

Is Quantum Chemistry a Degenerating Research Programme?

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Abstract

This note is intended to address one particular issue in the relative status of Quantum Chemistry in comparison to both Chemistry and Physics. It has been suggested, in the context of the question of the reduction relations between Chemistry and Physics that Quantum Chemistry as a research programme is incapable of furnishing useful guidance to practising chemists. If true, this claim will let us qualify Quantum Chemistry as a degenerating research programme, which, due to its complexity has difficulty to be applied to Chemistry. This claim is shown to be false. The replacement claim I wish to make is that Quantum Chemistry is perfectly capable of furnishing such guidance, but renders the ontological status of many models favored by chemists problematic. Quantum Chemistry, however, validates these models in an instrumental fashion. I will argue that Quantum Chemistry is a progressive research programme.

1 Introduction

In the 1970's Imre Lakatos [1], in response to the work of Kuhn [2] and others in the history of science, introduced the notion of a research programme. The con-

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cept of a research programme was aimed at reconciling Kuhn's theory of scientific paradigms with the ideas of falsification stemming from Karl Popper [3].

As is well known, a research programme in the sense of Lakatos is characterised by a succession of theories, for instance T and T' . The programme itself consists of a 'hard core' and a set of 'auxiliary hypotheses'. While researchers generally protect the 'hard core' from refutation, changes in the auxiliary hypotheses, also called 'problem shifts' are allowed. Theory change thus involves a change in the auxiliary hypotheses rather than the hard core of the theory.

A research programme can be progressive or degenerating. A research programme is progressive when a sequence of theories T and T' predicts new facts.

Andrea Woody, in a recent paper [4], discusses the explanatory weaknesses of *ab initio*¹ Quantum Chemistry in the context of reduction between Chemistry and Physics. I will leave the discussion of this reduction relation to a later paper. In this paper I want to take issue with her portrayal of Quantum Chemistry as, what in Lakatosian terms, can only be described as a degenerating research programme.

I only wish to note here that in the context of reduction relations I read Woody's paper (and her proposed strategy to deal with reduction) as follows: while Quantum Chemistry has been successful in post-dicting the energies of small molecules (such as the hydrogen molecule) with great precision, it struggles with delivering useful information to practicing chemists².

Therefore, while reduction ('as a standard deductive account of theory reduction' in Woody's terminology) can be held to be successful, the issue becomes one of 'reduction to what'—i.e. the claim is that it is ontological reduction that fails.

While I do not believe that Woody's picture of quantum chemistry is inadequate, it is misleading in that it both underestimates the usefulness of Quantum Chemistry to the practising (or 'bench') chemist and misunderstands the nature of reduction that is at play here. In the light of these inadequacies, I believe the set of critical conclusions concerning *ab initio* Quantum Chemistry around which a consensus has seemed to emerge in the recent literature needs to be revised.

Central to Woody's claims is the notion that Quantum Chemistry is a discipline which is constrained in its application to chemical problems by computational and representational complexity. This contention rests essentially on three claims, which are summarised by Woody as follows [4]:

¹'From the beginning', or first principles. This generally refers to a type of Quantum Chemistry that does not make use of 'semi-empirical' approximations. The latter type used to be quite common in the early days of Quantum Chemistry, when computer power was limited; these days, semi-empirical methods are less prevalent.

²As an aside, it is to some degree questionable how much of Woody's paper is a contribution to the reduction debate. The paper is cited by Scerri [5] as one of the more insightful contributions to the problem of reduction in Chemistry.

1. First, computational complexity restricts the scope of application severely (page S617).
2. Second, this same complexity restricts the utility of analyses that are within reach. The series formulation of the wavefunction prohibits easy identification of a molecule within the representation scheme. (S618)
3. More important, ab initio calculations comprise a set of unconnected derivations concerning the energetic states of particular molecules. The derivations have the same starting point, the stationary state Schrödinger equation, but are otherwise distinct (S618).

These claims, if true, paint a picture of a discipline mired in computational complexity which struggles to be useful to its field of application (claims 1 and 2). Moreover, it is only able to provide a very partial account of issues that concern practising chemists (claim 3).

While the the notion that on this account Quantum Chemistry is a degenerating research programme in this context is mine, it seems not too problematic to hold this view.

