



Electronegativity as a new case for emergence and a new problem for reductionism

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Abstract

The potential reducibility of chemical entities to their physical bases is a matter of dispute between ontological reductionists on one hand, and emergentists on the other. However, relevant debates typically revolve around the reducibility of so-called ‘higher-level’ chemical entities, such as molecules. Perhaps surprisingly, even committed proponents of emergence for these higher-level chemical entities appear to accept that the ‘lowest-level’ chemical entities—atomic species—are reducible to their physical bases. In particular, the microstructural view of chemical elements, actively developed and defended by emergentists, appears to hold that the explanatory power of nuclear charge justifies being reductionist about atomic species. My first task in this paper is to establish that nuclear charge cannot ultimately provide explanations sufficient to justify a reductionist approach to atomic species, unless we abandon the persuasive intuition that the presence of an element in a substance ought to explain the properties of that substance. The ‘missing piece’ for explaining the properties of substances by way of their elemental constituents is the electronegativity values of participant atoms. But electronegativity is a strikingly disunified concept that appears distinctly unamenable to analysis by way of fundamental physical principles. Through evaluating the uncertain physical identity of electronegativity, as well as its widespread and indispensable epistemic utility in chemical practice, I argue that electronegativity provides compelling grounds to seriously consider emergence for atomic species.

Keywords Reductionism · Emergence · Electronegativity · Microstructuralism · Nuclear charge · Chemical elements

Introduction

The reducibility of chemistry to physics has been a matter of debate since at least the development of quantum chemistry during the 1920s. In contemporary philosophy of chemistry, the debate is at somewhat of an impasse. Ontological reductionism asserts that physical systems are causally complete, so that all chemical properties ought in principle to

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be explainable in exclusive reference to constituent fundamental particles. The emergentist view is that since some chemical properties cannot at present be explained in reference to physical theory, there is no good reason to infer that the causal powers of higher-level chemical entities such as molecules are exhausted by those conferred by their physical bases. Evidential recourse thus far fails to decisively favour either position.

Yet there is at least one seemingly ontologically-reductionist view promoted by emergentists themselves. This is the microstructural view of chemical elements, which appears to hold that the causal powers of atomic species—the smallest unit still characterised as a chemical entity—are exhausted by those conferred by their physical bases, particularly nuclear charge. Only in specific instances, when equivalent fundamental constituents can produce diverse properties in substances so constituted, do emergentists assert the possibility of emergent properties for *molecules* and other higher-level chemical entities. Isomers are the iconic evidential basis upon which the emergentist claim is made.

My goal here is to question the evidential basis of microstructuralism-as-reductionism, and thereby extend the plausibility of emergence to chemical elements as the lowest-level chemical entities. I accomplish this in part through close attention to a key means by which chemists explain the chemical properties of substances in reference to their elemental constituents—the electronegativity of atomic species. Electronegativity is ordinarily understood as the power of an atom to draw electrons to itself under bonding conditions, and an analysis of the concept provides a striking new argument for the serious consideration of emergence for atomic species.

I establish microstructuralism as a reductionist view, and address some complexities regarding the relationship between ontological and intertheoretic reducibility, in “[Microstructuralism and reductionism](#).” “[Missing explanations from nuclear charge](#)” argues that nuclear charge is insufficient to provide satisfying explanations from the atomic constituents of substances to the properties of those substances, through a discussion of the role of bond polarity in explaining the distinct properties of isomers. “[Electronegativity and a new case for emergence](#)” considers and rejects the possibility that electronegativity, used to predict bond polarity, can provide explanations from the fundamental constituents of atoms to the properties of substances so constituted, and argues instead that the disunity of the electronegativity concept provides reasonable grounds to consider emergence for atomic species. Throughout, I emphasise the work of Robin Hendry, as perhaps the most prominent advocate of both microstructuralism about chemical elements and emergence for higher-level chemical entities.

