

# Autonomy and Automation

## Computational modeling, reduction, and explanation in quantum chemistry

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### abstract

This paper discusses how computational modeling combines the autonomy of models with the automation of computational procedures. In particular, the case of *ab initio* methods in quantum chemistry will be investigated to draw two lessons from the analysis of computational modeling. The first belongs to general philosophy of science: Computational modeling faces a trade-off and enlarges predictive force at the cost of explanatory force. The other lesson is about the philosophy of chemistry: The methodology of computational modeling puts into doubt claims about the reduction of chemistry to physics.

### 1. Introduction

In philosophy of science, there is a lively debate about the role and characteristics of models. The present paper wants to make a contribution to this debate about *computational* modeling in particular.<sup>1</sup> Although there is agreement about the importance of computers in recent science, often their part is seen as merely accelerating computations. Of course, speed is a critical issue in practices of computation, because it restricts or enlarges the range of tractability for computational strategies.<sup>2</sup> However, it will be argued in this paper that the conception of computational modeling, is not merely a matter of speed, i.e., not only amplifying already existing approaches, but has much wider philosophical significance.

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<sup>1</sup> There may be considerable overlap with the issue of simulation, but the argumentation of this paper does not depend on this part of terminology.

<sup>2</sup> This has been aptly expressed in the part of Paul Humphreys' book (2004) that deals with computational science.

This paper will discuss the case, or the family of cases, of *ab initio* modeling in quantum chemistry. Based on this analysis, two lessons will be argued for. The first is about a topic in general philosophy of science: Computational modeling faces a trade-off between explanation and prediction and enlarges predictive force at the cost of explanatory force. The second lesson belongs to the philosophy of chemistry: The methodology of computational modeling puts into doubt claims about the reduction of chemistry to physics.

Let us briefly elaborate on these two claims. The issues of explanation and prediction are very prominent topics in philosophy of science. While prediction seems to address pragmatic success in the world in a relatively straightforward way, explanation deals with the more intellectual side and has attracted controversial discussions. Of course, explanation and prediction are not independent. Peter Dear, for instance, has written an enjoyable book on two interacting strands - science as natural philosophy and science as instrumentality - that are related to explanation and prediction, respectively (Dear 2006). However, the usual accounts in philosophy of science perceive both concepts as being in line: Predictions follow explanations.

In the covering law account, explaining a phenomenon means to subsume it under general laws. These laws - complemented by initial and boundary conditions - in turn allow us to derive and therefore to predict characteristics of phenomena. Notwithstanding important differences, the causal account also sees explanation and prediction in line<sup>3</sup>. A causal mechanism does not only count as key to explanation, but also will give the means to make predictions about what follows from certain manipulations. One could also argue, though the case is a bit more complicated, that unification via identification of mathematical structures serves explanatory and predictive goals.

This paper wants to argue that computational modeling changes the relationship between explanation and prediction. They cease to be in line, rather there is a trade-off between prediction and explanation: Computational models can be good at prediction at the cost of explanatory force.

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<sup>3</sup> In general, this will not be entirely correct for probabilistic systems. However, this caveat will not be discussed in any detail, because causal explanations do not play an important role in the cases considered here.

For some readers, this thesis will not sound very spectacular. There is an instrumental use of mathematical techniques like curve fitting, or time series analysis, that aim at prediction but do not have clear relationship at all to explanation. This paper wants to establish a stronger thesis that scrutinizes the particular characteristics of computational modeling. To argue for the claim, a very particular terrain is chosen, but one in which a trade-off against explanation *prima facie* seems to be most unlikely, namely *ab initio* methods. These are methods in theoretical chemistry, more precisely in quantum chemistry, that are based on fundamental theoretical knowledge, which means that they are derived from the Schrödinger equation. They received their name as *ab initio* to mark the difference to more empirical methods. Their nature is of philosophical significance because they are applied in chemistry while their basis is in quantum theory, i.e., physics. Hence they assume a central role when issues of reduction are discussed.

