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THE EPISTEMOLOGICAL AUTONOMY OF CHEMISTRY

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Abstract

The “logicians’ program” or attempt to situate scientific methodology within a logical framework has come to a standstill following radical developments within the philosophy of science and science and technology studies. One of the most persistent concepts remaining from the traditional philosophy of science or logical empiricism however is the unification of science through the reducibility of chemical and biological phenomena to physical laws and explanations. Towards the end of the 19th century, chemistry underwent a physical revolution in order to describe dynamic processes and express chemical phenomena mathematically, and developments within quantum mechanics during the 1920s encouraged the assumption that chemistry is fully reducible to physics. Theoretical chemistry is briefly overviewed to reveal that quantum chemistry developed through the assistance of models developed within the “organic structuralist tradition” and empirical data to generate abstract approximations that are cumbersome to calculate. From these approximations, however chemists have produced powerful models, in particular molecular orbitals, that have become invaluable conceptual tools within chemistry since they “black box” quantum mechanical calculations and rationalize chemical processes. Despite shared ontology between physics and chemistry, since it is impossibly cumbersome to fully explain chemical phenomena at the particle level, there is the appearance of “emergentism” at the molecular level, and physics does not capture chemistry’s engineering ideology and “disciplinary matrices”, philosophical concepts including “supervenience” have been used to argue for the epistemological autonomy of chemistry. Logical empiricism is predominantly a philosophy of theoretical physics that privileges physics to ontology and forces reduction through the declaration that if an object is material, its properties and behaviours can be fully described by physical laws and explanations. This limiting aspect of our philosophy of science could be improved through imagining a more accommodating philosophy of science such as Kopylov’s (1999) in which the sciences are restructured as technical satellites of a shared, essential ontology.

Keywords: logical empiricism, scientific reductionism, epistemological autonomy, theoretical chemistry, intertheoretical relations

Reduction and the Unification of Science

Science is a process that systematically generates empirically verifiable knowledge that is valued for its predictive capability. The philosophy of science seeks to understand the nature and justification of science, in particular epistemology or knowledge and justification, ontology or material entities, and semantics or meaning. The traditional philosophy of science or logical empiricism, developed through the combined efforts of the Vienna Circle and Karl Popper, dismisses metaphysical or empirically unverifiable epistemology and instead emphasizes logic such that theories are linked to observations through deductive reasoning whereby conclusions follow the logical consequences of true premises to provide theories with strong epistemic evidence (Duran, 1998). The success of science lies in its method which is demarcated through the "falsifiability" of scientific hypotheses which are constructed such that they can be empirically disproven. The traditional philosophy of science describes the conceptual framework within which the majority of what Kuhn (1996) terms "normal science" takes place and is defined according to Hacking (1981) by the following concepts: 1) realism – science uncovers truths about the real world, for which unique descriptions exist, 2) demarcation – there exists a sharp distinction between scientific theories and other forms of belief such that science is factual, objective, truthful, and based on empirical evidence, 3) science is cumulative – science builds on what is already known, 4) observation-theory distinction – there exists a sharp distinction between observation reports and theoretical statements, 5) foundations – hypotheses and theories are justified through observation and experiment, 6) deduction – scientific theories are deductive and tested by deducing observation-reports from theoretical postulates, 7) precision – scientific concepts and terms are specific and fixed, 8) contexts of justification and discovery – the logical basis of a discovery is distinguished from its psychological and social circumstances, and 9) unification of science – one science describes one real world and complex phenomena are reducible to physical explanations.

The vision for a science unified through reduction began with Kant's notion of a systematically ordered ontology and evolved into the idea that complex systems are simply the sum of their parts, both ontologically and epistemologically, which places the sciences in a hierarchical order. Mayr (1988) writes that the two most common notions of reduction are “explanatory reduction”, whereby all phenomena and processes at higher hierarchical levels including chemistry and biology can be explained in terms of the actions and interactions of physical components, and “theory reduction” whereby theories and laws formulated in chemistry and biology are only special cases of physical ones since all matter is composed of physical particles and therefore governed by physical laws and explained by physical mechanisms. Similarly, perspectives on reduction can be separated into “philosophical reductionism”, which maintains that chemical and biological methods and principles do not differ from those within physics and that their reducibility will eventually be demonstrated such that biology is reducible to chemistry through molecular biology and chemistry is reducible to physics through quantum mechanics, and “pragmatic reductionism” which argues that although science is unified by fundamental laws and particles, science must be conducted at different hierarchical levels for ease of research since reductive explanations do not make pragmatic sense as it is impossibly cumbersome to discuses behaviour, for example, on the genetic, molecular, or elementary particle level (Webster, 2003).

