

Is Quantum Chemistry a Degenerating Research Programme?

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ABSTRACT. This paper is intended to address some particular issues in the relative status of quantum chemistry 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 briefly argue that quantum chemistry is a progressive research programme and outline some of the issues that have to be resolved for full Lakatosian reconstruction of quantum chemistry as a research programme.

KEYWORDS: Quantum Chemistry, Research Programme, Reduction

1. Introduction

In the 1970's Imre Lakatos¹, in response to the work of [Kuhn (1970)] and others in the history of science, introduced the notion of a research programme. The concept of a research programme was aimed at reconciling Kuhn's theory of scientific paradigms with the ideas of falsification stemming from Karl [Popper (1959)].

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.

This paper intends to address the question of whether quantum chemistry can be seen as a progressive research programme in the sense of Lakatos. A number of distinct questions become pertinent in this context. These questions, in the end, come down to two separate issues: whether quantum chemistry is progressive in the sense of generating novel facts, and what, if any, relationship quantum chemical considerations have to the explanatory notions of 'classical' chemistry. This paper will deal mainly with the second of these items but will have things to say about the first one as the argument progresses.

The first set of questions relate to whether quantum chemistry has made novel predictions in the sense of Lakatos. In the literature, there has been some argument about what a novel prediction exactly is, notably, the original notion of Lakatos was refined by [Zahar (1973)] and [Worrall (1978)]. For the purposes of this paper, the key aspect of novelty is that improvements are the result of a meaningful internal development of the programme, that is, there is, either in the hard core of the theories themselves or in their protective belts, a positive heuristic for further theoretical improvement.

The second set of questions relate to the relationship between quantum and

¹ See [Lakatos and Musgrave (1970), Radnitzky and Andersson (1978)] for an overview and critique of Lakatos' ideas, in particular the paper *Falsification and the Methodology of Scientific Research Programmes* on page 91–196 in [Lakatos and Musgrave (1970)].

‘classical’ chemistry. While one could think that quantum chemistry is in some sense a competitor for classical chemistry my argument will not be that quantum chemistry is progressive in precisely this sense. Rather, I will argue that the relationship between quantum chemistry and classical chemistry is to be seen as the relationship between a supply programme and a guiding programme in the sense of [Zandvoort (1986)].

Particularly important in the discussion of the relationship between quantum and ‘classical’ chemistry is the notion of reduction, and the related notion of explanation by reduction. Both explanation and reduction are, in a sense, concepts with many hues of gray, but are often depicted as consisting of black and white only. In particular, the idea that there are conceptual difficulties with relating the notions of ‘classical’ chemistry to quantum chemistry is sometimes taken as meaning that quantum chemistry has nothing (or very little) interesting to say with regard to classical chemistry.

In this context Andrea [Woody (2000)] has discussed the explanatory weaknesses of *ab initio*² quantum chemistry in the context of reduction between chemistry and physics. 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 Chemists³; hence, it is hard to see how reduction can be successful.

Therefore, while reduction (‘as a standard deductive account of theory reduction’ in Woody’s terminology) can be held to be successful, the issue be-

² ‘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.

³ As an aside, it is to some degree questionable how much of Woody’s paper is a contribution to the reduction debate, as it touches on reduction only occasionally, and, as I discuss later, her main claim with respect to reduction, as one of tokens rather than types, is a bit unclear. I will save a more detailed discussion of Woody’s claims with regard to reduction to a later paper, in which I intend to discuss the role of quantum chemistry in this context in more detail.

comes 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 (2000)] as follows:

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 wave function 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).

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.

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 (section 2) I will outline the methodology that quantum chemistry uses in its explanation of chemical data. In the next section (section 3) I discuss Woody's claims above and show that they are problematic. In the last section of this paper (section 4) I argue that quantum chemistry is indeed a research programme in the sense of Lakatos, and qualify it as a progressive research programme.

2. How Quantum Chemistry Explains

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 (1983), Primas (1998)] 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.

⁴ There are a large number of references that I could give here. I will restrict myself 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 (1969)], [McWeeny (1989)] or [Wilson and Dierksen (1992)].

H is the Hamiltonian operator, which corresponds to the property of energy

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

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 (2000)] 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 wave function) which ignores the effects of electron correlation. This wave function 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 wave function 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

⁵ Although 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.

⁶ Although 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.

(either Many Body Perturbation Theory (MBPT) or the more sophisticated Coupled Cluster (CC) approach).

6. Electronic properties than have to be predicted with these wave functions—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.