The case study will comprise two parts. The first will investigate the birth of the term '*ab initio*'. After giving a primer to quantum chemistry in section 2, section 3 will discuss how a new approach, based on computational modeling and the use of digital computers gave rise to *ab initio* methods. Notably, these were not in full continuity to an older principled approach. The second part of the case study (section 4) will treat a transformation in the conception of computational modeling that occurred around 1990. A new type of *ab initio* methods appeared that had an overwhelming success in practice. Arguably, density functional methods are the paradigm instance and the chapter will focus on them. Their predictive success is, or so will be argued, based on an exploratory mode of modeling that makes use of the cheap and easy availability of small, lab-scale computers. At the same time, this exploratory mode weakens the explanatory force.

Finally, section 5 will summarize the lessons to learn about the meaning(s) of *ab initio*, the relationship between explanation and prediction, and the issue of reduction of chemistry to physics.

## **2. Competing pathways - a primer to quantum chemistry**

In the early 20th century, chemistry had been firmly established as a discipline with a strong experimental culture, considered to be profoundly different from the rational-theoretical branch of physics. The difference was put into question when the new quantum theory was formulated,

and in particular when Schrödinger published his wave equation in 1926. This equation details the electronic structure of atoms and molecules which in turn determines their chemical properties, like bond energies. Hence quantum theory seemed to establish a bridge between theoretical physics and chemistry. At least such a bridge started to look like a real possibility: Shouldn't one be able to *compute* chemical properties from the Schrödinger equation?

More accurately, it was not clear by then whether the potential new field would lean more toward chemistry or physics. The early name of “chemical physics” indicates the somewhat combinatorial nature of what later became known as quantum chemistry.<sup>4</sup> In fact, two complementary views of how the combination of physics and chemistry should work opposed each other. The first camp can be called “principled theory” and foregrounds the physics-side, while the second camp is often denoted by “semi-empirical” and brought in the experimental traditions from chemistry. Both flourished from the start, i.e., shortly after the Schrödinger equation was published.<sup>5</sup> Let us give a brief outline of both standpoints to learn about the role of fundamental theory in quantum chemistry.

### *Visions of theory*

The basic consideration of the principled standpoint is that the Schrödinger equation contains all information about the electronic structure of molecules. Basically, the Schrödinger equation expresses the energy via a wavefunction  $\Psi(1,2,\dots,N)$  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

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<sup>4</sup> It may seem curious that Schrödinger's mathematical equation would trigger changes in how disciplines are framed. From the standpoint of history of science, the pioneering phase of quantum chemistry is the best researched phase. Scholars like Nye, Gavroglu, Simões, and others have laid out the field. The books by Nye 1993 and in particular the monograph “Neither Physics Nor Chemistry” by Gavroglu and Simões 2012 cover the history up to the late 1960's. Both end their narratives with the establishment of quantum chemistry as a subfield of chemistry.

<sup>5</sup> Some readers might wonder about the significance of Schrödinger's equation. It was neither the first formulation of the new quantum theory nor the mathematically most advanced. However, the mathematical form of a wave equation was important, because it highlighted the continuity to established mathematical techniques. Therefore it attracted scientists that had deep interests in chemistry but were somewhat scared by the more abstract matrix mechanics.

freedom (three dimensions of space, leaving spin aside), a number of discouraging cardinality in many circumstances. Practically, to solve  $\Psi$  is extremely difficult and computationally demanding – it can be seen as a paradigm of computational complexity.

Setting practical difficulties aside, it appeared to be possible to mathematically derive chemical properties, such as bond energy levels, i.e., extract them from the Schrödinger equation. Would quantum theory indeed allow to derive relevant knowledge about chemical properties? This question was answered in the positive very quickly. The 1927 joint paper by the German physicists Walter Heitler and Fritz London is widely acknowledged as the first seminal work in quantum chemistry. There they treated the simplest case, the hydrogen molecule, and argued that homopolar bonding could be understood as a quantum phenomenon. The argument was of mathematical nature: From the Schrödinger equation it follows that two electrons with antiparallel spin (a quantum concept) that aggregate between two hydrogen protons reduce the total energy. That result was taken as a proof that quantum theory could be more than a vision: The computation had in fact suggested that chemical bonds have a quantum nature. Although the calculated quantitative value of the bond energy was not very close to the value already known from experimentation, Heitler and London took their result as a great success. They saw questions of interpretation, namely seeing electron exchange (a quantum mechanical effect) as the source of chemical attraction, as far more important than the quantitative accuracy (cf. Nye 1993).

