Whole-Parts Strategies in Quantum Chemistry: Some Philosophical and Mereological Lessons

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Abstract: Philosophers mainly refer to quantum chemistry in order to address questions about the reducibility or autonomy of chemistry relative to quantum physics, and to argue for or against ontological emergence. To make their point, they scrutinize quantum approximations and formalisms as if they were independent of the questions at stake. This paper proposes a return to history and to the laboratory so as to emphasize how quantum chemists never cease to negotiate the relationships between a molecule, its parts, and its environment. This investigation will enable us to draw methodological conclusions about the role of history within philosophical studies, and to examine how quantum chemistry can clarify important philosophical and mereological issues related to the emergence/reduction debate, or to the way instruments and contexts are involved in the material making and the formal description of wholes and parts.

Keywords: *mereology, historicized epistemology, emergence, quantum chemistry, reduction, affordances.*

1. Introduction

Philosophers mostly refer to quantum chemistry in order to address questions about the reducibility or autonomy of chemistry relative to quantum physics, or to argue for or against ontological emergence. In this respect, they mainly direct their attention to:

(1) the status and legitimacy of approximations used in order to circumvent performing exact calculations (Hendry 1998, 1999);
(2) conceptual problems in standard quantum chemical models of the electron configurations of atoms (Scerri 1991a, 1991b, 1997, 2007a);
(3) configurational Hamiltonians, considering that they vindicate some ontological stance about emergence (Hendry 2006, 2010);

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(4) the epistemological meaning of emergence (Scerri 2007b, 2012, 2013; van Brakel 2000); or
(5) the possibility of redefining the concept of emergence in terms of singular asymptotic expansions and time-rescaling – using a contextual topology that fits the higher-level description of the system while still being compatible with lower-level basic theory (Primas 1983, 1998).

In this paper, we aim to report two complementary outcomes of a study that pays attention to the whole-parts strategies used by quantum chemists when they perform a calculation in order to determine a particular geometry or to quantify an energy. We would like to highlight the fact that the formalisms, theoretical tools, languages, and representations used within various chemical quantum methods were *constitutively* shaped by questions related to the relationships between a molecule, its parts, and the environment. In short, we would like to underline that the theoretical tools by means of which philosophers use to think about emergence and reduction *are not independent of the questions at stake*.

The later Wittgenstein clearly emphasized how relevant scrutiny of specific uses is for understanding a particular form of life, whether scientific or not (Wittgenstein 1953). Following Wittgenstein, our idea is to start from the study of chemical practices in order to identify what is at issue in a particular domain of chemical activities, and then to tackle the philosophical problems raised by chemistry. We envisage chemistry as a means to clarify philosophical issues that receive their meaning in other domains of knowledge, and sometimes to resolve them.

In her *Matière à penser: Essais d'histoire et de philosophie de la chimie* (2008) Bernadette Bensaude Vincent advocated that chemistry can be 'food for thought', or in French 'matière à penser'. This emerging question is the opposite of a more frequently-asked question, namely, what is the impact of philosophy on chemistry? Therefore, it merits fresh attention from both historians and philosophers. During the eighteenth century, the French philosopher Denis Diderot already held that studying chemistry should mean querying what chemists do and what is going on when chemical know-how and knowledge spread. Diderot aimed at characterizing chemical, technical and scientific practices by considering their specific sites, instruments, and goals (Diderot 1754). He advocated an image of chemistry as constantly adopting new techniques and pushing at the frontiers of neighboring fields of sciences.

That is what has been occurring for quantum chemistry since its beginning. In *Neither Physics nor Chemistry*, Ana Simões and Kostas Gavroglu make it obvious that quantum chemistry is a truly novel specialty. They say that "theoretical chemistry is first and foremost an enterprise whereby mathematical notions, numerical methods, experimental measurements, pictorial representations, and, above all, chemical concepts constitute an undivided whole." (Gavroglu & Simões 2012, p. 184) In other words, quantum chemistry is neither physics nor chemistry nor applied mathematics but an emergent whole clearly not reducible to its ingredients taken in isolation, or to their mere sum! What matters in order to address molecular issues is the way in which the whole approach is reinforced through the cross-linking and cross-fertilization of all these elements. In this respect, this recent book illustrates and widens the authors' previous work (Simões & Gavroglu 1997; Simões 1993) which established that the emergence of quantum chemistry is the convergent result of diverse scientific traditions.

Following this line of reasoning, our idea is to investigate what quantum chemists *actually do* in their laboratories. Our approach does not consist in applying types of mereology – that is to say types of logic of propositional reasoning concerning relations between wholes and parts – or prior concepts of emergence to chemical activities but, in contrast, in identifying the prerequisites that a concept of emergence or a type of mereology should have in order to address the questions raised by chemistry *as it is practiced*. It is in this sense that chemistry can become 'food for thought' and not just an application of concepts taken from other areas.

We divide our work into four parts. We first study how early quantum methods used orbitals – either molecular or atomic – in order to understand the formation and the reactivity of molecules. We will thus study how Robert S. Mulliken's 'Method of Molecular Orbitals' describes a molecule in terms of nuclei and electrons, and how Linus Pauling's 'Valence Bond Approach', in contrast, employs atoms or ions. Second, we will carefully examine a specific calculation based on Density Functional Theory (DFT) a method *which replaces orbitals by electron density*. This "rotation to laboratory", to use Roald Hoffmann's terminology (Hoffmann 2007), enables us to clarify the way quantum chemists connect a whole, its parts, and its environment, within a single calculation. Third, we will summarize how the current debate between the main protagonists and antagonists of the Quantum Theory of Atoms in Molecules (*QTAIM*) resembles and restates the opposition between Mulliken and Pauling as to whether a molecule is best considered an aggregate of atoms or a single, irreducible whole. We draw philosophical and mereological conclusions which could provide nourishment for the reflection of philosophers.

2. Whole-parts strategies in early quantum chemistry

In the late 1920s, the aim of many researchers was to create a molecular model which accounts for the various empirical facts of spectroscopy and chemistry. Among them, Mulliken was primarily concerned with the assignment of quantum numbers to electrons in molecules. He carefully studied the various molecular states obtainable when two atoms are imagined to come together. This problem is more difficult than determining the molecular states obtained from an atom if its nucleus were considered to be divided into two parts. Following Hund's principle (1927) according to which "no state is lost" during the formation of a molecule from two atoms, Mulliken aimed to find out correct relationships among the quantum states of: two isolated atoms, 'the united atom' (a fictitious entity obtained by coalescence of those two atoms) and the molecule, in which those two atoms were chemically combined (Mulliken 1928). (A helium atom made by fusing two hydogen atoms would be a 'united atom'.)