Lakatos translates Popper's well-known three requirements for the growth of knowledge into his statement that new theories are classified as 'scientific' if they lead 'to the discovery of novel facts. This condition can be analysed into two clauses: that the new theory has excess empirical content (acceptability₁) and that some of this excess content is verified (acceptability₂)'. He then goes on to argue that for the sophisticated falsificationist 'a scientific theory T is falsified if and only if another theory T' has been proposed with the following characteristics: (1) T' has excess empirical content over T , i.e. it predicts novel facts, i.e. facts improbable in the light of or even forbidden by T ; (2) T' explains the previous success of T , i.e. all the unrefuted content of T is included (within the limits of observational error) in the content of T' ; and (3) some of the excess content of T' is corroborated.'³

A degenerating research programme, on the other hand has none of these features. Theory succession is driven by failure to predict novel facts, and more and more 'ad hoc' additional hypotheses have to be introduced into the framework to keep connected to the facts.

We need one assumption. We have to assume that the scope of the 'facts' that Quantum Chemistry wishes to generate is a set of chemical facts. It can be argued that Quantum Chemistry produces useful facts for other, related physical sciences. For the purpose of this paper, however, I wish to evaluate Quantum Chemistry as targeted to chemistry rather than other disciplines.

³[1], page 116).

With this assumption we can evaluate Woody’s claim as a claim that Quantum Chemistry is a degenerating research programme. Woody’s first and third claims imply that the scope for the discovery of novel facts is limited—firstly because the scope of application is limited due to complexity, and mostly limited to unconnected energy states of molecules. Woody’s second claim, that quantum chemical analyses are not very useful, points in a similar direction—quantum chemical research on this account is primarily driven by internal considerations, but is not particularly connected to chemistry due to its complexity of interpretation.

This paper will proceed along the following lines. In the following section I will argue that Quantum Chemistry is indeed a research programme in the sense of Lakatos, and qualify it as a progressive research programme. In the last section I discuss the claims above and show that they are problematic.

2 Quantum Chemistry as a Research Programme

Quantum Chemistry attempts to explain chemical phenomena through a computational solution of the basic equations of quantum mechanics. The calculations of the Quantum Chemists rely on computer programs that capture the basic equations of quantum mechanics combined with a (significant) set of assumptions and a relevant context. It is the case that these computer programs are able to compute the properties of atoms and most small molecules with (almost arbitrarily) high precision⁴.

In the paragraph above, I use the word ‘computer program’ deliberately. The work of Primas [9, 10] discusses in detail the weaknesses in explanatory power of quantum mechanics when it comes to reduction of chemistry to physics. But the computer programs of the quantum chemists do not implement ‘pure’ quantum mechanics, but instead use an idealised form, one where the logical structure of the chemical problem is pre-supposed.

The key point is that the time-independent Schrödinger equation

$$H\Psi = E\Psi \tag{1}$$

provides little instruction in how it could be used to model atoms or molecules. H is the Hamiltonian operator, which corresponds to the property of energy

$$H = \sum_i h(i) + \sum_{i \neq j} g(i, j) \tag{2}$$

⁴There are a large number of references that I could give here. I will restrict ourselves to a relatively small number of overviews to substantiate the general points that I wish to make. A good overview of the methods which I will discuss is given in McWeeny and Sutcliffe [6], McWeeny [7] or Wilson and Diercksen [8].

where $h(i)$ is the one particle operator (consisting of kinetic and potential energy) and $g(i, j)$ is the electrostatic interaction between electrons i and j .

In actual practice, to solve the equations for a small or large molecule, the quantum chemist relies on the following idealisations and concretisations (see also Woody[4] for a slightly different enumeration⁵):

1. The geometrical structure of the molecule is put in to the program.
2. Relativistic effects are generally ignored⁶
3. With each atom there is an associated ‘basis set’ in terms of which the wave function will be expanded. The quality of the basis set has a direct influence on the quality of the overall result of the calculation. Basis set selection is in fact a bit of a fine art (black art?) in practical quantum chemistry.
4. Generally, the first level of solution is a ‘self consistent field’ solution (SCF or Hartree-Fock wavefunction) which ignores the effects of electron correlation. This wavefunction is an effective one-electron function (i.e. it ignores two electron terms and hence electron correlation) which satisfies the Brillouin condition. In general, the SCF wavefunction is a starting point for more complicated treatments. It should be noted that it is perfectly possible, with the Hartree-Fock solution in hand, to draw pictures of the Hartree-Fock orbitals and talk about its ‘orbital energies’.
5. Electron correlation is subsequently introduced through either Configuration Interaction (CI) or Multi-Reference methods (which are both variational methods), or so called ‘Many Body’ Perturbation Theory methods (either Many Body Perturbation Theory (MBPT) or the more sophisticated Coupled Cluster (CC) approach).
6. Electronic properties than have to be predicted with these wavefunctions—i.e. an ‘operator’ that corresponds with the property needs to be chosen.

