UTILIZATION OF OVERLAY AND AB INITIO FORCE FIELDS IN THE CONSTRUCTION OF EMPIRICAL POTENTIAL ENERGY FUNCTIONS FOR CONJUGATED MOLECULES

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SUMMARY

The optimization of the parameters in the molecular mechanics method is discussed. The utilization of spectroscopic force fields is described, and the advantages of utilizing molecular symmetry in the optimization of the parameters on the vibrational frequencies are stressed. The development of the potential functions for the benzene ring and for the vinyl group is briefly described, and the the application of these functions to calculate the geometry of the styrene molecule is discussed.

INTRODUCTION

The fast development of computers in the past few years has made it possible to study more and more complex organic molecules and molecular crystals with the molecular mechanics, molecular dynamics and Monte Carlo methods using empirical potential energy functions. The potential energy model adopted is usually of the form (refs. 1-3)

$$V = \tfrac{1}{2} \sum F_i(q_i - q_{i0})^2 + \sum_{i<j} f_{ij}(q_i - q_{i0})(q_j - q_{j0}) + \sum V_{\text{tor}} + \sum v_{\text{nb}}(r_{kl}) \qquad (1)$$

In the expression above the q_i:s are internal coordinates defined as in spectroscopic force field calculations, *i.e.* bond lengths and angles. V_{tor} is a periodical torsional potential while v_{nb} is a potential energy term for a nonbonded interaction between a pair of atoms, usually modelled as a Lennard-Jones or Buckingham potential. The Coulombic interactions are often included in the last term. The potential energy expression contains different types of parameters which have to be optimized: q_{i0} is the reference value for the internal coordinate q_i, F_i describes the stiffness of the coordinate q_i, while f_{ij} is the potential energy parameter for the simultaneous deformation of coordinates q_i and q_j from their reference values. V_{tor} contains the barrier height, and the nonbonded potentials contain at least two parameters for each type of atoms (if combination rules are applied). The geometry of the molecule

or crystal is obtained by minimizing the potential energy of the system with respect to the geometry of the system, usually expressed in Cartesian coordinates.

The reliability of the results of calculations using this type of potential is, of course, totally dependent on how well the potential energy model adopted describes the true intra- and intermolecular interactions, and how sensitive the properties studied are to the potential energy model. Especially for conjugated molecules this is important, since there are several significant interaction parameters f_{ij}. Furthermore, the stiffness as well as the reference value of a bond in a conjugated system depend on the bond order. Thus, there are significantly more independent parameters than in nonconjugated molecules. In this paper we discuss the optimization of the parameters mentioned above, and describe how the spectroscopic force field calculations, overlay or *ab initio*, can be utilized. As an example we describe the development of potential energy functions for the benzene ring and the vinyl group and the application of these functions to study the geometry of the styrene molecule.

OPTIMIZATION OF THE PARAMETERS

General

The optimization of parameters in the molecular mechanics method is far more tedious than the optimization of force constants in conventional spectroscopic force field calculations. The reasons for this are obvious. In the latter method the scope of the calculations is rather limited, most often the goal is only to reproduce or predict the vibrational frequencies. Furthermore, the only type of parameters we have to deal with there, are the force constants (closely related, but not equivalent to the parameters F_i and f_{ij} in eqn. (1) (refs. 2-4)), and the elements of the Jacobian matrix are readily calculated from the eigenvectors.

In the molecular mechanics method the situation is much more difficult. Firstly, the goal is more ambitious. We wish to calculate several types of molecular properties which depend on the potential energy function, including *e.g.* molecular geometries, conformational energy differences, barrier heights, heats of formation, vibrational frequencies, thermodynamic functions, dipole moments, and crystal structures and vibrations. Secondly, the calculation of the Jacobian matrix elements is tedious for most types of properties mentioned above, and for some types, such as conformational energy differences, it becomes impractically complicated and time consuming. A thorough discussion of the algorithms for the calculation of the Jacobian matrix elements has been given by Rasmussen (ref. 3). Furthermore, if a proper optimization strategy is not adopted, problems with correlations between the parameters in the potential energy function can arise.

The most severe problems with correlations can be avoided by dividing the optimization into smaller parts. For example, the lattice constants and energies, as well as the frequencies of the lattice vibrations of molecular crystals depend almost solely on the nonbonded interactions. Thus, the nonbonded interactions can be obtained by optimizing on the crystal properties (ref. 5). The barrier heights and conformational energy differences are sensitive both to the periodical torsional potential and to the nonbonded interactions. Molecular

geometries and the frequencies of the intramolecular vibrations are sensitive to the first two terms in eqn. (1), the other terms giving a significant contribution, also. Thus, the optimization of the parameters of these terms is tedious, especially for conjugated molecules, where a large number of cross terms have to be included.

