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Chemistry

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Computational chemistry has become an important area in all fields of chemistry; its significance in molecular physics and pharmacy is also well-recognized. In the design of new materials quantumchemical calculations to determine structural and stability properties of molecules or molecular aggregates are routinely performed parallel to experiments. Similarly, the calculation of energy surfaces to determine various minima (corresponding to isomers) or to locate reaction barriers is undertaken quite efficiently in cooperation with experimental work. Density functional (DFT) procedures are frequently the "work horse" because of their simplicity and because they account for some of the electron corelation. First principle simulations, i.e. a combination of electron structure calculation with molecular dynamic (MF) treatments are used for an increasing number of problems. In such calculations up to a few hundred particles and their motion may be treated in small time intervals. Such studies require large modern computer facilities such as the Jülich installation and cannot be done efficiently on small workstation clusters.

The examples chosen in this year's book show the impact of modern simulation techniques, a wide area of applications, the intense cooperation between computational and experimental work and the need for further theoretical developments in computational chemistry.

An unusual and novel study is the simulation of mechanically-induced chemical reactions. Such investigation is important for the detailed interpretation of single molecule Atomic Force Microscopy (AFM). At the same time it gives information on rupture processes, identifies mechanisms which lead to permanent deformation or ultimate material failure in elastomers. Tailor-made chemical modifications investigated on the computer can design ways to enhance material performance. The study of cooperative effects of various hydrogen bridges in biological materials and in solution requires also first-principle simulations and cannot be performed by molecular dynamics treatments based only on classical mechanics. One of the contributions shows how physical properties of water and ice depend on size and the geometrical arrangment of small clusters; treated are up to 24 particles.

The study of catalytic properties of transition metal ions and of surfaces are always in the main stream of computational chemistry work. This year's contributions are excellent examples of joint experimental and computational studies. The hydrogenation of an organic substance on a platinum surface (and an alloy of platinum with a second metal Sn) is investigated with high resolution electron energy loss spectroscopy (HREELS) in conjunction with DFT calculations. All of the measured peaks in the HREELS spectra could be assigned from the calculations and lead to a deeper understanding of the absorption complex and the catalytic mechanism. Another contribution related to catalysis treats the question of rearrangement and decomposition pathways of molecular (transition-metal containing)

complexes. This is a typical question in coordination and organometallic chemistry. The novel feature in this study is the characterization of more local properties in terms of the compliance matrix (related to the Hessian matrix) at a stationary point which describes the stiffness of a molecular system, i.e. its resistance against distortion. In this case more qualitative considerations can be extracted for further experiments.

The final contribution demonstrates again the large range of computational chemisty projects. It is basic quantumtheoretical work and deals with relativistic effects of small molecules with heavy atoms. The wavefunction is obtained in the 4-component form based on the Dirac and not the Schrödinger equation. Two compontens can be interpreted as the "usual" spin-dependent electronic wavefunctions while the other two describe anti-matter, i.e. positrons. This procedure is merged with the most accurate quantumchemistry methods (configuration interaction and coupled cluster treatment) which are designed to account for electron correlation. The resulting implementation is the best theoretical method available at present to determine with high accuracy spectroscopic properties of molecules containing heavy elements. So far its applicability is restricted to small molecules, however.

All articles show the impact of computational chemistry in various areas and at the same time underline the essential role of the John von Neumann Institute for such work.