It should come as no surprise that the problem for large molecules with high degrees of precision (i.e. large CI expansions or complex Coupled Cluster equations) can become intractable.

⁵Although Woody’s enumeration is somewhat different, I do in the main agree with her classification as well, though I believe my own to be more comprehensive.

⁶Although there is a significant research program in ‘relativistic quantum chemistry’, the equations to be solved tend to be an order of magnitude harder than the equations of non-relativistic quantum chemistry. The situation is not helped by the fact that relativistic effects are most pronounced for heavy atoms and molecules with heavy atoms—i.e. those areas of the Periodic Table where quantum chemistry can become practically intractable.

However, the *practical* intractability of some of these problems does not mean that they are *principally* impossible. In fact, for areas where quantum chemical solutions have been practically feasible (in general atomic calculations and small molecules) the results have been impressive, and there is little doubt that the mechanisms generally employed by quantum chemists are capable of producing these results for as yet unknown cases.

We are now in a position to consider how Quantum Chemistry can be conceived as a Lakatosian Research Programme. Our basic supposition will be the following:

- Its hard core consists of the basic equations of (time independent) quantum mechanics. These can be conceived of the time-independent Schrödinger equation, but also of a number of lesser-known theorems, such as Ehrenfest's theorem, the Hellman-Feynman theorem and the creation of operators that correspond to observables.
- Auxiliary hypotheses correspond to the idealisations and concretisations above. Auxiliary hypotheses thus consist of (i) Molecular Structure, (ii) Non-relativistic Schrödinger equation, (iii) Basis sets, (iv) 'One electron' SCF wavefunctions, and (v) Electron correlation methods

It now remains to show that Quantum Chemistry is a progressive research programme, i.e. that successive improvements in the auxiliary conditions have led to progressive problem shifts and still continue to do so.

(i) For molecular structure, there is not much to say. Generally, practising Quantum Chemists have to start with some notion of molecular structure, though the starting structure of a calculation does not have to correspond to the chemical equilibrium structure of a molecule. Quantum Chemists regularly calculates the electronic energies and properties of molecules outside their equilibrium state, and this leads to new insights in areas such as reaction dynamics. In particular, Quantum Chemists are able to make predictions on the stability of molecules that do not yet exist. All in all, there is little reason to suppose that the area of molecular structure poses serious questions.

(ii) The next auxiliary hypothesis is the neglect of relativistic effects. This neglect is not universal. Quantum Chemists are well aware that relativistic effects do have a bearing on their predictions of molecular energies and properties. There is a significant and fruitful research effort to quantify relativistic effects. The issue here is that relativistic effects can generally be introduced in either of two ways. The first is to consider relativistic operators as perturbations to the non-relativistic Hamiltonian. This method is perhaps more practical, but is theoretically less attractive. From the work of Dirac we know that the relativistic Schrödinger equation

takes on a form that is very different from the non-relativistic equation. It is so different that this equation is often referred to as the Dirac equation.

The relativistic research programme in Quantum Chemistry then consists of solving the Dirac equation with auxiliary hypotheses similar to the ones above. It is thus, on a strict interpretation of a Lakatosian research programme, a separate research programme since it has a different ‘hard core’.

(iii) We now come to the basis set. Basis set choice is something of an art in Quantum Chemistry in the sense that the selection of a poor basis set will have adverse results in the result of the calculation. However, basis sets are not the achilles heel of quantum chemistry. There is research being done in improving the quality of basis sets, and there is also a solid understanding of what quality basis sets are required to solve chemical problems of a certain complexity. For instance, calculation of molecular dipoles and quadrupoles requires addition of ‘polarisation functions’ to the basis set. These polarisation functions are not made up after the fact; we know they have to be there because a basic consideration of the symmetry of molecular integrals tells us that the calculation will be incomplete if these are not considered. It is thus the case that the form of the basis set can be decided ‘a priori’ with reference to the molecular property we want to calculate.

