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Austere quantum mechanics as a reductive basis for chemistry

Hinne Hettema

Abstract This paper analyses Richard Bader's 'operational' view of quantum mechanics and the role it plays in the the explanation of chemistry. I argue that QTAIM can partially be reconstructed as an 'austere' form of quantum mechanics, which is in turn committed to an *eliminative* concept of reduction that stems from Kemeny and Oppenheim. As a reductive theory in this sense, the theory fails. I conclude that QTAIM has both a regulatory and constructive function in the theories of chemistry.

Keywords Operational quantum mechanics · Operationalism · Atoms in molecules · Electron density · Reduction · Explanation

Introduction

In some recent papers, Richard Bader (2011a, b) proposes an 'operational' view of quantum theory, which is based on observables, equations of motion, and action theorems. This view on quantum theory applies the ideas of Dirac (1932 , 1958), Schwinger (1951) and Feynman and Hibbs (1965) to the molecular density. The aim of this view of quantum theory is to set up a quantum theory of open systems, which may be put to the task of showing how the Quantum Theory of Atoms In Molecules (QTAIM) forms a proper, (reductionist) basis for chemistry.

I will characterise Bader's approach with the term 'austere' quantum mechanics. Austere quantum mechanics, a term of my own making, is a form of quantum mechanics in which quantum mechanics is conceived in both an *operational* and *eliminative reductionist* framework. The manner in which these elements interact, leading to a strict interpretation of observables, which is furthermore conceived as eliminative and foundational, leads me to characterise this approach as 'austere': it does not leave room for (much) independent conceptual apparatus or theoretical development at the 'higher' levels.

To be of use, the term 'Austere Quantum Mechanics' must be precisely specified.

H. Hettema (✉)
Department of Philosophy, The University of Auckland, Auckland, New Zealand
e-mail: hhet001@aucklanduni.ac.nz

First consider operationalism. In the papers cited above, Bader specifically refers to his method as ‘operational’. Note, however, that the degree to which his theory exemplifies ‘operationalism’ (as a specific philosophical position on the interpretation of theoretical terms) is not entirely clear.

The operationalist conception of quantum mechanics is to a large extent connected to the operational interpretation of physics stemming from Bridgman (1932), which is discussed in detail in Chapter II of Frank (1954), as well as in Pap (1959). This view gained some popularity in philosophy of science in the 1950s, though its popularity was relatively short-lived. In the papers collected by Frank, there is broad agreement that the specific quantities of quantum mechanics are to be operationally defined as interpretations of an abstract calculus, though at some point there is a connection between the expectation value of an operator and the outcome of an experiment, where the latter involves a specific series of physical operations.

The specifics of the reductionist claim also require careful consideration. I will in particular contrast the reduction of theories and laws as discussed in Nagel (1961) with the concept of reduction *qua* elimination from Kemeny and Oppenheim (1956). Austere quantum mechanics requires reduction in the latter form, but not the former. The operational view of quantum theory proposed by Bader—which precludes the presence of theoretical concepts that do not have either an origin or a counterpart in the observables of quantum mechanics—only allows for reduction in the eliminativist sense, and thereby precludes the more liberal conception of reduction as envisaged by Nagel (1961).

At this point it is worth while to develop the thesis of ‘austere quantum mechanics’ in some detail, as constituting the following specific claims:

1. Operationalism (O): All theories of science (including physics and chemistry) are based on operations characterised as a series of operations that perform physical measurements, or (computational) deductions in a theoretical framework leading to predictions of such physical measurements.
2. Eliminative Reductionism (ER): The theories and concepts of a reduced theory are eliminated in the reduction, and instead of working with the reduced theory, it is more efficient to work with the reducing theory instead.
3. Austere Quantum Mechanics (AQM): System observables in the operational sense are given by quantum mechanics and carry all the information necessary for chemistry.

In this sense, (AQM) encompasses elements of both (O) and (ER).

The ‘austere’ take on quantum theory is not well aligned with the sort of use to which quantum theory is sometimes put in chemistry. In particular, it does not allow for the specific vocabulary of some chemical theories, in which ‘chemical bonding’ is explained in terms of individual orbitals and *Aufbau* models, models that rely on the attribution of a physical property to specific orbitals, or a strong differentiation between specific *types* of bonding, and these sort of chemical theories have been the target of Bader’s critique.

In the remainder of this introduction I sketch a brief characterisation and justification for classifying Bader’s views as a variety of austere quantum mechanics, noting that the details of *how* QTAIM differs from AQM will matter for what follows.

First consider the eliminativist character of the reduction. While Bader argued for the reduction of chemistry to physics, he does not precisely specify the details of this reduction, and his commitments need to be reconstructed to some degree.

In broad outline, the aim of operational QTAIM is to advocate ‘[…] a sea change in our attempts to predict and classify the observations of chemistry, […] to replace the use of simplified and arbitrary models with the full predictive power of physics, as applied to an atom in a molecule' (Bader and Matta 2012).

More specifically, the target of the operational interpretation of QTAIM is in significant measure the use that has been made in some contexts of the orbital model. In this vein, Bader (1990) argues that

> The orbital model has, however, been extended beyond its intended use of predicting and providing an understanding of the electronic structure of a system, by associating the forms of individual orbitals with the assumed spatially localized pairs of bonded or non-bonded electrons, and by attempting to define atomic properties in terms of coefficients of atomic-centred basis functions appearing in the expansion of molecular orbitals. These steps are admittedly arbitrary, as are attempts to define atoms through a partitioning of the Hamiltonian operator. This latter step violates the indistinguishability of the electrons from the outset. (Bader 1990, p. 131)

From this perspective, the aim of QTAIM is to facilitate a partially *eliminative* reduction of chemical concepts and theories, where the elimination can happen through two different mechanisms: (1) models and concepts that are arbitrary or inconsistent with the basic tenets of quantum mechanics *should* be eliminated, and (2) models and concepts that are consistent with the basic tenets of quantum mechanics *can* be eliminated. It is in this sense that I read Bader's 'no parallel universes' remarks: in the final analysis, for chemistry there remains only the physics of the electron density.[1]

In this paper, I conclude that Bader's QTAIM cannot be characterised as austere quantum mechanics in its entirety, and that the project of austere quantum mechanics fails in ways that recast QTAIM as both a regulative and constructive programme in the formation of chemical theories.

