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Disciplines, models, and computers: The path to computational quantum chemistry

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ABSTRACT

Many disciplines and scientific fields have undergone a computational turn in the past several decades. This paper analyzes this sort of turn by investigating the case of computational quantum chemistry. The main claim is that the transformation from quantum to computational quantum chemistry involved changes in three dimensions. First, on the side of instrumentation, small computers and a networked infrastructure took over the lead from centralized mainframe architecture. Second, a new conception of computational modeling became feasible and assumed a crucial role. And third, the field of computational quantum chemistry became organized in a market-like fashion and this market is much bigger than the number of quantum theory experts. These claims will be substantiated by an investigation of the so-called density functional theory (DFT), the arguably pivotal theory in the turn to computational quantum chemistry around 1990.

1. Introduction

Many disciplines and scientific fields have undergone a computational turn in the past several decades, including, for example, computational physics and computational fluid dynamics. How can such turns be characterized? Do they merely entail that a particular instrument, the computer, began to be utilized while the disciplinary organization remained unaffected? Or do they involve the creation of a new interdisciplinary field, e.g. in between physics and computer science? This paper analyzes this sort of turn by investigating one particular instance, namely quantum chemistry (QC). It will be argued that a computational turn is characterized not merely by the addition of expertise in computation, but by a more complex transformation involving the interplay of (at least) three components: technology, concepts, and disciplinary organization.

This paper will investigate the formation of quantum chemistry and the pathway it took to what is now called computational quantum chemistry. Both can be perceived as distinct and different configurations regarding disciplinary organization, conception of modeling, and (computational) instrumentation.

The field of quantum chemistry has its origins in a debated interdisciplinary subject falling between physics and chemistry—chemical physics, as it was called—and hence its trajectory tells a story about interdisciplinary exchange. This trajectory is a well-researched subject, most recently in Kostas Gavroglu's and Ana Simões' monograph with the aptly chosen title "Neither Physics Nor Chemistry" (2012). There, they vividly discuss the status of quantum chemistry as an "in-between discipline". More precisely, when one refers to the field as "quantum chemistry" one already takes for granted that it eventually was established as a subdiscipline of chemistry. Gavroglu and Simões argue, though, that there have been points where the trajectory had leaned towards physics, too.

Two claims will be put forward. The first one concerns the formation of quantum chemistry. While the historical literature is unanimous that the computer as an instrument played a major role in the establishment of quantum chemistry, it does not take into account changes and transformations related to different computing technologies. My account will focus on computational modeling and claim that it is an essential element in the formation

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of quantum chemistry. In particular, this claim is directed against a common misunderstanding that underrates the role that computational models play in scientific inquiry and sees the computer merely as an instrument to extract information from theory by computational power.

The second and main claim deals with the more recent trajectory of quantum chemistry. While it was firmly established as a subdiscipline of chemistry in the early 1970s—a re-configuration took place around 1990 that transformed (parts of) quantum chemistry into computational quantum chemistry. The main claim is that the transformation from quantum to computational quantum chemistry involved changes in three dimensions:

On the side of instrumentation, small computers and a networked infrastructure took over the lead from centralized mainframe architecture. Second, a new conception of computational modeling became feasible and assumed a crucial role. And third, the field of computational quantum chemistry became organized in a market-like fashion and this market is much bigger than the number of quantum theory experts. These claims will be substantiated by an investigation of the so-called density functional theory (DFT), the arguably pivotal theory in the turn to computational quantum chemistry around 1990.

2. Quantum chemistry—a subdiscipline of chemistry?

Although nowadays the answer seems to be obvious, it was not so obvious in the early decades of the field. Its trajectory can be depicted as a varied process in which the ties to both physics and chemistry were active and relevant. The trajectory starts with the Schrödinger equation and ends with the establishment of quantum chemistry as a subdiscipline of chemistry. There is excellent literature in the history of science that investigates and describes this process.[1] This section will briefly summarize some facets of the development of QC that are especially relevant as background against which the claims of this paper will be made clear.

