New implementation of the first-order perturbation theory for calculation of interatomic vibrational amplitudes and corrections in gas electron diffraction

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Abstract. The problem of computation of vibrational molecular parameters in models of gas electron diffraction is discussed. Some peculiarities of the standard for these purposes Shrink program are analysed. An alternative code has been written to implement the well established Sipachev’s first-order perturbation theory. It has been used for calculation of vibrational parameters of several molecules. Comparison of obtained results shows that the new program outperforms the available program Shrink in many aspects.

1. Introduction

A typical application of the gas electron diffraction (GED) method is to study geometrical structure and dynamics of free molecules.[1] Models of molecular part of electron diffraction in GED are usually expressed in terms of thermally averaged interatomic distances $r_a$ or $r_g$, mean amplitudes of their variations $l$ and asymmetry constants $\kappa$.[2, 3, 4] Successful interpretation of experimental electron diffraction patterns requires, excepting very simple cases, preliminary calculation of these geometrical and vibrational parameters. In structural analysis they are used for construction of initial model and as fixed constraints[5] or flexible restraints[6] to make the inverse problem stable. In addition, it is well known that the thermally average $r_a$ and $r_g$ distances are not geometrically consistent, which leads to a so-called "shrinkage effect".[7, 8] Therefore, in current practice GED structural analyses are internally done in terms of geometrically consistent $r_{h0}$, $r_{h1}$ or $r_e$ parameters.[9] This, in turn, requires corresponding corrections to interatomic distances $(r_{h0} - r_a)$, $(r_{h1} - r_a)$ or $(r_e - r_a)$, which are in most cases computed on the basis of theoretically optimized structures and calculated force constants. The usage of corrections to equilibrium structure $(r_e - r_a)$ is most preferable since they have clear physical meaning and provide common basis for combination of experimental data from different sources and for comparison of structures obtained by different methods.

For calculation of vibrational amplitudes $l$ and corrections for interatomic distances most of the modern GED structural studies utilize the first-order perturbation theory of Sipachev implemented in program Shrink using classical formalism.[10] The current implementation of the corresponding algorithm has, however, several limitations restricting studies of large molecules by GED method.
In this contribution we are extending the current Sipachev’s algorithm for the case of large molecules. This work has been done in scope of the UNEX project[11], a software platform for computational studies, simulations and inverse problems. Its second version UNEX2 provides a computer language and its implementation with standard library, which includes a toolkit for GED investigations. A new program VibModule has been written for calculations of vibrational amplitudes and corrections using standard Sipachev’s theory. As a next step this standalone program will be converted to a corresponding module for the standard UNEX2 library.

2. Implementation of the first-order perturbation theory

As already stated before the vast majority of modern GED structural studies use the Sipachev’s formulation of the first-order vibrational perturbation theory implemented in program Shrink [12, 13, 14] for calculations of vibrational amplitudes and distance corrections. Its algorithm uses a so-called ”curvilinear approach” by solving the vibrational problem in redundant internal coordinates and requires at least Cartesian coordinates and a harmonic force field of a molecule as the input information. Additionally, a cubic force field is required in general case for calculation of anharmonic distance corrections to equilibrium geometry. Altogether \( r_e - r_a \) corrections are calculated as:

\[
r_e - r_a = \frac{l^2}{r_e} - \langle \Delta r \rangle_{\text{har}} - \langle \Delta r \rangle_{\text{loc}} - \langle \Delta r \rangle_{\text{rot}} - \langle \Delta r \rangle_{\text{anh}},
\]

(1)

where \( \langle \Delta r \rangle_{\text{har}} \) is the shrinkage correction calculated in the curvilinear harmonic approximation [12], \( \langle \Delta r \rangle_{\text{loc}} \) is the local centrifugal distortion caused by intramolecular vibrational motions [14], \( \langle \Delta r \rangle_{\text{rot}} \) is the centrifugal distortion caused by rotational motion of a molecule [15] and \( \langle \Delta r \rangle_{\text{anh}} \) is the anharmonic part of the correction.[13] A comparison of such contributions for different interatomic distances of ethane molecule is given in Table 1. Amplitudes of interatomic vibrations \( l \) are calculated in the similar manner [12] and are also collected in Table 1. The theory performs well for relatively stiff molecules without large amplitude motions. Calculations for molecules with lowest frequency below 85 cm\(^{-1}\) can be unreliable.[10] Current implementation of the program Shrink has limitations, which complicate GED studies of large molecules. Firstly, numbers of internal coordinates, of atoms and their pairs are limited to 600 (empirical observation), and secondly, this program is too slow. It is possible that these disadvantages can be fixed in future. However, to our knowledge this code is not supported anymore and in this work it has been decided to write a new program, which implements the aforementioned theory. The new program VibModule is coded in C computer language and uses the UNEX mathematical library (UML) from the UNEX2 project.[11] It utilizes algorithms similar to those described earlier and used in program Shrink.[12, 13, 14, 15] VibModule has a number of advantages:

- virtually no limits on numbers of molecular parameters mentioned earlier;
- higher computational performance;
- automatic generation of internal coordinates;
- variety of input possibilities: Shrink input files, output files of Gaussian [16] and Firefly [17] quantum chemical packages;
- output data are ready to use in UNEX [18] and KCED [19] programs for GED structural analysis.

