In spite of numerous practical and theoretical difficulties it is already possible to model theoretically carbon-13 NMR spectra by using various easily accessible quantum chemistry programs. Under certain conditions the results of GIAO DFT method ensure reproduction of the experimental $^{13}$C chemical shifts with the accuracy of the order of 1 - 2 ppm within the reasonable computation time for molecules being of the practical interest for chemists. Recently, also the calculation of the indirect spin-spin coupling constants with reasonable accuracy and within the reasonable time has become quite feasible. It seems that it is not commonly realized that this new tool creates new possibilities of performing much deeper analysis of the experimental NMR spectra, which can deliver a wealth of chemically important information on investigated systems.

Let us remind that in the past the signals in NMR spectra were being assigned to particular atom nuclei in investigated molecules exclusively by extrapolating the empirical data. Generalizations originating from the experimental material accumulating in time had a form of more and more detailed tables listing the typical ranges of chemical shifts for specific structural situations such as aliphatic carbon-bonded carbons, aliphatic oxygen-bonded carbons, aromatic carbons, carbonyl carbons and so on. Further differentiation of the signals in the given spectrum relayed upon various - again empirically established - rules allowing to predict the influence of structural factors (substituent electronegativity, branching of aliphatic chains, heavy atom substitution, etc.) on chemical shifts. The signal position could be sometimes predicted quantitatively by using various empirical equations based on rough additivity of increments characterizing specific substituents or structural fragments. Such assignment methods are of course helpful and still in use, though they are certainly insufficient in numerous situations, e.g. when one is dealing with distinguishing stereoisomers. Generally, the smaller the chemical shift difference between considered signals the less reliable the conclusions based on such assignments. The application of the analysis of the spin-spin coupling networks and NOE data with the aid of the multidimensional correlation spectroscopy does, however, dissolve the assignment problems. In last years, owing to methods enabling theoretical calculation of NMR parameters, a completely independent method supporting and verifying the signal assignments has appeared. This type of application of theoretical data is probably the most obvious but certainly not the only and not the most important one.

Theoretical approach has been proven to be effective in investigating the influence of various structural factors on chemical shifts by performing calculations for a properly selected model compounds. Such a series of models may include real as well as hypothetical structures. Exploiting such a method we have modelled, for example, the electronegativity effect of the substituent on chemical shifts of carbon and nitrogen nuclei in cyano compounds. A "pure" inductive effect is expected to operate, e.g. in the series of ions possessing the acetonitrile-like structures, $\text{H}_3\text{XCN}$ ($\text{X} = \text{Li},...\text{Ne}$). Actually, only two members of this series, namely $[\text{H}_2\text{BCN}]$ and $\text{H}_2\text{CCN}$, are sufficiently stable to be investigated experimentally, but it is not a limitation for a computational approach. One can be naturally sceptical about the precision of the predicted shielding constants for such peculiar structures as $[\text{H}_3\text{LiCN}]^3$ or $[\text{H}_2\text{NeCN}]^{4+}$. Also the selection of a numerical measure of electronegativity of exotic substituents is somewhat arbitrary. Nevertheless, one may safely conclude that in this series
the theory predicts the existence of the monotonical relationship between the shielding constant of the nitrile carbon and the electronegativity of H₃X substituent. Moreover, these theoretical results have shown that the direction of this relationship is such that the enhanced electronegativity of X causes the shielding effect of cyano carbon, which is in agreement with the result of the Hammet-type analysis performed for a large set of the experimental data.

The most important - in my opinion - applications of the combined theoretical/experimental approach to NMR investigations concern analyses of the spectra of the systems in which molecules undergo exchange, rapid in NMR time-scale. In such a situation only the population-weighted averaged spectra are observed. Usually, not only the populations but even the structures of the species abundant in the investigated solution are not known a priori. Both these types of information are of interest for the physicochemical investigations and, essentially, both can be gained by numerical analysis of the experimental chemical shifts, using the shielding constants coming from the theoretical calculations. In favourable circumstances the analysis can answer which forms are actually present in the investigated solution and yield their populations. In the past this sort of information could seldom be gained from NMR spectra. Some examples of applications of NMR/DFT studies concerning the rapid conformational equilibrium, tautomerism (including determination of the position of the proton in the intramolecular hydrogen bond), and acid-base equilibrium will be presented.

It is obvious that the studies of this type require preservation of some preconditions concerning the experimental as well as theoretical data to be compared. An attempt at formulating a minimal set of such recommendations will also be undertaken.