Before we start our discussion, it is worthwhile making a few brief general comments.

It is first worth noting that as a quantum theory, the operational structure is almost directly derived from Paul Dirac's construction of quantum theory. A clear exposition of this construction is given in Dirac's in *The Principles of Quantum Mechanics* (Dirac 1958). This in itself provides us with some useful clues as to the operational characterisation of this approach. Bader proposes a more or less directly operational reading where he remarks that when Dirac

> […] did offer support for any branch of philosophy, it was that presented by the "logical positivists", who held that a statement had meaning only if it could be verified by observation. (Bader 2011b, p. 12667).

Note that this reading of Dirac's philosophical commitments is not universal. In a detailed study of Dirac's philosophical commitments Bokulich (2008) argues that Dirac's approach to quantum mechanics was more along the lines of *engineering*. Dirac's philosophical commitments in quantum mechanics, from the viewpoint of Bokulich, were primarily based on his notion of a 'open theory', in which the basic postulates of quantum mechanics stand in an *analogy* relation with classical mechanics. More specifically, Dirac's formulation of quantum mechanics is based on a thesis of non-reductive structural continuity with classical mechanics, in which, for instance, Poisson brackets correspond to quantum mechanical commutators, and the mathematical structure of quantum mechanics

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[1] The 'no parallel universes' comment is derived from the title of Bader (2011a) As an aside, it is interesting to note that the elimination of concepts in this way precisely follows the two horns of Hempel's *Theoretician's Dilemma* (Hempel 1958).

is analogous to that of classical mechanics.[2] The analogy relation is the key to determining the mathematical form of the operators that correspond to observables.

Secondly, the aim and purpose of QTAIM are put into a sharper focus by Coulson's comment in the Tilden lecture, that 'all the necessary information required for the energy and for calculating the properties of molecules is is embodied in the first- and second-order density matrices' (Coulson 1960, p. 175). In this vein, a number of 'atoms in molecules' theories have been developed,[3] which will not be discussed further in this paper.

The open questions thus centre around the strength of Bader's emendation of Dirac's approach to quantum mechanics as a strongly reducing theory—a reducing theory which does not only explain but also *eliminates*—as well as the sort of chemistry that can be constructed on its basis. Bader's operational approach, which is fairly strictly based on Dirac's approach to quantum mechanics, and which aims to base chemistry on the information contained in the electronic density *only*, is in this sense an interesting case study as a strongly reductive theory.

The structure of this paper is as follows. I briefly give an exposition of the argument for austere quantum mechanics in "The operational structure of quantum theory". I distinguish QTAIM from austere quantum mechanics, and argue that austere quantum mechanics makes stronger claims than QTAIM. In particular, QTAIM allows for concepts of chemistry where austere quantum mechanics does not.

In "Austere quantum mechanics as a strongly reducing theory" I critically evaluate Bader's operational theory as a strongly reducing theory of quantum mechanics in the sense of Kemeny and Oppenheim. I argue that QTAIM cannot be classified as a strongly reducing theory in this sense due to a variety of reasons.

In "Building chemical theories with electronic densities" I discuss the role that austere quantum mechanics might play in chemistry. To that end, I contrast Bader's 'operational' view of quantum theory with the (much older) philosophical position of 'operationalism' to which it is fairly closely related. To do so, my argument reflects an older argument by Pap (1959). For Pap, operationalism is subject to a dilemma: it falls short as a scientific explanation on the one hand, and is indispensable on the other. This dilemma has a bearing on the role that may be played by austere quantum mechanics in the theories of chemistry. Specifically, I will argue that as a result of this dilemma QTAIM plays a regulative as well as a constructive role in chemistry, but cannot be a theory of 'all there is'. The last section is a conclusion.

The operational structure of quantum theory

Let us first lay out Bader's proposed operational structure of quantum mechanics. The operational construction of QTAIM is derived from the quantum theory for open systems developed by Dirac (1932), Schwinger (1951) and Feynman and Hibbs (1965). Its application to the density in chemistry by Bader has a long history, starting from the paper by Srebrenik and Bader (1975), Bader et al. (1981), Chapters 5 and 8 of Bader (1990) and Bader (1994, 2007). The explicit 'operational' formulation of quantum theory is given in Bader (2011b). Its philosophical commitments are most clearly outlined in Bader (2011a) and Bader and Matta (2012).

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[2] This argument from analogy can for instance already be seen in Dirac's paper 'Quantum Mechanics and the Hydrogen Atom' (Dirac 1926).

[3] An example of such an early 'atoms in molecules' theory is found in the article by Moffitt (1951).

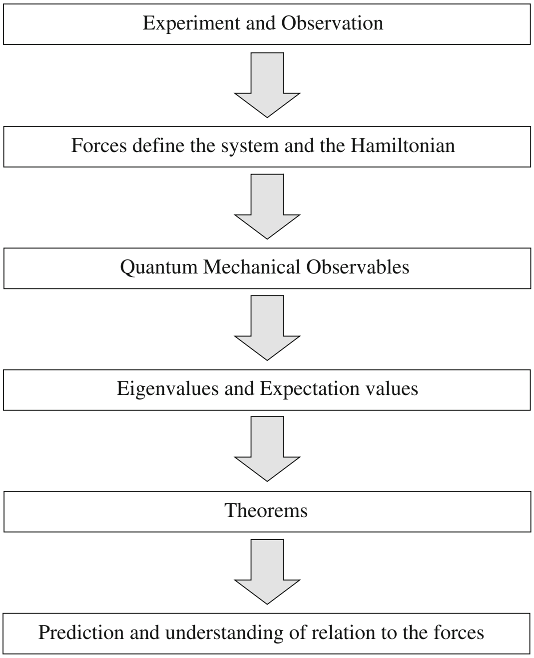

Fig. 1 Bader's proposed operational structure of quantum mechanics. The claim is that this operational structure can be deduced from the action principle, and also forms a reductive basis for chemistry

Bader's 'operational' view of quantum mechanics is presented in Fig. 1. It is based on the view that all of science (including physics and chemistry) is based on a theory of observations, which is subsequently subjected to theoretical analysis.

