A new scaling algorithm for predicting vibrational spectra of polyatomic molecules[†]

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Abstract.   We propose here a relationship between the off-diagonal and diagonal force constants which is valid theoretically under harmonic approximation provided the L matrix is available from some theoretical calculation using $L^{T}FL = \Lambda$.

1. Introduction

Theoretical prediction of vibrational spectra of polyatomic molecules has been the goal for a long time.[1–7] The recent advances in *ab initio* and density functional methods (DFT) met considerable success in the prediction of vibrational spectra of small molecules. Still the routine calculations of vibrational frequencies of medium and large molecules have substantial error compared to the experimental frequencies.[7] Finite basis set, partial inclusion of electron correlation, harmonic approximation are some of the reasons for the discrepancies.[7] The anharmonic calculations although available with Gaussian03[8] this option is very time consuming for medium or large molecules with a large basis set. Also, this option is available only for less symmetric molecules. The accuracy is similar to that achieved through scaling. The disagreements between calculated and experimental frequencies are empirically corrected by scaling algorithms which are either applied to force constants or to the frequencies. The assumption made is that the errors are systematic and the scale factor(s) empirically compensate the shortcomings of the theories used. Scaling the frequencies by a scale factor is the simplest although the results are not as good as scaling the force constants.[9] Also, the assignment of vibrational frequencies needs a normal mode analysis in terms of force constants. The most popular scaling algorithm for the force constants is Pulay's SQM approach.[7] Here

we get a small number of scale factors for the diagonal force constants and use their geometric mean for the off-diagonal scale factors.[7] However, there is no theoretical justification for this scaling procedure. The question whether there exists any theoretical relation between off-diagonal and diagonal force constants is addressed from the early days of scaling methods with out an answer. Here we propose a theoretical relation between the diagonal and off-diagonal force constants. These relations could be used successfully to scale the force constants and predict the vibrational spectra. It is to be noted that the force constant relations could be obtained only when the L matrix is available. The L matrix is usually obtained from the cartesian force constants calculated by some theoretical method like *ab initio* or DFT.

2. Methodology

The normal mode analysis is usually done in terms of Wilson's GF matrix formalism.[6] Here we define a set of internal coordinates (R) and from them we construct $3N - 6$ (N is the number of atoms) or $3N - 5$ local coordinates(s) depending on whether they are non-linear or linear. Using projection operator technique these local coordinates are converted to symmetry coordinates (S). Wilson's G matrix is constructed from the B matrix.[6] The cartesian force constants obtained from the *ab initio* or DFT methods are converted to local coordinates by $F(\text{local}) = [(UB)^{-1}]^{T}F(\text{cart})[UB)^{-1}]$ where $[(UB)^{-1}] = M^{-1}(UB)^{T}G(\text{local})^{-1}$. The local G and F Matrices are converted

to symmetric G and F and the frequencies and normal modes are obtained by solving $GFL = L\Lambda$ [6] where $\lambda_i = 4\pi\nu^2 i$ and L is the transformation matrix from symmetric to normal coordinates. The calculated frequencies are fitted to the experimental ones by adjusting the force constants and finally a set of scale factors are obtained in local coordinates for the best fit. The details of these calculations are given reference 10. The new methodology is as follows. The equations $GFL = L\Lambda$ and $LL^T = G$ leads to $L^TFL = \Lambda$[6]. Λ is diagonal matrix. If we keep the F elements in L^TFL as symbolic F elements and multiply L^T and F (symbolic) and L the LHS gives us a matrix where each element is a linear combination of force constants. A symbolic F has a number for each element instead of its value. All the off-diagonal elements of Λ are equal to zero. Hence, we get one linear relation among the symbolic force constants for each off-diagonal element. These equations form a set of linear homogeneous equations. These could be solved by Gaussian elimination or Gauss–Jordan elimination to get the relations between the diagonal and off-diagonal symbolic F elements. The number of force constants we have to know is equal to the number of frequencies. The other force constants are defined in terms of these known force constants. Gaussian elimination with full pivoting strategy gives a satisfactory answer. This method is exemplified using water molecule in table 1.

3. Benzene molecule

Benzene is one of the molecules well studied from 1955.[6] It has 34 symmetric force constants and 42 local force constants. Benzene has 20 unique frequencies excluding the degeneracy. This means the Λ matrix will have 20 unique diagonal elements. If we fix 20 force constants, rest of them could be obtained by the equations obtained by solving $L^TFL = \Lambda$. These relations are used to get the scaled off-diagonal force constants by fitting the calculated frequencies to the experimental ones[11] as described in reference 10 and the final force constants obtained along with the symbolic F and redundancy relations are given in the supplementary material which is available on request from the authors. The fitted frequencies are given in table 2. The RMS error is 5 cm^{-1}. The cartesian force constants are calculated at B3LYP/aug-cc-pvdz level of theory using Gaussian03 program and a locally developed program is used to do the normal mode analysis. To use the scale factors for prediction, one has the choice to use any convenient method including SQM methodology to fix the required number of force constants which is equal to the number of unique frequencies. The rest of the off-diagonal elements are obtained by solving the equations obtained from the transformation $L^TFL = \Lambda$. Which force constants are dependent and which ones are independent is decided by the full-pivot Gaussian elimination algorithm.

