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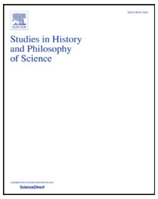

# Disciplines, models, and computers: The path to computational quantum chemistry

Johannes Lenhard

*University of Bielefeld, Germany*

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A B S T R A C T

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

*E-mail address:* johannes.lenhard@uni-bielefeld.de.

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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.

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[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.

## 3. Modeling and computation

The computational problems connected with solving the Schrödinger equation became a main focus of quantum chemistry. However, such problems were normally seen as strictly dependent on the theoretical equation. The art of computing then consisted in using mechanical desktop calculators or inventing computational tricks to numerically solve the complicated integral equations that were conceived as theoretically given. This viewpoint assigns merely a serving role to computational techniques. We will see, however, that this point of view is overly simplistic. The present section will put forward the complementary viewpoint, according to which computational modeling is not derived from theory but assumes an autonomous stance. It will be described how this second viewpoint slowly gained ground, and indeed became a major factor in the development of quantum chemistry.

An interesting case in point is the work of Cambridge mathematical physicist Douglas R. Hartree (1897–1958). He was a pioneer of computational methods and explored computational modeling at a time when it was not yet accepted as an essential part of quantum chemistry (see the study by Park, 2009). He invented a computational procedure to tackle the Schrödinger equation that could be iterated semi-mechanically. It formed the heart of the so-called self-consistent field (SCF) approach, which can be seen as an early example of how computational modeling acquired its status as an activity guided by considerations of its own.

Let us have a closer look. We already mentioned that the interaction of electrons causes insurmountable complexity. The SCF method takes a radical first step and ignores the infamous interaction potentials of electrons, replacing them in the Hamiltonian by one effective field. At first, this field is guesswork and only serves as starting point for the following iterative procedure: one electron is singled out and adapted to the field of the remaining electrons, this latter field assumed to be constant. The first electron is then ‘put back’ and its new, adapted value changes the overall field somewhat. Then the procedure is repeated with the second electron singled out and so on. After every electron has been treated in this way, all values and the effective field are mutually adapted. The entire process is then iterated until the point is reached where no further changes occur, and the field is said to be “self-consistent”.

Hartree’s philosophically significant step was to take into account an instrumental perspective. The whole strategy makes sense only when iteration steps can be performed (relatively) easy so that massive iteration is feasible in a quasi-mechanical manner. Hartree was ingenious in combining extant methods of computation and integration to devise a procedure that actually worked. As one might have expected, Hartree earned some severe criticism, because his approach was viewed as too artificial and even principally flawed. For Hartree, the computational virtues of his model outweighed dubious modeling assumptions (cf. Park, 2009). From our point of view, Hartree’s important move was to take numerical feasibility as a leading criterion, in this way allowing a certain autonomy to computational modeling. Such autonomy inevitably runs against the determinative role of theory.

Contributions that released computational modeling from its strictly secondary status slowly but steadily gained ground in quantum chemistry. One example is Boys (1950) who introduced Gaussian basis functions—at that time still a heterodox approach. This class of functions was initially held not to be an adequate choice, because there was no motivation from the quantum theoretical side and therefore a poor approximation quality was suspected. However, Boys advocated these functions on the grounds that they have excellent computational properties and therefore could serve as versatile building blocks in computational models. Another example in a similar vein is Roothaan’s widely cited paper (1951) that provided mathematical justification (and hence motivation) for the use of analytic basis sets in a Hartree-like numerical strategy. Thus, by the early 1950s issues that originated primarily from computational modeling received treatment from leading theoreticians of the field.

These cases all predate the advent of the digital computer. Some prototypes existed, but these were not accessible for quantum chemists. Without doubt, the digital computer would offer superior computational power and thus make procedures feasible that had been infeasible before. Hence it is correctly seen as a pivotal factor in the development of quantum chemistry. However, complexity remained a threat even with this new instrument at hand. I would like to maintain that it was not simply the computational power that mattered. Rather, the philosophically significant step consisted in perceiving computational modeling as an activity in its own right and not as a strictly secondary issue that is derived from the mathematical form of the theory.

