taken into account.[37] This means that the ratios between the elements in each line or each column of the matrix of force constants $\mathcal{F}$, calculated near the Hartree—Fock limit, are such that their successful linear correction is possible, in order to achieve a plausible agreement with the experimental vibrational frequencies.

Numerous calculations have shown (see, for example, Refs. 17, 19—33) that the number of scaling factors, determined by the number of dissimilar quasi-equivalent molecular coordinates, is quite sufficient for performing the corresponding correction of the force field. The application of the Pulay scaling[14,15] to force fields, calculated in the SCF approximation close to the Hartree—Fock limit, makes it possible to make the best use of the advantages of this approach, which include the most complete retention of the properties of quantum-mechanical force constants and the efficient allowance for the dynamic electron correlation.[40—42]

An extension of the basis set and inclusion of a certain part of the correlation energy (for example, in the second order of the Møller—Plesset perturbation theory) results in the empirical scaling factors approaching unity, the number needed for reproducing the experimental vibrational frequencies with a desired degree of accuracy decreasing simultaneously. This has been shown,[5] despite the fact that the *ab initio* calculation of the vibrational frequencies was carried out in the harmonic approximation, and the anharmonicity was efficiently taken into account by scaling factors. The observed transferability of the scaling factors in a series of related compounds obviously indicates that the corrections for anharmonicity in similar structural groups are constant.

As regards the minimal and maximal limiting cases of scaling, *i.e.*, homogeneous scaling and the solution of the inverse vibrational problem with a number of fixed force constants and also force constants taken equal to one another, the former is an ideal case, in which only one multiplier for all the coordinates is used, and scaling is accomplished most regularly. This leads to the complete retention of all the characteristic features of the force matrix (the distribution of signs and the ratio between the force constants) and, consequently of the quantum-mechanical values of molecular parameters such as, for example, the intensities of IR and Raman bands.

The inverse vibrational problem with a number of fixed and equal force constants (for example, determination of "regularized force fields"[38]) is actually a variant with the maximum number of scaling factors with no retention of the distribution of signs or the approximate ratio between the absolute values of the force constants, *i.e.*, it is the scaling carried out by the least regular procedure, and, therefore, it is the least acceptable approach. Attempts to reduce the number of variable parameters lead to the appearance of various ways of scaling (instead of the traditional solution of the inverse vibrational problem) based on the quantum-mechanical force field as the initial approximation. It should be stressed that theoretically justified scaling is possible only in the case where the quantum-mechanical force fields to be scaled have been obtained by an *ab initio* method of sufficiently high level.[37]

Other procedures for the empirical correction of the harmonic quantum-mechanical force field have been considered in a review.[40] Of the two variants of the correction of this force field[58] and the quantum-mechanical vibrational frequencies[35] suggested recently, the former possesses predictive possibilities, apparently, only for isotopomers of a molecule, while the latter is applicable only to the frequencies of one of these isotopomers.

The work was carried out with financial support of the Russian Foundation for Basic Research (Project No. 93-03-18386).