Many scholars question the success and motivation of reduction and whether complex processes could ever be fully explained by fundamental physical laws. Alternative perspectives have consequently developed within the philosophy of science including “emergentism”, where the whole is considered greater than the sum of its parts such that properties and phenomena exist at the chemical and biological level that cannot be fully explained by the sum of their physical components. Consider, for example that within biology, functions emerge within tissues that are not observed at the cellular level. The unification of science through reduction is widely acknowledged to have failed, including by Popper, Beckner, and Kitcher (Mayr, 1988). Janich (1998) writes that the concept remains inconclusive since 1) reduction, whether in principle or practice, remains to be demonstrated, 2) reduction is generally treated only in terms of theories and neglects “disciplinary matrices”, or Kuhn’s (1996) term for beliefs, techniques, models, metaphysical principles, problems, and exemplar solutions that enable scientific disciplines to be productive research domains, and 3) theories are treated as natural objects and not rational theory-constructions (Kuhn, 1996). Consequently, the “logicians’ program” or attempt to found the philosophy of science within a logical framework has reached its limits of usefulness, leaving important problems unanswered and no new directions of inquiry (Berson, 2003). Beyond the inconclusiveness of reduction, developments within the philosophy of science including Kuhn's (1996) concepts of disciplinary matrices and "incommensurability", Feyerabend's (1975) epistemological anarchism, Rorty's (1997) pragmatism, and social revelations within science and technology studies have further undermined the traditional philosophy of science. Consequently, philosophers of science have become increasingly interested in the role of semi-empirical methods, instrumentation, models, and approximations (Baird, Scerri, & McIntyre, 2005). Although many philosophies of science and reductionist programs overlook the significance of disciplinary matrices, scholars are becoming increasing aware of their ontological and epistemological consequences in the pursuit of scientific knowledge.

The traditional philosophy of science is predominantly a philosophy of theoretical physics, influenced by mathematical logic, and is an inadequate and inaccurate philosophy for most sciences however the notion of reductionism remains one of the most persistent ideas within the philosophy of science because of shared ontology between the sciences. Autonomists argue that chemistry and biology differ fundamentally from physics in subject matter, conceptual framework, and methodology and that the unification of science can only be achieved through adopting a broader philosophy of science that accommodates philosophical questions and concerns within chemistry and biology. Although the philosophy of biology emerged in the 1950s to address philosophical concerns within biology that were absent within the traditional philosophy of science, the philosophy of chemistry only established a research domain over the past 15 years as a consequence of strong reductive prejudices (Baird et al., 2005). Autonomy is essential for many academic fields since disciplinary domains and boundaries are important socio-economic distinctions that assist in securing funding and attracting new students. Since the question of autonomy seeks to legitimize disciplinary matrices, the central question within the philosophy of chemistry is: Is chemistry an autonomous science or is it reducible to physics? In order to address this question, however an appreciation of the conceptual link between physics and chemistry, namely theoretical chemistry is required.

Theoretical Chemistry

Chemists were alerted to the potential of quantum mechanics in rationalizing chemical phenomena when Heitler and London (1927) proposed their quantum model of molecular hydrogen. This model provided the first reasonable explanation for covalent bonding, which was difficult to comprehend within previous theoretical frameworks since it was assumed that repulsion forces between the two electrons would be too significant to permit bonding (Nye, 1993). As quantum mechanical approximation techniques developed and yielded increasingly accurate ground state energies for diatomic molecules, the reducibility of chemistry to physics was increasingly assumed. Indeed, this assumption is captured in Dirac's (1929) quietly accepted although recently questioned declaration that:

> The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations too much complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed which can lead to an explanation of the main features of complex atomic systems without too much computation. (p. 714)

The development of quantum chemistry was revolutionary since, for the first time, physical and mathematical principles were explicitly applied to dynamic chemical problems. Although the development of physical chemistry corroborated many of the structural considerations that had been so powerful in explaining chemical phenomena within the 19th century "organic structuralist tradition" and increased the significance and rate of chemical discoveries, these tremendous advancements clearly situated the chemical atom within the physical domain (Nye, 1993). Since then, advancements within particle physics have identified even smaller components of matter. Thus the "doctrine of physicalism", which dictates a dependence upon physical ontology and epistemology, has been upheld within chemistry (Hendrey, 2006).