At this point, the argumentation in this paper ties in with the debate on models and modeling in recent philosophy of science. A phrase that captures the gist of the present case especially well is Margaret Morrison’s slogan “models as autonomous agents” (Morrison, 1999). According to Morrison, models mediate between theory and phenomena but are not strictly dependent on either.[4]

## 4. Infrastructure and standardization

How was computation organized in the community of computational chemists? First, let us have a look at pre-computer times when evaluating integrals numerically was an extremely time-consuming work. A telling example is the NAS conference on quantum-mechanical methods in bond theory that Mulliken convened in 1951 on Shelter Island, and which gathered most of the leading people working in this new field.[5]

Computational problems were a dominating issue at the conference: “The need felt most acutely was a reliable table of the difficult integrals which inevitably turn up in valence calculations. Everyone agreed that a conference on such integrals would be desirable, both to find out which integrals would be most useful, and to avoid duplication of effort in computing them.” (Parr & Crawford, 1952, p. 547). The participants decided to build an “Integrals Committee”, located at the University of Chicago, whose task was to identify integrals of common interest, to organize the evaluation of these integrals by different groups, to collect the information, and then distribute tables of numerical values.

The setting changed fundamentally with the introduction of the digital computer. Indeed, “speed matters”.[6] The establishment of quantum chemistry as a subdiscipline of chemistry is in large part the result of the introduction of digital computing machines that changed what computational strategies could count as tractable.[7] However, this was not only matter of speed, but also of access.

Bernard Ransil’s work may serve as an illustration. He received a Ph.D. in molecular physics and used the SEAC computer at the National Bureau of Standards to compute wavefunctions of the $H_3$ radical. In 1956, he moved to Mulliken’s group at the University of Chicago and worked on the design and construction of a computer

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[4] Morrison’s paper is a chapter in Morgan and Morrison (1999) where one can find a succinct introduction to the modeling debate. Additionally, Schweber and Wächter (2000) provide an account of modeling as a new style of reasoning.

[5] See the report about this conference by Parr and Crawford (1952). On the role of founding conferences like this one see Schweber (1986).

[6] So the accurate motto of Humphreys (2004) to characterize computational science.

[7] In the background there is the important issue of meaning and significance of *ab initio* methods that will be addressed in a separate paper.

program to generate wavefunctions (cf. Bolcer & Hermann, 1994, p. 8) This program was written in machine language for a UNIVAC (Remington-Rand 1103) that was located not in Chicago but at the Wright Field Air Force Base in Dayton, Ohio. Mulliken and Roothaan contracted excess computing time from the military. This meant that Ransil had to travel from Chicago to Ohio with a stack of prepared punch cards and work overnight with the UNIVAC.[8]

Nevertheless, after much back-and-forth between Chicago and Ohio, the program ran and delivered adequate results. That was the occasion for Mulliken and Roothaan (1959) to announce "Broken Bottlenecks and the Future of Molecular Quantum Mechanics". In this paper they compare quantum chemistry with the quantitative application of Newtonian mechanics: it took many years to find efficient mathematical formulations to treat problems quantitatively. Now, the authors claim, this time has come in quantum chemistry. They report about the machine program that calculates (important aspects of) wavefunctions of diatomic molecules. "The importance of such a machine program is illustrated by the fact that the entire set of calculations on the $N_2$ molecule which took Scherr (with the help of two assistants) about a year, can now be repeated in 35 minutes … ." (cited acc. to Simões, 2003, p. 396).[9]

When the bottleneck of computing power was gradually removed, the bottleneck of access became more relevant. Researchers were urged to accomplish 'the' right model including correct values for all parameters before they fed the information into the computer, because adaptation and modification of the model or the computer program was laborious and the related multiple use of the computer was expensive.

By the early 1960s, quantum chemistry was the specialty of a relatively small group. In this situation, standardization was pivotal to making quantum chemistry more popular. Rendering software portable was a key goal, but several problems had to be addressed first. One issue was whether users would have access to the code of the software they use. Another point was compatibility, because many types of machines were in use, like IBM 7094, CDC 3300, TR, or IBM 360, that additionally complicated the situation by working with different word lengths (24, 36, 48 bit). The portability of code was a non-trivial problem that had to be addressed when one intended to work on different machines or to distribute the code to other researchers. A third question was how to organize distribution—a question that directly affected the identity and progress of quantum chemistry.

The Quantum Chemistry Program Exchange (QCPE) started in 1962 in Indiana as a platform for the distribution of software. Initially founded with funding from the military, it quickly changed into an academic endeavor in 1966. The goals of QCPE were the collection and distribution of software, including basic verification, i.e. a check whether the program runs, not whether models are valid. QCPE was founded by Harrison Shull, a theoretical chemist at Indiana University, Bloomington. His goal was to create a "central, international repository of software used by quantum chemists," (Lipkowitz & Boyd, 2000, v).