Utilization of spectroscopic force fields

In the following we concentrate on the first two terms in eqn. (1). If vibrational frequencies are not used in the optimization, it is necessary to include experimental geometries both from nonstrained and strained molecules in the set of observables used for optimization. If there were no data from strained molecules, the values obtained for parameters with dimensions of force constants would be highly unreliable. For many classes of compounds there are no experimental data for strained molecules. However, if both molecular geometries and vibrational frequencies are available for nonstrained molecules, the parameters can be optimized. In nonstrained molecules there is only little correlation between the q_{i0} and the F_i parameters. The parameters q_{i0} are thus readily obtained by optimizing on the molecular geometries.

The parameters with dimensions of force constants are more difficult to optimize, since these parameters are often badly correlated, and, furthermore, it is often difficult to choose good initial values for the optimization. At this stage spectroscopic force fields are of great help (ref. 4). If the Newton-Raphson method is used in the final minimization then the Hessian matrix in the minimum is equal to the spectroscopic force constant matrix in Cartesian coordinates. By subtracting the contributions of the nonbonded interactions and the periodical torsional potentials from the spectroscopic force constant matrix expressed in Cartesian coordinates, we obtain the second derivatives of the first two terms in eqn. (1). The derivatives are of the form

$$
\left(\frac{\partial^2 g_{ij}}{\partial x_{k\alpha} \partial x_{l\beta}} \right) = f_{ij} \left\{ \left(\frac{\partial q_i}{\partial x_{k\alpha}} \right) \left(\frac{\partial q_j}{\partial x_{l\beta}} \right) + \left(\frac{\partial q_i}{\partial x_{l\beta}} \right) \left(\frac{\partial q_j}{\partial x_{k\alpha}} \right) \right.
$$
$$
\left. + \left(\frac{\partial^2 q_i}{\partial x_{k\alpha} \partial x_{l\beta}} \right) (q_j - q_{j0}) + \left(\frac{\partial^2 q_j}{\partial x_{k\alpha} \partial x_{l\beta}} \right) (q_i - q_{i0}) \right\}
$$

$$(2)$$

where $x_{k\alpha}$ is the Cartesian coordinate α ($\alpha = 1, 2, 3$) of the atom k. For nonstrained molecules the terms with second order derivatives of q_i:s with respect to the Cartesian coordinates are negligible, and what we are left with can be identified as the transformation of the force constant matrix from internal coordinates to the Cartesian coordinates. Initial values for the parameters F_i and f_{ij} can then be obtained by a least squares fit of the parameters to the Cartesian force constant matrix after the subtraction mentioned above. The approximations used in the molecular mechanics method need not be the same as in the spectroscopic force field, and in fact much cruder approximations are usually applied, if accurate vibrational frequencies are not needed.

Now, when fair initial values for the parameters are available, it is in principle a rather straightforward task to optimize the parameters F_i and f_{ij} on the known experimental frequencies. In practice, however, the situation is not so simple, since when the mass weighted Hessian matrix is diagonalized, we get all the vibrational frequencies, but we have no guarantee that they are in the correct order, *i.e.* the assignments may change. This is true particularly when we use cruder approximations. In fact, this caused us serious problems in the past. These problems can be overcome by transforming the Hessian into Cartesian symmetry coordinates for each irreducible representation. If this is done, the optimization is rather straightforward, even from very bad initial values (ref. 6).

The spectroscopic force field can be either an overlay or a scaled *ab inito* force field (ref. 7). Occasionally we have to treat classes of molecules for which there are no experimental frequencies available. In these cases the best we can do is to calculate a scaled *ab initio* force field and use the parameters obtained from the least squares fit to the subtracted force constant matrix.

CALCULATIONS AND RESULTS

As a starting point we chose the overlay force field developed earlier (ref. 8). The q_{i0} parameters were first adjusted to reproduce the experimental geometries of ethene, butadiene and benzene. The values of these parameters are of course close to the bond lengths and anglesin these nonstrained molecules. Then the subtraction of the contribution of the nonbonded interactions was performed as described above. The parameters of the type F_i and f_{ij} thus obtained were then optimized on the experimental frequencies of several isotopomers of ethene, butadiene, benzene and styrene. Initially we did not utilize symmetry in the optimization, but the preservation of the correct symmetry of the normal modes for all molecules simultaneously during the optimization proved to be extremely difficult, if not impossible. By utilizing the symmetry as described above, however, the optimization became rather straightforward. The full results will be published elsewhere (ref. 6). Here we merely give some illustrative examples, listed in Table 1. The notations for the parameters are the same as in refs. 4 and 8.

