”Seeing” the molecules
- using DFT calculations and periodic boundary conditions -

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What happens to matter during and after exposure to ionizing radiation? In order to find out, it is important to know what the radiation damaged molecules look like and especially: how they interact with their environment. These properties can only be observed indirectly in the lab. Quantum chemical calculations, on the other hand, provide structures and electron distributions in the molecules directly, and are increasingly used to complement experimental investigations. At the EPR lab at the University of Oslo, this combination of experiment and computations has become a significant part of the research activity.

The calculations are performed using a method known as Density Functional Theory (DFT) which has been extensively used for the last two decades due to its great time efficiency and power to reproduce experimental results. In the solid state, molecules are so close to each other that the interaction between them is important in determining their structures. A time efficient method is of essence when one is trying to describe a solid because a great number of molecules need to be represented in the computation. At present some hundred atoms in one calculation do not cause a problem. But clusters of this size are still quite small and boundary effects occur which may influence the results.

To circumvent the problem of boundary effects some computational packages allow for the use of periodic boundary conditions (PBC). The use of PBC results in a simulation of an infinitely large system with a repetitive character. And only a (relatively) small number of atoms need to be represented explicitly. Such a system is physically more realistic than a molecular cluster in vacuum. The periodic boundary conditions therefore allow for a great improvement of the quality of the computations without a comparable increase in computational time costs.

Examples will be presented of how DFT has been applied to gain more insight in the radiation damages that occur in crystalline lattices. Furthermore, examples on how the use of PBC has improved the quality of the descriptions of proton transfers along chains in crystals and geometrical conformations of biomolecules will be presented.

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