Staff at QCPE was minimal, but the number of users steadily increased in the 1960s and 1970s. For instance, in 1969, 1251 members were listed and 1929 programs were sent out, while in 1970 already 1700 users worldwide contacted QCPE (cf. Bolcer & Hermann, 1994, p. 33). QCPE remained active until the 1990s, when it shut down due to new modes of software distribution being practiced on networked computers.

By 1970, the field of quantum chemistry had consolidated into a subdiscipline of chemistry. The historical accounts by Nye and by Gavroglu and Simões 'zoom out' at this stage and consequently do not pay attention to later developments in computing technology and to related conceptions of computational modeling. However, these developments are highly relevant when one wants to extend the analysis of quantum chemistry to the 1980s and beyond.

A telling example is the software package 'Gaussian', first released in 1970. John Pople, a mathematically minded chemist working at Carnegie Mellon, was a leading figure in the development of Gaussian. He assembled a 'club' of expert groups that contributed various modules to the package that comprised a suite of numerical methods for quantum chemistry. Pople advocated standardization in a theoretical sense. He introduced "model chemistries" as standardized test beds, i.e. classes of well investigated cases that were built into the program so that the performance of new models could be tested against already known results. Secondly, Pople promoted standardization in a technical sense. When researchers used Gaussian, they geared their work towards cases and questions that fit the scope of the program.

In the 1970s and 1980s, the establishment of quantum chemistry meant that a particular configuration of three interrelated components had locked in, comprised of computational modeling, the digital computer as an instrument, and the way the subdiscipline was organized. Thus one claim of the present paper has been shown: computational modeling plays an important role in the configuration of quantum chemistry. We now move on to the second part of the paper that deals with the claim about the 'computational' turn that occurred around 1990.

## 5. New infrastructure—new models

It will be argued that the transition to computational quantum chemistry (CQC) involved changes in all of three components discussed here: conception of computational modeling, computing instrumentation, and disciplinary organization. The transition did not occur abruptly in any of these dimensions. Nonetheless, the years around 1990 will be singled out as the decisive years when the three new components reached a mutual fit. The argument put forward here will rest on the investigation of so-called density functional theory.

First, however, let us have a look at the late 1980s and the changes in computing technology that heralded the computational turn.[10] On the technological side, the so-called "VAX revolution" occurred. The VAX 11/780, manufactured by DEC, was the first "small" machine in the sense of a lab-scale computer, called "superminicomputer", i.e. a computer that would be located in some room in the department or laboratory and directly accessed by researchers—as opposed to a centrally maintained and located mainframe machine with regulated access for various departments and groups. The new technology brought two important changes. First, access to the computer became cheap—when a department had purchased the machine, it was interested in researchers using it. Second, these computers enabled researchers to work interactively, using visualization and graphics displays. Together, these changes encouraged the building of models that needed extensive checking and adapting—instead of the carefully crafted single model demanded in Ransil's times. The VAX types of computer

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[8] For a more colorful version of this story, see Mulliken's "Life of a scientist" (1989).

[9] The group of Boys at Cambridge, working on the EDSAC II computer, reached complete automation at roughly the same time (Boys & Cook, 1960).

[10] The technology did not simply determine this turn, rather it is a matter of the mutual interrelationship between several contributors.

were only the first instances of a fast-paced evolution of small machines like workstations and PCs.[11]

On a bibliometrical register, it has been ascertained that the late 1980s and early 1990s saw an upswing of computational modeling. In quantum chemistry, many journals adjusted titles and subjects to highlight the topic of computational modeling (see Lipkowitz & Boyd, 1997 for more details). This turn to computational modeling directly poses the following questions.

- What are the essential characteristics of the purported turn ‘from QC to CQC’ around 1990?
- How did the change affect the practices and products of modeling?
- What were the implications for (inter)disciplinarity?

These questions will be addressed by examining the trajectory of density functional theory (DFT). This theory has been chosen because it is of special relevance for my argument.[12] One would expect an upswing of the computational branch of quantum chemistry to be a consequence of the general dissemination of computational power. DFT, however, stands out: “The truly spectacular development in this new quantum chemical era is density functional theory (DFT)” (Barden & Schaefer, 2000, p. 1415)—an opinion that the CQC community largely shares. One can readily read off the “spectacular development” also from bibliometric data. A statistical survey of all journals of the American Chemical Society reveals that the number of articles that contain DFT in title or abstract languishes around 30 a year during the 1980s but around 1990 quickly rises by two orders of magnitude to a staggering 4000 per year.