In the diagram, a system is defined by its forces, which in turn determine the Hamiltonian. Subsequently, quantum mechanics is developed on the basis of a complete set of commuting observables (CSCOs), something Bader calls 'Dirac observables'.[4]

The use of Dirac observables requires some more attention. CSCOs are primarily used to develop a *characterisation* of the wave function. The construction of CSCOs is approached in the following manner. A *complete set of commuting observables* is defined as 'a set of observables which all commute with one another and for which there is only one simultaneous eigenstate belonging to any set of eigenvalues' (Dirac 1958, p. 37). Cohen-Tannoudji et al. (1977) present extensive detail on the role played by CSCOs.

Briefly, consider an operator $\hat{A}$, a basis $\{|x_i^n\rangle\}$ and a set of eigenvalues $\{a_i\}$. If there are no degenerate eigenvalues, then the eigenstates can be labelled by the index i only and the basis is the set of eigenstates $\{|a_i\rangle\}$. If there are degenerate eigenvalues, we choose a second operator $\hat{B}$ which commutes with $\hat{A}$ and we construct an orthonormal basis of eigenvectors common to $\hat{A}$ and $\hat{B}$. Hence the CSCO procedure lets us define a basis and lets us define the 'q-numbers' which characterise the quantum state. A *complete* set of commuting observables generates a complete description of the quantum state.

Bader's approach to operational quantum mechanics is in addition driven by the need to define a set of quantum principles for an atom in a molecule, which is defined as a (physical) *bounded region of space* Ω, for which there is a zero-net flux condition (Bader, 1990) over a bounding surface $S(r)$:

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[4] The term 'complete set of commuting observables' stems from (Dirac 1958) and is also a key element of the development of quantum mechanics in (Cohen-Tannoudji et al. 1977).

$$\nabla \rho_{S(r)} = 0 \quad \text{or} \quad \nabla \rho(r) \cdot n(r) = 0; \quad \forall r \in S(r) \tag{1}$$

The claim of operational quantum theory is that the quantum equations may be derived for real bounded spaces as a variation on the procedure developed by Schrödinger and later developed by Feynman and Hibbs (1965) and Schwinger (1951).

This problem is most easily approached by considering the Schrödinger formulation of quantum mechanics. Austere quantum mechanics is developed as an extension of the original derivations of either Schrödinger or Feynman / Schwinger for these real spaces,[5] based on the theory of variations of a quadratic functional $L(q, p)$. In what follows, I will first outline Bader's exposition, followed by some historical remarks.

Quantum mechanics in an open system

As is outlined by Bader (2007) and Jammer (1989), Schrödinger's approach was to optimise the Hamilton-Jacobi equation $H[q, \partial S / \partial q]$ by substituting S by $K \log \Psi$.

The quantum action integral (Bader 2007) is based on the quadratic form

$$G\left(\Psi, \frac{K\partial\Psi}{\Psi\,\partial q}\right) = \int_{-\infty}^{\infty} dr \frac{\hbar}{2m}(\nabla\Psi)^2 + \frac{2m}{K^2}(V - E)\Psi^2 \tag{2}$$

so that the variational problem can be written as

$$\delta G = \delta \int G dr = \int \frac{\partial G}{\partial \Psi}\delta\Psi + \int \frac{\partial G}{\partial \nabla\Psi}\delta\nabla\Psi \tag{3}$$

The last term can be further evaluated through integration by parts and using the identity $\nabla\Psi \cdot \delta\nabla\Psi = \nabla^2\Psi\delta\Psi + \nabla \cdot (\nabla\Psi\delta\Psi)$. This leads to two conditions, of which the first is the Schrödinger equation

$$\nabla^2\Psi + \frac{2m}{K^2}(V - E)\Psi = 0 \tag{4}$$

and the second condition can be written, using Gauss' theorem, as a surface integral

$$\oint dS(r_s)(\hbar^2/2m)\nabla\Psi \cdot n(r)\delta\Psi = 0 \tag{5}$$

It is the second condition that is the key to the quantum theory of atoms in molecules as a quantum theory of a region with finite boundaries. In the Schrödinger case the term vanishes because at infinity, $\delta\Psi = 0$.

Bader's proposal is to modify the Schrödinger derivation in terms of a variation in $\Psi, \nabla\Psi$ and a surface Ω. Running through the steps again the variation procedure yields the same terms as previous, and an added term due to the variation $\delta\Omega$. This problem can be tackled, as outlined in Bader (2007), by imposing a *zero flux condition*. This allows the equations to be written as

$$\delta G(\Psi, \nabla\Psi, \Omega) = (-i\hbar/2m) \oint dS(\Omega, r_s)\delta j(r) \cdot n(r) + \text{cc} \tag{6}$$

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[5] For a brief illumination of the different formulations of quantum mechanics, see for instance the paper by Styer et al. (2002).

where

$$\delta j(r) = (\hbar/2mi)\{\Psi^* \nabla(\delta\psi) - (\nabla\Psi^*)\delta\Psi\}. \tag{7}$$

This term can be written as

$$\delta G(\Psi, \nabla\Psi, \Omega) = -(\epsilon/2)\{(i/\hbar)\langle\Psi|[H, G]_\Omega|\Psi\rangle\} + \mathrm{cc} \tag{8}$$

where the commutator $[., .]_\Omega$ is taken over the bounded region. This last formulation leads to the equation of motion of the generator and thus allows us to extract a *mechanics* from the theory of atoms in molecules by identifying the 'generator' G with particular operators.