Quickly a small group of quantum theorists, typically physicists, became convinced that quantum chemistry was covered by known fundamental physical laws. The next steps in the principled branch were to tackle (slightly) more complicated cases and to produce more accurate values. One should note, however, that in general results were not predictions but retrodictions of values already known from experiment. Thus, although the principled approach saw quantum chemistry as a genuinely theoretical endeavor, when it came to concrete values and the question of accuracy, the supremacy of experimental results was not challenged.

Dirac's notorious quote, cited in virtually every portrayal of quantum chemistry, expresses the situation:

“The underlying physical laws necessary for the mathematical theory of (. . .) 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, 714)

This quote transports several theses and was received in interestingly different manners. It suggests a complexity barrier, but many quantum chemists of later decades found it overly pessimistic, because new methods and strategies of computational modeling had been able to yield increasingly sophisticated approximations, thus making the barrier penetrable. The quote also suggests a reduction of chemistry to quantum physics, but some historians and philosophers have argued that this would overstate the case. Definitely, the issue is one of intense debate in the philosophy of chemistry.<sup>6</sup> This paper will make a point against reduction exactly from the way in which computational modeling contributes to the success of quantum chemistry.

The principled program was, however, plagued by the computational quagmire that the mathematical strategies ran into. In 1933 James and Coolidge reached a veritable impasse: They used trial functions and were willing to add as many terms as were necessary to obtain an accurate fit. The quantitative results about the hydrogen molecule indeed looked satisfactory, but it became clear that the computation was forbidding - it took more than one year of intense work for them to finish the computations (Schaefer 1986, Park 2009). Moreover, it turned out that, from a computational perspective, pairs of electrons constitute very special (and relatively easy) cases and that the numerical strategy would break down in other cases.

At the time, these problems seemed to be unsurmountable for the principled approach. The mathematician and chemist Charles Coulson recalled in retrospect that after the early 1930s the development of wave mechanics came to a full stop and “despondency set in” (Coulson 1948, cited acc. to Nye 1993, 239).

### *Semi-Empirical Approaches*

The second camp followed a different methodology. Proponents of this camp accepted right from the start that the appropriate strategy to overcome - or rather circumvent - computational difficulties would be to resort to known experimental results. When computational procedures involved terms, say integrals with physical significance, but too complicated to compute, one

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<sup>6</sup> The reductionist viewpoint is widely distributed. For a recent example, see Hettema 2012. A significant number of historians and philosophers of chemistry hold that the applicability of quantum mechanics does not imply reduction, see Gavroglu and Simões 1994, Harris 2008, Scerri 1994, Schweber 1990, Simões 2003.

could interrupt the computation, plug in experimentally obtained values for these terms, and then resume the procedure to compute other terms from there. This approach is usually called semi-empirical, and it avoided 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)

Semi-empirical approaches did not follow one coherent theoretical framework, rather they were orientated toward prediction (or retrodiction) and based on a pragmatic combination of experimental results, theory, and computational modeling. A typical instance is John Slater’s proposal to approximate a molecular orbital. There existed two competing approaches: On the one side, the valence bond (VB), with Linus Pauling as a main proponent, sees molecules as comprised of atoms and works with localized individual electrons that build bonds. On the other side, the molecular orbital (MO) approach, advocated by Robert Mulliken, assumes a mixture of uncorrelated electrons that are shared by a molecule. Slater proposed to approximate a molecular orbital, i.e., a non-localized orbital that belongs to a whole molecule, by a linear combination of atomic orbitals, the so-called LCAO method. In mathematical terms, to model the combination as linear brings maximum tractability and adjustability. In this way Slater made computationally compatible the two complementary approaches – in the service of obtaining (predicting) accurate numerical values.<sup>7</sup>

One might notice that both theory and experiment were crucial parts in the semi-empirical approach and therefore claims for reduction of chemistry to physics are seriously undermined. We come back to this issue later. The consideration of the pioneering phase of quantum chemistry has shown that it was the pragmatic, semi-empirical approach that was dominant while the principled one encountered serious, seemingly unsurmountable, difficulties.