Thus, the obvious question is: what happened to DFT around 1990? DFT was not a brand new theory by then; it originated in solid state physics in the mid-1960s, but has gained outstanding relevance in quantum chemistry around 1990. How and for what reasons did it become relevant in chemistry? It will be argued that the sudden movement of DFT in the 1990s from periphery to indicates the transition from quantum to *computational* quantum chemistry. This turn in the 1990s reflects the availability of small networked computers and also the adoption of a certain conception of computational modeling, which went hand in hand with a new organization of the field. Together these factors make up a new configuration. To explain and justify this claim, we first have to introduce DFT.

## 6. Density functional theory

This section aims at a brief and non-technical introduction to DFT. Quantum chemistry deals with the electronic structure of atoms and molecules. DFT is a theory of this structure that starts with the Schrödinger equation, but then makes a particular move to greatly reduce its complexity. The Schrödinger equation expresses the energy via a wavefunction $\Psi\,(1, 2, \ldots, N)$ that has as variables all $N$ electrons of an atom, molecule, or bunch of molecules. The electrons interact and hence $\Psi$ has $3N$ degrees of freedom (three dimensions of space, leaving spin aside), a number of discouraging cardinality in many circumstances. Practically, to solve $\Psi$ can be seen as a paradigm of computational complexity. DFT, however, expresses the energy in terms of the (joint) electron density, which is an object in space and only has 3 degrees of freedom.

The computational advantages of such a reduction of complexity brought this approach into practical and heuristic use in engineering fields already in the 1960s, but the legitimation behind it was not clear. The theoretical condensed matter physicist Walter Kohn played a major part in producing this legitimation when he and his colleague Pierre Hohenberg proved two theorems (Hohenberg & Kohn, 1964).

The first theorem of Hohenberg and Kohn states that the ground state energy is indeed uniquely determined by the corresponding electron density $\rho(r)$, that is, $E = E\,(\rho(r))$. This equation has to be read as saying that the energy $E$ can be expressed as a function of only the density $\rho$. Recall that the Schrödinger equation expresses $E$, too. The second theorem is a mathematical variational principle: $E[\rho_{\text{trial}}] \geq E[\rho]$, and hence: “the exact ground state energy and density can be calculated without recourse to the Schrödinger equation, at least in principle.” (Bickelhaupt and Baerends, 2000, p. 3). So, in principle DFT is an *ab initio* theory. Furthermore, it is an *ab initio* theory that potentially avoids the Schrödinger equation and its devastating complexity. However, as Bickelhaupt and Baerends aptly write, the promise is one “in principle”, whereas in practice one gets out of the frying pan into the fire.

The 1964 results proved that there exists a function f that gives the energy and that it depends only on the electron density.[13] However, this existence is meant in a mathematical sense, that is, the sheer existence of such a functional relationship between $E$ and $\rho$ is proved, but the theorem does not give any clue as to how that function looks like or how it can be determined. The space of mathematical functions is extremely large (definitely larger than a haystack!), hence to actually determine one particular function might be very difficult.

Kohn was aware of this shortcoming and in the following year he introduced, together with his co-worker Liu Sham, a practical computational scheme (Kohn & Sham, 1965). This scheme postulates a reference system of $N$ non-interacting electrons—a deliberately counterfactual assumption—moving in an effective external potential, the so-called Kohn–Sham potential, instead of the electrostatic potential of the nuclei. The (hypothetical) Kohn–Sham potential is an attempt to deal with the unknown functional relationship by assuming an idealized situation. It places a numerical handle on the problem of how to approximate the unknown functional and has been the main basis for most of the recent developments in DFT.

The mentioned 1964 and 1965 publications were immensely influential papers. Indeed, they are the most cited papers of all times in the flagship journal Physical Review (Redner, 2004).[14] Eventually, in 1998, Kohn received the Nobel Prize “for his development of density functional theory”. This reflects the path breaking role of Kohn’s theoretical contributions.

