The Changing Relationship Between Simulation and Experiment: The Case of Quantum Chemistry

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The role simulation and computational modeling play in the sciences clearly hinges on the advent of electronic digital computers. Since then, both computing technology and simulation modeling have been developing further in close connection. Over the course of their evolution, the conception of computational modeling has changed and the relationship between simulation and experiment has taken on different characteristics. The case of computational quantum chemistry (CQC) will be discussed and three phases of its development will be discerned. These phases differ in the conceptions of computational modeling, in the computing technologies they use, and in the relationship between simulation and experiment.

(i) pre-computer visions

The famous starting point of quantum mechanics is the Schrödinger equation (1924). This equation describes the interaction of electrons in atoms and molecules. The immediately emerging vision among quantum theorists was that chemistry could be made computational. On the qualitative side, it was confirmed that some chemical concepts could be interpreted in quantum theoretical terms. However, due to computational complexity, quantitative results were limited to the most simple cases. Experimental chemistry had a clear leading role. It was the goal of the leading edge computational work to achieve a reasonable fit with experimental data. Only very few and limited quantitatively satisfactory results were achieved in this phase.

From a general perspective, the common viewpoint about computational methods was that there is an exact solution given in mathematical form and that this exact solution should guide the process of computational modeling like a fixed star. Computational modeling then approximates this exact solution step-by-step. As I will argue, the fixed-star viewpoint of approximation arrived at an impasse. Only the acceptance of a partial autonomy for computational modeling *and* a new technology, the digital computer, led to a new dynamics.

(ii) mainframe maturity

Based on the arrival of mainframe digital electronic computers, a full-fledged numerical programme is developed in the 1950s/60s and reaches its maturation during the 1970s/80s. At this point, simulation became full partner of experiment - and computational chemistry an

established (sub)discipline. The history up to this point has received scholarly attention, see for instance Gavroglu and Simões (1994), Simões (2003), or Nye (2003).

A small community emerged that started with pre-computer integration methods but quickly concentrated their interests on digital machines. So-called *ab initio* methods became popular, accompanying semi-empirical methods, but aiming to separate computational models from empirical, experimentally motivated influences. As a defining factor of maturation, I take the systematization and standardization that computational models and methods underwent to make consequent use of the computer. Around 1980, computer methods became "full partner" of experiment. A prime example is Methylene (CH_2) whose computed geometry (bent, not linear) contradicted experimental results (linear, not bent). After several years of controversy, the computational side won. This was an early instance of CQC giving reason to revise experimental

results.

Little by little, computational modeling was conceived as a task in its own right. Regarding the conception of computational modeling, the overall tendency was to trade a strict approximation of the Schrödinger equation for practical numerical methodologies. Criteria for what counts as a "solution" became bargaining chips.

(iii) networked markets

This phase starts in the 1990s and features a new combinatorial type of modeling, networked small computers, and a market-like exchange dynamics. Phase (iii) and the spectacular take-off of CQC, in particular *density functional theory*, will be a main issue of my talk.

DFT is a theory of the *electronic structure* of atoms and molecules. It starts with the Schrödinger equation, but reduces its complexity greatly. In 1998, Walter Kohn, a theoretical physicist, got the Nobel prize in *chemistry* "for his development of density functional theory". This reflects the pathbreaking role of Kohn's theoretical contributions back in the 1960s. DFT immediately played a role in physics since then, but the significant step was that it acquired very quickly an *extraordinary* role in computational chemistry since the 1990s.

John Pople, a mathematically minded chemist, got his half Nobel prize "for his development of computational methods in quantum chemistry". That is, the Nobel Prize gets *computational* - this is a noteworthy combination.

The most important point is that DFT brings to the fore a transformation in the methodology of computational modeling, entailing also a fundamental re-adjustment in the relationship between experiment and simulation.

There is a telling distinction between approaches to electronic structure theories. They are divided in *ab initio* methods and in semi-empirical ones, both traditional but in tension one with the other. The former try to avoid empirical parameters, whereas the latter actively *introduce* parameters to simplify equations and to create an approximate form. This approximate form, then, is solved by fitting parameters to known experimental data. DFT per se is open to both approaches. Semi-empirical functionals became popular in phase (iii). The *ab initio* view, leading in phase (ii), that tries to minimize the number of empirical parameters now has become a minority view. Thus, exploring tentative adjustments, incorporating experimental results, and calibrating good-working parameter constellations, has become an integral part of computational modeling.

The following characteristics of phase (iii) will be discussed:

- the rapid take-off in terms of market and audience,
- the new technology of widely distributed and networked smaller computers,
- the combinatorial nature of computational modeling.

These characteristics are interrelated and support a new conception of computational modeling and simulation. A major feature of the modeling process is that experiment and simulation get inextricably interwoven.

Cited literature

Kostas Gavroglu and Ana I. Simões, The Americans, the Germans, and the Beginnings of Quantum Chemistry: The Confluence of Diverging Traditions, in: HSPS 25(1), 1994, 47-110. Mary Jo Nye: From Chemical Philosophy to Theoretical Chemistry, Berkeley, CA: University of California Press, 1993.

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