

# Crossing the Interface between Chemistry and Mathematics

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**N**umerous researchers have crossed the boundary between mathematics and physics, and the resulting interaction has benefited both disciplines. In contrast, there has been relatively little interaction between mathematicians and chemists.

There are many reasons for this. Historically, the typical chemist has not been interested in problems that have led to tractable mathematical questions. Chemists have traditionally spent the bulk of their time in a laboratory, and the discipline of theoretical chemistry has evolved only recently.

During the last few decades, the situation in chemistry has been changing, largely because of the development of powerful computers. Large-scale numerical computations have been extremely useful in chemistry, and there are now significant numbers of theoretical and computational chemists.

These scientists are working on problems that are very different from those of traditional

laboratory chemistry. Many of their questions and techniques are mathematical in nature, and research opportunities now exist that span the boundaries between chemistry and mathematics. Several such opportunities are described in a report, *Mathematical Challenges from Theoretical/Computational Chemistry*, published by the National Academy Press, which is available on the Internet from the World Wide Web site <http://www.nas.edu/>. This report contains descriptions of many diverse areas in theoretical/computational chemistry where significant mathematical problems have arisen.

Several audiences are addressed in the report, such as individual researchers, funding agencies, professional societies, editors, and college departments of chemistry and mathematics. The report contains descriptions of cultural and institutional barriers to interdisciplinary research, as well as several ideas to improve communication and to foster collaboration between chemists and mathematicians. One suggestion is to encourage students in the disciplines to take courses in the other discipline. Another is for editors to solicit review articles that will help researchers bridge the gap between the subjects. Yet another suggestion is to have more interdisciplinary conferences or simply to have speakers from one discipline occasionally present seminars in the other department.

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The report contains specific examples of successful collaborations between mathematicians and chemists. It also contains descriptions of a large number of diverse areas in chemistry that would benefit from input from mathematicians. A small subset of these areas includes: strategies for the design of new drugs and agricultural chemicals, development of molecular dynamics algorithms, optimization problems, folding of proteins, transport across biological membranes, coiling and uncoiling of DNA, the structure of crystals and quasicrystals, the relationship between quantum mechanics and simpler approximate models, and a wide range of numerical analysis problems. It is conceivable that essentially any area of mathematics could be applied somewhere in theoretical/computational chemistry. In fact, page 44 of the report has a chart in which the authors indicate their guesses as to which areas of mathematics are most likely to make contributions in various areas in chemistry.

A mathematician who wishes to begin working in the area would be best advised to attend appropriate conferences and to consult researchers who are active in the particular subfield of interest. Although the report might serve as a starting point for a newcomer to the area, one should be forewarned that parts of it are superficial, and it does not review all aspects of the subject.

For example, the report does not mention one very successful interaction between mathematicians and chemists that concerns the study of quantum mechanical resonances. Physically, resonances are states with long but finite lifetimes. They play very important roles in chemical reactions.

In the early 1970s, mathematicians working in Schrödinger operators developed a technique that involved embedding certain quantum Hamiltonian operators in analytic families of unbounded operators. Their original motivations involved spectral and scattering theory, and they eventually settled on the name of “dilation analyticity” for the whole process. Among other things, dilation analyticity provided an alternative mathematical definition for resonances. After a few years, some chemists used dilation analytic ideas to develop numerical algorithms for computing resonances, and they gave the process the new name “complex coordinate rotation”. These algorithms were very successful, and the chemists tried to use them in certain circumstances where the original dilation analytic theory did not apply. One of these circumstances involved quantum systems in constant electric fields. Prodded by the chemists, mathematicians studied this situation, which led to interesting new mathematical results. They concluded that

one could indeed use dilation analytic ideas to study resonances in such problems, although the analysis was very subtle. One small surprise that emerged was the realization that the operator

$$-\frac{\partial^2}{\partial x^2} + \lambda x,$$

defined on a suitable domain in  $L^2(\mathbf{R})$ , had no spectrum if  $\lambda \in \mathbf{C}$  was not real. (For real  $\lambda$ , the operator is self-adjoint; when  $\lambda = 0$ , the spectrum is  $[0, \infty)$ ; when  $\lambda$  is real but nonzero, the spectrum is the whole real line.)

Another circumstance where the chemists could not use the original dilation analytic theory involved fixing the positions of the nuclei in a molecule and trying to apply dilation analyticity ideas to the Hamiltonian for the electrons. No one was able to make this work directly, but mathematicians developed a replacement technique for this situation that is usually called “exterior complex scaling”. This technique is much more general than the original dilation analyticity, and the chemists have used it as the basis of successful numerical algorithms. Readers who are interested in this topic should consult Chapter 8 of [3] and [2, 4, 5, 6, 8] for chemistry, mathematics, and physics review articles.