(iv) The one electron SCF wave function is a common starting point for further calculations involving electron correlation. With computers less powerful, Quantum Chemists have long lived with a situation in which these wave functions were the best they could do (generally the sixties, seventies and much of the eighties of the last century). At present, however, calculation of an SCF wavefunction for small to midsize molecules is more or less routine.

The case of the SCF wavefunction is of particular importance for our discussion and I will discuss it briefly in some more detail. A completed HF calculation specifies a set of atomic or molecular orbitals ψ_i , (which can be plotted as density graphs) and a corresponding set of eigenvalues (‘orbital energies’) ϵ_i . There are, moreover, occupied and empty (virtual) orbitals.

The particular minimal condition that has to be satisfied by the HF wavefunction is the Brillouin condition, which requires that matrix elements of the Fock operator between virtual and closed (or occupied) shell orbitals vanish. The Brillouin condition is thus a relatively weak condition, which allows for an arbitrary large number of orbital sets to satisfy the HF equation. The most often used representation is the ‘canonical’ HF equation, where the orbitals diagonalise the entire Fock matrix.

It is not the case that the Hartree-Fock description of atomic and molecular properties yields descriptions that are chemically irrelevant. There are (see [7] page 164-166) a number of relevant molecular properties that may be derived from this wavefunction. (i) The HF eigenvalues ϵ_k for the occupied correspond to the

ionisation energy I_k needed to produce a positive ion by removing an electron from ψ_k . (ii) Similarly, the eigenvalues ϵ_m represent empty places that can be taken up by an additional electron, and the difference between orbital energies provides a first approximation to the excitation energies of the system. (iii) The HF wavefunction will support the calculation of spatial electron densities.

This is not to claim that the HF method is the best possible answer to these entities (it is not), but serves as a reminder that the HF wavefunction, if desired, supports the type of diagrammatical interpretation which features in the second half of Woody's paper. I also want to note that the HF wavefunction is not the only wavefunction that supports this type of interpretation, other types do it as well (though with more mathematical and computational effort).

The 'if desired' qualification is of key importance here. While the HF function will support these interpretations, it also renders them ontologically problematic (see for instance McWeeny [7] page 135 and page 200-206).

Since the minimal condition to be satisfied for an HF wavefunction is the Brillouin condition, the occupied and virtual wave functions are unique up to a unitary transformation that separately mixes occupied and virtual orbitals. There is thus a large degree of arbitrariness when one applies Quantum Chemical wavefunctions to, let's say, an analysis of the number of electrons in a given chemical bond ('population analysis') and it is possible to come up with various spatial representations, dependent on the methods deployed to 'localise' these orbitals.

Nevertheless, there are limits to this ontological arbitrariness. As McWeeny points out, even while there are different localisation criteria, for many cases they tend to come up with similar results ([7], page 203):

Usually, when applied to molecular closed shell ground states, the various localization methods lead to orbitals that are concentrated either around individual nuclei (for example inner shell orbitals not very different from those in free atoms) or in the "valence regions" (for example, lone pair orbitals, mainly on *one* centre, and bond-pair orbitals, confined mainly to adjacent centres) .

(v) The last auxiliary hypothesis of Quantum Chemistry is the method chosen to consider electron correlation. There are generally two approaches here (Woody mentions only one). The variational approach leads to Configuration Interaction (CI) or multi-reference approaches, where the wavefunction is written as an expansion of many configurations of like symmetry.

In addition, there exist perturbational methods which view the effects of electron correlation as a perturbation on the effective one-electron hamiltonian that governs the self-consistent field solution. There are further branchings in this field,

for instance between Many-Body Perturbation Theory (MBPT) and Coupled Cluster (CC) approaches.

These approaches generally result from Quantum Chemists being well aware what the limitations of the one-electron SCF equation are.

We have so far sketched only a brief summary of quantum chemistry, without going in too much detail. However, we have enough to come to a conclusion. In sum, Quantum Chemistry can be viewed as a Lakatosian research programme with a positive heuristic. Improvements in the auxiliary hypothesis are driven mainly by Quantum Chemists' understanding of what the shortcomings are in previous theories, and result from mitigating these problems.