By comparing sets of spectroscopic and thermodynamic data, Mulliken managed to compare molecular and atomic electron quantum numbers and states, thus gathering the molecules formed by the elements of the first two rows of the periodic table. At first he noticed that the nature of the dissociation products of a given molecular state depends as much on its position on the energy scale as on its electron configuration, *i.e.* the distribution of the molecular electrons in various orbits. Then he noticed that, during the formation of a molecule from two atoms, some of the electrons must undergo rather radical changes in their quantum numbers – *changes that Mulliken dubbed 'electronic promotion'* – in order to satisfy the demands of the Pauli Principle regarding the molecule and the united atom (Llored 2010).

The gradual connection between the two early versions of quantum theory, chemistry, and spectroscopic analyses gave birth to the correlation diagrams (Mulliken 1932a). The position of a molecule in this type of diagram made it possible to assess the degree of likeness between a molecule and its separated atoms – or between a molecule and its united atom – thanks to empirical knowledge concerning inter-nuclear distances and charges of *nuclei*. Knowing the experimental characteristics of a molecule, it was possible to represent the negative energy of ionization of the electrons in the diagram and to make predictions both of energy parameters and the bonding, non-bonding, or anti-bonding function of the electrons in their different specific orbits around the *nuclei* of the molecule. In so doing, Mulliken proposed the curve representing the evolution of the molecular electronic state. This curve is an interpolation between two extremes cases: the electronic state of the united atoms on the one hand, and that of the separated atoms on the other. In this respect, he never reduced a molecule to atoms – *either isolated or unit-*

ed –, but, on the contrary, endeavored to elucidate the type of energy continuity between their respective states within a transformation (Llored 2010).

Mulliken rejected the concept of valence as an intrinsic property of an atom. By contrast, he referred to the 'binding capacity' of an electron in a given molecular orbit; considering that each orbit is delocalized over all the *nuclei* – or over a part of them – and could contribute, depending on each specific case, a stabilizing or a destabilizing energy contribution to the total energy of the molecule. In this respect, the notion of orbit depends upon the molecule as "a self-sufficient unit and not as a mere composite of atoms." (Mulliken 1967) The sum of the energy contributions of each electron in its orbit determines whether the electronic configuration allows for the existence of a stable molecule, *i.e.*, whether its energy is stabilizing overall. For Mulliken, in a molecule the atom no longer existed. He stated (1931, p. 369):

> In the 'molecular' point of view advanced here, the existence of the molecule as a distinct individual built up of nuclei and electrons is emphasized, whereas according to the usual atomic point of view the molecule is regarded as composed of atoms or of ions held together by valence bonds. From the molecular point of view, it is a matter of secondary importance to determine through what intermediate mechanism (union of atoms or ions) the finished molecule is most conveniently reached. It is really not necessary to think of valence bonds as existing in the molecule.

The '*electronic state*', the '*binding capacity*', the '*electronic promotion*', and '*the energy-bonding-power*' are among the many theoretical tools that Mulliken built in order to explain the capacity of electrons to be linked to *nuclei* and to form a molecular whole. The language of his orbits approach is thus underpinned by a specific representation of the whole-parts relation. His challenge was to understand why the new molecule displays properties that the reactive reagents or the atoms do not, knowing that the decomposition of a molecule allows recovering the separate atoms in particular electronic states. This type of investigation is reminiscent of the questions raised by Aristotle concerning the difference between an aggregate and a true "mixt" (Bensaude-Vincent 2005) or, closer to us, of the classical whole-parts discourses developed by the British emergentists (Llored 2013). *From the outset, the approximations and the language developed by Mulliken were constitutively shaped by the problem of emergence*. This remark remained relevant when, in 1932, Mulliken replaced the notion of molecular *orbit* by that of molecular *orbital*. We would like to point out that 'the approximation of molecular orbitals' modified the previous whole-parts strategy by introducing the environment into the calculation, often implicitly.

The notion of 'orbital' took its meaning from Max Born's probabilistic interpretation, according to which the square of the one-electron molecular wave function (orbital) in a region of space corresponds to the probabilitydensity of finding an electron in there. In addition, Mulliken (1932b, p. 50) asserted:

> By an atomic orbital is meant an orbital corresponding to the motion of an electron in the field of a single nucleus plus other electrons, while a molecular orbital corresponds to the motion of an electron in the field of two or more nuclei plus other electrons. Both atomic and molecular orbitals may be thought of as defined in accordance with the Hartree method of the self-consistent field, in order to allow so far as possible for the effects of other electrons than the one whose orbital is under consideration.

Mulliken explicitly interpreted this picture *as a model* on which to base calculations of the numerical values of chemically relevant molecular properties such as 'bond strengths' or 'atomic populations'. Mulliken's occasional ontological remarks support the view that the formation of molecular orbitals as linear combinations of atomic orbitals, namely the LCAO-MO approximation, does not entail that molecules are additive conglomerates of independent *nuclei*. Let us consider the simple but, methodologically speaking, generalizable case of a calculation involving a molecule made of two *nuclei*. The molecular wave function ψ can be expressed using two atomic orbitals φ_1 and φ_2:

$$\psi = c_1\varphi_1 + c_2\varphi_2 \tag{A}$$

The weighting coefficients c_1 and c_2 are determined using the variational principle in order to reach the minimal electronic energy. This minimization *technically* implies that the determination of *each* coefficient depends upon two integrals: (1) the Coulomb integral which is related to the electron energy in a unique atomic orbital φ_1 or φ_2, and (2) the exchange integral which deals with the energetic coupling between the two atoms *inside* the molecule.[1] As this type of coupling exists once the molecule is created, we can conclude that *each coefficient depends upon the whole molecule, and not solely upon its corresponding atom or nucleus!*

In the same way, the determination of 'atomic populations' depends on the contribution of *all* the electrons belonging to *all* the molecular orbitals that are occupied. Indeed, Mulliken ascribed the 'net charge', $c_1^2+1/2(2c_1c_2S_{12})$, to the atom corresponding to the atomic orbital φ_1. This atomic charge depends upon the whole molecule through: (1) the 'overlap population'[2] S_{12} which expresses the part of the electronic density that refers to the two atomic functions *at the same time*, and (2) the coefficient c_1 itself. *The whole and the parts are thus co-defined*. The atoms whose cores constitute the basic architecture of molecules are thus 'parts' insofar as they belong to the nuclear contribution of the global molecular wave function; but they are also 'parts' because calculations enable chemists to ascribe an atomic charge to each atom in the molecule in order to explain the reactivity and the selectivity of the chemical reaction under study.

