QUANTUM MECHANICAL MODELING: A POWERFUL SUPPORT FOR THE STUDIES OF STRUCTURE AND REACTIVITY OF SOLIDS

Jernej Stare
National Institute of Chemistry, Ljubljana, Slovenia
E-mail: jernej.stare@ki.si

ABSTRACT

The significance of molecular modeling and quantum chemical calculations, particularly under periodic boundary conditions, is presented. Quantum calculations find application in a variety of chemical disciplines, including the structure and function of zeolite materials. Our recent experience with the modeling of the structure and catalytic activity of TS-1, probably the best known representative of zeolite catalyst, is briefly discussed. Application of periodic methods to problems of structure and dynamics in solid-state chemistry is also outlined.

Keywords: quantum chemistry, periodic calculations, TS-1, catalysis.

INTRODUCTION

The rapid development of new technologies provides a constant demand for new and improved materials. Detailed characterization of the structure, dynamics, reactivity and other properties represents one of the most essential steps in the efforts to design new materials with desired properties or improve existing ones. The complexity of required information calls for the usage of complementary methods of characterization. In this sense, computational methodologies represent a valuable support to experimental techniques, since they enable reliable qualitative and quantitative determination of properties of matter at very low costs. Among the variety of computational approaches, those based on quantum mechanics (QM) provide the most detailed insight into matter – namely at the level of electron structure – thus facilitating the interpretation of a variety of properties at the very fundamental level, which is often beyond the reach of experimental methods. In cases when experimental characterization is difficult or impossible, computational methods can even become, at least to a certain degree, an efficient substitute for experimental work.

MOLECULAR MODELING METHODS

Computational techniques for the treatment of molecular systems are commonly known as molecular modeling, and can be divided into two major groups according to the underlying physical background. The so called classical modeling treats the matter as assembly of particles (atoms) connected by elastic springs (bonds); electrostatic and WDV interactions can also be added. All the interactions are expressed in the form of simple mathematical functions, empirically parametrized to experimental data or to calculations of higher accuracy; the entire set of parametrized functions is called the force field. These models operate entirely in terms of classical (Newtonian) physics; because of simplicity they allow for treatment of very large systems (thousands of atoms), but carry no information on the electron structure. Also, the usage of force fields is normally restricted to a relatively narrow group of related compounds, and (re)parametrization of force field often represents a prerequisite for further work.

The other major kind of molecular modeling is quantum-mechanical (QM). QM methods are based on the solving of the Schrödinger equation for the electron structure of the system. As such, they are much more accurate and closer to the first principles than the classical methods. QM methods feature much less empirical parameters (if any) than classical

ones. The major drawback of QM methods originates in their complexity and much higher computational costs; depending on the level of applied theory, the usage of QM methods is in the best case limited to a few hundred atoms, but often to even much less than that.

QM methods for the prediction of structure and other properties of molecules in the gas phase have reached a mature stage and are used as a regular supporting tool to experimental studies. QM calculations such as geometry optimization, vibrational analysis, calculation of atomic charges, NMR chemical shifts, electric potential maps etc. have found place in many research assignments which are otherwise conventionally "experimental". A variety of programs for QM modeling of isolated molecules and molecular clusters is available, of which probably the most known is the GAUSSIAN program package [1]. Supporting most of to-date theoretical formalisms for calculation of electron energy and atomic or molecular properties, it has become readily used not only by theoretical research groups but also by primarily experimental labs. In the field of crystalline solid state research, there is slightly less experience with QM modeling, mainly due to high computational costs. Nevertheless, the formalism for the implementation of periodic boundary conditions has been for a while used in a number of QM program packages such as VASP [2], CRYSTAL [3] and CPMD [4]. Due to the enhanced hardware capabilities, QM studies of crystalline systems have recently become one of the fastest growing disciplines in computational chemistry.

The heart of most QM methods is the expression of the searched all-electron wave function in terms of pre-defined functions ("orbitals"), called basis functions or basis set. Various forms of basis sets are available, and for isolated systems they most often consist of Gaussian-type functions centered on atomic nuclei, while for periodic systems plane-wave (PW) sine-type functions are probably most commonly used due to their intrinsic periodicity. Another popular form of periodic basis sets is based on localized atomic Gaussian functions periodically modulated over the infinite lattice by means of Bloch functions.