Reductive prejudices are frequently upheld with little awareness of the historiography of ideas (van Brakel, 2003). Chemistry was traditionally the exemplar, ontologically strict science that reduced all phenomena and explanations to measurable macroscopic quantities including weights and volumes. The "realism-instrumentalism debate" between Mach and Planck during the early 20th century however saw chemistry adopt scientific realism and surrender the ancient notion of the atom to physicists (Fuller, 2000). The majority of efforts to demonstrate that chemistry is reducible or irreducible to physics have addressed the question from a theoretical perspective, in particular through examining links between the two disciplines at the quantum mechanical level. Thus, questions concerning the autonomy of chemistry require an appreciation of theoretical chemistry, which provides a mathematical description of and theoretical basis for experimental chemistry.

Quantum mechanics evolved through a number of landmark realizations. In 1901 Planck proposed the "quantum hypothesis" in which the energy (E) of electromagnetic radiation is quantized as a multiple integer (n = 0,1,2,3...) product of the frequency (f) of electromagnetic ration and Planck's constant (h) such that $E = nhf$. The quantum hypothesis ultimately resolved the "ultraviolet catastrophe" arising from Rayleigh's 1900 incomplete mathematical description of radiation emission from an ideal "black-body", which absorbs all electromagnetic radiation and emits light as a function of temperature (Cox, 1996). Rayleigh's equation, outlined in Equation 1, describes the energy (E) emitted from an ideal "back-body" increases infinitesimally as a function of decreasing wavelengths (λ) at a constant temperature (T) and using the Boltzmann constant (k) and erroneously predicts that a "black-body" emits both within the visible and ultraviolet regions at room temperature.

$$dE = \rho d\lambda \qquad \text{where} \qquad \rho = \frac{8\pi\kappa T}{\lambda^4} \tag{1}$$

Rayleigh's equation however is improved to closely match experimental observations at all wavelengths where p incorporates Planck's equation as illustrated in Equation 2, where c is the speed of light and h is Planck's constant.

$$\rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda\kappa T} - 1)} \tag{2}$$

In the early 17th century, the nature of light was hypothesized to be either a particle, according to Newton's "corpuscular theory" or a wave, confirmed by "Young's slits" experiments in which light is projected through slits in two screens and onto a third screen (Cox, 1996). Specifically, light is projected through a narrow slit in the first screen and two narrowly spaced slits in a second screen to yield periodic light intensity on the third screen called "fringes". The only reasonable interpretation of these fringes is that they result from constructive and destructive wave interferences. Although these experiments uphold the wave nature of light, Einstein remarkably evoked the particle nature of light in his rationalization of the "photoelectric effect" in which light or ultraviolet radiation projected onto metal, for example emits electrons as confirmed by the detection of a current (Ritchie & Sivia, 2000). Several observations concerning the photoelectric effect do not suit the wave notion of light, including the frequency and not the intensity dependency of 1) the kinetic energy of the emitted electrons, and 2) the minimum threshold below which electrons are not emitted (Ritchie & Sivia, 2000). Einstein proposed that a particle of light, or "photon" must collide into an electron with sufficient energy (Φ) to eject the electron from the substrate, as mathematical described in Equation 3 where m is the mass and υ is the velocity of the electron, h is Planck's constant, and v is the frequency of the incident radiation. The discovery of the wave-particle duality of light was a fundamental clue in the development of quantum mechanics since it suggests that the microscopic world is more complex and less accessible than the macroscopic world.