### **3. Automation, prediction, and complete prediction**

The situation gets a new twist when so-called *ab initio* methods were developed. The Latin term “*ab initio*” can be translated as “from the beginning” and has many usages in scientific as well as extra-scientific domains. In science, it is often used synonymously with “from first principles”.

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<sup>7</sup> See Michael Weisberg (2008) for a philosophical examination of the structural conception of co-valent bonding.

The term was first coined in quantum chemistry and the description would fit well to the principled account where computing-from-the-beginning meant deriving from the Schrödinger equation. However, the term *ab initio* was not in use back then, it made its first appearance in Parr et al. (1950), nearly two decades after the principled approach had dried up. The appearance of *ab initio* is closely related to computational modeling and it will be argued that its meaning therefore differs in important ways from the first-principles idea.

To compute something “from the beginning” suggests a certain purity, in the sense that the results obtained will be justified exactly by the principles one had started with. That would amount to a reduction of the computed phenomena to the principles and, at the same time, would amount to an explanation of the phenomena by these principles. For chemistry in particular, the phenomena would be explained by quantum theory (the Schrödinger equation). According to this understanding, the computational modeling part would present a neutral instrument, a tool that makes mathematical derivation feasible and computation effective. This picture is deeply flawed as will be argued.

In quantum chemistry, *ab initio* methods were developed and advocated by a small group from the 1950's onwards and they achieved a leading role in the 1970's and 1980's. Their success was based, however, on something different from what the older principled approach wanted to achieve, namely it rested on a conception of computational modeling that depended on a much more flexible relationship to the Schrödinger equation than the derivation picture suggests. Again, a brief look into the historical development will be useful.

For Parr and others, when they brought up the term *ab initio*, the computational aspect was key. In their paper on configuration interaction in benzene (1950) their point was that the computation could run from start to result without the insertion of empirically measured values. That is, *ab initio* intentionally denotes the negation of semi-empirical. If you have in mind the computational barrier that had blocked the principled approach in the 1930's, how could *ab initio* look like a promising idea in the early 1950's?

First of all, this is not directly due to computer use. Although the electronic computer should become a major factor very soon, such machines were not yet available for quantum chemists. Rather, the new perspective came from a conception of computational modeling that pre-dated the digital computer. The key point was to liberate computational modeling from the task to deliver a numerical solution.



Of course, all computational procedures and strategies have to deliver numerical results. And it is equally admitted that numerical procedures normally are of an approximative nature, not yielding the exact solution. But there are also cases in which a model is constructed for reasons of computational tractability. It is important to see this as a separate case. It is one case to choose a model that treats things as more coarsely grained than a theory would require. It is another case to replace a too complex procedure by something that is tractable but does not have a clear relationship to the original theory.

In short, there can be a trade-off between tractability and derivational accuracy. That means, some modeling choices can be oriented at making the procedure manageable even if there is no justification for why these choices are adequate. A telling example is the work of Boys (1950) where he introduces Gaussian basis functions. These functions have a special “Gaussian” form that guarantees them excellent computational properties, therefore they led to computationally tractable integrals, and thus opened up the pragmatic possibility for predictive success. Initially, quantum chemists were skeptical, because there was no justification from quantum theory that the computational virtues of the class of functions would make the treatment of quantum chemical problems more accurate. Without such a justification in quantum theoretical terms, the approximation quality was cast into doubt. However, the proposal of Gaussian basis functions became a great success on the basis of its good results.<sup>8</sup>

Thus we have seen the attempt to devise methods - *ab initio* methods - that avoid the use of values obtained from empirical measurements. Here, *ab initio* is used in the sense of automation: The goal was to specify a model and implement it as a program and then assign particular initial conditions to this program as input to the computation. The result then would be produced automatically, without further intervention.

