

Editorial

Introduction: the impact of theoretical methods on solid-state chemistry

“What are these calculations good for?” When I read quotes like this one—and I happened to receive such a review when one of my last year’s manuscripts containing a little theory here and there did not find enthusiastic approval by a synthetic chemist,—I sometimes believe that computational/theoretical approaches still have a long way to go until being fully appreciated by the majority of the solid-state chemical community.

Strange, isn’t it, that we still have to defend the most complete and powerful theory—quantum mechanics—for solid-state chemical questions at the beginning of the 21st century? A moment of reflection, however, reveals that the skepticism of some of our synthetic colleagues is understandable, at least to a certain degree, in terms of the historical development.

As we all know, the puzzle of chemical bonding was ingeniously clarified in 1927, not for a crystalline solid but for the hydrogen *molecule*. The rapidly emerging scientific discipline *quantum chemistry* also focused on the molecular parts of chemistry both because of technical and “political” reasons: let us not forget that the most important quantum-chemical workhorse (Hartree–Fock theory) has been particularly resistant to adapt to the solid state, and we surely must be aware of the fact that the solid-state chemical community is limited in size such that the number of “costumers” for quantum chemists is relatively small. As a sad consequence, the solid-state chemists have been left alone for some decades when it comes to questions of theoretical understanding although Bloch’s theorem dates back to the year 1929! Go and try to find the “solid state” in introductory textbooks of quantum chemistry!

Theoretically isolated, the solid-state chemistry community had to find other ways to rationalize their synthetic, structural findings, for better or for worse. Let me just mention the tremendously useful (but intrinsically non-quantum-mechanical) Zintl–Klemm concept or, to give another prominent example, the oversimplifying notion of trying to understand solid-state compounds *only* by considering their electrostatic (Madelung) energies. Oddly as it may seem, the latter concept is still being used today although Hans Hellmann already showed in the early 1930s that

quantum systems comprising only potential but no kinetic energy are thermodynamically unstable. Also, as Roald Hoffmann had carefully observed in 1988, the dominating philosophy within solid-state chemistry had isolated the community even more by not seeing chemical *bonds* between the atoms. Even in 2003, a freshman chemist will probably get the false idea, by looking into regular chemistry textbooks, that molecules are held together by covalent bonds whereas solids are taken care of by ionic forces. Isn’t that weird?

Nonetheless, the changing prospect for quantum-theoretical solid-state chemistry were already laid within the early 1960s when *semi-empirical methods* such as extended Hückel theory were invented. These were simple enough (but not too simple) to allow for semi-quantitative accuracy, they were not too difficult to understand and, quite importantly, they could be easily transferred to large systems, a prerequisite for the solid state; this fundamental step opened the way towards an understanding of solid-state compounds in terms of quantum chemistry. Second, *density-functional theory* was founded at approximately the same time and, over the years, further developed by the solid-state *physics* theorists. Sometimes it seems to me that the present tools of theoretical solid-state chemistry may be looked upon as illegitimate children of semi-empirical/qualitative molecular orbital theory on the one side and density-functional electronic structure theory on the other. But I may be biased.

Due to the exploding growth of computational resources within the 1980s and 1990s which was mostly due to improved hardware (in chemical terms: better solid-state materials!), the new theoretical techniques could be applied to real solid-state systems, i.e., those that you make in the laboratory. At the present time, there is available a whole arsenal of great methods (semi-empirical, density-functional and, yes, Hartree–Fock, too) to solve Schrödinger’s equation for complex solids. In addition, we know of a number of powerful tools such as bonding indicators or localization functions needed to extract the chemical information from the incredibly complicated as well as complex wave functions. Ingenious techniques

for time- or temperature-dependent (solid-state) chemical problems such as the Car–Parrinello method were invented, and there are also other non-quantum-mechanical approaches of computational science on the horizon.

Consequently, this special volume of the Journal of Solid State Chemistry is intended to give the reader an overview of the present status of (quantum) theory within solid-state chemistry, thereby showing the growing importance of theory within solid-state chemistry, its capabilities, its future potential and, also, its present limitations. I am not aware of any prior special volume covering this particular topic and I am therefore especially grateful to the Editors of this very journal for letting me organize this special issue.