One of the essential aspects of periodic QM formalisms is the support for symmetry features of the system, both in terms of restrained atomic positions and symmetry of the electron density. This is important because it enables mimicking of the actual structure as close as possible, but also allows for exploring the influence of symmetry restrictions on the structure of the system. The available packages greatly differ in this aspect, but many of them can recognize and maintain the symmetry. The CRYSTAL program package offers full and rigorous support of space group symmetry according to the crystallographic conventions.

Another important aspect is the support of molecular dynamics (MD) simulation. MD provides information on a real-time behavior and allows for calculation of dynamical quantities such as vibrational spectra. While most of the available packages based on PW representation of the electron structure support MD, CRYSTAL is currently restricted to time-independent formalism.

Below are shown some examples of our recent computational work related to zeolite research and studies of crystalline materials.

EXAMPLES

Titanium site preference in TS-1 zeolite catalyst. In the parent MFI zeolite framework there are 12 inequivalent Si-sites, of which some are replaced by titanium (Fig. 1). The concentration of Ti is relatively low (~2.5 atomic %), but no consensus has been reached on distribution of Ti over the available sites. While some experimental studies show preference of certain sites over another, some studies suggest that the distribution is entirely random and/or is mainly kinetically controlled in the course of synthesis of the material. There have been many computational studies devoted to this problem, but most of them relied on rather

simplified models in which the TS-1 structure was represented by isolated clusters cut out from the MFI crystal lattice and terminated by saturating the dangling valences with hydrogens [5]. As with experimental studies, these treatments gave mixed results regarding the Ti-siting. Our approach was based on the fully periodical 3D model, strictly following the restraints of the experimental *Pnma* space group and the Hartree-Fock and Density Functional Theory quantum methodology with an all-electron atomic basis set. In order to account for lower Ti concentrations, we also modeled the system using the following subgroups of lower symmetry: *P*2$_1$/c, *Pc* and, ultimately, *P*1. Our results show that the Ti-preference is rather modest, the energy span over the sites being about 4 kcal/(mol Ti). The preference order is in good agreement with the experimental findings that suggest non-random siting of Ti in TS-1 [6].
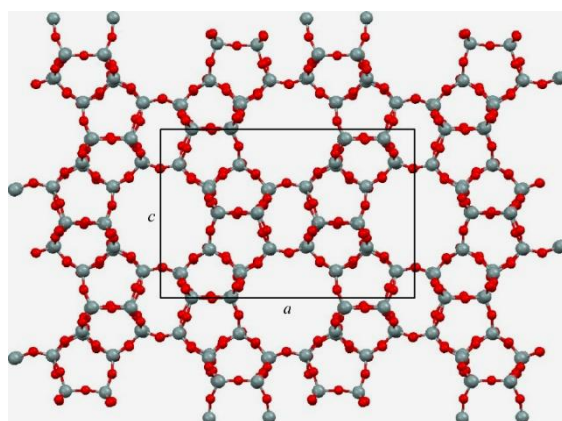

Figure 1. Crystal structure of TS-1 viewed along *b* axis with the unit cell indicated.

Catalytic mechanism of propene epoxidation in the TS-1 framework. The importance of TS-1 derives from the fact that it is able to efficiently catalyze a variety of technologically relevant oxidation reactions of small organic molecules. Despite considerable experimental and computational studies, many aspects of the source of catalytic activity and the corresponding reaction mechanisms remain poorly understood [7]. In our work we studied the propene epoxidation reaction (Fig. 2) which is one of the most widely used catalytic applications of TS-1. At the initial stage we studied in detail the reaction in the gas phase and assessed the factors that have notable influence on the reaction mechanism and on the energy barrier [8]. Among the latter are the external electric field and the presence of water molecules. We have recently started calculations on the reaction mechanism within the explicit crystalline zeolite environment of TS-1 using the program package VASP. Preliminary results show that the reaction energy is comparable to the one in the gas phase. Advanced optimization techniques will be applied in order to evaluate the reaction pathway and energy barrier.
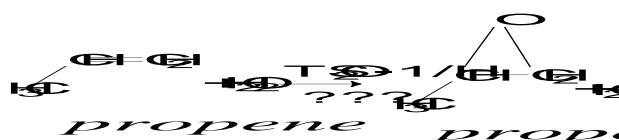

Figure 2. Propene epoxidation reaction.