If these methods are based on computational modeling and if the latter is oriented more at tractability than at derivation from theory, then the following question seems natural: How is such modeling guided? Apparently, computational cost should not be minimized - that would be

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<sup>8</sup> Klaus Ruedenberg’s work (1951), or Roothaan’s widely cited paper (1951) are further instances of fairly systematic investigations into strategies of computational modeling. Douglas Hartree’s self-consistent field method - it follows an iterative strategy and takes consistency of the model with itself as a criterion - would be another (an even earlier) example for the liberation of computational modeling.

a silly criterion and definitely result in an inappropriate model. The guidance cannot come from (quantum) theory, rather it has to come from predictive (or retrodictive) quality. Thus the pivotal criterion is how accurate do the calculations match the measured values. Quantum chemists can do research on the computational feasibility of certain strategies, but the relevance of such work is dependent on extant computing technology that allows us to get actual predictions about interesting cases. Only then can such strategies prove (or disprove) their predictive potential.

The electronic digital computer was exactly the instrument that let the automation strategies get off the ground. Toward the late 1950's, the first computational models were running on computers without any intermediate insertion of empirically determined values. The first computation of this kind was Bernard Ransil's work on nitrogen.<sup>9</sup> That is, the conception of computational modeling and the computing technology together opened up a new avenue for quantum chemistry.

Based on this development, Robert Mulliken and Clemens Roothaan, the leaders of the Chicago lab of which also Ransil was a part, rushed to announce "Broken Bottlenecks and the Future of Molecular Quantum Mechanics" (1959). The bottleneck to which they referred was the complete automation of computing. They reported Ransil's machine program that calculated (important aspects of) wave functions of diatomic molecules.

"The importance of such a machine program is illustrated by the fact that the entire set of calculations on the N<sub>2</sub> molecule which took Scherr (with the help of two assistants) about a year, can now be repeated in 35 min ... " (1959, 396).

Consequently, this kind of procedure was also called 'complete prediction'<sup>10</sup> to make clear the difference from semi-empirical methods where computation does need empirical values as an extra input and therefore is incomplete. On the other side, 'complete prediction', or automation, may rely on ad-hoc assumptions and computational strategies that are justified by performance rather than derivation from first principles. A group of quantum chemists, like Mulliken (Parr was in his group, too), became strong advocates of computer use in quantum chemistry. Quickly, the term *ab initio* became established to discern the camp that aimed at

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<sup>9</sup> Ransil was a member of Mulliken's lab at Chicago, while the computer he worked with was owned by the military and was located at Wright Air Field, Ohio.

<sup>10</sup> See for example Boys et al. 1956, or Boys and Cook 1960.

‘complete prediction’. With increasing computational capacities and increasing sophistication of computational modeling, the *ab initio* camp steadily grew in importance and arguably assumed a leading role in quantum chemistry through the 1970’s and 1980’s.

Thus, complete prediction, or *ab initio* methods, rest not only on computational capacity but also on a new conception of computational modeling. This conception requires measures that have *neither* a principled *nor* a semi-empirical character. A principled strategy would have to specify a model from quantum theoretical considerations. A semi-empirical strategy would plug in empirically obtained values of physical significance. Instead, the measures required are taken according to computational virtues, including parameters that are adapted (in interactive iterations) according to their performance.

Hence we can discern two different dimensions, or two senses of *ab initio*. One is the principled sense in which *ab initio* computation means derive and compute from the Schrödinger equation. The other is the computational sense, i.e., achieving complete predictions - which tolerates computational models that do not rest on quantum theoretical considerations. While some parts of the reputation of *ab initio* methods may well rest on the principled understanding of this term, our point is that computational modeling normally will go with the second, computational sense.

It should be remarked that tractability is a necessary condition of all computational science, as for instance Paul Humphreys pointed out (2004). Also, there is a great affinity to Bob Batterman’s arguments about idealization in modeling and how they blur the character of models as representations (see e.g. 2010). In a sense, both aspects get combined: Here, idealization is not about simplifying *objects* like turning planets into point masses, rather idealization is about making *procedures* computationally tractable.

To ignore the difference between computational *ab initio* and first-principle *ab initio* would suggest the misleading picture that the success of the computer has made true the old rational-mechanical dream of first-principle based derivation. Such viewpoint neglects the significance of computational modeling, which is not a matter of theoretical derivation but rather a matter of mediation between theory, experiment, phenomena, and computational technology. While the recent discussion in philosophy of science - I dare to omit the usual references - about models and modeling has convincingly supported this standpoint, this paper wants to point out the ramifications for *ab initio* methods.