References

1. M. V. Vol'kenshtein, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Vibrations of Molecules*], Gostekhizdat, Moscow, 1949, **1**, 600 pp. (in Russian).
2. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York—London—Toronto, 1955.
3. S. J. Cyvin, *Molecular Vibrations and Mean Square Amplitudes*, Universitetforlaget, Oslo, 1968.
4. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Vibrations of Molecules*], Nauka, Moscow, 1972, 699 pp. (in Rissian).
5. Ch. W. Bock, Yu. N. Panchenko, and V. I. Pupyshev, *J. Comput. Chem.*, 1990, **11**, 623.
6. C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.
7. T. Ziegler, *Chem. Rev.*, 1991, **91**, 651.
8. A. Bérces and T. Ziegler, *J. Chem. Phys.*, 1993, **98**, 4793.
9. J. Florián and B. G. Johnson, *J. Phys. Chem.*, 1994, **98**, 3681.
10. P. Pulay and W. Meyer, *J. Mol. Spectrosc.*, 1971, **40**, 59.
11. W. Bleicher and P. Botschwina, *Mol. Phys.*, 1975, **30**, 1029.
12. C. E. Blom and C. Altona, *Mol. Phys.*, 1976, **31**, 1377.
13. K. W. Hipps and R. D. Poshusta, *J. Phys. Chem.*, 1982, **86**, 4112.
14. G. Fogarasi and P. Pulay, *Annu. Rev. Phys. Chem.*, 1984, **35**, 191.
15. G. Fogarasi and P. Pulay, in *Vibrational Spectra and Structure*, Ed. J. R. Durig, Elsevier, Amsterdam, 1985, **14**, 125.
16. V. I. Pupyshev, N. F. Stepanov, S. V. Krasnoshchiokov, G. R. De Maré, and Yu. N. Panchenko, *J. Mol. Struct.*, 1996, in press.
17. Ch. W. Bock, Yu. N. Panchenko, S. V. Krasnoshchiokov, and V. I. Pupyshev, *J. Mol. Struct.*, 1985, **129**, 57.
18. Yu. N. Panchenkò, P. Pulay, and F. Török, *J. Mol. Struct.*, 1976, **34**, 283.
19. Ch. W. Bock, Yu. N. Panchenko, S. V. Krasnoshchiokov, and R. Aroca, *J. Mol. Struct.*, 1987, **160**, 337.
20. Yu. N. Panchenko, S. V. Krasnoshchiokov, and Ch. W. Bock, *J. Comput. Chem.*, 1988, **9**, 443.
21. Ch. W. Bock, Yu. N. Panchenko, and S. V. Krasnoshchiokov, *Chem. Phys.*, 1988, **125**, 63.
22. Ch. W. Bock and Yu. N. Panchenko, *J. Mol. Struct. (THEOCHEM)*, 1989, **187**, 69.
23. Ch. W. Bock and Yu. N. Panchenko, *J. Mol. Struct.*, 1990, **221**, 159.
24. Ch. W. Bock, R. McDiarmid, Yu. N. Panchenko, V. I. Pupyshev, and S. V. Krasnoshchiokov, *J. Mol. Struct.*, 1990, **222**, 415.
25. Ch. W. Bock, Yu. N. Panchenko, and S. V. Krasnoshchiokov, *Chem. Phys.*, 1990, **147**, 65.
26. Yu. N. Panchenko, S. V. Krasnoshchiokov, P. George, and Ch. W. Bock, *Struct. Chem.*, 1992, **3**, 15.
27. Yu. N. Panchenko and Ch. W. Bock, *Struct. Chem.*, 1992, **3**, 27.
28. S. H. Chough, Yu. N. Panchenko, and Ch. W. Bock, *J. Mol. Struct.*, 1992, **272**, 179.
29. Yu. N. Panchenko, G. R. De Maré, and Ch. W. Bock, *J. Mol. Struct.*, 1992, **272**, 161.
30. G. R. De Maré, Yu. N. Panchenko, V. I. Pupyshev, and N. F. Stepanov, *Vestn. Mosk. Univ., Ser. Khim.*, 1993, **34**, No. 1, 3 [*Moscow Univ. Chem. Bull.*, 1993, **48**, No. 1, 3 (Engl. Transl.)].
31. G. R. De Maré, Yu. N. Panchenko, and Ch. W. Bock, *J. Phys. Chem.*, 1994, **98**, 1416.
32. G. R. De Maré and Yu. N. Panchenko, *J. Phys. Chem.*, 1994, **98**, 8315.
33. G. R. De Maré and Yu. N. Panchenko, *Zh. Fiz. Khim.*, 1994, **68**, 1270 [*Russ. J. Phys. Chem.*, 1994, **68**, 1148 (Engl. Transl.)].
34. J. D. Goddard and D. J. Clothier, *J. Chem. Phys.*, 1982, **86**, 5039.
35. J. Y. Lee, O. Hahn, S. J. Lee, B. J. Mhin, M. S. Lee, and K. S. Kim, *J. Phys. Chem.*, 1995, **99**, 2262; J. Y. Lee, O. Hahn, S. J. Lee, H. S. Choi, H. Shim, B. J. Mhin, and K. S. Kim, *J. Phys. Chem.*, 1995, **99**, 1913.
36. J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem., Symp.*, 1981, **15**, 269.