The reader may wonder how this story about theoretical physics in the 1960s can possibly be turned into a story about computational chemistry in the 1990s. The first step is the observation that Kohn, a theoretical physicist, got the Nobel Prize in chemistry (to his own surprise). DFT played an important role in physics more or less immediately after Kohn’s seminal papers came out. The Kohn–Sham potential was accepted as a workable scheme that provided (approximated) functionals, useful in solid state physics, but these functionals did not provide results accurate enough for properties

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[11] This evolution affected a great number of disciplines and quantum chemistry is only one among many cases of a more comprehensive turn. Johnson and Lenhard (2011) address the development in a broader context of a “new culture of prediction”.

[12] An additional motivation lies in the fact that DFT has not yet received a study in the philosophical literature.

[13] The density itself is a function and functions of functions are often called functionals—hence the name density functional.

[14] Redner also documents the steady flow of citations from the physics community that set in more or less instantly after the publication.

of chemical interest. This situation changed around 1990 and DFT quickly acquired an extraordinary role in computational quantum chemistry.

The second step is the observation that Kohn shared the 1998 Nobel Prize with John Pople, the mathematically minded chemist who has already entered our investigation as a prominent figure in the formation of computational modeling in quantum chemistry. Notably, he was awarded his half Nobel prize "for his development of computational methods in quantum chemistry". That is, the Nobel Prize gets computational—for the first time in its history. While Kohn and Pople may initially appear as strange bedfellows, this couple was a very appropriate pick, because it was the combination of Kohn's and Pople's achievements that underlies the outstanding performance of DFT.

This claim may appear surprising. Pople was a leading proponent of the standardization of computational modeling software, especially the package "Gaussian", which is still the market leader in QC-software. Nonetheless, and somewhat ironically, up to the late 1980s Gaussian did not include DFT. And it excluded DFT for a reason: DFT was based on a function that has been merely shown to exist, and had no chemically promising approximation at the time. However, this assessment changed around 1990 and Gaussian started to include DFT. What made the prospects of DFT look different was a new conception of modeling.

## 7. The combinatorial character of DFT

The extraordinary success of DFT rests on theory as well as on a pragmatic conception of computational modeling that in turn hinges upon the new, compact and easily available computing technology. To argue for this claim, let us consider more closely how DFT works.

How does DFT devise machinery that circumvents the complexity of the Schrödinger equation? After all, the interaction of electrons that we already identified as a main reason of computational complexity does take place in reality. Electron exchange and correlation effects also are included into DFT. However, the approximation scheme of Kohn and Sham assumes that most of this computational 'mess' can be expressed in the form of a *local* potential $v_{xc}(r)$ that contributes to the "effective" (fictitious) external potential $v_s(r)$:

$v_s(r) = v(r) + V_{Coul}(r) + v_{xc}(r)$, where $v(r)$ is the electrostatic potential of the nuclei and $V_{Coul}(r)$ the energy.

This assumption is a crucial idealization, because it opens up paths for computational treatment.[15] As clarified by the practitioners themselves, "This leaves us with an effective one-electron formulation of the quantum many-body problem, which is used in essence by all current implementations of DFT. Note, however, that the exact exchange-correlation potential $v_{xc}(r)$ is not known as some analytical expression in the density $\rho(r)$. Thus, approximations to $v_{xc}(r)$ have been developed: for example, the local density approximation (LDA) or the generalized gradient approximations (GGA or nonlocal DFT), whose quality determines the level of density theory applied." (Bickelhaupt and Baerends, 2000, p. 3).

The details of the mentioned approaches do not matter here (they are the core business of scientists developing DFT-methods). Most DFT approaches work on the basis of the Kohn–Sham scheme. Thus, DFT per se is an *ab initio* method that is potentially computationally very efficient. However, one important gap remains: the mathematical formulation works with an unknown functional $E(\rho)$, whose approximation is based on idealizing (and deliberately false) assumptions.

Given that the exchange and correlation effects can be included in the local potential $v_{xc}(r)$ to a sufficiently appropriate degree, one still needs to decide how they are specified, i.e. which (computationally tractable) mathematical form should be assumed for $v_{xc}(r)$ and which values should be chosen. The form is only approximately specified, with various sophisticated approaches to find a computationally effective approximation. Normally there is a theoretically informed ansatz, like local density approximation, accompanied by the adaptation of this ansatz to known experimental data, or to model chemistries. Thus actual approximations rely on semi-empirical methods and the quality of approximations is judged by the accurateness with which they capture known cases or make predictions.

