

Calculation and Prediction of Molecular Structures and Reaction Paths

The atomic arrangement of molecules and the changes that take place when molecules react is a central problem in chemistry, molecular and condensed matter physics, and molecular biology. It is not surprising that enormous effort has been expended to calculate these quantities, and supercomputers have played a prominent role.

Geometrical arrangements and reaction paths could be predicted if one could calculate the total energy of a system for all atomic positions. Stable structures correspond to local minima in the energy "surface", and the energy required to perform the transition from one structure to another (the energy "barrier") determines the rate at which the reaction can proceed. Accurate solutions of the Schrödinger equation for the many-electron wave function

would lead, in principle, to this information and much more, but this approach is restricted to systems containing few atoms. The description of the forces in the system by adjusting the parameters of a potential function (a "force field") provides an alternative, but the results are sensitive to the way the parameters are fixed.

Experience over the past 20 years or so has shown that the density functional formalism can provide energy differences that have predictive value. The range of applications has been overwhelming: reactions at surfaces, the structure and magnetic properties of metallic multilayers, catalytic reactions in bulk systems, etc.. The formalism states that the energy (and many

other properties) can be determined from a knowledge of the electronic density. It results in equations that have a form that is similar to that of the Schrödinger equation, but much simpler to solve numerically. Approximations are still unavoidable for one contribution to the energy (the "exchange-correlation energy"), but there has been significant progress on this front as well.

A recent application of density functional methods is provided by the reaction of water with adenosine 5'-triphosphate (ATP). ATP is the most important energy carrier in cellular metabolism, and each human being produces its own weight in ATP every day. The ATP molecule is shown in Figure 1, where carbon atoms are grey, hydrogen white, oxygen red, nitrogen blue, and phosphorus orange. The situation in biological systems is complicated by the presence of water and many other molecules and ions, and we show in Figure 2 the model system for which we have studied two reactions in an aqueous environment: an associative reaction involving the attack of

one water molecule, and a dissociative reaction involving the scission of the terminal bridging P-O bond. Magnesium ions (green) are catalysts in these processes.

The calculations were performed with the CPMD program (J. Hutter et al., IBM Zürich and MPI für Festkörperforschung, Stuttgart), which uses a plane wave basis and makes extensive use of the fast Fourier transform (FFT). The program runs on many platforms, and it is used by research groups in