Microstructuralism and reductionism

Microstructuralism as reductionism about chemical elements

To be an ontological reductionist about chemistry is to claim that since physical systems are causally complete, all chemical phenomena must be determinately caused by the mass, charge, and motion of fundamental particles (protons, neutrons, and electrons, for my purposes here) governed by a few fundamental forces (see e.g. le Poidevin 2005). *Contra* ontological reductionism is the emergentist view. As articulated by Hendry (2010: 185, emphasis in original), the essential tension is that “the ontological reductionist thinks that [the properties of chemical entities] are no more than their physical bases because the causal powers they confer are a subset of those conferred by their physical bases; the emergentist

sees them as distinct and non-reducible just because the causal powers they confer are *not* conferred by their physical bases.” Hendry articulates this latter emergentist claim in specific reference to ‘higher-level’ chemical entities, e.g. molecules.

But there is at least one ontologically-reductionist claim that emergentists themselves promote. This is the *microstructural* view concerning chemical elements. Microstructuralism holds that “the discreteness of the elements is explained by the nomologically required discrete variation in a physical quantity, namely nuclear charge” (Hendry and Needham 2007: 340). As per Hendry (2006: 869), “the presence of an element in a compound explain[s] the chemical properties of the compound. It is nuclear charge... that overwhelmingly determines the chemical behaviour of both elements and compounds, via the electronic structure of free and bound atoms.”

Arguments for microstructuralism are ordinarily articulated in the context of natural kinds debates. The intended philosophical heft of the position is therefore that nuclear charge provides an observer-independent delineation of atomic species. But, as identifiable in the above, microstructuralism is *evidenced* by a claimed causal dependence from nuclear charge to the properties of substances.

Thus, when discussing superheavy elements, Hendry (2020: 134, emphasis added) argues that “an object of a particular kind can be said to exist only if it is in principle possible for it to exert the *causal powers* that are characteristic of members of that kind. For an element [to exist] requires... electronic structure, and the chemistry that that structure makes possible.” In conjunction with the view that an element’s presence in a substance serves to explain the chemical properties of that substance, the implication of such a claim is that the distinct causal powers of atomic species are exhausted by those conferred by their discrete nuclear charges.

Of course, the isotope effect, and relativistic effects in the heaviest elements, contradict the claim that nuclear charge is the sole determinant of the chemical properties of substances in every case. Hendry (2006: 868) acknowledges as much while maintaining the emphasis on nuclear charge since, in the majority of cases, “nuclear charge is the overwhelming determinant of chemical behaviour, and atomic weight a negligible factor.” Microstructuralism-as-reductionism therefore consists of the claims that (a) all atomic causal powers are directly conferred by the causal powers of their constituent fundamental particles, and (b) nuclear charge is the physical property that overwhelmingly determines atomic causal powers, particularly those distinct causal powers associated with discrete elements.

Ontological versus intertheoretic reducibility

Two issues are worth noting immediately. First, there is an apparent inconsistency in the emergentist view as I have thus far characterised it: claiming that molecules and other higher-level chemical entities can display causal powers beyond those conferred by their physical bases seems inconsistent with the claim that nuclear charge overwhelmingly determines the chemical properties of substances. The second is that arguments for microstructuralism make appeal to successful explanations to justify their ontological stances without clarifying the relationship between explanation and ontology. These issues are related, and some attention to the distinction between ontological and *intertheoretic* reduction will clarify the situation.

Intertheoretic reduction for some aspect of chemical theory is the complete explanation of that aspect in exclusive reference to physical theory.¹ That successful intertheoretic reduction has ontological implications is an intuitive view, and in broader epistemology it is not uncommon to presume that intertheoretic reductions denote ontological reducibility (see e.g. Sankey 2021). But, as established by Dupré (1993: 96–9), there is no necessary corollary between intertheoretic and ontological reducibility, and the relationship between the two remains a matter of dispute (cf. Chang 2017).

Although emergentism is clearly an ontological position, proponents do not make positive ontological claims. Instead, for Hendry (2010: 190), if chemical theory can provide explanations for some chemical property that physical theory cannot equally explain, emergentists argue that it is as justifiable to infer that the property is an emergent one as it is to infer ontological reducibility. This resolves the apparent inconsistency indicated above: the emergentist endorses the view that intertheoretic reducibility can evidence ontological reducibility but demands that intertheoretic reductions occur before ontological reducibility can be justifiably inferred. Meanwhile, microstructuralism both endorses this evidential relationship between intertheoretic reductions and ontological reducibility and maintains that sufficient intertheoretic reductions have been demonstrated to warrant accepting that the causal powers of atomic species are exhausted by those conferred by their physical bases.