Now we come to the main point of the argument. It concerns the way this unknown part of the function is specified. For instance, the (unproven) ansatz of Kohn and Sham is that for every system of interacting electrons moving in an external potential, there exists a local potential such that a system of non-interacting electrons will obtain the same density. The status of these assumptions was debated. "For some time a physical meaning of these KS orbitals has been denied" (Bickelhaupt and Baerends, 2000, p. 5). The negative evaluation changed with practical success. The computational scheme, plus its later refinements, where very successful—judged by their predictive quality, not by principled derivation. The theoretical justification of the whole approach was cast into doubt only as long as the performance was not convincing.

The success of DFT resulted from the combination of two approaches. On one side the stunning *ab initio* theory from the mid-1960s contributed to the credibility of DFT. This is not to say that the theoretical part has not seen any progress since Kohn's papers; Perdew et al. (2005) give a detailed account of this progress and suggest a picture of DFT as a still developing, in-principle-*ab-initio* method. However, they also acknowledge that the semi-empirical perspective has won hegemony in DFT. This second, exploratory aspect of modeling practice, where approximation schemes are iteratively adapted to certain cases of interest, stands behind much of the practical success of DFT. The "physical meaning" that had been cast into doubt was established for reasons of performance, not from theoretical derivation.

Prior to around 1990 the quantum chemistry community had looked at DFT with suspicion: an unknown functional whose approximation did not yield accurate predictions did not seem like a promising route to go. Consequently, DFT was not included in Gaussian (in 1970s and 1980s). The success of DFT in quantum chemistry was not yet established at this time. What happened around 1990? How could an approach of such combinatorial nature get off the ground?

These questions bring us back to the claim about the new configuration that marks CQC as different from QC. A performance oriented, explorative and iterative mode of modeling was key. There is no other way to handle 'artificial' parameters, which have to be justified by performance. Moreover, their values have to be assigned through an exploratory procedure. Such procedures, in turn, require easy availability, direct feedback and cheap access to the computer. These were the conditions at place around 1990. Then, and only then, a new combination became attractive: in-principle theory complemented by a layer of semi-empirical adaptation. It is worth noting that the older semi-empirical stance in quantum chemistry worked differently as it did not perceive this strategy as part of modeling.

The tide began to turn when new families of functionals where proposed by Becke (exchange), Lee–Yang–Parr, and Perdew (correlation) in the late 1980s. These functionals worked for model

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[15] Deliberate falsity is a common motive in mathematical modeling. For instance, Ernan McMullin (1985) describes Galilean idealization as falsity for reasons of mathematization.

chemistries, i.e. met the standards of the established (non DFT) quantum chemistry. Success in predictions was unanimously acknowledged in the community and the popularity of DFT increased quickly in the early 1990s. DFT was then—to return to our indicator software suite—included in Gaussian.

It is a consequential development that DFT quickly diversified into quite a zoo of various functionals. In chemistry it is a well established tradition to use instruments that are shaped for specific classes of materials and purposes—in our case these are functionals that are adapted to specific conditions of applications, or to specific materials. The combinatorial nature is further exemplified by so-called hybrid functionals. For instance, the Becke three-parameter functional B3 works with exact exchange, and is combined with a correlation functional to build B3LYP, a very popular variety. Such hybrids are regularly built in the *ad hoc* manner of a weighed average. Which combination works best depends on the case under consideration and is determined by iterative-exploratory testing with the materials or cases of interest.

The major point for the acceptance of DFT were speed, i.e. relatively low order of computational complexity, and good accuracy in predictions.[16] To the extent that users can easily and cheaply access computational resources, the need to adapt functionals to specific cases of interest is no drawback. All sorts of combinations with previous computational approaches were tried to optimize performance of density functionals. Nonetheless, from a theoretical point of view, current functionals remain *ad hoc* insofar as their relation to the correct functional is not clearly known (cf. Barden & Schaefer, 2000).

Up to this point, I have shown how instrumentation and computational modeling are interrelated in the case of computational quantum chemistry. The issue of disciplinary organization will be addressed in the concluding section.