Beyong this technical aspect, Vemulapalli (2003) clearly highlighted that the application of the variation principle in the calculation of the ground state of a molecule, strictly speaking, presupposes energy transfer with its environment. As a consequence, the *molecular whole, its parts, and the surroundings are required at the same time within the calculation.*

In contrast to Mulliken, Pauling developed a Daltonian scheme in which atoms are treated as the actual components of molecules, retaining their integrity in the compound they form. The use of accurate thermodynamic and crystallographic data enabled him to notice that the sum of the calculated covalent radii of the bonded atoms approximated the measured bond lengths well. He then linked the calculated binding energies with experimental heats of formation of gaseous molecules. The key step was to choose a set of molecules that could supply the data necessary for extracting those binding energies. This approach enabled him to express the total energy of formation of the molecule as a mere sum of energy terms characteristic of the different bonds; assuming that the molecule was obtained from separate atoms (Pauling 1932).

To understand Pauling's molecular description, one needs: (1) to connect the molecular structure to the properties of its constitutive atoms; (2) to study how those atoms interact from within the molecule. Each atom has stable atomic orbits, 2s, 2p for instance, that are used to form stable bonds inside a molecule or to induce *ad hoc* directed valence (Pauling 1931, Slater 1931). He stated that bonds resulted from the overlapping of two atomic eigenfunctions: the larger the overlap, the stronger the bond.

The study of diatomic molecules enabled him to propose the concept of 'normal' covalent bond and to express what he called the 'normal' covalent molecular wave function as a mere sum of covalent and ionic terms. Such contribution enabled him to develop the quantum counterpart of his definition of electronegativity (Pauling 1932).

The language and the theoretical tools developed by Pauling within the framework of his Valence Bond Theory are thus underpinned by a specific representation of the whole-parts relation. From the outset this work was shaped by questions related to the deduction of the properties of the whole from the properties of the parts. In addition, it is interesting to bear in mind that Pauling also used the variation principle in order to determine the weighting coefficients of each atomic orbital of the linear combination used to define a particular 'hybrid orbital.' As it was the case in Mulliken's work, the whole, the parts, and the surroundings are thus implicitly interwoven in Pauling's approach.

To conclude, Mulliken's and Pauling's approaches are not mere applications of quantum physics to the domain of chemistry. It is the *contingent* connection between chemistry, quantum mechanics, and instrumentation which frames the content of a particular approach. The two basic methods we have described *translate mereological questions into chemical language*. In a nutshell, early chemical quantum methods, their logical relations, and their related languages have been concerned with the problem of emergence from the beginning. The relations between a whole and its parts – atoms of different types, fragments, nuclei, electrons – are specifically at stake within those languages and formalisms. It is now time to turn to our second point and to return to laboratory in order to analyze a current calculation using DFT.

3. Study of a current DFT calculation

In 2010, we immersed ourselves in the workaday research activities of the French laboratory DCMR, the '*Laboratoire des Mécanismes Réactionnels*' at the Ecole Polytechnique. Our aim was to study quantum chemists at work. This laboratory determines mechanisms which account for molecular reactivity, using quantum calculations, mass spectrometers, and fluorometers. Our starting question was: What do quantum chemists do when they calculate a molecular geometry or a molecular energy? We will present the summary of the key results of our investigation. Fine-grained developments can be found in Llored 2012.

The researchers we worked with used Kohn-Sham density functional theory (Kohn *et al*. 1996). This method is different from quantum chemical methods based on wave functions. The molecular space is divided into grids of cubes, and researchers define an electronic density for each cube of this space. The total energy is calculated as a *functional* of the electronic density, *i.e.* a function having electron-density distribution as basic variable.

Some researchers develop *tailor-made* functionals for each atom or for each specific physical effect within a molecule. To achieve this difficult task, they change the number and values of parameters thereby shaping a new mathematical functional form that is designed to take physical phenomena and chemical results into account. They then use databases to appraise the reliability of the new functional, and pragmatically modify it again and again until they stabilize the 'best performers' for a specific purpose, that is until they obtain a functional that is not further improved (for the purpose of interest) by variation in the number or value of parameters (Zhao & Trulhar 2008).

Choosing a functional of electron density depends upon: (1) the desired accuracy, (2) the chemical system, and (3) the time required for calculation. These calculations also require choosing a set of functions called a *basis* for *each atom*. The basis changes according to the type of atoms, three main types are available: (1) the Gaussian Type Orbital of the form exp(-ar^2), (2) the Slater Type Orbital of the form exp(-ar), and (3) plane waves. Chemists can also use a linear combination of those three types if necessary. The basis also changes with other effects such as diffusion, polarization, pseudo potentials for core electrons, and the size of functions *depending on the circumstances*. The functional and its relative basis set define a 'level of calculation'. The calculation process depends upon the use of a computer program such as 'Gaussian' type or 'Turbomole'.

The process of calculation then combines information about: (1) the whole system: its geometry that chemists first define from the outset of the calculation, often using X-ray crystallography determinations; (2) the parts: a functional for each atom or groups of nuclei, each molecular orbital, each particular physical effect, and so on; (3) and the solvent: what is outside the whole. The calculation uses the three levels – the molecular whole, its parts, and the environment – *at the same time* in order to: (1) minimize energy, (2) calculate an energy barrier, (3) determine a transition state, and (4) postulate a type of geometry by means of *different* levels of calculation.

The model of the solvent is related to the solvation free energy of each compound. This quantity is defined as the required amount of energy necessary to transfer a molecule of gaseous solute into the solvent. The crucial step is to appraise how the solvent becomes involved in a chemical reaction. Its action can be direct if some molecules of solvent take part in the chemical process, or indirect if the solvent – then labeled the 'bulk medium' – only modifies the reactivity of the reactants compared with that of the same molecules in the gas phase. Chemists discuss the nature of the reaction pathway according to factors that influence solvation free energy – *including* the size and form of the cavity occupied by the solute, the solvent reorganization, the polarization between the solvent and the solute, and the entropic contribution (Llored 2011).

An iterative calculation based on the variational optimization of orbitals can then start. Loops of calculations are carried out until the the energy of the whole system reaches a convergent minimum value. If calculations are not convergent, researchers can change the functional, the size of the grids, and convergence thresholds in order to optimize geometry or to calculate molecular energy. Each step requires know-how, chemical experience, and pragmatic compromises. The calculation always uses both the variation principle and the molecular structure determined by experiments. The interaction with the environment may be either implicit, as it is the case with the use of the variation principle, or explicit when the specific interactions of the solvent are taken into account.

A particular level of calculation – a particular functional and its basis – is designed to answer a specific question only and *excludes* others. One cannot study all the molecular characteristics by means of a single calculation. When quantum chemists study the energy barrier of a chemical reaction, they have to choose a functional, its basis, and best estimates[3] for each level – atoms, molecule, and the solvent. They thus tailor a useful tool to understand and predict a defined characteristic (a rate constant or activation energy, say) and not another one, such as the geometry of a particular active site within a protein. 'Complementary' levels of calculation are thus necessary to achieve a global molecular description. They cannot be used within a particular calculation *at the same time*, because of their incompatible parameters. The global method used is *relative to* a family of chemical compounds and depends upon the entanglement of inter-calibrated tools. The method is *one* way not *the* way to *account for a* characteristic of the whole from its parts and its environment. In this respect, a quantum chemical method is a practice of articulation which negotiates an explanation from a particular whole-parts-environment strategy.