From Table 1 it is apparent that the changes in parameter values are in most cases small, as expected, since we are dealing with nonstrained molecules. There are only two large changes in the F_i parameters. Both F_{α_b} and F_{α_s} decrease significantly, as expected. Still, there are only relatively small changes in most of the interaction parameters.

It is now of interest to look closer at the geometry of the styrene molecule, which is more strained due to the interaction between the *ortho-* and *cis-β-* hydrogen atoms. Styrene has recently been studied by the *ab initio* method using the 6-31G basis set (ref. 9) and by microwave Fourier transform spectroscopy (ref. 10). In the microwave study the geometry was taken from the *ab initio* calculation (ref. 9), and the only parameter varied was the $C_1-C_\alpha=C_\beta$ angle. Bock *et al.* (ref. 9) calculated a value of 127.6° for the $C_1-C_\alpha=C_\beta$ angle, while Carminati *et al.* (ref. 10) obtained 125.6° for this angle. From the molecular

mechanics calculations described here we obtained 126.8°, in good agreement with the others (refs. 9-10). The reference value for the C-C=C angles used was 122.4°, and in butadiene we calculated 123.4° for the C-C=C angle. It should be noted that all the q_{i0} parameters used for styrene are the same as the corresponding parameters for benzene and butadiene, except for the C-C bond, where we have 1.458 Å for butadiene and 1.467 Å for styrene. The latter value is adjusted to reproduce the C-C bond length in styrene (ref. 9). This small increase of the reference value for the C-C bond in styrene as compared to butadiene is also in agreement with the corresponding spectroscopic force constants (ref. 8).

TABLE 1

Some illustrative cases of parameters in different phases of the optimization. All the parameters apply also to styrene, except F_{Rw}, which is for butadiene. For styrene the optimized F_{Rw} is 684.4, and the spectroscopic value is 676.5. The parameters marked with (f) are fixed during the optimization. For further details see the text. The units used are kcal (energy), Å (bond lengths) and rad (angles)

Parameter	Spectroscopic	Subtracted	Optimized
F_{R_S} (f)	1312.7	1310.7	1312.7
F_{R_b}	950.1	944.1	927.9
F_{R_W} (f)	722.4	720.5	722.4
$F_{\alpha'}$	97.9	92.9	93.1
F_{α_S}	165.6	152.5	116.4
F_{α_b}	184.5	154.3	153.0
F_{β_b}	148.6	143.9	141.9
F_{β_v}	143.2	129.8	135.2
$F_{\beta'}$	160.1	151.9	151.4
$f_{R_b R_b, o}$	112.0	107.8	106.4
$f_{R_b R_b, m}$	-54.1	-62.1	-57.9
$f_{R_b R_b, p}$	38.9	29.1	33.2
$f_{R_S R_W}$ (f)	85.2	97.2	85.2
$f_{\alpha_b \alpha_b}$	0.0	-15.0	-14.8
$f_{\alpha_S \alpha_S}$	22.3	27.7	23.6
$f_{\alpha_b \beta_b}$	-15.1	-15.6	-17.4
$f_{\alpha_S \beta_v}$	20.1	26.0	21.9
$f_{R_b \alpha_b}$	45.2	40.0	31.9
$f_{R_S \alpha_S}$ (f)	60.8	53.2	60.8
$f_{R_W \alpha_S}$ (f)	21.7	19.8	21.7
$f_{R_S \beta_v}$	-54.9	-44.2	-57.8
$f_{R_W \beta_v}$	-20.4	-13.2	-20.4
$f_{R_b \beta_b, o}$	-36.1	-33.4	-30.7
$f_{R_b \beta_b, m}$	-8.5	-9.1	-8.7
$f_{R_S \alpha'}$	-38.7	-32.1	-35.0

We also optimized a diagonal molecular mechanics force field for benzene and butadiene on frequencies from several isotopomers of these molecules to demonstrate the effect of this crude approximation on the molecular geometries. The optimized values of the parameters F_{R_S}, F_{R_t} and F_{R_W} are 1047.8, 684.2 and 589.8 kcal/Å^2, respectively. Assuming that the difference between the F_{R_W} parameters for butadiene and styrene in the diagonal approximation is the same as in the more accurate model, we obtain for F_{R_W} in styrene a value of 551.7 kcal/Å^2. The changes in the angle parameters are much smaller. This crude model does of course not adequately predict vibrational frequencies of related molecules. The approximations affects the styrene geometry to some extent, since the C-C bond is softer in the diagonal approximation. The strain in this model is decreased by the increase of the C-C bond length from 1.475Å to 1.484Å while the valence angles are opened slightly less than in the more accurate model (ref. 6). Thus, although styrene is not strongly strained, the effects of the approximations are already evident.

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