#### 4. A new computational turn: density functional theory

Computational quantum chemistry experienced a remarkable upswing since around 1990. Among quantum chemists, there is widespread agreement on the special role that density functional theory plays among a couple of *ab initio* methods: “The truly spectacular development in this new quantum chemical era is density functional theory (DFT).” (Barden and Schaefer, 2000, 1415)

Different from other *ab initio* methods from Hartree-Fock to coupled cluster, DFT had rarely been in use before in quantum chemistry. Hence we can formulate a riddle: DFT had its origins in the 1960's in condensed matter physics and was an influential theory in physics since then, but marginalized in chemistry. However, around 1990 an avalanche of applications started in chemistry. In the timespan of a few years, scientific papers went up from around 30 per year to a level of more than 4000. This avalanche certainly calls for an explanation.

The following analysis will show that the success of DFT is based on a twist in the conception of computational modeling that now includes adaptive feedback loops between (tentative) models and known empirical data. This section will first present DFT and its astonishing (inter)disciplinary trajectory, before its character as *ab initio* is critically discussed.

What is density functional theory (DFT)? Quantum chemistry deals with the *electronic structure* of atoms and molecules. DFT is a theory of this structure that circumvents the problem of solving the Schrödinger equation. DFT expresses the energy in a different way, namely in terms of the (joint) electron density - roughly the more likely electrons visit a certain location in space, the higher the density. The density hence is an object in space and has only 3 degrees of freedom.

The computational advantages of such a reduction of complexity had brought this approach in heuristic use in engineering fields, even before the theory was formulated. The theoretical condensed matter physicist Walter Kohn played a major part in advancing this approach to the level of theory. He and his colleague Pierre Hohenberg produced the two founding theorems (Hohenberg and Kohn 1964) that state that the ground state energy indeed is uniquely determined by the corresponding electron density  $\rho(r)$ , that is,  $E = E(\rho(r))$ . Thus, the energy can be calculated without reference to the Schrödinger equation, at least in principle.

Therefore, DFT is an *ab initio* theory (in the principled sense discussed previously) that potentially avoids the Schrödinger equation and its devastating complexity. However, the promise is one *in principle*, whereas *in practice* one gets from the frying pan into the fire.

Note that the reported 1964 results did prove that there exists a function  $f$  that gives the energy and that is dependent only on the electron density.<sup>11</sup> While the energy entirely depends on the form of this function, the theorem does not give a clue what that function looks like or how it can be determined. The space of mathematical functions is extremely large, definitely larger than a hay stack, 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 and Sham 1965). This scheme postulates a reference system of  $N$  non-interacting electrons - a deliberately counterfactual assumption - moving in an (hypothetical) effective external potential  $v_s(r)$ , the so-called Kohn-Sham potential. It is an attempt to deal with the unknown functional relationship by (counterfactually) assuming an idealized situation. It does so to place 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 - and still are - immensely influential papers. One can read this off from bibliometrical evidence: Indeed, they are the most highly cited papers ever in the flagship journal *Physical Review* (Redner 2004). Eventually, in 1998, Kohn received the Nobel prize “for his development of density functional theory”. The reader might wonder how this story about theoretical physics in the 1960’s can possibly throw light upon the 1990’s turn in computational quantum chemistry.

Well, the first step is the observation that Kohn, theoretical physicist, got the Nobel prize in chemistry (to his own surprise). The Kohn-Sham potential had been accepted as a workable scheme that provided (approximated) functionals, useful in solid state physics, but not good enough for predicting properties of chemical interest.

“However, the correct functional of the energy is unknown and has to be constructed by heuristic approximation. Initial functionals, based principally on behavior of the electron gas ( . . .

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<sup>11</sup> The density itself is a function and functions of functions are often called functionals - hence the name density functional.

.) [the Kohn-Sham scheme, j], were lacking in the accuracy required for chemical applications. Breakthroughs over the past two decades (. . .) have led to the development of functionals capable of remarkable accuracy and breadth of applicability (. . .).” (Friesner and Berne 2005, 6649)<sup>12</sup>

So, the question remains what enabled the “breakthroughs” in accuracy? Kohn shared the 1998 Nobel prize with John Pople, a mathematically minded chemist who had a leading role in promoting computational modeling in quantum chemistry. Pople was awarded “for his development of computational methods in quantum chemistry”.<sup>13</sup> Kohn and Pople might appear as strange bedfellows, but it was a twist in computational modeling, as we will see, that enabled the outstanding performance of DFT (though this twist did not come from Pople’s work).