To conclude, this typical calculation clearly illustrates what explaining a structure or a mechanism, or predicting a transformation amounts to. Quantum chemists use many interrelated tools within a large and sophisticated network which combines mathematical functions and devices, empirical outcomes, computer engineering, quantum and classical physics, and chemical knowledge and know-how. The molecule, its 'parts', and the environment are required *at the same time*. They are *co-defined* within the calculation. Investigators negotiate what an explanation of the one from the others means. There is no room for deduction in this type of activities. Let us now study how recent debates in quantum chemistry summarize and modify those questions.

4. Whole-parts and the reduction debates in the atoms-in-molecules approach

The point that we have defended so far can be extended to quantum chemical methods that deny any overlap between atoms, as it is typically the case in Richard Bader's 'Quantum Theory of Atoms in Molecules' (Bader 1990). This approach is based on a topological description of the electronic density of the molecule. Chérif Matta (2002) states:

> It is the topology of the electron density that determines the boundaries of an atom which in turn determine its shape which in turn determines its properties inside a molecule [p. 28]. [...] A consequence of this topological feature of the density is the association of an atom with a region of space, each region being dominated by a given nucleus, with boundaries evident in the minima that exist between the nuclear maxima. The boundaries are determined by the balance in the forces that the neighbouring nuclei exert on the density [p. 29]. [...] The definition of an atom and its bounding surface are made both qualitatively and quantitatively apparent in terms of the patterns of trajectories traced out by the gradient vectors of the density. [...] The gradient exhibits a maximum at each nucleus in any plane that contains the nucleus, the nucleus acts as a *global attractor* in the gradient vector field of density. As a consequence, the three-dimensional space of the molecule is divided into atomic basins, each basin being defined by the set of trajectories that terminate at a given nucleus. *An atom is defined as the union of a nucleus and its associated basin*. [...] A bond path provides a universal indicator of bonding, linking all pairs of bonded atoms, regardless of the nature of the interaction [p. 32]. [...] Nuclear motions can induce topological changes in the density that correspond to the making and breaking of chemical bonds and to a change in molecular structure [p. 40]. [Emphasis added].

In this approach, an 'atom' is defined as the union of an *attractor – the nucleus – and its associated atomic basin.* Using its usual vocabulary, the atom has an 'inner' structure expressed by the 'intrinsic' geometry of the gradient field vector. Bader goes on to say that "[t]he quantum theory of atoms in molecules, QTAIM, demonstrates that every measurable property of a system, finite or periodic, can be equated to a sum of contributions from its composite atoms." (Bader 1990, p. 10) In other words, there are no gaps between atoms carved out of a given molecule: they perfectly match and compose the whole molecule. In this sense, the atoms literally add up to form the molecule they are part of. Matta and Bader thus define a reductionist program, according to which the molecule becomes the sum of 'topological atoms'. They assert that "[t]he time has arrived for a sea change in our attempts to predict and classify the observations of chemistry, time 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 & Matta 2013, p. 253).

The linguistic shift is clear. An atom *in* a molecule is now considered as a non-overlapping and bounded unit. As it seems, all is in the right place at the right time to deduce the whole from its parts. Nevertheless, Paul Popelier (2000), another leading expert of the field, qualifies this statement by claiming:

> We recollect that the gradient vector field *naturally* partitions the molecules into atoms, *i.e.* the gradient of ρ carves the atoms by the term *molecular atoms* as opposed to free or isolated atoms. Thus, every molecule falls apart into non-overlapping molecular atoms. [...] Every type of nucleus appears inside thou-

> sands of possible molecular atoms. In fact, there are millions of carbon (molecular) atoms because each atom is cut of a particular chemical molecular environment of which there are as many as there are molecules. In a manner of speaking, every molecular atom is endowed with properties it inherits from the molecule of which it is a part. In other words, the atom reflects the features of its particular chemical environment (p. 35). [...] There are literally many millions of molecular atoms because there are millions of molecules which all give rise to a set of constituent atoms. Nevertheless the sometimes bewildering shapes of atoms have been criticized as being contrary to chemical intuition. This should not be disconcerting, rather it could be interpreted as an expression of the richness of chemistry. Indeed, the amazing variety of atoms is a result of quantum systems cutting themselves into fragments, each leaving behind on the fragments detailed fingerprints of the total molecule. Is it possible, then, to find exactly the same atom more than once coming from different molecules? (p. 49) [Italics in the original, emphasis by underlining added.]

Chemists reply negatively to this last question, due to the dependence on the environment within the very definition of any part. Popelier prefers to use the expression ‘molecular atoms’ instead of that of ‘topological atoms’ in order to insist on this context-dependence. Once again, local density needs the whole molecule to be defined. In other words, the molecular level and the atomic level are co-defined. Following this line of reasoning, Popelier questions the transferability of atoms from one molecule to another. He adds (Popellier 2000):

> [I]t is not possible to cut an atom from on molecule and insert it exactly into a corresponding cavity of another molecule. Thus it is impossible to transfer perfectly an atom from one molecule to a different molecule. Transferability is possible to some extent. The ‘zoo’ of atoms does reveal subsets containing atoms with striking patterns of mutual similarity that can be analysed using mathematical techniques collectively known as *cluster analysis*. It should be emphasized, though, that transferability is something one *observes* in chemistry rather than *imposes* on it. Supported by the faith that a method reveals the correct degrees of transferabilities, this information can be used to set up a library of atoms, enabling a rapid and accurate construction of large ensembles of atoms such as proteins. It is important to realize that transferability is a continuous rather than binary (yes/no) concept for it depends on what errors in information transfer are allowed [p. 50]. [...] Perfect transferability of atoms from one system to another is an unattainable limit but, if observed and present, a large degree of transferability will faithfully be revealed by AIM [p. 51]. [Italics in the original, emphasis by underlining added.]

The expression ‘the richness of chemistry’ used in the former quotation, and that of ‘the zoo of atoms’ present in the later remind us of the diversity of life forms which depends on the environment. This parallel to evolution and biology clearly drawn by Popellier is reminiscent of Diderot’s clear stand both in favor of the heterogeneity of matter (1754), and against Fontenelle’s proposal to derive chemistry from mechanics (Fontenelle 1669). Notwithstanding their obvious differences, the debate between Popelier, Matta and Bader about the whole-parts strategy developed within QTAIM and the significance of its main theoretical tools reminds us of the debate between Mulliken and Pauling as to whether a molecule is an aggregate of atoms or, by contrast, an irreducible whole. Furthermore, Bader and Matta also use variational methods for minimizing energy which, in turn, implicitly strengthens the co-dependence of the whole, its parts, and the environment.