Towards austere quantum mechanics

The explanatory approach of Bader's QTAIM focuses on the extraction of the necessary chemistry from the electronic density alone. It can be classified as an 'austere' quantum mechanics in the sense that it does not leave room for dynamical properties that do not correspond to a mathematical expression for the generator G. In this sense, properties that do not correspond to an operator do not 'exist'.

However, QTAIM is not entirely identical to austere quantum mechanics: where austere quantum mechanics is the 'mechanics of an atom in a molecule' QTAIM is a richer theory that allows for chemistry to be constructed on the foundations of austere quantum mechanics (for instance, QTAIM can include a theory of bonding whereas austere quantum mechanics cannot).

As outlined in the introduction, austere quantum mechanics is predicated on the view that all that matters in science is prediction (or explanation) of observables, that there is a direct identity relationship between the operators of quantum theory and such predictions, and that, in a strong sense, that is all there is (eliminativism). In this way, the claims of austere quantum mechanics lead us to a primarily *mechanical* picture of molecules in which material equivalence of the quantum equation of motion and the equations of classical mechanics determines behaviour, and determines it completely.

QTAIM commits to the three claims of AQM with varying degrees of enthusiasm. The precise degree to which QTAIM can be classified as austere quantum mechanics therefore requires further elucidation, attribution and justification.

The existence claims for the various properties of molecules are based on observation of *physical* properties of molecules. A fairly strict adherence to the first claim, that all that matters in science is prediction, is supported by a number of explicit statements in Bader's recent writings. As Bader writes:

> QTAIM is predicated on the premise that a theory of an atom in a molecule must predict what can be measured in the laboratory. (Bader 2007, p. 50).

A detailed discussion of the properties that do correspond to such observables is given in Matta and Bader (2006) and in Bader (2007).

What is striking about these properties is that they capture physical properties of atoms, while properties that feature in chemical theory building—such as valence and a distinction in various *types* of bonding, are not capable of corresponding directly to operators in the sense intended by QTAIM.

At this point QTAIM as well as austere quantum mechanics construct a *normative* argument for concept elimination: concepts that are not reconcilable with the basic tenets of quantum mechanics *should* be eliminated from our theories. It is in this sense that the quantum mechanics proposed by Bader is *austere*—it is primarily aimed at extracting chemistry from the laws of physics, while not 'adding' anything in the process.

It is in this sense that Bader has argued that 'there are no parallel universes' [see the title of Bader (2011a)], and that, in the terminology of his last paper, 'the single most important characteristic of the atom or a functional grouping of atoms defined within QTAIM is that all of its properties, even those induced by externally applied fields, are determined by its form in real space' (Bader and Matta 2012). Similarly, Bader's comment with regard to apportioning of atomic charges sums up the idea of the whole program:

> The choice is, in fact, clear to use physics as opposed to one of the many arbitrary definitions of atomic charge, ones choice being dictated by finding the set of charges that agrees best with ones personal prejudices. (Bader and Matta 2012).

This claim amounts to a form of explanatory exclusion, in which the aim is to eliminate competing theories that are not based on austere quantum mechanics. As I will discuss in the last section, QTAIM's commitment to explanatory exclusion is however only partial and there are some exceptions. As an example, QTAIM does not universally deny the use of the orbital model in *all* chemical explanations. Orbital explanations are admissible to the extent that they adhere to our basic tenets of quantum mechanics.

Austere quantum mechanics as a strongly reducing theory

Apart from its operational character, Bader's QTAIM makes a number of claims about the reduction of chemistry.

It is my aim in this section to raise a number of objections against the role of operational (or austere) quantum mechanics as a reductive basis for chemistry. In the next section I will propose the role that austere quantum mechanics might play as a theory of furnishing building blocks for theories of chemistry.

Technical objections

Let us first consider some technical objections. A first objection, raised by Cassam-Chenaï and Jayatilaka (2001), is that the determination of 'atoms' in terms of zero-flux regions of real space is not unique. Firstly, there are some spurious 'zero flux' basins in a molecular density, which do not correspond to 'atoms'.[6] Somewhat more serious, however, is the observation that the atomic partitioning breaks down at nodes in the vibrational wave function and that the theory is incapable of correctly apportioning 'atomic' basins in excited vibrational states. QTAIM s in this sense not always capable of correctly predicting the location of topological 'atoms' given a molecular electronic density.

Another problem appears if we consider the density as an *observable*. Electronic densities are not directly empirically accessible, but rather correspond to observables that are

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[6] This issue has has been discussed at length in the literature. To address it, Nasertayoob and Shahbazian (2009) define a concept of 'Quantum Divided Basins' (QDBs), and to propose these QDBs as an alternative structure which may be amenable to theoretical investigation. However, that still leaves open the question of how much of the theory of atoms in molecules actually deals with *atoms* as opposed to arbitrary zero-flux regions. As an example, in the final analysis given in Nasertayoob and Shahbazian (2009) topological atoms are defined on the basis of 'chemical intuition' rather than robust mathematical analysis.

the result of a more convoluted operational procedure. In another set of papers Bader (2009, 2010) argues that bond paths correspond to an electronic density operator

$$\hat{\rho}(\vec{r}) = \sum_i \delta(\hat{\vec{r}}_i - \vec{r}). \tag{9}$$

This 'bond path operator' is generated by projecting the density along the bond paths originating at the critical points and terminating at the location of the nuclei.

The density in this sense is not an operator which corresponds clearly to a defined set of eigenvalues and measurements, and by implication the same is true for bond path. These concepts are central to QTAIM, but are only reconcilable with AQM with some difficulty. The example of atomic force microscopy, presented in Bader and Matta (2012), is in this regard somewhat unconvincing, since alternative theories, based on orbitals and repulsive forces in ways that cannot be reconciled with AQM are equally well capable of explaining the phenomena.