This interchange, which benefited both mathematics and chemistry, was driven by the efforts of a few individuals. Personal contacts played an important role, as did conferences that were attended by both mathematicians and chemists. However, one can see the presence of several barriers to interdisciplinary research. The mathematicians published their articles in mathematics journals; the chemists published theirs in chemistry journals. The two groups have continued to use separate nomenclature. The mathematical articles strove to treat very general situations; the chemistry articles concentrated on specific situations.

A related story illustrates a cultural difference between chemistry and mathematics. The main point of this example is that while mathematicians hold proofs in the highest esteem, chemists are often more impressed by a numerical computation than a proof. Suppose one considers the ground state of an atom or ion with nuclear charge  $Z$  and two electrons (for  $Z = 1$  this is  $\text{H}^-$ , for  $Z = 2$  it is  $\text{He}$ , for  $Z = 3$  it is  $\text{Li}^+$ , etc.). The energy of this ground state is given by a convergent power series in  $\lambda = 1/Z$  if  $|\lambda|$  is less than the radius of convergence  $\lambda^*$ . At some critical value  $\lambda^{crit}$ , the ground state energy coincides with the bottom of the continuous spectrum of the system. In 1966 a chemist, Frank Stillinger, made a conjecture [9] that  $\lambda^{crit} < \lambda^*$ , based on a few assumptions and the behavior of the first 21 coefficients in the power series. This led him to make the physically interesting conjecture

that for  $\lambda \in (\lambda^{crit}, \lambda^*)$ , the system might have a bound state embedded in its continuous spectrum. In 1977 another chemist, William Reinhardt, used a dilation analyticity argument to prove [7] that the precise behavior of an embedded bound state conjectured by Stillinger could not occur. Although this mathematical proof completely answered the physically interesting question, it did not terminate interest in the problem among chemists, partially because Reinhardt's proof did not provide specific information about the value of  $\lambda^*$ . The problem was laid to rest to the satisfaction of the chemical physics community by a spectacular numerical computation by Jonathan Baker, David Freund, Robert Hill, and John Morgan [1] in 1990. They numerically computed the first 401 coefficients in the power series and used them to estimate the values of  $\lambda^{crit}$  and  $\lambda^*$ . They concluded that  $\lambda^{crit} = \lambda^* = 1.09766\dots$

There are several other cultural and institutional barriers that inhibit collaboration between chemists and mathematicians. A researcher in one field who publishes papers in the journals of another field risks being unappreciated in either field or denied tenure or a promotion as a result. Furthermore, there are few people who know both subjects well, and there are relatively few review articles that deal with subjects on the boundary between the two disciplines. If these barriers can be overcome, there are many challenging opportunities at the interface between these two disciplines.

Many chemical questions lead to extremely difficult mathematical problems. For example, suppose one wants to know some detail about the dynamics of a water molecule. The Schrödinger equation that describes this molecule can be written down immediately. Unfortunately, it is a partial differential equation in 40 independent variables (3 for each of 13 particles, and 1 for time). By using conservation of total momentum and total angular momentum, one can separate a few of the variables, but one still faces a PDE in high dimension with singular coefficients. A direct attack on the problem is essentially hopeless, but chemists generate useful information by using a variety of approximations and numerical techniques they have developed. There are plenty of mathematical opportunities here. Are the approximations valid? Are there useful rigorous error bounds? Are the numerical algorithms converging to the correct results? Can one develop better numerical techniques? Water, of course, is a simple molecule. One would like to be able to study much more complicated molecules, such as polymers or biological molecules. The study of chemical reactions is even more challenging, since the num-

ber of independent spatial variables is the sum of those for the individual reactant molecules.

Many chemical questions bear a similarity to this example. One can model the problem at a very basic level, but there is no hope of finding a solution at that fundamental level. The chemists frequently replace the basic model with some approximate model, and they usually resort to computer calculations before reaching any conclusions. Along the way, they leave plenty of opportunities for mathematicians.

Mathematicians who pursue these opportunities will be tackling difficult problems, but they face the prospect of rich rewards. The main messages in *Mathematical Challenges from Theoretical/Computational Chemistry* are that chemistry could provide a source of excellent problems in many areas of mathematics and that increased interaction would benefit both disciplines.

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