37. V. I. Pupyshev, Yu. N. Panchenko, Ch. W. Bock, and G. Pongor, *J. Chem. Phys.*, 1991, **94**, 1247.
38. G. M. Kuramshina, F. Weinhold, I. V. Kochikov, Yu. A. Pentin, and A. G. Yagola, *Zh. Fiz. Khim.*, 1994, **68**, 401 [*Russ. J. Phys. Chem.*, 1994, **68**, 358 (Engl. Transl.)].
39. T. Kato, *Perturbation Theory for Linear Operators*, Springer Verlag, Berlin, Heidelberg, New York, 1966.
40. Yu. N. Panchenko and N. F. Stepanov, *Zh. Fiz. Khim.*, 1995, **69**, 592 [*Russ. J. Phys. Chem.*, 1995, **69**, 535 (Engl. Transl.)].
41. N. F. Stepanov, G. R. De Maré, and Yu. N. Panchenko, *J. Mol. Struct. (THEOCHEM)*, 1995, **342**, 9.
42. Yu. N. Panchenko, G. R. De Maré, and N. F. Stepanov, *J. Mol. Struct.*, 1995, **348**, 413.
43. S. V. Krasnoshchekov, A. V. Abramenkov, and Yu. N. Panchenko, *Zh. Fiz. Khim.*, 1996, **70**, in press [*Russ. J. Phys. Chem.*, 1996, **70**, in press (Engl. Transl.)].
44. P. P. Shorygin, K. Ya. Burshtein, *Usp. Khim.*, 1981, **50**, 1345 [*Russ. Chem. Rev.*, 1981, **50**, 701 (Engl. Transl.)].
45. T.-K. Ha, R. Meyer, and Hs. H. Günthard, *Chem. Phys. Lett.*, 1978, **59**, 17.
46. Yu. N. Panchenko, G. R. De Maré, and V. I. Pupyshev, *J. Phys. Chem.*, 1995, **99**, 17544.
47. M. M. Mestechkin, in *Nestabil'nost' khartri-fokovskikh uravnenii i molekulyarnaya stabil'nost'* [*Instability of Hartree—Fock Equations and Molecular Stability*], Naukova dumka, Kiev, 1986, 176 (in Russian).
48. G. Fogarasi, P. G. Szalay, P. L. Liescheski, J. E. Boggs, and P. Pulay, *J. Mol. Struct.*, 1987, **151**, 341.
49. J. E. Boggs, in *Accurate Molecular Structures*, Eds. A. Domenicano and I. Hargittai, Oxford University Press, New York, 1992, Ch. 13.
50. V. M. Tatevskii, in *Stroenie i fiziko-khimicheskie svoistva molekul i veshchestv* [*Structure and Physicochemical Properties of Molecules and Substances*], Izd. Moskovskogo Gos. Univ., Moscow, 1993, 40 (in Russian).
51. V. M. Tatevskii, *Vestn. Mosk. Univ., Khimiya, Ser. II*, 1995, **36**, 187 [*Moscow Univ. Chem. Bull.*, 1995, **50** (Engl. Transl.)].
52. V. M. Tatevskii, *Vestn. Mosk. Univ., Khimiya, Ser. II*, 1996, **37**, in press [*Moscow Univ. Chem. Bull.*, 1996, **51** (Engl. Transl.)].
53. Yu. N. Panchenko, *Vestn. Mosk. Univ., Khimiya, Ser. II*, 1991, **32**, 561 [*Moscow Univ. Chem. Bull.*, 1991, **46**, No. 6, 25 (Engl. Transl.)].
54. P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, 1979, **101**, 2550.
55. Ch. W. Bock, Yu. N. Panchenko, R. Aroca, and G. R. De Maré, *Struct. Chem.*, 1996, in press.
56. M. Aoyagi, I. Ohmine, and B. E. Kohler, *J. Phys. Chem.*, 1990, **94**, 3922.
57. V. I. Pupyshev and Yu. N. Panchenko, *Zh. Prikl. Spektrosk.*, 1991, **55**, 945 [*J. Appl. Spectrosc.*, 1991, **55** (Engl. Transl.)].
58. A. Vijay and D. N. Sathyanarayana, *J. Mol. Struct. (THEOCHEM)*, 1994, **311**, 87; 1994, **328**, 269.

Received December 1, 1995