Structure and symmetry of hydrogen bond in crystalline tetraacetylethane (TAE). TAE is a benchmark example of short, symmetric hydrogen bond with two equivalent equilibrium positions of the proton (Fig. 3). Because of the chemical symmetry of the TAE molecule one

would expect to find two equivalent sites for the hydrogen-bonded proton in crystalline TAE. Rather than that, the proton location is preferably closer to one oxygen than to another, and the proton potential energy function is notably asymmetric [9]. The reason for this is in the fact that the potential energy function is coupled to the torsional orientation of methyl groups. Since the methyl groups are "anchored" to the neighboring TAE molecules by weak C-H…O interactions, methyl rotation barriers are high, which prevents the proton potential from being symmetrized in the course of MD. Our CPMD simulations clearly demonstrate that in the free TAE molecule the hydrogen bond is symmetric while in the crystal it is not.
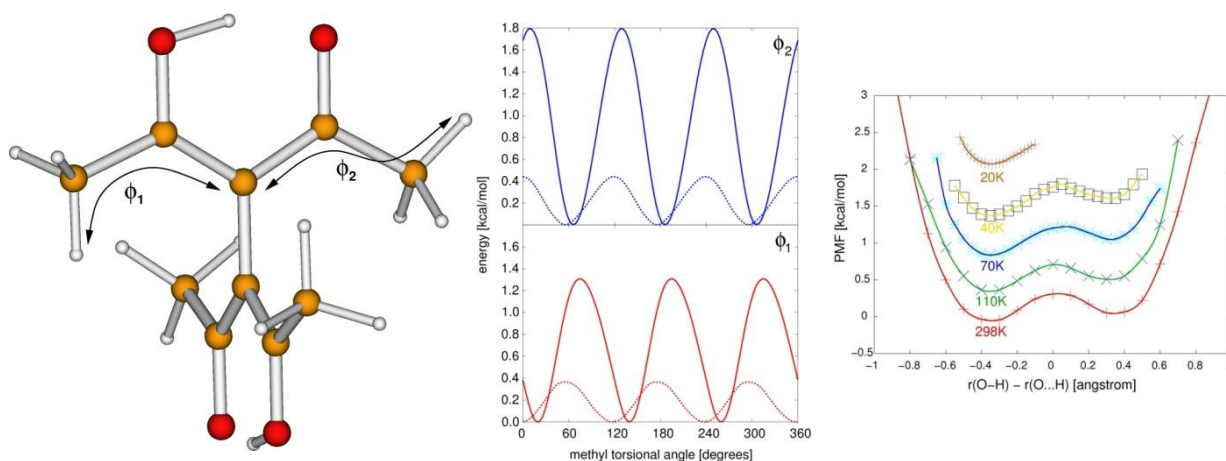
Figure 3. Left: structure of tetraacetylethane (TAE); middle: torsional potentials of methyl groups; right: potential energy profiles for proton transfer at various temperatures.

CONCLUSION

Molecular modeling techniques represent a challenging and versatile tool for the characterization of the structure, dynamics, reactivity and other properties of crystalline solid materials, includeing zeolites. Providing a detailed insight into the structure of matter, they are valuable for the improvement of our knowledge on many aspects of materials and their properties.

REFERENCES

[1] M. J. Frisch *et al.*, *Gaussian 03, Revision B.03.* Gaussian, Inc., Pittsburgh, PA, 2003.

[2] G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54,** 11169.

[3] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Acro, M. Llunell, *Crystal06 User's Manual*, University of Torino, Torino, 2006.

[4] M. Boero, A. Curioni, J. Hutter, A. Isayev, A. Kohlmeyer, N. Nair, W. Quester, Ł. Walewski, *Car-Parrinello Molecular Dynamics* (1990-2008).

[5] See ref. [6] and references cited therein.

[6] G. Pirc, J. Stare, *Acta Chim. Slov.,* 2008, **55,** 951.

[7] See ref. [8] and references cited therein.

[8] J. Stare, N. J. Henson, J. Eckert, J. Chem. Inf. Model., 2009, **49,** 833.

[9] P. M. B. Piccoli, T. F. Koetzle, A. J. Schultz, E. A. Zhurova, J. Stare, A. A. Pinkerton, J. Eckert, D. Hadži, *J. Phys. Chem. A,* **2008,** 112, 6667.