$$\frac{1}{2}m_e\upsilon^2 = hv - \Phi \tag{3}$$

In 1924 de Broglie fascinatingly extended the theory of wave-particle duality to other particles, including electrons such that the wavelength (λ) of a particle with momentum p can be expressed using Planck's constant (h) as shown in Equation 4.

$$\lambda = \frac{h}{p} \tag{4}$$

An important realization made concerning the wave-particle duality of matter by Heisenberg during his development of "matrix mechanics" is that pairs of unknowns, such as the position (x) and momentum (p)

of a particle cannot be simultaneously known without some degree of uncertainty (Cox, 1996). Heisenberg's celebrated Uncertainty Principle is mathematically described in Equation 5, where $\hbar$ is a modification of Planck's constant such that $\hbar = 2\pi/h$.

$$\Delta p \Delta x \geq \frac{1}{2}\hbar \tag{5}$$

Schrödinger extended de Broglie's relation to mathematically express particle-waves, as shown in the time independent form in Equation 6 where m is the mass and x is the position of a particle, $\hbar$ is a modification of Planck's constant such that $\hbar = 2\pi/h$, ψ is the wavefunction, V is the potential energy of the particle, and E is the total energy of the particle (Cox, 1996).

$$\frac{-\hbar^2 d^2\Psi}{2mdx^2} + V(x)\Psi = E\Psi \tag{6}$$

The Schrödinger equation is one of the most important statements within quantum mechanics and the primary goal within quantum chemistry is to solve more complex variations of Schrödinger's equation for the wavefunction of an electron. Critically, the square of the wavefunction yields the probability density of finding the electron at position x. The wavefunction for the hydrogen electron can be completely solved for all theoretical energy states and further interpreted to yield spatial coordinates or atomic orbitals that describe the area probability of finding the electron in various energy states. Unfortunately, because of the many-body problem and the necessity to consider electrostatic interactions, the Schrödinger wavefunction cannot be solved for any systems larger than the single electron hydrogen atom. Excellent approximations however can be made including reasonable orbital approximations from the solution for the hydrogen atom. The Born-Oppenheim approximation separates the electrostatic and nuclear components of a wave function by assuming that since nuclei are much heavier than electrons and therefore move relatively slowly, they can be treated as stationary relative to electrons (Atkins & de Paula, 2006). By fixing the location of nuclei, the Schrödinger equation can be solved for the electron alone so that wavefunctions of larger atoms and molecules can be approximated. Therefore although Schrödinger's equation cannot be definitively proved, it can be employed in combination with other theories to rationalize and statistically predict phenomena including electron tunneling, chemical bonding, molecular structure, electromagnetic radiation absorption and emission, and periodic trends.

The development of valence bond theory, which assists in evaluating the strength and spatial arrangement of chemical bonds, is one of the strongest links between quantum mechanics and empirical observations concerning molecular structure (Atkins & de Paula, 2006). Quantum chemistry, which chemists consider to be the foundation of chemistry, emerged in 1928 when Pauling explained the Heitler-London (1927) interpretation of molecular hydrogen to be attractive instead of repulsive because of the Pauli Exclusion Principle, which states that no more than two electrons can occupy an orbital, in which case their spins must be paired, and the Heisenberg-Dirac “resonance” phenomenon whereby paired electrons couple, perturbing each other’s harmonic oscillations such that the frequency of one is increased whilst that of the other is reduced to yield electronic attraction instead of repulsion (Nye, 1993). These revelations led Pauling to develop valence bond theory which rationalizes favourable pairing of electrons from atomic orbitals of different atoms such that electrons are paired with opposing spin and their orbitals merge to form an electron cloud during bond formation, as corroborated by approximate wavefunction calculations which yield electron density plots (Atkins & de Paula, 2006). Wavefunction descriptions within valence bond theory can explain concepts including “hybridization” or orbital mixing that gives rise to new orbital shapes through wavefunction interference such as in the formation of methane where three sp^3 hybrid orbitals are formed between three hydrogen 1s electrons and three carbon 2p electrons, and a fourth sp^3 orbital is formed between a hydrogen 1s electron and a carbon 2s electron “promoted” to the 2p atomic orbital (Atkins & de Paula, 2006).