### *The exploratory option*

How does DFT circumvent 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. Hence, electron exchange and correlation effects somehow have to be included in every *ab initio* approach. The approximation scheme of Kohn and Sham makes the crucial assumption about the effective potential - an idealizing and deliberately false assumption that greatly simplifies the computational task (see Bickelhaupt and Baerens 2000 for an introduction.)

What are the ramifications of such modeling assumptions? Given that the (real) exchange and correlation effects can be included in the (hypothetical) potentials to a sufficiently appropriate degree, how are they specified in the context of the model, i.e., which (computationally tractable) mathematical form has this potential and, furthermore, which parameter values should be chosen?

The predictive quality of early functionals was only moderate. They employed only a few parameters, often justified by mean value considerations. These functionals were interesting, because they were ‘computationally cheap’ and the low level of adaptability was not a great

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<sup>12</sup> The authors detail the achievements of various *ab initio* methods in accuracy and computational efficiency.

<sup>13</sup> For the first time that a Nobel prize was awarded for computational methods, but not for the last time as the chemistry prize of 2013 shows.

concern for physicists, namely crystallographers where materials with highly regular structures prevail. In chemistry, materials typically are much more complicated and DFT in general had a predictive quality too low to be useful.

This situation changed, however, around 1990 when a couple of new functionals became available, all of them with a relatively high number of adaptable parameters. To tune these functionals calls for an exploratory mode of modeling that uses extensive feedback loops to adapt parameters and steer model behavior to match known cases. Thus - and this is the key point - we have a two-tiered computational model with a functional that is motivated by theoretical considerations but not fully specified by them. The specification, i.e., adaptation of parameters, is done via iterative and exploratory studies.

In a situation like Ransil's in the late 1950's where it was a tedious task to complete but one run of 'the' right model, an exploratory strategy was not an option. Additionally to computational power, researchers needed easy and direct access to tentatively adapt their models. These conditions were met from the late 1980's onwards when computers were small and cheap enough to be set up locally in laboratories.<sup>14</sup>

One can detect this turn in the trajectory of "Gaussian", the leading software package in quantum chemistry. Pople was a leading proponent behind the standardization of computational modeling, especially in the development of Gaussian that was first released in 1970. Researchers in quantum chemistry started to use this software, because it offered algorithmic solutions hard to achieve when developing software by themselves. Gaussian was and still is the market leader in quantum chemistry software, but up to the late 1980's, it did not include DFT. And it excluded DFT for a reason that we guess from the previous discussion: An only 'mathematically existing' function with not even a chemically promising approximation available appeared dubious and of little use.

However, this assessment completely changed around 1990 when Gaussian started to include DFT. Gaussian nowadays offers a choice of more than a dozen different functionals and, moreover, competes with more than hundred other software packages that include DFT. Most of

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<sup>14</sup> Johnson and Lenhard 2011 argue that a new culture of prediction is connected to the technology of small and networked computers.

the functionals follow different rationales about how to build in parameters and therefore are hardly comparable.

DFT quickly diversified into quite a zoo of various functionals that can be adapted to specific conditions of applications, or materials. For example, the user can build so-called hybrid functionals that are weighed averages of other functionals. With which functionals to start and which weighing factors to choose is dependent on the case under consideration and can be determined by iterative-exploratory calibration only. Derivation from density functional theory does not help when it comes to decide upon which functionals, parameters, and parameter values one should choose. Rather, performance is the pivotal criterion, i.e., the predictive quality as tested by matching known cases. Consequently, Gaussian advises its users always to try several of the functionals on offer and not to trust any particular one.

Thus, predictions play a pivotal role: computing properties of certain materials and adapting the models to known cases gives researchers confidence that properties of similar materials can be predicted (computed) successfully. Many theoreticians are concerned about this development and bemoan, correctly I think, that the impressive dynamics in application of DFT is more based on ongoing adaptation of models to special cases than to general theoretical progress.