The research about the nature of chemical combination and the relationships between a molecule and its components is like a thread which holds those chemical explanations together. Every method described in this paper expresses a particular whole-parts strategy, which refers, implicitly or not, to the environment in which these properties are displayed. In this respect, mereological assumptions have always played an important role in the debates which frame the history of quantum chemistry. But we could have easily referred to many similar debates in other domains of chemistry at different periods of its history. Did not Pierre Duhem fight against atomism and molecular models by means of a holistic energy approach? In the same vein, did not Gaston Du Clos reject the corpusculian interpretation proposed by René Descartes and Robert Boyle using what he called ‘natural mixts’? Last but not least in this brief and non-exhaustive list of examples, did not Georges Ernst Stahl focus chemistry on the notion of the mixt against other reductionist interpretations of his time? According to Bernadette Bensaude-Vincent (2005), much more characteristic is the recurrence in the history of chemistry of those two possible interpretations of what a body must be: a mixture or an aggregate. The chemists were always confronted with this dichotomy and, according to the period and the problems at stake, they have opted for one interpretation or another, or even tried to reconcile the two. But the pluralism of possible interpretations does not cease to be present in chemistry.

5. Concluding remarks: some mereological and philosophical lessons

We would like to insist on three main lessons which, among others, can be drawn from this investigation.

The first one is methodological, and concerns the way one can study science philosophically. From the 1920s to today, and from isolated or united atoms to topological ones, quantum chemical methods have always been *constitutively* concerned with, and shaped by, different questions about the relationships between the molecule, its parts – atoms, electrons, and nuclei –, *and the environment*. Researchers never cease to develop new languages, representations, theoretical tools, algorithms, computerized methods, instruments, and formalisms in order to explain and predict chemical transformation and molecular reactivity. The type of laboratory in which they work changed accordingly.

Quantum chemists gradually proposed new methods and approximations in order to circumvent the impossibility of performing full analytical calculations, and to make the language of classical structural chemistry and that of quantum chemistry compatible. Those methods are not mere transpositions from quantum physics to chemistry: many *translations* – in the sense used by Michel Callon (1995) – and transformations occurred especially with the view to answering the whole-parts questions involved in research. Chemists' starting point is not Schrödinger's, but a contextualized problem of chemical reactivity to be solved in terms of the molecular structure at hand. As Gavroglu and Simòes (2012) show, the history of quantum chemistry is also a history of the attempts of chemists to establish the autonomy of their theories and methods with respect to physical, mathematical, and biological theories. Philosophers should bear in mind the role played by this quest for autonomy in the constitution of the basic chemical tools to which they refer in order to illustrate or develop their philosophical perspectives.

Even though further historical studies should be done concerning the autonomy and self-sufficiency of chemistry, quantum chemical methods always revolve around whole-parts-environment strategies. The debate between the practitioners of *ab initio* and semi-empirical methods has always involved underlying scientific and metaphysical assumptions about the possibilities for reaching a complete description of the world.

As we have pointed out, the mereology used by quantum chemists entangles the whole, its parts, and, sometimes, its environment. It is not a classical transitive mereology. A careful study of the way quantum chemists work shows that their approaches are neither holistic descriptions within which the whole is necessary to define the parts, nor reductionist analyses that only need the parts to define a whole. Quantum chemical practices both need and interweave the whole, the parts, and the rest of the world at the same time. Quantum methods are neither purely holistic nor purely reductionist. They always negotiate the co-existence of different levels of description within a network which assembles chemistry, physics, computers, and mathematics. Chemists have contrived specific methods within which the whole and its parts are constitutively co-defined (Llored 2012).

This mutual connection is a condition of possibility of chemical reasoning, in that it enables chemists to correlate chemical composition and structure with chemical reactivity and 'properties'. Both analytic and historical studies of chemical language must be undertaken in order to understand what chemists actually do. It is of crucial importance to study chemical languages and their logical implications. But, insofar as the languages and formalisms at stake include mereological and philosophical assumptions, it is also of primary importance to consider them as deeply embedded in human life, that is to say, as being engaged in a particular practice which combines symbols and action in order to understand and transform the world (Hottois 1996). Understanding whole-parts strategies used in quantum chemistry and in other domains of sciences, and philosophizing from and about them require the connection between philosophy and a historicized epistemology of chemical activities. Each approach is appropriate and relevant. But their concerted and joint effort is far more fruitful than their separated contributions.

We should 'follow the process' of scientific activities in order to grasp what is at stake within the work of scientists (Stengers 2000). In this respect, when philosophers aim at connecting the concept of emergence with quantum chemistry using a careful study of theoretical equations, they should bear in mind that the formalisms under study are constitutively concerned with the problem of emergence. This is a methodological point that leaves questions about the role and status of history within philosophical studies open.

The second lesson we draw from this investigation is about the relationships between levels of organization. Parts may differ in quantum chemistry: they can be, for instance, atoms, electrons, nuclei, or groups of atoms according to the group theory approach or to nuclear magnetic resonance (Llored 2010). Methods can differ as well: they can be based on molecular orbitals, functionals of density, or even consist of a mixture of the two. The molecular 'whole' can differ too, depending on the project involved: it can be either a protein or an active site within it. It can also be a local complex with includes some molecules of solvent into the site. Chemists can also study some parts with classical models while using quantum methods to investigate others. The synchronic use of incompatible models or methods depends both on the scale of the description involved and the problem at stake.

In addition, a philosopher who carefully studies chemical activities cannot but highlight: (1) *the co-definition of relations and relata* (Schummer 1998), and (2) the constitutive role of the modes of intervention in the definition, always open and provisional, of chemical bodies (Bachelard 1940). Parts, wholes, and local environments are *constitutively* dependent on the mode of access – instrumental or cognitive. *They are not 'monadic' but relational* (Llored & Bitbol 2013). In other words, they are 'affordances', *i.e.* products of the interaction of equipment and the world (Harré & Llored 2011).[4] Parts and wholes cannot be detached from the way chemists act upon or describe a sample of bodies in a particular context.