In order to test the accuracy of results obtained with VibModule several molecules have been processed and corresponding parameters have been compared with values calculated by Shrink. Results for two of these objects, relatively small ethane (C\(_2\)H\(_6\)) [20] and large [30]trithia-2,3,5,10,12,13,15,20,22,23,25,30-dodecaazaazahexaphyrin (C\(_{30}\)N\(_{15}\)H\(_{15}\)S\(_3\)) [21] molecules, are summarized in Table 2. The small values of the root-mean-square deviations (RMSD) demonstrate the consistency of the results of both programs.
An another test has been done in order to measure the improvement in computational speed of VibModule. Magnesium octa(m-trifloromethylphenyl)porphyrazine (MgC_{72}H_{32}N_{8}F_{24}) has been chosen as a test object, which is probably the largest molecule ever studied by GED method.[22] Calculations have been performed on a computer running under 64-bit Windows 7 operating system. The running times for VibModule and Shrink were 46.5 and 316.1 minutes, respectively. It should be noted that, in contrast to VibModule, Shrink was not able to process the full set of interatomic pairs for the test molecule due to the limitations mentioned earlier. A calculation of all required parameters would require 23 runs. Thus, the real effective timings were 46.5 and 7270.3 minutes for VibModule and Shrink, respectively.

3. Conclusions
A new program has been developed for calculations of interatomic vibrational amplitudes and corrections using the first-order perturbation theory. This code together with the well-known Shrink program has been used for processing of data for several test molecules of different sizes. Comparisons of the obtained parameter values have shown that both programs produce consistent results. The new code has, however, significant technical advantages including much higher computational speed and possibility of processing data for large molecules.

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Table 1. Amplitudes of vibrations and corrections for different pairs of atoms in C_2H_6 and C_{30}N_{15}H_{15}S_3 molecules calculated using VibModule program, [Å].

| Molecule | r_e | l | (Δr)_{bar} | (Δr)_{loc} | (Δr)_{rot} | (Δr)_{anh} | r_e − r_a |
|----------|-----|---|------------|------------|------------|------------|-----------|
| C_2H_6   |     |   |            |            |            |            |           |
| C—H      | 1.095 | 0.077 | 0.0000 | 0.0037 | 0.0002 | 0.0176 | -0.0161 |
| C—C      | 1.530 | 0.051 | 0.0000 | 0.0010 | 0.0115 | -0.0107 |
| H...H    | 1.766 | 0.123 | -0.0063 | 0.0053 | 0.0271 | -0.0178 |
| H...C    | 2.182 | 0.107 | -0.0062 | 0.0032 | 0.0250 | -0.0176 |
| H...N    | 2.542 | 0.182 | -0.0055 | 0.0055 | 0.0321 | -0.0199 |
| C_{30}N_{15}H_{15}S_3 |     |   |            |            |            |            |           |
| C—H      | 1.083 | 0.070 | 0.0000 | 0.0038 | 0.0000 | 0.0125 | -0.0118 |
| N...N    | 2.462 | 0.064 | -0.0069 | 0.0050 | 0.0142 | -0.0107 |
| C...N    | 13.165 | 0.246 | -0.2352 | 0.0173 | 0.0822 | 0.1395 |
| C...S    | 13.648 | 0.254 | -0.2658 | 0.0137 | 0.0937 | 0.1622 |
| H...H    | 17.553 | 0.260 | -0.3469 | 0.0194 | 0.1268 | 0.2036 |

Table 2. Root-mean-square deviations between results obtained with VibModule and Shrink programs for C_2H_6 and C_{30}N_{15}H_{15}S_3 molecules, [Å].

| Molecule | RMSD(l) | RMSD(r_e − r_a) |
|----------|---------|-----------------|
| C_2H_6   | 4.08 · 10^{-5} | 4.08 · 10^{-5} |
| C_{30}N_{15}H_{15}S_3 | 1.06 · 10^{-3} | 4.69 · 10^{-4} |
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