### *Shades of ab initio*

The findings from the study of computational modeling in quantum chemistry raise the question what the correct characterization of *ab initio* methods is, or should be. The case of density functional theory (DFT) has revealed two sides. On one side the stunning theorems from the mid 1960's go into it. On the other side, the success of DFT in quantum chemistry depends also on an exploratory mode of modeling that adapts model parameters according to overall performance.

This type of procedure does not fit the principled approach of early quantum chemistry that has been discussed in chapter 2, because the parameters and their values play a crucial role in the model and are not simply derived from quantum theory. It does not fit the (traditional) semi-empirical approach either, because the parameters in question do not have physical significance and their values cannot be empirically measured. In effect, computational modeling has opened up an additional category that combines traits of both older approaches in a new way. In fact, the case study has shown that exploratory computational modeling can be called semi-empirical, insofar as models are adapted, and also can be called *ab initio* in the computational or procedural sense, insofar no empirically measured values are inserted.

Having this in mind, one should be careful when reading about *ab initio* or semi-empirical in the context of computational modeling, if these terms are used without qualification. Engel and Dreizler (2011), for a typical recent example, distinguish the “*ab-initio* or *first principles* approach” which is based on the “true, fundamental Hamiltonian” from a model-based approach that studies a “suitable *model* Hamiltonian”. For them, *ab-initio* can have adjustable parameters, but only for “technical approximations”, not “adjustable physical parameters” (2011, 1/2). The model-based approach, according to Engel and Dreizler, tries to construct a simpler model as basis for calculations. Then physical parameters might be introduced and determined from sources external to the model, like empirical experiments.

Engel and Dreizler do not engage in a terminological discussion, rather they take the notion of *ab initio* as unproblematic. However, the distinction they make suggests that an *ab initio* approach would *not* be model-based. But such a view is misleading, because *ab initio* approaches rely on computational modeling. Engel and Dreizler might want to subsume such modeling steps under the category of “technical approximation”. This would, however, mask the autonomous status of computational modeling. We have seen in the case study that

computational modeling assigns non-physical parameters a central role - a fact that arguably is widespread in scientific practice, but cannot be adequately captured in the traditional terminology Engel and Dreizler use.

## **5. Conclusion: Reduction and Explanation**

From these arguments about the characteristics of computational modeling follows a lesson about a most discussed topic in the philosophy of chemistry, namely a lesson about the issue of reduction. There seems to be a strong argument for irreducibility, or at least against reduction in a certain sense. The case of *ab initio* methods should be the strongest case in favor of reduction, because they promise to use a physical theory for deriving the facts of chemistry, much in the spirit of the Dirac quote given on the first pages of this paper. However, we have seen that *ab initio* methods (typically, probably not always) rely on autonomous modeling steps that do not have a quantum theoretical rationale. Hence the results of such methods can hardly count as being derived from quantum theory. And if one is willing to take predictive accuracy as indicator for reduction, then reduction loses much of its epistemic relevance.

In brief, we are confronted with a somewhat ironical situation: The conception of *ab initio* methods entails a strong reductionist claim. The computer was decisive to leverage *ab initio* methods, but the characteristics of computational modeling undermine their reductionist claim.

In one further step, we arrive at the conclusion concerning the issue of explanation and prediction. It has been argued that the quality of predictions systematically plays a pivotal role in computational modeling. It does so, because the performance regarding predictions (including retrodiction, i.e., matching known cases) is often the only criterion to judge the adequacy of modeling steps like parameter adaptation.

However, all the iterative refinements that increase predictive success, at the same time decrease the explanatory force. The fact that quantum chemists deal with a compound of principled theory, (autonomous) modeling steps, and adaptive loops shows that quantum theory plays a decisive role - as a part of the compound, but at the same time it shows that epistemic opacity looks inevitable. It gets difficult to attribute model performance or certain parts of model performance to certain model assumptions. Epistemic opacity has been identified as an important

characteristics of simulation modeling (see, for instance, Humphreys 2009). Put briefly: Even *ab initio* methods are plagued by epistemic opacity. Over the course of adaptations, epistemic opacity grows and therefore prediction is not in line with explanation, rather works against it.

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