The most fruitful structural tool arising from quantum mechanical calculations is molecular orbital theory within molecular wavefunctions are constructed as a linear combinations of atomic orbitals (LCAO) to generate molecular orbital (MO) wavefunctions that spread across entire molecules (Atkins & de Paula, 2006). Depending on the electronic distribution probabilities expressed within these wavefunctions, LCAO-MOs can be described as bonding, non-bonding, and anti-bonding orbitals such that wavefunctions for bonding orbitals express a higher probability of electrons being located between nuclei, localize the electron predominantly over one atom in non-bonding orbitals, and are destabilizing in anti-bonding orbitals. Molecular orbital theory has been developed more extensively than valence bond theory and forms the basis for much of computational quantum chemistry. Thus although many-electron wavefunctions are too cumbersome to calculate beyond molecular hydrogen, orbital approximations based on precisely calculated hydrogen orbitals can be made, taking into account nuclear charges and interactions between electrons, such that first approximations to an exact wavefunction are obtained by considering each electron to be occupying its own orbital (Atkins & de Paula, 2006).

Although approximations from Schrödinger's equation closely predict a number of experimental phenomena, its statistical interpretation troubled its founders and divided them into two philosophical camps, namely those who believed that the theory is incomplete and that with further developments, definitive solutions can be achieved including Planck, Einstein, de Broglie, and Schrödinger, and those including Bohr and Heisenberg who accepted the statistical interpretation which implies that nature is probabilistic, known as the "Copenhagen interpretation" (Ballentine, 1970). The Copenhagen interpretation is largely recognized to have succeeded since later generations of scholars have become more comfortable with the statistical scenario. Therefore despite the statistical nature of quantum mechanics, it is a foundational concept employed within physical chemistry to rationalize and predict a number of chemical phenomena, in particular molecular bonding and structure, and atomic radiation absorption and emission spectra, results from which have corroborated much of quantum mechanics, in particular the notion of discrete energy levels and the shell structure of the atom proposed by Bohr. One of the most satisfying outcomes from the quantum conception of the atom is the *aufbau* or "building up" principle for filling electrons into atomic orbitals during the construction of the periodic table since it rationalizes periodic trends including ionization energies and electron affinities (Ritchie & Sivia, 2000). This principle follows the Pauli Exclusion Principle and Hund's "maximum multiplicity rule" whereby electrons are distributed first within ground state orbitals so as to maximize the number of unpaired electrons. Since the periodic table is so foundational in organizing chemical explanations – indeed within chemistry it has a law-like status – it is clear that chemistry has deep foundations within quantum physics.

However, although quantum mechanics does provide a structural and spectroscopic theory for chemistry, it does not provide a theory for the dynamics of chemistry, which is considered within statistical thermodynamics.

Statistical thermodynamics can be described as a unifying foundation of chemistry. It combines the empirical predictive power of classical thermodynamics, which does not accommodate a theory of microstructure, with the quantum mechanical understanding of matter, thus linking structure to function and macroscopic phenomena such as temperature to a microscopic, molecular perspective (Maczek, 1998). Within statistical mechanics, macroscopic ensembles are statistically appreciated as a function of their constituent parts. In particular, statistical mechanics facilitates the interpretation of spectroscopic data using classical thermodynamics in order to predict equilibrium rates under specific conditions and predict the behaviour of molecules in real systems. Most chemical processes occur in solution, which can profoundly influence reaction rates and the structural conformations molecules adopt through screening electrostatic interactions. Simply consider how a complex process like protein folding ultimately occurs through countless small changes in intermolecular forces as a consequence of hydrophobic and hydrophilic solvation effects on amino acid side chains (Grant & Richards, 1995). Molecules are dynamic and statistical mechanics facilitates a theoretical understanding of dynamic molecular structure beyond bond rotations.

The central question in statistical thermodynamics concerns the distribution of energy over identical systems through the assistance of the Boltzmann distribution, and the partition function (Maczek, 1998). The Boltzmann distribution, outlined in Equation 7, provides information on the relative population ratios of two different energy states and the temperature dependence of this equilibrium, which is a central consideration in much of physical chemistry. Specifically, the fractional number of particles in the energy state n_i is dependent upon the temperature (T) difference of the two energy (ε) states where k is the Boltzmann factor.