Moreover, the role that the bonding operator would play in austere quantum mechanics is somewhat unclear: it is not a generator with a definite equation of motion, but neither is it a clear observable in the sense of a CSCO. I conclude that the occupational role of the bond operator in austere quantum mechanics is in need of further elucidation.

Historical and philosophical objections

In addition to these technical issues, a number of historical and philosophical issues need to be considered.

The first one of these concerns the question whether austere quantum mechanics a correct characterisation of Dirac's approach to quantum mechanics. A recent study by Bokulich (2008) has considered the underlying approach to theory formation that is inherent in Dirac's approach to quantum mechanics and has characterised it in terms of an 'open theory', which is amenable to future revision. Dirac thus leaves a role for theoretical development where AQM sees only observables. Bokulich has argued that Dirac's approach to quantum mechanics was based on this notion of an open theory, with further development through the establishment of *analogies* with the form of equations in classical mechanics.

A detailed consideration of Dirac's philosophical commitments to quantum mechanics as an 'open theory' leads Bokulich to conclude that the relationship between classical and quantum mechanics is best characterised as a non-reductive relation of 'interstructuralism', in which the analogies are heuristic *guides*, rather than strict empirical prescriptions, for the further development of the theory. In this context, Bokulich notes that Dirac's 'disavowals of philosophy' are based on a conception that quantum mechanics is not yet the correct theory (p. 71). As I have already noted, Bader's interpretation of the same fact seems to be that Dirac was committed to logical positivism (to which operationalism is closely related).

In Bokulich' view, Dirac's approach to the development of quantum mechanics is based on a principle of *correspondence* with the laws of classical mechanics. It is in this context useful to outline what an 'analogy' in the sense intended by Dirac amounts to. In his discussion of the action principle in both quantum and classical physics, Dirac remarks that

> The variation with time of the Heisenberg dynamical variables may thus be looked upon as the continuous unfolding of a unitary transformation. In classical mechanics […] the whole motion be be looked upon as a continuous unfolding of a contact transformation. We have here the mathematical foundation of the analogy between the classical and quantum equations of motion, and can develop it to bring out the

> quantum analogue of all the main features of the classical theory of dynamics. (Dirac 1958, p. 125)

This ‘quantum analogue’ of the ‘main features of classical dynamics’ is in important part the mathematical form of the operators that correspond to classical observables.

Somewhat unconvincingly, Bokulich (2008) argues that Feynman ‘was unable to understand what Dirac meant by “corresponds” or ”analogous” [and] decided to set the quantum and classical expressions equal to one another’ (p. 53).[7] Bader (2007) does also recognise the role of correspondence in Dirac’s theory, where he writes that

> In 1933 such thinking led Dirac to write a paper wherein he posed the question of what would correspond to the limiting classical expression for the quantum transition amplitude that determines the dynamic behavior of the system with time. Dirac was asking for the correspondence of quantum mechanics with the Lagrangian method of classical mechanics, a formulation he considered to be more fundamental than that based on Hamiltonian theory. (Bader 2007, p. 49)

Bader also notes that the *identification* was only made by Schwinger. However, austere quantum mechanics *relies* on the *identification* of the variations both of and on the zero-flux surface with the action of infinitesimal generators, and in this sense, the derivation of the dynamical laws for the equations of motion of the generators in QTAIM is dependent on this identification step.

Where Dirac thus sees scope for a development of *quantum* pictures along classical lines,[8] austere quantum mechanics is focused on extracting the classical picture out of the quantum system, and leaves no room for the possibility that the quantum picture may in a sense be determined by classical structures. Bokulich argues that

> Dirac develops a way to reintroduce particle trajectories into quantum mechanics—something that he takes to be an important extension of the analogy between classical and quantum mechanics. (Bokulich 2008, p. 55)

It is however not quite clear how a move from Feynman and Schwinger’s identity of the contact transformations of classical mechanics and the unitary transformations of quantum mechanics to Dirac’s principle of analogy extension may affect philosophy of chemistry. In the philosophy of chemistry, this move may to some degree rehabilitate the orbital picture, but this is an area that needs more in-depth technical and philosophical research. I have outlined some of my initial thoughts in the “Appendix”.

It is therefore not the case that QTAIM adheres to AQM throughout. Under the Dirac perspective, the dynamical structures that emerge from QTAIM become features of chemical theories that *correspond* to dynamical features of quantum theory, but that on the other hand do not *preclude* chemical explanations in terms of entities that are not captured in the language of QTAIM. It is in this context interesting to note that Richard Bader does recognise the correspondence:

> Once the quantum mechanics has been used to determine $\rho(r)$ and the dressed densities, then the theorems that govern a systems behavior are of the same form as

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[7] She does not expand on this statement in detail.

[8] Note that in another chapter Bokulich argues that there is room to suppose that *classical* trajectories of particles in a particular class of quantum system influence the (semi-classical) quantum trajectories, and hence she argues that in this sense the classical structure may *determine* the quantum solution. For details, see her Chapter 5.

> the expressions from classical mechanics that describe a corresponding macroscopic system. (Bader and Matta 2012)

In this sense, Bader thus seems to oscillate between the perspectives of austere quantum mechanics and those of Dirac.

A last, and relatively minor, issue appears if we consider the claim in Bader and Matta (2012) that ‘atoms’ are non-overlapping. Specifically, Bader writes that

> The notion that atoms overlap one another stems from the use of atomic-like functions (improperly termed atomic orbitals) in the expansion of a molecular orbital or in expressing a valence bond wave function. (Bader and Matta 2012)

However, the notion of ‘overlapping atoms’ can historically be found in the papers by (Lewis 1916) (his item no. 4 on p. 768), and is would not seem to be a feature of the orbital model.