In 1926, the physicist Erwin Schrödinger presented his famous wave equation, formulating the new quantum mechanics in a traditional mathematical way that caught attention from the physics as well as the chemistry communities of his day. The equation described the interaction of electrons and therefore promised to entail the full information about the electronic structure of atoms and molecules. Hence, given that the many-electron equation captures the situation adequately, it should be possible to mathematically derive chemical properties, i.e. to extract them from the Schrödinger equation.

A small number of researchers were immediately intrigued by the prospects of a theoretical or quantum chemistry, a field that would be located in between chemistry and physics. Alternative labels used to designate the budding field were ‘chemical physics’ and ‘molecular quantum mechanics’. At that time, very different disciplinary cultures came into contact. In chemistry, experimentalists had the say and theory played a serving role, whereas in physics, quantum theory was a revolutionary development of theory. It was contested whether the envisioned chemical physics should follow the lead of physics or chemistry. As Gavroglu and Simões (2012) aptly point out, researchers in the new field sat uneasily between these disciplines.

With only a moderate degree of oversimplification, one can discern two main lines of research that were pursued: a principled and a semi-empirical one. The principled view originated among German physicists and aimed to derive everything from the Schrödinger equation, the relevant law of nature. The second stance can be called pragmatic, or semi-empirical, and was advocated by young American scholars.[2]

The founding work of the first stance was presented by the young German physicists Walter Heitler and Fritz London (1927) who treated hydrogen bonding, the mathematically simplest case of one pair of electrons. They showed that two electrons with antiparallel spin that aggregate between two hydrogen protons reduce the total energy. Hence homopolar bonding depends on spin and thus must be understood as a quantum effect.[3] Their result was taken as a proof that quantum theory was indeed relevant for chemistry; though in quantitative terms the result was not very close to the value for the binding energy known from experiment.

While Heitler and London were primarily interested in qualitative interpretation, the shortcomings in quantitative accuracy turned out to be of a deep mathematical character. The principled view was hampered by the computational difficulties involved in handling even a very small number of electrons. Electrons influence each other, and this typical case of computational complexity made the treatment of the Schrödinger equation an extremely demanding task. Paul Dirac, in his notorious note, described the situation thus:

> “The underlying physical laws necessary for a mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” (Dirac, 1929, p. 714)

This quote expresses faith in theory and at the same time acknowledges problems on the computational side. Indeed, in further work along this first principled line of development computational problems seemed to become insurmountable, as computing time with extant methods (slide rule, desktop calculator) had to be counted in months or even years. This led to the conviction that chemically interesting cases are out of reach. The principled viewpoint arrived at an impasse and came to a (temporary) end in the early 1930s (cf. Park, 2009 and also Nye, 1993, p. 239).

A second—pragmatic—strand of methodology complemented the first one from early on. Proponents of this camp accepted from the start that experimental approaches should be used as valuable resources. The strategy to circumvent computational difficulties was to resort to known experimental results. This means that if computational procedures get stuck with quantities that have physical significance, but are too complicated to compute, one would plug in values that are determined by experimental means and then go on with the procedure. This approach was called ‘semi-empirical’ and it did not face the impasse of the first approach. “Devising semi-empirical approximate methods became, therefore, a constitutive feature of quantum chemistry, at least in its formative years.” (Simões, 2003, p. 394). Scientists like Linus Pauling and Robert Mulliken—young American researchers with a strong educational background in quantum theory—pursued this line of inquiry.

[1] The two books by Mary Joe Nye (1993) and by Kostas Gavroglu and Ana Simões (2012) stand out as comprehensive accounts. Further references can be found there. In particular, these books make clear that the term “quantum chemistry” was established only as a *result* of (sub)disciplinary formation.

[2] Gavroglu and Simões (1994) give a historical account that highlights the differences between German and American cultures of science.

[3] Carson (1996) discusses the work of Heitler and London as a contribution to the notion of exchange forces.