Table 1. H_2O molecule as example. Water has $3N - 6 = 3$ frequencies. So we need three force constants. the f_4 is automatically fixed from f_1, f_2 and f_3. In C_1 symmetry, all the off-diagonal elements are fixed by the diagonal force constants because $3N - 6 =$ number of frequencies = number of diagonal force constants.

$$\begin{bmatrix} -0.719 & -0.719 & -0.014 \\ 0.048 & 0.048 & -1.520 \\ 0.731 & -0.731 & 0.000 \end{bmatrix}\begin{bmatrix} 1 & 3 & 4 \\ 3 & 1 & 4 \\ 4 & 4 & 2 \end{bmatrix}\begin{bmatrix} -0.719 & 0.048 & 0.731 \\ -0.719 & 0.048 & -0.731 \\ -0.014 & -1.520 & 0.000 \end{bmatrix} = \begin{bmatrix} 1 & 4 & 0 \\ 4 & 2 & 0 \\ 0 & 0 & 3 \end{bmatrix}$$

$$\quad\quad L^T \quad\quad\quad\quad F \quad\quad\quad\quad L \quad\quad = \quad \Lambda$$

$$1 = \lambda_1 = 1.035*f_1 + 0.000*f_2 + 1.035*f_3 + 0.041*f_4$$
$$2 = \lambda_2 = 0.005*f_1 + 2.312*f_2 + 0.005*f_3 - 0.294*f_4$$
$$3 = \lambda_3 = 1.070*f_1 + 0.000*f_2 - 1.070*f_3 + 0.000*f_4$$
$$4 = 0 = -0.032*f_1 + 0.010*f_2 - 0.032*f_3 + 1.000*f_4$$

When we have several equations like 4, they constitute a set of linear homogeneous equations which could be solved by Gaussian elimination to get relations among the force constants

Table 2. Scaled frequencies of Benzene after fitting to the experimental frequencies. The scaled frequencies are in parenthesis followed by experimental values.[11]

A_{1g}
3074(3078); 993(995);

A_{2g}
1350(1365);

B_{2g}
990(992); 707(707);

E_{1g}
847(846);

E_{2g}
3057(3055); 1600(1601); 1178(1172); 608(608);

A_{2u}
674(677);

B_{1u}
3057(3048); 1010(1005);

B_{2u}
1310(1315); 1149(1155);

E_{1u}
3065(3069); 1484(1474); 1038(1039);

E_{2u}
967(966); 399(399);

RMS error 5 cm^{-1}

4. Glycine molecule

Glycine exists as a neutral molecule in the gas phase. The vibrational spectrum of glycine in the gas phase has been studied recently by theory and experiment.[12] To check the methodology we tried MP2/6-311++G** calculations on the most stable conformation of glycine. All the experimental frequencies of the four isotopomers reported in reference 12 are fitted to the calculated frequencies. The RMS error between the experimental and final calculated frequencies is 10 cm^{-1}. The assignments are similar to that reported earlier. The scaled frequencies are in better agreement with experimental frequencies. From the scale factors obtained for glycine, predicting the spectra of other related molecules like alanine and serine are in progress. Since

the assignments are similar to the reported one we are not repeating it here.

5. Conclusions

A method is proposed to obtain the theoretically justified relationship between the off-diagonal force constants and diagonal force constants in C_1 symmetry molecules. In symmetric molecules some (independent) off-diagonal and diagonal force constants equal to the number of unique frequencies have to be fixed and from these other off-diagonal force constants (dependent) could be obtained. The independent off-diagonal force constants could be fixed by any convenient method including SQM in using the scale factors for predicting the vibrational spectra.

Supplementary information

The supplementary information table S1 to S4 are provided in the online version (www.ias.ac.in/chemsci).

References

1. Kozmutza K and Pulay P 1975 *Theor. Chim. Acta* **37** 67
2. Blom C E and Altona C 1976 *Mol. Phys.* **31** 1377
3. Torak F, Hegedus A, Kosak and Pulay P 1976 *J. Mol. Struct.* **32** 93
4. Botschwina P 1974 *Chem. Phys. Lett.* **29** 580
5. Baker J, Jarzecki A A and Pulay P 1998 *J. Phys. Chem.* **A102** 1412
6. Wilson Jr E B, Decius J C and Cross P C 1980 *Molecular vibrations* (Dover Publications, Inc)
7. Fogarasi G and Pulay P 1985 *Vibrational spectra and structure* (ed.) J R Durig (Elsevier) Vol. 14, p. 125
8. Frisch M J *et al* 2004 Gaussian03, Gaussian Inc, Wallingford, CT
9. Merrick J P, Morgan D and Radom L 2007 *J. Phys. Chem.* **A111** 11683
10. Ragubanshi D, Maheshwary S and Manogaran S 2001 *J. Mol. Struct.* (*Theochem.*) **574** 245
11. Berger R, Fischer C and Klessinger M 1998 *J. Phys. Chem.* **A102** 7157
12. Stepanian S G, Reva I D, Radchenko E D, Rosado M T S, Duarte M L T S, Fausto R and Adamowicz L 1998 *J. Phys. Chem.* **A102** 1041