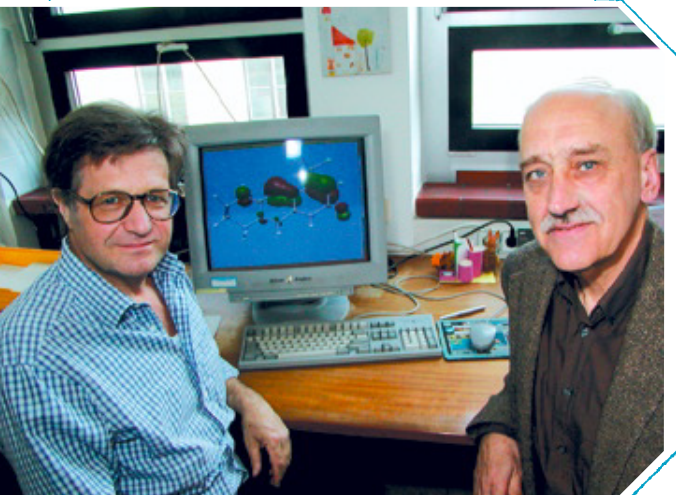


## COMPUTATIONAL CHEMISTRY

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The research areas of our group comprise the theoretical study of states of neutral and ionized small molecules, design of functional dyes, reaction mechanisms, thermochemistry, and properties of solids.

### Personnel

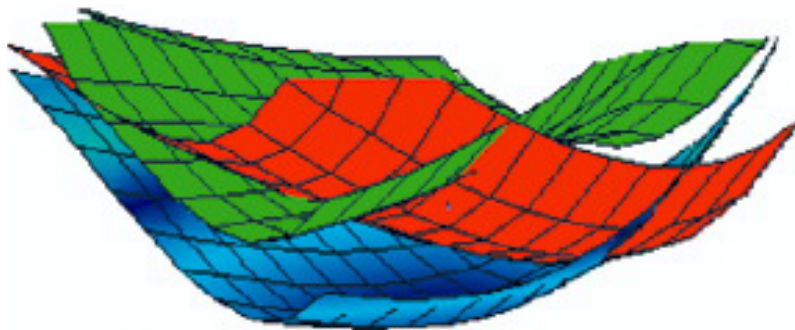
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### References Part 1

- Benedict, H., Limbach, H. H., Wehlan, M., Fehlhammer, W. P., Golubev, N. S., Janoschek, R. (1998). Solid State  $^{15}\text{N}$  NMR and Theoretical Studies of Primary and Secondary Geometric H/D Isotope Effects on Low-barrier NHN-Hydrogen Bonds: *J. Am. Chem. Soc.*, *120*, 2939-2950.
- Stefan, T., Janoschek, R. (2001). How relevant are S=O and P=O Double Bonds for the Description of the Acid Molecules  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$ , respectively?: in *Highlights in Computational Chemistry*, T. Clark (ed.), Springer, Berlin, Heidelberg, New York.
- Janoschek, R. (2001). Quantum Chemical B3LYP/cc-pvqz Computation of Ground-State Structures and Properties of Small Molecules with Atoms of Z 18 (H to Ar): IUPAC Technical Report: *Pure and Appl. Chem.* *73*, 1521-1553.
- Uray, G., Verdino, P., Belaj, F., Kappe, C. O., Fabian, W. M. F. (2001). Absolute Configuration in 4-Alkyl- and 4-Aryl-3,4-dihydro-2(1H)-pyrimidones: A Combined Theoretical and Experimental Investigation: *J. Org. Chem.*, *66*, 6685-6694.
- Fabian, W. M. F., Kappe, C. O., Bakulev, A. A. (2000). Ab Initio and Density Functional Calculations on the Pericyclic vs Pseudopericyclic Mode of Conjugated Nitrile Ylide 1,5-Electro-cyclizations: *J. Org. Chem.*, *65*, 47-53.

Computational Chemistry has become a versatile research tool in all areas of chemistry. The development of a variety of methods now allows the calculation of molecular properties with high precision as well as the treatment of large molecules with predictive power.

The methods we employ range from semiempirical and ab initio SCF over sophisticated electron correlation procedures and density functional theory approaches to molecular mechanics and QSAR modeling techniques.



Since density functional theory (DFT) achieved a remarkable breakthrough in computational chemistry, the important question "How reliable are quantum chemical calculations for spectroscopic properties and thermodynamical functions" should be answered anew. In two IUPAC projects DFT is applied to hundreds of small molecules, and calculated properties are compared with experimental ones. The above question is answered by the mean absolute deviation between calculated and experimental data. For some systems, dubious experimental values were detected.

Many anions are important precursors in producing neutral radicals or short-lived intermediates, which are hardly accessible by other means than electron photodetachment. Therefore, the systematic screening of molecules for electron affinities, stable electronically excited states and structural changes upon electron attachment or detachment yields