Looking Back at 45 Years of Computational Physics and Chemistry

When I agreed to write this editorial column some months ago, I hadn’t given much thought to what I could contribute that would be of general interest to this publication’s intellectually diverse readers. I could have discussed opera and great singers, a passion of mine, or my experiences meeting legendary blues musicians such as Muddy Waters, Buddy Guy, Otis Rush, and James Cotton while I was a graduate student in the chemistry department at the University of Chicago. I could spin some interesting stories about that period (1964–1968), but the subject matter seemed a bit far from the purpose of this magazine and the interests of its readership. As the deadline drew closer, I decided to focus on what I felt were the most influential computational ideas in my own field of atomic and molecular physics (AMP). At the outset, I fully admit that I’m heavily influenced by my training as a theoretical chemist, and while I hope my biases aren’t too dominant, they’re certainly present.

To begin, AMP was an early beneficiary of the advent of mechanical and later electronic computing machinery. This was primarily a consequence of the fact that the interactions are essentially electromagnetic and well understood. The Schrödinger equation for simple atomic and molecular systems could be solved using techniques such as finite difference and variational approaches tailored to treat atomic and molecular collisions. Looking back, a number of early calculations gave good insight into the collisions of electrons with simple atoms and even molecules. In the early 1960s, interest grew in trying to better understand the scattering of electrons from atoms as well as heavy particle collisions. Not coincidentally, this was the early age of digital computing, and the “power” of those machines enabled these approaches to be used to their full potential. The numerical solution of truncated close-coupling approaches applied to electron hydrogen and helium scattering, along with photoionization, revealed the presence of long-lived, temporarily bound excited states embedded in the continuum not yet seen but later confirmed by experiment.

Again, while it was possible to apply these approaches to simple one- and two-electron systems, the complexities of the many-body problem for the continuous spectrum required the development of newer and more robust approaches. The most powerful of these methods relied on expanding the scattering wave function in some set of basis states and then optimizing the linear (and perhaps nonlinear) parameters via a variational method. These methods came in many flavors, such as the R-matrix method, the Harris, Kohn, J-matrix, and so on, and they had many features in common with each other and with bound-state variational methods in that they relied on placing the heaviest computational burden on basis functions that vanished at infinity. Representations on a grid were replaced by coefficients in the expansion of the scattering wave function in the basis, obtained by diagonalizing a matrix or solving a set of linear equations. These operations could be done quite efficiently on existing and emerging computational platforms and were commonly used in quantum chemistry. The main role of the continuum functions was to provide the link between the inside region, where all the complex, many-body physics was taking place, and the outer region, where simplified approaches were being used to extract scattering information. Indeed, it was necessary to find efficient approaches to computing what are called bound-free and free-free
matrix elements, but this could be done easily for atomic systems. For molecules, especially polyatomic molecules, this wasn’t possible, and approximate methods were developed to ease the computational burden. The great similarity to problems in chemistry drew the interest of several theoretical and computational chemists, and many critical advances came from their camp. In addition to these methods, other approaches such as complex rotation, complex exterior scaling, and complex basis functions were also used to “beat the continuous spectrum” and turn these collision problems as much as possible into bound-state problems, well known to theoretical chemists.

The following few decades saw many applications of these approaches to atoms, diatomic molecules, and eventually to complex polyatomic molecules. By the late 1990s, even the great “unsolved” problem, the impact ionization of hydrogen, was attacked by both advanced close-coupling and complex exterior scaling to produce results impressive in their agreement with experiment for very detailed energy and angularly resolved cross-sections. Attention then turned to modifying these approaches to the interaction of short, intense radiation with such targets, an essentially time-dependent problem. This story is still ongoing, but there has already been notable progress.

To close, importing the technology of theoretical chemistry to AMP has led to very significant progress in explaining a diverse set of collision problems involving electrons, photons, and heavy particles. This progress was clearly enabled by the digital revolution and the development of fast, cheap processors and memory. Supercomputers also played a significant role for the most computationally intense tasks. But it would be disingenuous not to also acknowledge the role of novel algorithm development and software. This latter aspect played as significant a role in AMP’s progress as the computers themselves. If neither were present, it’s unlikely we would be where we are today.

My closing message is to urge new, young investigators to read the older papers, learn what we had to learn, and push on to even greater challenges. There’s still a lot to learn and a lot to discover. Enjoy.