This clarifies microstructuralism and emergentism and explains how both positions can be held simultaneously. But it raises the question of whether the reductionist implications of arguments for microstructuralism should be viewed as a genuinely ontological position, or a disguised epistemological position regarding the availability of explanations from nuclear charge to the properties of substances. Microstructuralism is articulated as an ontological claim: that chemical elements are observer-independent natural kinds. But the appeal to causal dependence of the properties of substances on nuclear charge is made in order to warrant this view on natural kinds, and hence it is not clear that the reductionist aspect of microstructuralism can be so neatly characterised as an ontological position in its own right.²

Ultimately, little may hang on this particular point. Since intertheoretic reductions are used as the evidential basis for ontological reductionism, an argument against the intertheoretic reducibility of atomic species will extend the plausibility of emergence to the level of chemical elements. Since it is difficult to envision arguing for or against ontological reductionism without substantially engaging with intertheoretic reducibility, I propose understanding the issue by way of *causal explanation*.

Causal explanation neatly encapsulates the subtle relationship between intertheoretic reductions and ontological reducibility. The full causal explanation of some higher-level entity in reference to its lower-level constituents, while being an ultimately epistemic accomplishment (Potochnik 2015), provides strong intuitive grounds to infer ontological reducibility (cf. Beebe 2016). In the case of microstructuralism-as-reductionism, then, we ought to understand the claim to be that successful intertheoretic reductions (in the form of causal explanations) from the physical bases of atomic species to the properties

¹ E.g., the explanation of valence via electron shell capacity constitutes a successful intertheoretic reduction from chemistry to physics.

² Hendry's (2020) appeal to the causal powers of atomic species seems to recommend the ontological interpretation. But elsewhere, the emphasis on the explanatory power of nuclear charge (Hendry 2006; Hendry and Needham 2007) might suggest the epistemological view.

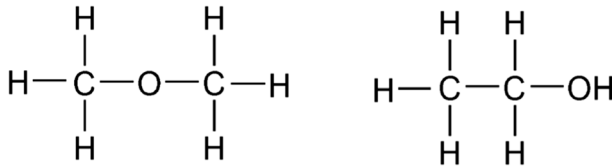


Fig. 1 Two-dimensional representation of molecular configuration for methoxymethane (left) and ethanol (right). Compare with shared chemical formula C_2H_6O . Note that, along with the positioning indicated here, three-dimensional bond length and bond angle are also significant aspects of molecular configuration

of substances so-constituted have occurred; and that these permit inferring the ontological reducibility of chemical elements. With this clarification in place, my goal in the next section is to show that no such sufficient causal explanations are available; that the causal powers of atomic species have not been intertheoretically reduced to their constituent fundamental particles.

Missing explanations from nuclear charge

Isomers and the case for emergence in higher-level chemical entities It is well-acknowledged that physical descriptions can give no explanation for the diverse chemical properties of chemical isomers.³ Isomers are those substances with a shared chemical formula, yet different molecular configurations and chemical properties. Take ethanol and methoxymethane (Fig. 1). Despite sharing the chemical formula C_2H_6O , these are substances with clearly distinct chemical properties, e.g. respective boiling points of $78.4\text{ }^\circ\text{C}$ and $-24.9\text{ }^\circ\text{C}$. Physical descriptions of molecules—molecular Hamiltonians, the results of Schrödinger equations solved for molecules—take into account only the mass and charge of particles. Thus, the molecular Hamiltonians for ethanol and methoxymethane are the same on the basis of their equivalent elemental constituents. But this means that a purely quantum-mechanical view cannot tell us which molecule of formula C_2H_6O will be realised under which circumstances.

Configurational Hamiltonians, Schrödinger equations solved for molecules while applying the Born-Oppenheimer approximation, can adequately distinguish isomers in physical terms. But making such use of the Born-Oppenheimer approximation, being the assumption that the positions of nuclei are fixed during quantum-mechanical analysis of electronic structure, requires as per Hendry (2017: 154, emphasis in original) “putting in *by hand* the parameters that specify [molecular configuration].”⁴ On this basis, configurational Hamiltonians cannot be considered purely quantum-mechanical descriptions, since they rely on information underivable from physical theory or the properties of fundamental particles.