In their contributions, the authors cover the whole range of solid-state materials, i.e., insulators, semiconductors, metals and intermetallics, extending from one to three dimensions. The computational methods used include force fields for computer modeling, machine-learning algorithms, semi-empirical quantum chemistry, density-functional or Hartree–Fock techniques, with or without (full-potential) shape approximations for the individual atoms. The basis sets are either totally delocalized (plane waves, preferred by our physicist friends) or localized (atomic-like), adapted to the valence electrons only (pseudo-potentials) or to all the electrons. The scientific focus ranges from fundamental questions touching upon the roots of density-functional theory and electronic correlation to macroscopic quantum phenomena such as (cooperative) magnetism and superconductivity. In order to understand the “chemistry” behind, these phenomena as well as structure rationalization and prediction are typically performed by use of bonding analyses, electron localization, and total-energy calculations. Questions of solid-state chemical reactivity, a relatively new field, are also covered.

As it seems, there is good reason to believe in a bright future for theory in solid-state chemistry, already being of tremendous service to the whole community, even more if a couple of grand challenges will be addressed in the coming years. For example, we have already witnessed, within the last decade, that structure, energetics and physical properties of many solid-state compounds can be successfully modeled, independently checked, and also chemically understood using the above-mentioned numerical tools. Also, theory’s *predictive power* has been impressively demonstrated in the realm of structure (phase) prediction for relatively simple phases such as elements and, say, binary compounds. It remains to be seen whether similar successes can be repeated for ternaries, quaternaries etc. or whether the sheer compositional complexity will render computational approaches difficult or impossible, even if “combinatorial”, parallel

computer technologies will be explored, simply because of the “combinatorial explosion”. Complexity *is* a problem but only if understanding is lacking. Remember that, in chess playing, a slow but *intelligent* human brain can impressively challenge (and sometimes outperform) incredibly fast but dumb parallel computers.

Here’s another grain of salt: While the solid-state theorist’s most important numerical companion—density-functional theory—has turned out astonishingly useful in the past, let us not forget about the breathtaking simplicity of some of the underlying, operational assumptions; it seems that many inhomogeneous solid-state systems seem to be quite tolerant upon being described with homogeneous approaches! But there are a number of serious DFT failures, and it is not at all straightforward how to correctly *improve* and not just “patch” DFT. Even a perfect functional, however, would fail for excited state questions that arise in the interaction of solid-state materials with electromagnetic radiation—the notorious band gap problem. Will we have to struggle for truly correlated methods such as post-Hartree–Fock for periodic systems? What about a temperature-dependent many-electron theory for the solid state? If these materialize, we could put even more trust in the simulation of solid-state chemical properties, irrespective of being cooperative in nature (magnetism and superconductivity) or touching upon analytical probes such as NMR. Coming back to computational power, many believe—I agree—that time-dependent phenomena will set the standard within the coming decades. We all would certainly love to observe solid-state chemical *reactions* (or solidification, or devitrification) correctly computed and displayed by a computer (program), wouldn’t we?

And yet, there is the big challenge to eventually break barriers of language and culture between solid-state experimentalists and theorists. This process is on its way already, but a lot more needs to be accomplished. I was once told that there must have been times when crystallographic techniques were considered not being part of solid-state chemistry, even contrary to its spirit! For the benefit of our science, these obstinate prejudices have disintegrated into nothing, and I would like to see theory become an essential part of solid-state chemistry. If experimentalists would use theoretical methods more naturally and theorists would rephrase experimental wisdom and understanding into more powerful theories, solid-state chemistry would surely blossom and exert an even greater impact on our lives. Let me make myself very clear: I am *not* thinking of yet another numerical/computational trick which lets us solve Schrödinger’s equation a little faster or to a higher precision—the reductionist’s dream. No, the ultimate goal surely lies in novel theoretical concepts, signposts, chemical

descriptors of which there are not so many in solid-state chemistry. It is certainly much more difficult to skillfully *imagine* composition and structure of a room-temperature superconductor than to theoretically compute the superconducting transition temperature of a known material. Again, I may be wrong, and only

the future will tell. What a wonderful situation to be part of !

Richard Dronskowski
Aachen, Germany