EFFECT OF SCALING OF A QUANTUM MECHANICAL FORCE FIELD ON THE FREQUENCIES AND FORMS OF MOLECULAR VIBRATIONS

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The effect of scaling of an ab initio quantum mechanical force field on the frequencies and forms of normal vibrations are studied in terms of first- and second-order perturbation theory. Scaling the force constant matrix according to Pulay using certain assumptions in first-order perturbation theory is equivalent to scaling vibration frequencies and does not modify the form of vibrations. In this case, the second-order corrections to the frequencies and forms of vibrations become zero. The first-order perturbation theory formulas are used to verify the assumptions by calculating the frequencies and matrices of transition to perturbed forms of vibrations of ethane, propane, ethylene, cyclopropene, and isobutene molecules from quantum mechanical force fields found with the 6-31G basis set. It is shown that the vibration frequencies calculated by the formulas of first-order perturbation theory are in good agreement with exact values; the matrix of transition to perturbed eigenvectors is rarefied, with only ≈1% of its elements being markedly nonzero.

INTRODUCTION

A combined analysis of experimental vibrational spectra and theoretical quantum mechanical calculations of normal vibrations (frequencies and forms) of molecules affords information about the intramolecular potentials near the equilibrium point and allows one to find certain tendencies in series of related structures. In some cases, studies of molecular vibrations are the only source of structural data.

Ab initio quantum mechanical calculations actually present a unique opportunity to reliably determine the force fields of polyatomic molecules. However, the results of such calculations demand certain empirical corrections, for example, in view of systematic exaggerations in the Hartree–Fock method.

This correction may be applied by different methods. One of the most rational and justified methods is Pulay's scaling method [1-6]. According to this method, the diagonal force constants are multiplied by correction coefficients whose typical values (e.g., for hydrocarbons) are of the order of 0.8 and the off-diagonal force constants are multiplied by the geometrical mean of the multipliers corresponding to the diagonal force constants. Scaling of this kind implies that determination is equally accurate for the diagonal and off-diagonal elements; this holds near the Hartree–Fock limit. The scaling factors are evaluated by solving the inverse problem [7, 8], which is well-posed, in contrast to the inverse vibrational problem.

The scaling method of empirically correcting the force field has a certain theoretical rationale. Earlier, it was shown [4] that scaling is an effective way to calculate electron correlation effects. In this case, the force constants corresponding to the results of calculation near the Hartree–Fock limit are in approximately linear relation to the exact force constants obtained by the full configuration interaction method with the same basis set.

An advantage of the scaling method is few multipliers compared to the number of vibration frequencies and especially to the number of force constants, as a multiplier is used for several quasiequivalent internal coordinates. Another important advantage is transferability of the scaling factors when using the same quantum mechanical
approximation and basis set for calculations of related molecules. The advantages of Pulay's method are treated in
detail in [9-13].

Determination of the quantum mechanical molecular force field with further correction with scaling factors is
currently becoming a standard procedure in routine calculations. Some aspects of Pulay's method are discussed, e.g.,
in [6]. It is of interest to examine the effect of scaling on the normal vibrations of molecules in more detail. Perturbation
theory is the most suitable tool for this purpose.

USING PERTURBATION THEORY

Evidently, for a problem with arbitrary scaling factors, one can take a problem with equal multipliers as an
unperturbed problem. The form of vibrations of the initial problem without scaling factors does not change, and the
frequencies are multiplied by a single coefficient.

The initial equation for an unperturbed force field is
\[ GF_0L_0 = L_0\Lambda_0. \]  (1)

The problem is first solved in general for an arbitrary small perturbation of the force matrix; then scaling is
considered as a particular instance. Perturbation theory is used for nondegenerate states, when \( \lambda_i \neq \lambda_j \).

A perturbed matrix \( F \) may be represented as
\[ F = F_0 + \mu F_1, \]
where \( \mu \) is a scalar parameter. Initial equation (1) is transformed into
\[ GF_1L_0 = L_0\Lambda_0. \]  (2)

As usual, perturbed frequencies and forms of vibrations are represented as power series in \( \mu \), i.e.,
\[ L = L_0 + \mu \delta^1L + \mu^2\delta^2L + \mu^3\delta^3L + \ldots, \]
\[ \Lambda = \Lambda_0 + \mu \delta^1\Lambda + \mu^2\delta^2\Lambda + \mu^3\delta^3\Lambda + \ldots, \]  (3)

where \( \delta^iL \) and \( \delta^i\Lambda \) are \( i \)th-order corrections to \( L \) and \( \Lambda \). Substituting these expansions into Eq. (2), we obtain
\[ G[F_0L_0 + \mu(F_0\delta^1L + F_1L_0) + \mu^2(F_0\delta^2L + F_1\delta^1L) + \ldots] = L_0\Lambda_0 + \mu(L_0\delta^1\Lambda + \delta^1L\Lambda_0) + \mu^2(L_0\delta^2\Lambda + \delta^1L\delta^1\Lambda + \delta^2L\Lambda_0) + \ldots \]

The condition of equality of coefficients with equal powers of \( \mu \) on the left and right sides of this expression
leads to the following set of equations:
\[ \mu^0: \quad GF_0L_0 = L_0\Lambda_0, \]
\[ \mu^1: \quad G(F_0\delta^1L + F_1L_0) = L_0\delta^1\Lambda + \delta^1L\Lambda_0, \]  (4)
\[ \mu^2: \quad G(F_0\delta^2L + F_1\delta^1L) = L_0\delta^2\Lambda + \delta^1L\delta^1\Lambda + \delta^2L\Lambda_0. \]  (5)

The first equation is the initial unperturbed equation. Taking into account normalizations, we find that
\[ L_0^+F_0L_0 = \Lambda_0, \]
\[ G = LL^+ = L_0L_0^+. \]  (6)

Equation (4) is recorded as
\[ \Lambda_0L_0^{-1}\delta^1L + L_0^+F_1L_0 = \delta^1\Lambda + L_0^{-1}\delta^1L\Lambda_0. \]