Is there any 'ground' or 'foundational level' in this mereological scheme? The way quantum chemical methods are set up and used prevents us from attributing a unique basic ground from which the higher level chemical bodies derive or emerge. *There is no basic level to be found within those chemical activities but only co-dependent levels involving the molecule, what it contains, and the surroundings – solvents, other chemical bodies, photons, electromagnetic fields, or instruments*. The 'primary thesis' according to which entities on the 'fundamental' level are primarily real and the rest are at best derivative, if they are real at all, strongly needs to be qualified, and even to be put into questions as soon as chemistry is used as 'food for thought'. All those mathematical tools, structural macroscopic characteristics, empirical outcomes, and auto-coherent computational devices are co-dependently arising and are, in turn, similarly connected with other events or phenomena by means of fine-grained correlations. "The overall process of which we partake by our action and cognitive relations has no fundamental level on which everything else rests. It has no absolute fundamental level and no absolute emergent level either, but it has co-emergent order." (Bitbol 2007, p. 303)

This lesson drawn from chemistry already gave rise to philosophical developments and discussions. In agreement with Earley (2008), Banchetti and Llored (2014) propose that the 'hard problem' of consciousness (Chalmers 1995) should be approached in a manner similar to that used to address parallel problems in philosophy of chemistry. In this respect, they show how the co-dependence of levels in quantum chemistry can be of help in order to avoid a reductionist account of the relationships between physical *phenomena*, such as brain states, on the one hand, and experience, *i.e.* phenomenal consciousness, mental states, or events with phenomenal qualities or '*qualia*', on the other. Other works took this lesson seriously and tried to move from an ontological emergence to a relational one in order to address the philosophical, ethical, and political questions raised by the consequences of the actions of chemical bodies upon ourselves, the other forms of life, and the whole Earth (Llored 2013).

This lesson taken from chemistry can help elucidate important philosophical concepts, considering that: (1) there is no asymmetric emergence of high-level properties out of basic properties, but *symmetrical co-emergence* of microscopic low-level features and high-level behavior; (2) there is no emergence of large-scale absolute properties out of small-scale absolute properties, but *co-relative* emergence of *phenomena*. Those *phenomena*, in turn, are to be construed as *relative to* a certain experimental context, with no possibility of separating them from this context (Llored & Harré 2014). The notion of emergence thus gains credibility, at the very same time it loses ontological content (Bitbol 2010, Llored 2012). According to this approach, both 'emergent' and 'submergent' properties are considered *relational properties*, and this leads to the proposal of an extended, non-classical mereology that accounts for the relationality, co-dependence, and mutual constitution of parts and wholes in quantum chemistry, but also in chemistry at large. In this respect, it brings new analytical tools pertaining to chemistry into the history and philosophy of sciences.

The third and last main lesson is therefore related to some mereological consequences of our investigation. As soon as wholes and parts are co-defined using, whether explicitly or not, the environment within a particular operative framework, two mereological fallacies endanger philosophical discussions and should be avoided (Harré & Llored 2013). It is sometimes a fallacy to ascribe to a part of an entity or chunk or mass a predicate that receives its meaning from its use for ascribing an attribute to the whole from which the part comes. A holistic predicate is not *necessarily* a part predicate insofar as those predications are context-sensitive. It is also a fallacy to infer that substantive products of an analytical procedure are parts of the substance on which the procedure was performed (though not in every case).

Mereology is the general theory of the grammar of part-whole discourses, and so particularly apt for analyzing the discourses of chemistry as they have developed since the corpuscularianism of Robert Boyle. However, there are different conceptions of 'part' having distinctive grammars and distinctive roles to play in chemistry. There is mereology as the grammar for parts of mass substances, as explored by Needham in a deservedly well-known paper. He distinguished a distributive and a cumulative condition that underpin mereological discourse about the parts of mass substances, such as buckets of sea water with respect to the sea. Molecules are parts in a sense that is expressed by Needham's distributive and cumulative mereological conditions (Needham 2005, p. 103).

While this mereology is interesting for the most part, chemistry has drawn on a mereology of parts and wholes where the parts are capable of *independent existence* when abstracted from the whole in which they have been resident, and preserve their identity when related with other such parts in constituting the whole. Along with this part-whole layout has been developed a simple explanatory theory-style: the behavior of chemical wholes is explained by reference to constituents and the relations between them that create wholes. Some of these relations must be invariant if the whole is to count as a chemical entity, say a molecule. There is a further aspect of this Boylean mereology: the results of certain analytical manipulations conducted on samples of the substance in question are not only products of the manipulation, but also constituents of the wholes from which they have been derived. The physics of chemical states, entities, and processes nevertheless suggests that this mereology is overly simplistic.

Remarks by Mulliken (1932a/b) suggest that he took 'molecule' to denote a bounded, material entity, localizable in space and having a self-identical trajectory in time and with a certain shape and volume – the technique of creating molecular orbitals as functions of atomic orbitals did not license the mereological principle that molecules are entities with atoms as their *constituents*. However, Mulliken did accept the mereological principle that *nuclei* of the atoms of the elements that entered into a molecule could be thought of as constituents standing in certain spatial relations to one another.

We could express this insight in a mereological principle: Constituent atoms of molecules are not parts of those molecules when we look at the total entity in the light of molecular orbitals. Unlike chair parts which preserve their material properties whether in the chair or on the bench. Nor are they parts in the sense that buckets of water are parts of the ocean. However, parts of chairs, atoms and the contents of buckets of water are extracted from the wholes of which they are parts by some procedure. Looked at from the point of view of the whole, chairs, molecules, and oceans *afford* things; looked at from the point of view of their constituent parts they are potentialities (Earley 2005), not the things that are thereby afforded.

'*Molecule*' is one of the three main ontological categories in organic chemistry, the others being '*atom*' and '*electron*'. All three words purport to refer to the mereological elements of material stuff. The relations between these apparent constituents include 'part-whole' and 'structure-element.' That these categories are not of the same status follows from the fact that as chemistry has developed *via* molecular orbitals, while 'atom' as 'atom-core' does *function* mereologically as the name of actual parts of molecules, 'electron' does not follow this pattern. If we do subsume them under the same mereology it can only be as a category of constituents of a certain long standing and powerful *model*, that is an *iconic representation* using spatial relations among *imagined* material entities. This situation seems to call for the use of the concept of 'affordance' to make the seemingly paradoxical role of 'electron' in chemistry intelligible (Harré & Llored 2013).

At some point in the hierarchy of 'constituents' of entities in the standard chemical model, in which molecules are made of atoms related to one another in space, we pass from affordances as constituents to affordances as dispositions. How does this affect the status of 'molecule' as referring to a structure of lower level 'constituents'? If 'proton' is not a constituent of 'atom' but an affordance of a certain class of manipulations, appearing as a constituent only as part of the standard model of chemical structure, then the use of part-whole mereological rules in sub-atomic discourse *restricts it to descriptions of and reasoning about an iconic model*. In this respect, whole-parts relationships in quantum chemical methods imply considering nuclei as parts of a heuristic iconic model which enable chemists to connect their classical representations of molecular structures with probabilistic sub-atomic electron density calculations.