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon i}}{\sum_i e^{-\beta\varepsilon i}} \qquad \beta = \frac{1}{kT} \tag{7}$$

The molecular partition function is derived from the Boltzmann distribution, describes how particles distribute over accessible quantum states, and is employed in the calculation of internal energy and statistical entropy, linking statistical and thermodynamic entropy. Further, the canonical partition function is derived from the molecular partition function and considers the interaction of individual particles (Maczek, 1998). By using the concept of "indistinguishability", micro- and macroscopic theories are linked and the Massieu Bridge, described in Equation 8 can be derived where *k* is the Boltzmann constant, *Q* is the canonical partition function, *T* is temperature, *A* is the Helmholtz free energy, and *J* is the Massieu function, namely *–A/T.* The Massieu Bridge is the strongest link to classical non-equilibrium thermodynamics, and the most fundamental statistical thermodynamic equations within chemistry are derived from it including that for: 1) internal energy, 2) the equation of state, 3) heat capacity, 4) entropy, 5) enthalpy, and the 6) Gibbs function (Maczek, 1998).

$$J = \frac{-[A - A(0)]}{T} = k \ln Q \tag{8}$$

One of the most important tools of theoretical chemists is computational chemistry. With the assistance of computers, many extensive and cumbersome quantum mechanical and statistical thermodynamic calculations can be completed to yield predictions for molecular structure, conformation, bond lengths and angles, ionization potentials, reactivities, and beyond. Rate constants however remain one of the most elusive chemical properties to predict (Grant & Richards, 1995). Computational techniques utilize various orbital approximation methods to calculate wave functions for molecular orbitals including *ab initio* techniques, which are purely theoretical, and semi-empirical methods which contain some empirical data in the method parameters. Many theoretical concepts however, cannot be computed and therefore molecular mechanics, which conceives as atoms as spheres joined by springs, applies classical mechanics to molecular systems and has evolved as an important domain within theoretical chemistry. This technique was first developed by spectroscopists and has had numerous applications in structural computational calculations of materials since the calculations for Newtonian forces are less cumbersome than quantum mechanical ones (Grant & Richards, 1995).

Theoretical chemistry is clearly founded upon the physical principles of quantum mechanics and thermodynamics although remarkable efforts have been made by physical chemists to link these principles to chemical phenomena. Most arguments for the autonomy of chemistry suggest that theoretical chemistry, in particular concepts developed within statistical mechanics, have undergone so many approximations that, although they are inspired by physical concepts, they are not reducible to them, and that although they are reducible in theory, it would be far too cumbersome to explain chemical phenomena in terms of physical forces anyways therefore it makes sense to retain a chemical level of explanation. Finally, some scholars write that our philosophical conception of science is misguided and that chemistry can remain an autonomous discipline despite its connections with physics.

Is Chemistry Reducible to Physics or is it an Autonomous Science?

The Physical Revolution

The emergence of physical chemistry in the late 19th century and the application of quantum mechanics to chemical phenomena beginning in the 1920s revolutionized the understanding of chemical phenomena by expressing chemical processes mathematically and dramatically increased the rate of progress through developments including molecular orbital theory. Despite the fact that the majority of chemists adopted the theoretical formulation of quantum chemistry, the persistence and continued success of the organic structuralist tradition, with the advent of the “curly arrow” and reaction mechanisms rationalized through concepts including “electrophiles” and “nucleophiles”, for example have prevented the physical revolution from being fully recognized (Tomasi, 1999). Frenking (1998) similarly writes that developments within quantum chemistry should have been revolutionary however were for a large part ignored since 1) chemistry was already a successful science, 2) quantum mechanical language is different from proven chemical models, and 3) experimental chemistry did not immediately benefit from an improved understanding of the chemical bond. The continued co-existence of these two traditions suggests that either chemistry is still undergoing a physical revolution or properties exist at the molecular level that cannot be efficiently and satisfactorily explained by quantum chemistry. However, since developments within quantum chemistry have corroborated much of the organic structuralist tradition, it is likely that the physical revolution is ongoing (Nye, 1993). Interestingly, Frenking (1998) writes that understanding and manipulation are not equally valued within chemistry, which remains an engineering program focused on material manipulation, and that progress within chemical understanding will continue to be hindered until the physical revolution is embraced.