As successive theories are improved, their computational load tends to increase quite rapidly. It is only fair to say that the scope of Quantum Chemistry is rapidly widened by improvements made in computer hardware⁷.

3 Is Quantum Chemistry degenerating?

We now turn to the paper by Woody. I do not have a problem with Woody's summary of the early history of Quantum Chemical calculations. Before the advent of computers, which could handle large complex calculations with relative ease, quantum chemical calculations were tiresome⁸.

Woody does make the point, where she discusses the James-Coolidge calculation that Quantum Chemistry produces a reduction of Chemistry to Quantum Mechanics:

The James-Coolidge calculation, in contrast [to the Heitler London calculation of 1927], was valuable as a confirmational exercise; it demonstrated the new quantum theory's sufficiency for empirically adequate predictions of particular energy states. The calculation is also significant because it eschewed reliance on outside knowledge in solving the Schrödinger equation; it was to be an *ab initio* calculation. In this respect, the James-Coolidge calculation sits comfortably beside standard deductive accounts of theory reduction. A fact from one do-

⁷Again, I have first hand experience of this. While working on my research in MCSCF quadratic response functions (hyperpolarisabilities) I initially worked on a mini mainframe. Full compilation of our program took a whole night on this computer. When the next line of RISC processors came out with a new set of compilers, compilation could be achieved in 25 minutes. Speed improvements in running the program were equally impressive.

⁸In my degree programme in Quantum Chemistry the students still had to perform a calculation of the Beryllium atom with a $3s$ basis set by hand. I thus have first hand experience of exactly how boring such a calculation can get.

main of inquiry was captured completely by the theoretical structure of another domain. (page S615).

It is hard to see how one could interpret the notion that the capture of the fact from one domain of inquiry is completely captured by the theoretical structure of another as anything but a reduction. However, Woody's problem seems to be with the usefulness of Quantum Chemistry to practising Chemists. To reiterate the claims made by Woody[4]

1. First, computational complexity restricts the scope of application severely (page S617).
2. Second, this same complexity restricts the utility of analyses that are within reach. The series formulation of the wavefunction prohibits easy identification of a molecule within the representation scheme. (S618)
3. More important, *ab initio* calculations comprise a set of unconnected derivations concerning the energetic states of particular molecules. The derivations have the same starting point, the stationary state Schrödinger equation, but are otherwise distinct (S618).

The remainder of her paper, having established the conceptual inadequacy of Quantum Chemistry, goes on to deal with the pictorial methods that are in common use in theories of the chemical bond.

Of these, the latter assertion is simply false. Quantum Chemistry *does* produce more than a set of 'unconnected derivations concerning the energetic states of particular molecules'. Quantum Chemistry computes a wavefunction in a complex numerical representation, one that is difficult to handle for a human, but easy for a computer. Once this wavefunction is obtained, a proper operator will enable us to compute the desired property. If the operator is a Hamiltonian, the property will be an energy, but there is no reason why the chosen property cannot be a dipole or multipole operator, in which case the property will be a dipole or multipole moment. Going even further, one can derive higher order properties by perturbation theory⁹.

The first assertion is problematic in our view. Quantum chemistry has benefited greatly from improvements in computer speed and architecture, and will continue to do so. There is thus a strong external driver which will enable expansion of the scope of Quantum Chemistry. However, progress is also being made in developing more and more 'compact' formulations of the wavefunction, such as Coupled Cluster methods or Multi-Reference wave functions. The further development of

⁹See my PhD thesis in Quantum Chemistry for one example.

these representations form a strong internal dynamic in the research programme of quantum chemistry.

The second assertion requires more careful consideration. Woody goes on to say (page S618):

With no internal relations among treatments of different systems, there also will be no significant guidance for the representation of new systems. There is no underlying *aufbau*, no line of reasoning to aid further theory development.

As our discussion of the HF wavefunction shows, the assertion is false. The HF wavefunction can be interpreted as supporting *aufbau*, and its interpretation into quantities of chemical interest is relatively straightforward¹⁰.

The deeper philosophical question is whether a knowledge representation that exists in a computer (as the wave function in a Quantum Chemical calculation) is inherently less useful for analysis than one that exists, lets say, on the back of an envelope. A negative answer here (as I am inclined to give) brings into question the validity of the second assertion.