This example shows how the careful study of chemical quantum methods can ‘feed’ current debates in current metaphysics and mereology.

Quantum chemistry points out the necessity for logicians and philosophers to tailor new mereologies. Quantum chemistry, and chemistry alike, could stimulate the creation of new types of mereology. Using the concept of ‘fusion’, Lewis refines the simple Lesniewskian scheme with alternative axioms for a mereology of sets and subsets (Lewis 1991, p. 74), in particular by adding (c) below.

(a) Transitivity: If x is a part of some part of y, then x is a part of y.
(b) Unrestricted Composition: Whenever there are some things, then there exists a fusion of those things.
(c) Uniqueness of Composition: It never happens that the same things have two different fusions.

Philosophers who bear in mind whole-parts strategies in quantum chemistry, but also chemical works on stereo-isomers, non-stoichiometric compounds, eutectoïds, or the co-dependence of the internal structure, the size of grains, and the chemical device in nanochemistry, to quote but a few examples, will surely find the principle of uniqueness of composition unintuitive, and inadequate to those rules for chemical parts-whole reasoning that are required to accommodate the role of chemical entities in structures, such as atoms in ‘polyatomic’ ions. They are likely to question the relevance of transitive mereology whenever the whole molecule and the parts are co-dependent, and relative to a specific environnement or action. There is no doubt that they will aim to develop “an extended mereology applicable to chemical combinations” (Earley 2008, p. 1) and to many others fields, including the philosophy of (nano)technology and material sciences, and the philosophy of mind.

Notes

[1] Using Paul Dirac’s notation, where H is the molecular Hamiltonian, $d\tau$ a volumic element, and ψ_i^* the conjugate of the complex function ψ_i:

$< \psi_i |H| \psi_i > =_{\text{space}}\int \psi_i^* H\psi_i \, d\tau = H_{ii}$ is the Coulomb integral

$< \psi_i |H| \psi_j > =_{\text{space}}\int \psi_i^* H\psi_j \, d\tau = H_{ij}$ is the exchange integral

[2] With the same notation:

$< \psi_i | \psi_j > =_{\text{space}}\int \psi_i^* \psi_j \, d\tau = S_{ij}$ is the overlap integral

[3] A ‘best estimate’ is the best theoretical calculation available at the time of the calculation. It may be, directly or not, connected to an empirical value.

[4] An affordance can be broadly defined as a disposition or capacity as ascribed to a certain material being to yield an observable effect when acted upon in a certain manner. It may be, for instance, a gas as the product of a chemical reaction when certain chemical bodies are acted on during a particular electrolysis. An affordance is relative to context, in particular to the specific interaction between some human beings and the material world.

References

Bachelard, G.: 1940, *La philosophie du non: Essai d'une philosophie du nouvel esprit scientifique*, Paris: Presses Universitaires de France [Engl. trans: *The Philosophy of No: A Philosophy of the New Scientific Mind*, New York: Orion Press, 1968].

Bader, R.F.W.: 1990, *Atoms in Molecules: A Quantum Theory*, Oxford: Oxford University Press.

Bader, R.F.W. & Matta, C.F.: 2013, 'Atoms in Molecules as Non-Overlapping, Bounded, Space-Filling Open Quantum Systems', *Foundations of Chemistry*, **15**(3), 253-76.

Banchetti, M. & Llored J.-P.: 2014, 'Reality Without Reification: Philosophy of Chemistry's Contribution to Philosophy of Mind', in: E.R. Scerri & G. Fisher (eds.), *An Oxford Handbook on the Philosophy of Chemistry*, Oxford: Oxford University Press, forthcoming.

Bensaude-Vincent, B.: 2005, *Faut-il avoir peur de la chimie?*, Paris: Les empêcheurs de penser en rond.

Bensaude-Vincent, B.: 2008, *Matière à penser: Essais d'histoire et de philosophie de la chimie*, Paris: Presses universitaires de Paris-Nanterre.

Bitbol, M.: 2007, 'Ontology, matter and emergence', *Phenomenology and the Cognitive Science*, **6**, 293-307.

Bitbol, M: 2010, 'Downward Causation without Foundations', *Synthese*, **180**, 1-23 [republished in: J.-P. Llored (ed.), *The Philosophy of Chemistry: Practices, Methodologies and Concepts*, Newcastle: Cambridge Scholars Publishing, 2013, pp. 675-705].

Callon, M.: 1995, 'Four Models for the Dynamics of Science', in: S. Jasanoff, G. Markle, J. C. Peterson & T. Pinch (eds.), *Handbook of Science and Technology Studies*, London: Sage, pp. 29-64.

Chalmers, D.: 1995, 'Facing up to the problem of consciousness', *Journal of Consciousness Studies*, **2**(3), 200-19.

Diderot, D.: 1754, *Pensées sur l'interprétation de la nature*, Paris: Pissot.

Earley, J.E.: 2005, 'Why there is no salt in the sea', *Foundations of Chemistry*, **7**(1), 85-102.

Earley, J.E.: 2008, 'How philosophy of mind needs philosophy of chemistry', *Hyle: International Journal for Philosophy of Chemistry*, **14**(1), 1-26.

Fontenelle, B. le Bovier de: 1669, *Histoire de l'Académie Royale des Sciences*, vol. 1, Amsterdam: Pierre Mortier.

Gavroglu, K. & Simões, A.: 2012, *Neither Physics nor Chemistry. A history of Quantum Chemistry*, Cambridge, MA: MIT Press.

Harré R. & Llored J.-P.: 2011, 'Mereologies as the Grammars of Chemical Discourses', *Foundations of Chemistry*, **13**(1), 63-76.

Harré R. & Llored J.-P.: 2013, 'Mereologies and molecules', *Foundations of Chemistry*, **15**(2), 127-44.

Hendry, R.F.: 1998, 'Models and Approximations in Quantum Chemistry', in: N. Shanks (ed.), *Idealization in Contemporary Physics* (*Poznan Studies in the Philosophy of the Sciences and the Humanities*, vol. 63), pp. 123-42.

Hendry, R.F.: 1999, 'Molecular Models and the Question of Physicalism', *Hyle: International Journal of Philosophy of Chemistry*, **5**(2), 117-34.

Hendry, R.F.: 2006, 'Is there Downward Causation in Chemistry?', in: D. Baird, E.R. Scerri & L. McIntyre (eds.), *Philosophy of Chemistry: The Synthesis of a New Discipline*, Dordrecht: Springer, pp. 173-90.

Hendry, R.F.: 2010, 'Ontological reduction and molecular structure', *Studies in History and Philosophy of Modern Physics*, **41**(2), 183-91.

Hoffmann, R.: 2007, 'What might philosophy of science look like if chemists built it?' *Synthese*, **155**(3), 321-36.