ATP molecule

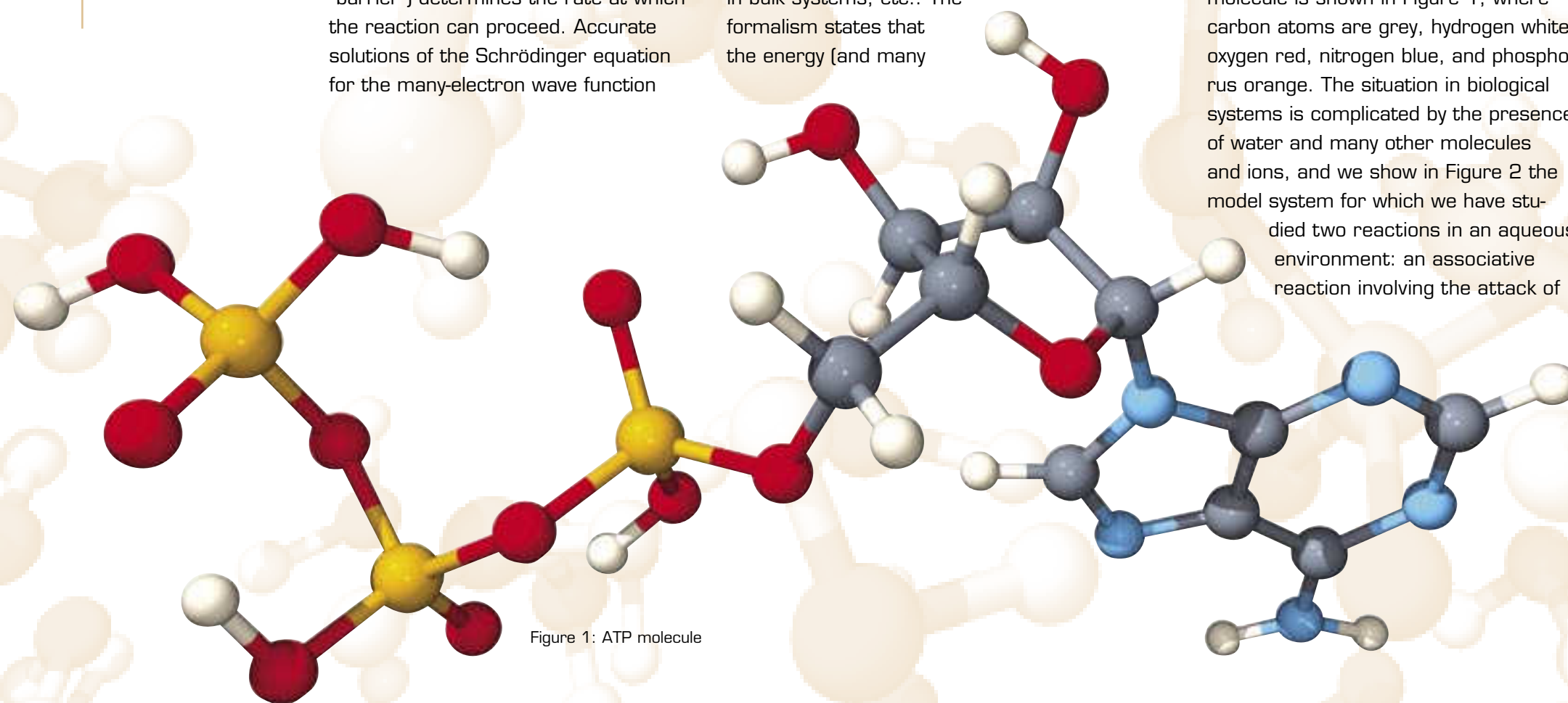


Figure 1: ATP molecule

ATP molecule

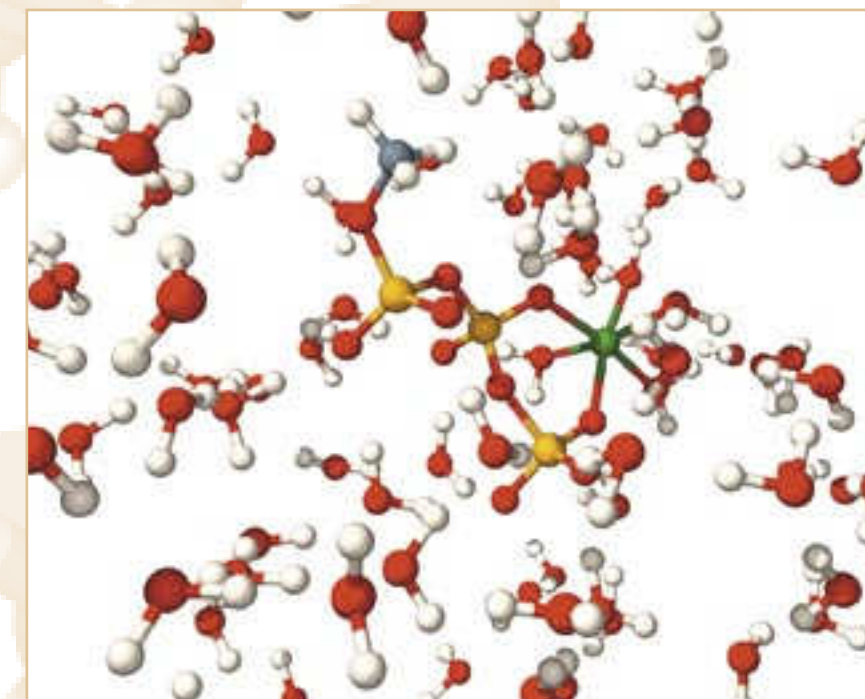


Figure 2:
Chemical reactions of ATP in an aqueous environment

many parts of the world. There are, of course, implementations of the density functional approach in many other program packages.

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