Reduction and elimination

Austere quantum mechanics is committed to an eliminativist form of reductionism. Eliminativism is a form of reductionism which derives from the ‘reduction qua replacement’ theory from Kemeny and Oppenheim (1956) and which needs to be contrasted with a more moderate, non eliminativist, view on reduction developed by Nagel (1961).[9]

The reduction scheme of Kemeny and Oppenheim (1956) was formulated at the same time as the Nagelian scheme. In opposition to the model of Nagel, which requires that the reduced and reducing theories are specified in detail, the Kemeny and Oppenheim model focuses on the empirical *consequences* of both theories. The operational definition of reduction that is employed by Kemeny and Oppenheim (1956) is embodied in the following statement:

> In a reduction we are presented with two theories T_1 and T_2 and with the observational language of today represented by the complex sentence ${}^tO$. (The superscript is added to emphasise that this is the body of observations available at a given time *t*.) The theoretical vocabulary of T_2, Voc(T_2), contains terms which are not in Voc(T_1). (And, of course, we must require that these terms be not definable in terms of Voc(T_1). We add this additional requirement once and for all—it will not be explicitly mentioned from here on.) But it turns out that T_1 can explain all that T_2 can, and it is no more complex. Hence we drop T_2 from our body of theories and strike out all terms in Voc(T_2) which are not in Voc(T_1). Then we say that T_2 has been reduced to T_1. (Kemeny and Oppenheim 1956, pp. 8–9).

Kemeny-Oppenheim reduction thus focuses on empirical strength in an operationalist sense, and moreover requires that reduced theories are eliminated.

In the context of the present discussion, AQM is committed to reduction in this eliminativist sense.

Austere quantum mechanics as eliminative reduction

Austere quantum mechanics is committed to an eliminative form of reduction in the sense of Kemeny and Oppenheim. Bader’s QTAIM approach to quantum mechanics shares a number of features with the Kemeny-Oppenheim theory: its commitment to observation as

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[9] For a discussion of the Nagelian perspective in the reduction relationship between chemistry and physics, see Hettema (2012).

the leading feature of a scientific theory, as well as the desire to eliminate certain aspects of the reduced science (chemistry) from the lexicon are the most obvious points of agreement.

Yet some of the problems associated with QTAIM suggest that QTAIM is not a reducing theory in the sense of Kemeny and Oppenheim.

QTAIM is based on zero-flux basins, but not all zero-flux basins correspond to atoms. Hence QTAIM is not eliminative for the concept of 'atom' in this sense. Similarly, the role of the 'bonding operator' in QTAIM needs further clarification.

Furthermore, a *calculation* of the densities on which QTAIM is based requires the specification of a molecular system in the terminology of quantum chemistry. The specification of such a system is not possible without specific commitments from chemistry about for instance the correspondence between 'atoms' and nuclei with a particular charge, and the specification of a molecular 'shape' through the Born-Oppenheimer approximation. Hence the system specification of QTAIM already contains significant aspects of chemistry in its construction.

It is not easy to see how QTAIM, as a theory of the quantum mechanics of a closed region of space, could be possible *a priori*—that is, without these pre-existing concepts of 'atoms', 'structure' and 'molecules' in a sense that would be required if QTAIM were a subspecies of AQM. Certainly, 'direct' calculations of the densities of such subsystems do not seem to be possible. In this sense, austere quantum mechanics is best characterised as an 'interpretational' device that assists in the evaluation of quantum chemical calculations, rather than as a device that can facilitate such calculations directly without intervention from chemistry.

Finally, the inability to 'pick out' the individual atoms and the somewhat confusing role of the 'bonding operator' suggest that there are aspects of QTAIM that are not 'simpler' than their corresponding theories of chemistry.

For these reasons I conclude that QTAIM is not a strongly reducing theory in the Kemeny-Oppenheim sense. It is at the same time not clear whether the inability to be reconstructed as an example of a Kemeny-Oppenheim reduction is actually a drawback of the theory: to my knowledge, there are no convincing proposals for reducing theories in the Kemeny-Oppenheim sense that are at the same time sensitive to the peculiarities of the sciences they deal with. QTAIM is certainly sensitive to chemistry, and therefore has a role to play in the development of chemical theories.

As opposed to austere quantum mechanics, the aim of QTAIM with respect to the theories of chemistry could be said to be the more limited goal of eliminating *some* uses of quantum mechanical concepts from the chemistry lexicon, as opposed to eliminating an entire branch of science.

This provides the necessary context for the consideration of the role of orbitals. Is QTAIM sufficiently strong to demonstrate that the 'orbital' picture should be removed from the chemical lexicon?

To correctly approach this question it should be noted that at this point, Bader's position seems to deviate in important details from austere quantum mechanics, since the positive role of MO theory is recognised in some instances.[10] However, as Bader notices, the orbital model is sometimes misused, particularly when molecular properties are ascribed to individual orbitals.

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[10] Specifically, as summarised in Bader and Matta (2012), MOs have a role to play in the explanation of the relative ordering of excited states, and considerations where symmetry plays an important role. Similarly, orbitals play a role in understanding the phenomenon of polarisability.

In this debate, QTAIM plays a regulatory role. One issue is that orbital partitioning schemes are in general not unique[11] and the apportioning of molecular properties across contributions from various orbitals is similarly, in the words of Bader, a matter of 'personal prejudices'. In this sense, QTAIM is indeed aimed at eliminating *some* uses of quantum mechanical concepts in chemistry: those that lack a proper physical basis.

From this perspective, it is not clear whether Richard Bader was committed to the strong eliminative tenets of austere quantum mechanics all along. Rather, his position seems to oscillate between an 'austere' and a Dirac perspective. Where austere quantum mechanics is based on a restriction of the Dirac perspective to an 'operational' perspective (in which there is no room for 'parallel universes'—(i.e. chemistry and physics explanatorily exclude each other), there is room, within QTAIM, for certain uses of the orbital model and the use of orbitals in an *instrumental* sense.

My conclusion, which I will defend in the last section of this paper, is that QTAIM is best conceived as a *building block* for theories of chemistry, and also provides a 'health check' for the resulting theories.