Do Quantum Mechanical and Statistical Thermodynamic Approximations Made to Fit Existing Chemical Models and Empirical Evidence Constitute Proof of Reduction?

Woody and Glymour (2000) declare that developments within quantum chemistry have not informed chemists of anything new and doubt whether empirically adequate Schrödinger wavefunctions would have ever been discovered in the absence of experimentally derived chemical bond energies, bond lengths, and dielectric constants, for example. Similarly, Hendry (2006) writes that abstract theories including quantum mechanics require a model of the system in question in order to be of any use. Since quantum mechanical theories corroborate many findings from the organic structuralist tradition, Woody and Glymour (2000) question: Why does the Born-Oppenheim approximation work? Why is statistical thermodynamics unable to translate phenomenological concepts including temperature and boiling point? Extensive approximations in quantum chemistry necessitate the continued use of “paper tools” or structural models developed within the organic structuralist tradition, despite ongoing improvements within computational chemistry, in order to rationalize outcomes that do not fit experimental data and guide future developments (Klein, 2001; Christie & Christie, 2000). Therefore reduction fails simply because it is intractable. Indeed, Hoffmann (1988) writes: “Most of the useful concepts of chemistry (for the chemist: aromaticity, the concept of functional group, steric effects, and strain) are imprecise. When reduced to physics they tend to disappear" (p. 1597).

Intertheoretical Relations

Despite shared ontology amongst the sciences, scholars are increasingly considering how to capture and accommodate the success and uniqueness of disciplinary matrices within the philosophy of science. A fascinating example is reported by Scerri (2000), who advocates for an intermediate position between the realism of chemical models and their reducibility to quantum mechanics, acknowledging chemistry's ontological dependence or reducibility to physics however benefitting from emergentism and the epistemological autonomy of its models through the concept of "supervenience", which defines an ontological relationship between two domains such that a change in the property of one object affects a change in a dependent object. Interestingly, van Brakel (2003) has declared a moratorium on concepts including supervenience, emergentism, unification, determination, equivalence, and approximation, all of which can be encompassed in the neutral term "intertheoretical relations", in attempts to account for the autonomy or reducibility of chemistry relative to physics since each position has only inconclusively been substantiated by empirical evidence. Further, van Brakel (2003) is frustrated by vague language used to conceal insufficient attempts to address the question of reduction including the verbs constituting, causing, controlling, determining, contributing, and underlies since they conceal insufficient attempts to properly address the question of intertheoretical relations. Instead, van Brakel (2003) writes that detailed case studies and further discussions are required concerning specific questions including: 1) "Can the notion of chemical bond be defined in purely quantum mechanical discourse?", 2) "What is the quantum-mechanical correlate of thermodynamic entropy?", 3) "How does the Pauli principle fit into quantum mechanics?", 4) "How is chemical reactivity brought about in terms of the four fundamental physical forces?", and 5) "Can we give a statistical mechanical description of the three-phase line between one solid and two immiscible liquids?" (p. 32). The unification of science through reduction is currently not a meaningful question since chemistry and physics cannot be clearly demarcated and what is to be reduced, specifically theories, concepts, properties, laws, causes, or explanations, for example, has not been articulated (van Brakel, 2003).

The Epistemological Autonomy of Chemistry

Chemistry has been revolutionized through the development of physical chemistry, in particular quantum mechanical explanations of chemical phenomena. Although the 19th century organic structuralist tradition enjoyed considerable industrial success, physical principles were only applied to chemical phenomena following Ostwald's declaration that questions concerning the dynamics of matter need to be addressed. The physical revolution within chemistry enabled chemical phenomena to be expressed mathematically for the first time, which improved understanding and productivity. The extent of this revolution however has been questioned since many of the structural outcomes of quantum chemistry corroborate models and theories first developed with the organic structuralist tradition, including the tetrahedral geometry of carbon. The impact of the physical revolution however is underappreciated since it developed over a relatively long period of time and in conjunction with advancements made within the organic structuralist tradition, in particular theories and models concerning reaction mechanisms (Frenking, 1998). Since models employed within the organic structuralist tradition, in particular molecular orbitals essentially "black box" mathematical and theoretical developments within quantum chemistry in particular, the two traditions are essentially commensurate, which makes it easy to under appreciate the significance and impact of the physical revolution.