Hottois, G.: 1996, *Entre symboles et technosciences. Un itinéraire philosophique*, Paris: Collection Champ Vallon.

Hund, H.: 1927, 'Zur Deutung der Molekelspektren. 1', *Zeitschrift für Physik*, **40**, S742-64 [English trans: 'On the Interpretation of Molecular Spectra I', in: H. Hettema (ed.), *Quantum Chemistry: Classic Scientific Papers*, World Scientific Publishing, 2000, pp. 214-34].

Kohn, W.; Becke, A.D. & Parr, R.G.: 1996, 'Density functional theory of electronic structure', *Journal of Physical Chemistry*, **100**(31), 12974–80.

Lewis, D.: 1991, *Parts of Classes*, Oxford: Blackwell.

Llored, J.-P.: 2010, 'Mereology and quantum chemistry: The approximation of molecular orbital', *Foundations of Chemistry*, **12**(3), 203-21.

Llored, J.-P.: 2011, 'The role and the status of thermodynamics in quantum chemistry calculations', in: J.C. Moreno (ed.,) *Thermodynamics – Interaction Studies – Solids, Liquids and Gases*', Rijeka: INTECH, pp. 469-90.

Llored, J.-P.: 2012, 'Emergence and Quantum Chemistry', *Foundations of Chemistry*, **4**(3), 245-74.

Llored, J.-P.: 2013, Chimie, chimie quantique et concept d'émergence : étude d'une mise en relation (*Chemistry, Quantum Chemistry and the Concept of Emergence: Study of a connection*), Ph.D. Dissertation, Ecole Polytechnique, Paris & Free University of Brussels.

Llored, J.-P. & Bitbol, M.: 2013, 'From Chemical Practices to a Relational Philosophy of Chemistry', in: J.-P Llored (ed.), *The Philosophy of Chemistry: Practices, Methodologies, and Concepts,* Newcastle: Cambridge Scholars Publishing, pp. 385-415.

Llored J.-P. & Harré, R.: 2014, 'Developing the mereology of chemistry', in: C. Calosi & P. Graziani (eds.), *Mereology and the Sciences*, London: Springer, pp. 189-212.

Matta, C. F.: 2002, *Applications of the Quantum Theory of Atoms in Molecules to Chemical and Biochemical Problems*, Ph.D. Dissertation, McMaster University.

Mulliken, R.S.: 1928, 'The Assigment of Quantum Numbers for Electrons in Molecules', *Physical Reviews*, **32**, 186-222.

Mulliken, R.S.: 1931, 'Bonding power of electrons and theory of valence', *Chemical Reviews*, **9**(3), 347-88.

Mulliken, R.S.: 1932a, 'Interpretation of Band Spectra, Part III. Electron Quantum Numbers and States of Molecules and their Atoms', *Reviews of Modern Physics*, **4**(1), 1-86.

Mulliken, R.S.: 1932b, 'Electronic structures of polyatomic molecules and valence II. General consideration', *Physical Reviews*, **41**, 49-71.

Mulliken, R.S.: 1967, 'Spectroscopy, Molecular Orbital and Chemical Bonding' (Nobel lecture), *Science*, **157**, 13-24.

Needham, P.: 2005, 'Mixtures and modality', *Foundations of Chemistry*, 7(1), 103-18.

Pauling, L.: 1931, 'The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules', *Journal of American Chemical Society*, **53**(4), 1367-400.

Pauling, L.: 1932, 'The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the relative Electronegativity of Atoms', *Journal of the American Chemical Society*, **54**(9), 3570-82.

Popellier, P.: 2000, *Atoms in Molecules. An Introduction*, London: Prentice Hall.

Primas, H.: 1983, *Chemistry, Quantum Mechanics and Reductionism*, 2nd edition, Berlin: Springer.

Primas, H.: 1998, 'Emergence in Exact Natural Sciences', *Acta Polytechnica Scandinavica Ma*, **91**, 83-98.

Scerri, E.R.: 1991a, 'Electronic Configurations. Quantum Mechanics and Reduction', *British Journal for the Philosophy of Science*, **42**(3), 309-25.

Scerri, E.R.: 1991b, 'Chemistry, Spectroscopy, and the Question of Reduction', *Journal of Chemical Education*, **68**(2), 122-6.

Scerri, E.R.: 1997, 'Has the Periodic Table been Successfully Axiomatized', *Erkentnnis*, **47**, 229-43.

Scerri, E.R.: 2007a, 'The Ambiguity of Reduction', *Hyle: International Journal of Philosophy of Chemistry*, **13**(2), 67-81.

Scerri, E.R.: 2007b, 'Reduction and Emergence in chemistry', *Proceedings of the Philosophy of Science Association (PSA)*, **74**(5), 920-31.

Scerri, E.R.: 2012, 'Top-down causation regarding the chemistry-physics interface: a skeptical view', *Royal Society Publishing*, **2**(1), 20-5.

Scerri, E.R.: 2013, 'Philosophy of chemistry: Where has it been and where is it going?', in: J.-P. Llored (ed.), *The Philosophy of Chemistry: Practices, Methodologies and Concepts*, Newcastle: Cambridge Scholars Publishing, pp. 208-25.

Schummer, J.: 1998, 'The Chemical of Chemistry I: A Conceptual Approach', *Hyle: International Journal for Philosophy of Chemistry*, **4**(2), 129-62.

Simões, A.: 1993, *Converging trajectories, diverging traditions: chemical bond, valence, quantum mechanics and chemistry, 1927-1937*, Ph.D. dissertation, University of Maryland.

Simões, A. & Gavroglu, K.: 1997, 'Different legacies and common aims: Robert Mulliken, Linus Pauling and the origins of quantum chemistry', in: J.L. Calais & E.S. Kryachko (eds.), *Conceptual perspectives in quantum chemistry*, Dordrecht: Kluwer, pp. 383-413.

Slater, J.C.: 1931, 'Directed valence in polyatomic molecules', *Physical Reviews*, **37**, 481-9.

Stengers, I.: 2000, *The Invention of Modern Science*, trans by D.W. Smith, Minnesota: University of Minnesota Press.

Van Brakel, J.: 2000, *Philosophy of Chemistry*, Leuven: Leuven University Press.

Vemulapalli, G.K.: 2003, 'Property reduction in chemistry. Some lessons', in: J.E. Earley (ed.), *Chemical Explanation. Characteristics, Development, Autonomy*, New York (*Annals of the New York Academy of Sciences*, vol. 988), pp. 90-8.

Wittgenstein, L.: 1953, *Philosophical Investigations*, Oxford: Blackwell.

Zhao, Y. & Truhlar, D.G.: 2008, 'Density Functionals with Broad Applicability in Chemistry', *Accounts of Chemical Research*, **41**(2), 157-67.

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