Building chemical theories with electronic densities

If austere quantum mechanics is not a strongly reducing theory in the sense of Kemeny and Oppenheim, it needs to be asked what its relationship to chemistry might be. In this section it is my aim to discuss a number of connections between 'austere' quantum mechanics, QTAIM and chemistry, and focus on how we build theories in chemistry. Bader's argument for austere quantum mechanics, with its modifications, clarifies that we cannot hope to build such theories *ignoring* quantities of physics. Yet, at the same time, there is a sense in which these quantities of physics are not 'all there is'.

A dilemma of operationalism

In an interesting paper, Pap (1959) has argued that the term 'operational definition' is in need of clarification. Specifically, Pap argues that terms that feature in scientific theories are on the one hand not capable of operational definition, yet, for the theories to have empirical import, these terms must have operational significance.

While I do not wish to rehash Pap's argument in detail, it boils down to the contention that while operational terms must in some sense be *measurable*, theories cannot be only about things that are measurable operationally, since theories rely on an interplay between measurement and calculation. Theoretical frameworks serve a dual function: they are on the one hand used for prediction, but they also feature in the *computation* of inferred values, leading to further predictions.[12] The 'calculation' function that Pap refers to differs from the 'systematising' or 'organising' criterion mentioned by Kemeny and Oppenheim: 'calculation' allows for a constructive aspect of theorising in a way that 'organising' does not.

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[11] It is also worthwhile to note in this context that orbitals themselves are unique only up to a particular set of transformations—for instance in the Hartree-Fock scheme a sufficient requirement for a correct HF solution is the Brillouin condition, which stipulates that matrix elements of the Hamiltonian between the ground state and single-excited states must vanish. This conditions does not fully determine all orbitals.

[12] The specific example Pap mentions, that the framework of mechanics stipulates that the mass of the electron, the mass of the sun and the mass of a football all refer to the same quantity 'mass' serves a key role in the explanatory strength of mechanics. Yet in a purely operationalist framework, these three different masses are measured in a different manner and should therefore refer to different quantities.

In other words, it is a key feature of theories that the terms that feature in them serve a dual purpose, both as ‘anchors’ to an experimental reality, as well as building blocks for future theories.

Chemical theories

Pap’s dilemma suggests that QTAIM, as an ‘operational’ theory, has a dual purpose as a regulatory and constitutive element of chemical theories.

Bader’s various comments on orbital theory should be read as part of this regulatory programme. Chemists sometimes *do* read too much into the properties of individual orbitals, and QTAIM provides, through its foundation in austere quantum mechanics, a timely warning that orbitals are mathematical tools with a somewhat suspect ontological identity. Similarly, QTAIM has a regulatory function with regards to the different ‘types’ of bonding that chemical theories sometimes distinguish, and is there to remind us that all these ‘types’ are in the final analysis aspects of the same phenomenon of bonding.

The constructive approach that is furnished by austere quantum mechanics through its ‘extension’ into QTAIM sees molecules primarily in *mechanical* terms, with a ‘chemistry’ that derives from the computed electronic densities. Bader (1990) contains numerous examples of how this ‘chemistry’ manifests itself in calculated electron densities, for example in a clarification of the Lewis electron pair model.

In this paper I have argued that to some degree this ‘extraction’ approach relies on the identification of classical contact transformations and the continuous transformations of quantum theory, and that the approach favored by Dirac, which is based on an analogy between the two rather than an identification, may leave room for typical ‘chemical’ concepts to enter into the quantum densities, although the technical detail of that project is entirely unclear.

Yet, there are a sufficient number of explanatory and technical difficulties associated with QTAIM to ensure that the theory is not in its entirety a form of ‘austere quantum mechanics’ and hence is not reductive in the eliminative sense intended by Kemeny and Oppenheim. On the other hand, the theory has much to contribute to our understanding of chemistry, and has a significant role to play in grounding chemical theories. That fact should ensure the future of QTAIM as a scientific theory for many years to come.

Conclusion

It is finally worth noting that the recent paper by Bader and Matta (2012) starts with a quote from Aristotle, taken from Russell (1945), that “form” is a distinguishing property of atoms. In Bader’s theory of course, this Aristotelian ”form” becomes identical with ‘shape’. However, Aristotle introduced ‘form’ as a term to distinguish it from ‘substance’. For Aristotle, a substance can only become a ‘thing’ by assuming a certain ‘form’—a shape, configuration and plan.

My reading of QTAIM as a regulative and constructive theory of chemistry suggests that we take this wider reading of Aristotelian ‘form’ seriously: the theory gives ‘form’ not only to the concept of atoms in molecules, but also to important parts of chemistry itself. Shape does play a role in that reconstruction, but is not the only contributing factor.

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Appendix: Possible implications of the Dirac perspective in the philosophy of chemistry

Austere quantum mechanics is based on a significant *restriction* of the Dirac perspective on theories, one in which 'analogies' become 'identities', one in in which prediction trumps everything, and, most importantly, one in which there is no room for 'open theories'. Hence it makes sense to ask whether adopting Dirac's particular perspective to the relationship between chemistry and physics can save both the positive achievements of Bader's QTAIM as well as a significant portion of classical chemistry.

To determine this question, it makes sense to ask what Dirac used the analogy for. Its main purpose was determining the *form* of operators that correspond to particular observables. In the specific sections of *The Principles of Quantum Mechanics* that deal with the action principle, Dirac uses the analogy between the unitary transformations of quantum mechanics and the contact transformations of classical mechanics to derive dynamical behaviour in both systems that is of the same form. Dirac also notes, that the analogy is not complete, however, since in classical mechanics the action S has to be real while there is no corresponding requirement in quantum mechanics (p. 130).

In chemistry, there are no clear equations of motion that can be cast in terms of either Poisson brackets or quantum mechanical commutators, and there is no 'chemistry' that clearly corresponds to a CSCO. Hence the *direct* application of austere quantum mechanics to chemistry is not possible. It is precisely in this sense that austere quantum mechanics is eliminative: it claims that the lack of such a *direct* application is the result of the non-existence of the theoretical entities of chemistry.