However, the *practical* intractability of some of these problems does not mean that they are *principally* impossible to be solved. 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. The auxiliary hypotheses thus consist of (i) Molecular Structure, (ii) Non-relativistic Schrödinger equation, (iii) Basis sets, (iv) ‘One electron’ SCF wave functions, 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 quadrupole 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 wave function for small to mid size molecules is more or less routine.

The case of the SCF wave function 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 wave function 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 [McWeeny (1989)] page 164-166) a number of relevant molecular properties that may be derived from this wave function. (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 wave function 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 wave function, if desired, supports the type of diagrammatic interpretation which features in the second half of Woody's paper. I also want to note that the HF wave function is not the only wave function 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 [McWeeny (1989)] page 135 and page 200-206).

Since the minimal condition to be satisfied for an HF wave function 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 wave functions 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 ([McWeeny (1989)], 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 wave function is written as an expansion of many configurations of like symmetry.

In addition, there exist perturbation 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 into 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 confirmation 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 domain 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 [Woody (2000)]

⁷ Again, 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.

⁸ In 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.

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 wave function 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 wave function in a complex numerical representation, one that is difficult to handle for a human, but easy for a computer. Once this wave function 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 my 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 wave function, such as Coupled Cluster methods or Multi-Reference wave functions. The further development of 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):

⁹ See my PhD thesis in quantum chemistry, [Hettema (1993)] for one example.

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 wave function shows, the assertion is false. The HF wave function 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, let's 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 wave function *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 parametrisation 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 wave function 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

¹⁰ One 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.

very useful in chemistry, 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 untethered 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 often 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.

¹¹ One 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.

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 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, wave functions provide little grip on well-established categories of chemical practice. (page S619).

While I agree with Woody here in the sense that wave functions 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.

4. Notes on Quantum Chemistry as a Lakatosian Research Programme

I now wish to turn to a brief discussion of how quantum chemistry could function as a Lakatosian research programme. My remarks here should not be taken as constituting a full reconstruction of quantum chemistry as a Lakatosian research programme, rather, my aim is to explicate in sufficient detail some of the salient points that could assist in such a reconstruction, with the idea that the full story might be told later.

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.'¹²

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.

In this section we will discuss some aspects of a Lakatosian research programme as they apply to quantum chemistry in more detail. In particular, we include a brief section on novel facts and a longer section on explanation by reduction and inter-theory relationships in Lakatosian research programmes.

Lakatos' notion of novel facts was significantly refined by [Worrall (1978)] and [Zahar (1973)]. Specifically, what these proposals add to the Lakatosian notion of the research programme is the importance of heuristics. That is, in the overall evaluation of whether a research programme is progressive or degenerating it somehow becomes important how facts were arrived at. As [Worrall (1978)] puts it

The methodology of scientific research programmes regards a theory as supported by any fact, a 'correct' description of which it implies, provided the fact was not used in the construction of the theory. This seems quite a modest proposal and it seems to be the obvious solution to the problem posed by the ease with which *ad hoc* explanations of *given* facts may be generated. The proposal does, however, have the effect of bringing questions of how a theory was arrived at, questions of 'heuristic', into the methodological assessment of the empirical merits of a theory (page 50).

In the case of quantum chemistry the question of the extent to which the particular approximations we discussed in section 2 of this paper (basis sets and independent orbital approximations and such like) are determined by the state of affairs to be accounted for becomes particularly pressing. There are two points at issue here which I will discuss briefly.

In the first place, some of the approximations that are commonly made are inconsistent with the basic framework of quantum mechanics. A well known

¹² In Lakatos [Lakatos and Musgrave (1970)], page 116.

example of this is the clamped nucleus approximation which underpins the majority of quantum chemical calculations. A more complete discussion of these issues has been given in [Hendry (1998)] in the context of a ‘proxy defence’. But it is easy to find other examples of this, such as for instance in ‘frozen core’ approximations or ‘valence electron only’ methods. There is thus a *prima facie* case to be made that in quantum chemistry, the auxiliary approximations can be inconsistent with the theoretical core of the theory, and a fuller exploration of this in the context of Lakatosian research programmes would make a rewarding project.

In the second place, there seems to be little evidence that the specific choice of the particulars of these approximations does indeed constitute ‘use’ of chemical facts in the construction of a quantum chemical model. Having said that, there is at least an interesting complication.

In the case of basis sets, it is a well known fact that any chosen basis set needs to have enough *flexibility* to describe the chemical fact in question. For instance, in the correct calculation of molecular properties such as multipole polarisabilities the basis set needs to have higher angular momentum functions in order to be able to correctly describe the molecular integrals that contribute to these properties.