Woody's issue seems to be that a wavefunction *in general* is too complex to make sense of for chemists. In the case of Quantum Chemistry, this complexity is captured in a complex set of parametrisations which are stored in computer memory. These complex wave functions do not easily translate into chemical notions such as reactivity. She also notes that one cannot give a description of the wavefunction of CO₂ to a practising chemist and ask her to compare this to a similar function for, say SO₂. This misses the point entirely.

In Quantum Chemistry, wave functions themselves are of only limited value. Quantum Mechanics, and Quantum Chemistry by extension, connects to empirical reality by calculating the expectation values of operators over a wave function. The empirical claim is that the computed expectation value is the one that can be compared to experiment.

It is, incidentally, perfectly possible to compute the 'pretty pictures' that many chemists have come to see as an orbital, whether that be the spatial representations or the energy levels of such orbitals. Many of them have graced the front covers of PhD theses in Quantum Chemistry. But for most practising Quantum Chemists, that is precisely what these representations are: cover art. This is not to diminish the notion that such pictorial representations are at times very useful in Chemistry,

¹⁰One could object here that the quantities are in fact stemming more from a physical than a chemical tradition, in the sense that ionisation energies and excitation energies are supportive of molecular spectroscopy rather than chemical reactivity. I wish to postpone discussion of this till a later paper, and will note for now that an account of chemical reactivity as supervenient upon these properties is at least in principle possible.

it is to claim that while they have explanatory value, their ontological value is very limited.

What we are faced with is the fact that Quantum Chemistry renders dubious some notions, such as ‘orbitals’, ‘aufbau’ and the like that we know are useful as explanatory models in Chemistry. Many writers have therefore concluded that these notions ‘add’ something inherent to our understanding of the atom and it is for those reasons that the notion of a reduction of Chemistry to Physics has to be resisted. This seems to be certainly Woody’s claim, where she argues that

There are, broadly speaking, two battles one could fight here, and it is best to keep them separated. One may argue either:

1. In the particular case of chemistry, the proper relations do not hold and therefore reduction fails, or
2. There is something systematically, and more generally, wrong with reductive accounts of intertheoretic relations such that they cannot capture meaningfully the connections between chemistry and quantum mechanics.

At the end of her paper, she concludes that the reduction that we are talking about is most likely a reduction of ‘tokens’ without the corresponding types.

While I cannot claim to fully understand what she means here, I would suggest that, as an account of reduction, this fails to distinguish between three types of reduction that are generally talked about in the philosophy of science. These are (i) reduction of laws, (ii) reduction of models and (iii) ontological reduction.

Since Quantum Chemistry tends to furnish results that can ‘save the phenomena’ (i.e. results that to the best of our knowledge are consistent with empirical facts¹¹), we are led to conclude that reduction types (i) and (ii) are actually successful even on Woody’s account, but that it is reduction (iii) that fails on her account. The reason why it fails is moreover instructive. Quantum Chemistry has a tendency to render these diagrammatic schemes problematic as ontological entities, even though it validates them as models. The latter validation, moreover, is the primary reason why reduction (ii) succeeds.

Perhaps we are too hard on Woody here. As a conclusion of her section on *ab initio* Quantum Chemistry, she states

I do not intend to deny the virtues of computational chemistry. Precise predictions are in certain contexts invaluable, not to mention that the

¹¹One may well argue that the molecular energies, which are among the prime results of Quantum Chemical calculations are not in themselves observables. One would be right. However, the energies are the primary sources for quantities that are observable, such as atomic distance in molecules, energy differences between excited states etc.

types of reliability afforded by automated digital computation make possible methods of inquiry clearly beyond the range of unassisted human cognition. I aim instead to display the insufficiency of principled manipulations of a foundational mathematical theory; standing alone, wavefunctions provide little grip on well-established categories of chemical practice. (page S619).

While I agree with Woody here in the sense that wavefunctions provide little grip on well-established categories of chemical practice, I disagree with her overall conclusion that there is some inherent insufficiency in these ‘principled manipulations’ of a ‘foundational mathematical theory’—at the end of inquiry, these manipulations provide a tractable set of empirical predictions that can be compared to experiments, and that is what science should be about.

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