In the main text of the paper I have argued that austere quantum mechanics plays a regulatory role *vis a vis* the concepts of chemistry—i.e. that it assists in *interpreting* the results of quantum chemical calculations in terms of a mechanical model of the molecule. At the same time, to leave room for chemistry, this mechanical model is not 'all there is'. 'Parallel universes' are possible, but in a limited sense.

However, relaxing the notion of identity of contact transformations and unitary transformations to one of analogy seems to suggest that the introduction of chemical concepts is possible in a more direct way. For instance, it would be interesting to consider the unitary group characterisation of open shell systems and the concept of valence along these lines.

References

Bader, R.F.W.: Atoms in Molecules: A Quantum Theory. Oxford Science Publishers, Oxford (1990)

Bader, R.F.W.: Principle of stationary action and the definition of a proper open system. Phys. Rev. **49**(19), 348–356 (1994)

Bader, R.F.W.: The Lagrangian approach to chemistry. In: The Quantum Theory of Atoms in Molecules, Chap. 2, pp. 37–59. Wiley-VCH, New York (2007)

Bader, R.F.W.: Bond paths are not chemical bonds. J. Phys. Chem. **113**, 10391–10396 (2009)

Bader, R.F.W.: Definition of molecular structure: by choice or by appeal to observation? J. Phys. Chem. A **114**, 7431–7444 (2010)

Bader, R.F.W.: On the non-existence of parallel universes in chemistry. Found. Chem. **13**, 11–37 (2011a). doi:10.1007/s10698-011-9106-0

Bader, R.F.W.: Worlds apart in chemistry: a personal tribute to J. C. Slater. J Phys. Chem. A **115**(45), 12667–12676 (2011b)

Bader, R.F.W., Matta, C.F.: Atoms in molecules as non-overlapping, bounded, space-filling open quantum systems. Found. Chem. **14**, 1 (2012)

Bader, R.F.W., Nguyen-Dang, T.T., Tal, Y.: A topological theory of molecular structure. Rep. Prog. Phys. **44**(8), 893–948 (1981)

Bokulich, A.: Reexamining The Quantum-Classical Relation: Beyond Reductionism and Pluralism. Cambridge University, Cambridge (2008)

Bridgman, P.: The Logic of Modern Physics. Macmillan, New York (1932)

Cassam-Chenaï, P., Jayatilaka, D.: Some fundamental problems with zero flux partitioning of electron densities. Theor. Chem. Acc. **105**, 213–218 (2001)

Cohen-Tannoudji, C., Diu, B., Laloë, F.: Quantum Mechanics. Wiley, Nwe York. Translated from the French by Susan Reid Hemley, Nicole Ostrowsky and Dan Ostrowsky (1977)

Coulson, C.A.: Present state of molecular structure calculations. Rev. Mod. Phys. **32**(2), 170–177 (1960)

Dirac, P.: Quantum mechanics and the hydrogen atom. Proc. R. Soc. A **110**, 561–579 (1926)

Dirac, P.A.M.: The Lagrangian in quantum mechanics. Physikalische Zeitschrift der Sowjetunion **3**(1), 64–72 (1932)

Dirac, P.A.M.: The Principles of Quantum Mechanics, 4th edn. Oxford University Press, Oxford (1958)

Feynman, R.P., Hibbs, A.R.: Quantum Mechanics and Path Integrals, 4th edn. McGraw-Hill, New York (1965)

Frank, P.G. (ed.): The Validation of Scientific Theories. American Association for the Advancement of Science, Washington (1954)

Hempel, C.G.: The theoretician's dilemma. In: Feigl, H., Scriven, M., Maxwell, G. (eds.) Concepts, Theories, and the Mind-Body Problem, Vol. 2 of Minnesota Studies in the Philosophy of Science, pp. 37–98. University of Minnesota Press, Minneapolis (1958)

Hettema, H.: Reducing Chemistry to Physics: Limits, Models, Consequences. Createspace (2012)

Jammer, M.: The Conceptual Development of Quantum Mechanics, 4th edn. Tomash Publishers, American Institute of Physics, Annapolis (1989)

Kemeny, J.G., Oppenheim, P.: On reduction. Philos. Stud. **VII**, 6–19 (1956)

Lewis, G.N.: The atom and the molecule. J. Am. Chem. Soc. **38**, 762–785 (1916)

Matta, C.F., Bader, R.F.W.: An experimentalist's reply to What Is an Atom in a Molecule? J. Phys. Chem. A **110**(19), 6365–6371. PMID: 16686473 (2006)

Moffitt, W.: Atoms in molecules and crystals. Proc. R. Soc. Lond. A **210**, 245–268 (1951)

Nagel, E.: The Structure of Science: Problems in the Logic of Scientific Explanation, 4th edn. Routledge and Kegan Paul, London (1961)

Nasertayoob, P., Shahbazian, S.: Revisiting the foundations of the quantum theory of atoms in molecules: toward a rigorous definition of topological atoms. Int. J. Quantum Chem. **109**, 726–732 (2009)

Pap, A.: Are physical magnitudes operationally definable? In: Churchman, C.W., Ratoosh, P. (eds.) Measurement: Definitions and Theories, Wiley, New York (1959)

Russell, B.: A History of Western Philosophy, 4th edn. Simon and Schuster, New York (1945)

Schwinger, J.: The theory of quantized fields. I. Phys. Rev. **82**, 914–927 (1951)

Srebrenik, S., Bader, R.F.W.: Towards the development of the quantum mechanics of a subspace. J. Chem. Phys. **63**(9), 3945–3961 (1975)

Styer, D.F., Balkin, M.S., Becker, K.M., Burns, M.R., Dudley, C.E., Forth, S.T., Gaumer, J.S., Kramer, M.A., Oertel, D.C., Park, L.H., Rinkoski, M.T., Smith, C.T., Wotherspoon, T.D.: Nine formulations of quantum mechanics. Am. J. Phys. **70**(3), 288 (2002)