Is chemistry, however epistemologically reducible to physics as a consequence of this physical revolution? The synergism of the organic structuralist tradition and quantum chemistry cannot be overlooked since extensive approximations made to determine empirically suitable wavefunctions continue to be guided by pre-existing chemical models. Additionally, the mathematical complexity involved in solving for wavefunctions in many-bodied problems, despite the use of super computers, means that approximations must continue to be made and verified against empirical evidence until either more powerful computers are developed or a revolutionary reconsideration within quantum theory is made. Since many of the useful concepts within chemistry cannot be fully understood at the quantum mechanical level and because of the appearance of emergentism, the reducibility of chemical epistemology remains to be demonstrated. Even if chemical epistemology was pragmatically irreducible to physics, discussions on reduction continue to totally ignore the importance of disciplinary matrices.

Chemistry has historically been preoccupied with material change and its synthetic tradition has profoundly influenced its character and ideology. Consider that chemistry has adopted more of an engineering outlook, aimed at preparing molecules that do not exist in nature, than physics and biology, which are preoccupied with answering deep cosmological and anthropological questions including "What is life?" and "What is the nature of the universe?" (Ball, 2006). One profound outcome of this ideological distinction between chemistry and physics is that chemists are more inclined to adopt pragmatic realism whereas physicists are much more likely to uphold Platonic Realism (Hoffmann, 2007). The ultimate goal of science is the generation of empirically verifiable knowledge, regardless of scientific methodology. Since logical empiricism was primarily established by philosopher physicists and analytic philosophers with a rigorous emphasis on *a priori* considerations, it is not surprising that notions including realism and unification through reduction suit their ideology. However, it does not necessarily follow that their philosophy is an adequate philosophy for all of the sciences.

Despite radical developments within the philosophy of science, the notion of unification through reduction remarkably persists. Disciplinary domains are socially important, especially for securing funding and attracting new students, and therefore the idea that chemistry and biology can be appropriated by physics simply through the notion of reduction is alarming and therefore resisted. Logical empiricism was constructed such that physics maintains privileged access to ontology. Indeed, physics is seen to own ontology to the extent that if an object is material, then its properties and behaviours can be entirely described by physical laws and explanations. This misguided aspect of our philosophy of science, which forces the notion of reduction, could be improved through imagining a different organizational structure for the sciences within which ontology is shared.

Kopylov (1999) proposes a novel organizational structure for the sciences in his “engineering chemical world concept” within which each science is imagined as a technical satellite of an essential ontology. What is refreshing about this philosophy is that it can accommodate the epistemological autonomy of disciplines since it does not force the question of reduction by establishing research domain hierarchies on the basis of ontological levels of complexity, namely particles, atoms, and molecules, through to organisms. Additionally, since Kopylov (1999) proposes that within this structure, each science should be considered a “constructive-technical paradigm”, the importance of disciplinary matrices, which are critical for disciplinary coherence through modes of explanatory discourse, and the role of technology as an epistemological mediator between object and observer can be acknowledged (Queraltó, 1998). Finally, Kopylov’s (1999) vision accommodates “big science”, which is more concerned with synthetic activities than generating knowledge about the real world, and promotes overlap and collaboration between research domains (Lelas, 1993). This philosophy of science does however dismantle physicists’ and analytical philosophers’ authoritative, pinnacle position on the “epistemic-ontological hierarchy of disciplines” which grants them special access to Truth, as enjoyed within the traditional philosophy of science (Rorty, 1997).

Investigations into connections between theoretical chemistry and physics yield an appreciation for the collaboration between the two disciplines and processes through which science progresses. Despite the fact that chemistry has benefitted from a physical revolution, the case can be made for the epistemological autonomy of chemistry since predominantly chemists developed quantum chemistry and they used their models originating from the organic structuralist tradition and empirical data to guide the development and application of increasingly abstract and approximated quantum theory to complex systems including molecules. Through this process, chemists have generated powerful visual models, in particular molecular orbitals, which have proven invaluable in inspiring, organizing, explaining, predicting, and designing chemical processes (Baird et al., 2006).

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