So even while it is not the case that basis set choice (to stick with this example) is exclusively made with the aim to find agreement with some chemical fact, it is certainly the case that the flexibility required in the basis set is determined by the nature of the chemical fact. It is however possible to determine this required flexibility *a priori* based on the symmetries of both the operators involved and the symmetry of the orbital in question. Again, working out this problem in the context of a Lakatosian account of ‘novel facts’ could make a rewarding project¹³.

We now turn to the problem of reduction. The argument in section 2 should have made it clear that, whatever one’s opinion may be with regard to the issue of reduction, quantum chemistry does not provide a ‘standard deductive account of theory reduction’ in Woody’s sense. It is therefore open to question what sort of reduction relation is at work here.

It helps to realise that several reduction concepts have been proposed in the literature and these are sometimes confused. One obvious distinguishing feature

¹³ I hope to undertake these projects one day.

of reduction concepts is the content of the reduction concept itself. Nagelian reduction is focused primarily on the internal structure of the reducing and reduced theory, while, for instance, the notion of Kemeny and Oppenheim is primarily focused on empirical content.

One other factor that seems to run alongside the former distinction distinguishes reduction concepts on the basis of theory replacement. For instance, [Kim (1993)] contrasts Nagelian reduction, which he calls *conservative* reduction to indicate that the reduced theory survives¹⁴, to the concept of reduction from [Kemeny and Oppenheim (1956)] and characterises the latter as entailing a replacement reduction (i.e. the theory that is reduced does not survive¹⁵).

My proposal is that in the case of quantum chemistry it is perhaps most instructive to consider it as a case of Nagelian reduction, and thereby imply that there is an interesting way in which ‘classical’ chemistry can coexist alongside quantum chemistry. Kim notes that

A general principle like the following seems to be at work here: *If a theory is confronted by another that explains more, the only way it can survive is for it to be conservatively reduced to the latter.*

It seems possible to say with confidence that quantum chemistry did not, in the course of its history, replace ‘classical’ chemistry; neither could it be argued that that was its aim in the first place¹⁶. Hence, the concept of reduction that interests us in this particular context is the concept of Nagelian, rather than Kemeny-Oppenheim, reduction.

A Nagelian reduction also implies that a significant amount of logical work

¹⁴ In [Nagel (1961)] we find the following quote supporting this reading:

However this may be, the reduction of one science to a second—e.g., thermodynamics to statistical mechanics, or chemistry to contemporary physical theory—does not wipe out or transform into something insubstantial or “merely apparent” the distinctions and types of behaviour which the secondary discipline recognises. Thus, if and when the detailed physical, chemical and physiological conditions for the occurrence of headaches are ascertained, headaches will not thereby be shown to be illusory (page 366).

¹⁵ Kim mentions the example of the phlogiston theory here, which was reduced in the sense of Kemeny and Oppenheim to the oxidation theory and did not survive.

¹⁶ Notwithstanding a few well-known quotes from early quantum chemists to the opposite effect.

must be done to effect the reduction. In the Nagelian concept of scientific theories, this work is done by the ‘bridge principles’ or ‘reduction postulates’, which are themselves fairly non-trivial statements that relate terms of the theory to be reduced to the reducing theory. From the argument in this paper we have enough evidence to state that whatever the relation at work might be, it will certainly be non-trivial.

While I do not wish to give a detailed account here of how such a Nagelian reduction might work, for now I wish to notice that, if reduction is at work, it has to be Nagelian rather than Kemeny and Oppenheim reduction, and note that the question of how quantum chemistry can meaningfully capture the relations between quantum Mechanics and chemistry is still largely open.

To conclude this discussion, it seems useful to consider the proposal made by [Zandvoort (1986)] for ‘guiding’ and ‘supply’ programmes. A ‘guiding programme’ provides the ‘set problems’ to other programmes while the ‘supply programme’ aims to provide solutions to these problems.

In this context, it might be useful to think of quantum chemistry as a ‘supply programme’ for the ‘guide programme’ of classical chemistry and this is indeed the line taken in [Zandvoort (1986)] (page 234-236), based on the problem of an ‘ion pump’ through an alpha-helix. It is interesting to note that in this context Zandvoort notes that the model of guide and supply programmes leaves room for what he calls ‘Lakatosian competition’.

In sum, it seems at this point that a detailed Lakatosian reconstruction of quantum chemistry *vis a vis* ‘classical’ chemistry could well shed an interesting light on an as yet unexplored set of philosophical issues.

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