## 8. Conclusion

On a market, goods are distributed that meet demands and customers are experts in using, rather than building these goods. CQC is organized in a similar fashion. The turn to CQC around 1990 is marked by a rapid expansion in terms of market and audience, accompanied by ongoing commercialization. Quite tellingly, the market leader Gaussian included DFT around the same time that Gaussian went commercial, i.e. changed from the academic setting at Carnegie Mellon to “Gaussian, Inc.”. From then on Gaussian addressed a broadened audience of experimentalists and engineers, promising an instrument that is worth its price. Simultaneously, Gaussian started to support the Microsoft operating system, thereby opening up CQC to a much bigger market of non-specialized users that work on smaller machines. Although Gaussian is still the market leader, it has a significant number of competitors that offer a diverse range of functionals. A preliminary search on the internet has indicated that there are about a hundred DFT-related packages on the market, 25% of which are open, 35% academic, and 40% commercial.

The conception of modeling supports an increasing diversity of functionals. If one functional is known to work well for one class of substance and another functional for another substance, perhaps the weighed average (so-called hybrid) is a good compromise when substances are mixed? Questions such as these are answered through computational trial and error. Consider again Gaussian: nowadays it includes not only DFT but more than a dozen density functionals. Its manual encourages users to try several of them and even to combine different functionals, i.e. to customize them, in order to optimize results. There is no advice regarding which functionals should be used in which cases. Instead, the only advice is never to rely on only one functional. Any one functional has to be justified by its performance in the case at hand. Typically, laboratories and working groups maintain their own inventory of functionals and adaptation techniques along with internal comments of how and when to use each of them.

Scientists who work with DFT usually have considerable expertise in finding the right way to work with and modify functionals. It is exactly the goal of the software to make it easy for users to work with functionals, even though users may not be experts in their derivation. For a similar reason, scientists do not need great expertise in programming. Most of them purchase or download the software rather than develop it. Often users may not even be able to view the software code because it is proprietary (as is the case with Gaussian).

In sum, the success of DFT in the practice of CQC is better explained by the dynamics of a market more than it resembles theoretical progress in science. It is fueled by the re-combination and adaptation of building blocks in a networked infrastructure that allows additional cases to be covered, rather than by the quest to reveal the deep structure of QC or to find something like the correct functional.

Should we regard computational quantum chemistry as a new subdiscipline or as an interdisciplinary field? In my view, the more appropriate diagnosis would be that the development of computational quantum chemistry indicates a loosening of boundaries between disciplinary identities. A comparison might be useful here. In 1951 at Shelter Island, the participants in the conference were identifying and discussing a set of problems and computational skills that eventually framed the new disciplinary identity of quantum chemistry. There was considerable interdisciplinary exchange, and several physicists and chemists became scientists in this new (sub)discipline (see the accounts of Nye, 1993 and especially Gavroglu & Simões, 2012).

In CQC, interdisciplinary exchange again plays an important role, but in a quite different manner. On the one hand, computational modeling has become the central topic of CQC, requiring a (albeit not entirely) new set of skills. On the other hand, this has not led to a new disciplinary identity. Instead, many practitioners of CQC work at arm’s length from relevant parts of the modeling activity. The users of DFT-related software, the developers of such software, and the theoreticians of DFT are not identical groups. This is a very different organizational pattern than the one we saw in earlier times at Shelter Island and the “Integral Committee”. The latter marked a common focus that integrated the field. In CQC, different communities interact on a networked architecture.

Thus CQC is marked by three interrelated turns in instrumentation, conception of modeling, and disciplinary organization. The resulting new configuration involves much more distributed expertise and consequently the ‘modeler’s autonomy’ increases—an observation that supports the “models as autonomous agents” viewpoint (Morrison, 1999). Incidentally, this increased autonomy is taken by some QC researchers as a warning sign and as a reason to insist on a stronger guidance by theory.

The case of CQC is arguably only one among a variety of more or less similar cases of computational turns. The art of user-friendly, adaptable, computationally affordable modeling is prevalent in various computational subdisciplines, from CQC and computational fluid dynamics to dozens of new specialties that have been named after established disciplines or subdisciplines with the addition of a

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[16] There are several other methods in use with a much higher accuracy, but also much higher demand of computing power. The use of supercomputers has not vanished during the computational turn. In chemistry, the computationally cheapest method always can be made to pose highest demands for computing power if one considers a big enough chunk of material.

"computational" prefix. These new specialties face questions and problems similar to the ones discussed above. Consider the widespread use in science, engineering, and industry of a great variety of black-boxed software packages. The recent computational turn, our analysis suggests, is not only geared towards a technology of computation, but also relies for its success on a reorientation towards performance at the cost of theoretical explanation.

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