Physical theory has no apparent basis upon which it can begin to explain the fact that, e.g., ethanol and methoxymethane respectively boil at $78.4\text{ }^\circ\text{C}$ and $-24.9\text{ }^\circ\text{C}$. Chemical theory, meanwhile, can provide partial explanations for the distinctive properties of isomers, so that the explanatory salience of chemical over physical theory is clear in this

³ Some influential accounts establishing as much include: van Brakel (2000: 50–3), Scerri (2007) and Hendry (2010, 2017).

⁴ This information is ‘put in by hand’ in that the specific, fixed positions assigned to nuclei when using the Born-Oppenheimer approximation are taken directly from chemical theory regarding molecular configurations, and cannot be derived from physical theory.

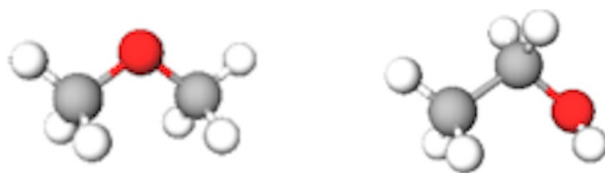


Fig. 2 Visual guide to bond polarity in molecules of methoxymethane (left) and ethanol (right). All of the bonds in which oxygen (red) is participant are polar covalent. Those between hydrogen (white) and carbon (grey), and carbon and carbon, are non-polar covalent

instance. The emergentist claim is therefore as follows: since no intertheoretic reductions from the distinct properties of isomers to the properties of their constitutive fundamental particles has occurred, it is just as plausible to infer that some molecular properties are emergent as it is to assume that these higher-level chemical entities are ultimately ontologically reducible.

Explaining chemical properties via bond polarity

Despite isomers constituting the iconic evidence against the wholesale reducibility of chemistry to physics, the ways in which chemical theory can explain isomers' distinct chemical properties ordinarily receives scant attention from philosophers. But chemists certainly have the means to (at least partially) provide such explanations. Many factors contribute to these explanations, but for current purposes the key factor of bond polarity will give sufficient indication of the available means.

Bond polarity concerns the relative in/equality with which two atoms participating in chemical bonding share their electrons, and resultant charge distribution within a molecule.⁵ Figure 2 provides a visual guide to the polarities of bonded pairs in methoxymethane and ethanol. The key distinction is in the bonds formed by oxygen. Methoxymethane's oxygen forms polar covalent bonds with both atoms of carbon, with each carbon atom forming non-polar covalent bonds with three hydrogen atoms. The situation is a little more complex in ethanol, wherein oxygen forms two polar covalent bonds, one each with an atom of carbon and an atom of hydrogen. In ethanol both carbon atoms are in a non-polar covalent bond, with the carbon bonded to oxygen also in non-polar covalent bonds with two atoms of hydrogen, and the other bonded to three hydrogen atoms as in methoxymethane.

We can explain the distinct boiling points of ethanol and methoxymethane via the distinct bond polarities present therein. In ethanol, the hydrogen atom in a polar covalent bond with oxygen has a slight positive charge due to the unequal sharing of electrons. In methoxymethane, each hydrogen atom has a neutral charge, being in non-polar covalent bonds with carbon. In both ethanol and methoxymethane, oxygen has a slight negative charge,

⁵ If two bonded atoms share their electrons fully, the bond is non-polar covalent, and the overall charge of the bonded pair remains equally dispersed. An ionic bond constitutes the full transfer of an electron from one atom to another in a bonded pair, resulting in the transferring atom having overall positive charge and the receiving atom having overall negative charge. More common than ionic bonding is a partial imbalance of charge distribution between bonded pairs. The relative category of a polar covalent bond covers these. Metallic bonds are often distinguished from non-polar covalent bonds on the basis of the delocalisation of electrons in metallic substances. For now I set them aside, as at least in regard to charge distribution between atoms under bonding conditions, metallic bonds are non-polar covalent bonds.

being the receiving atom in two polar covalent bonds. Thus, in a collection of ethanol molecules, the positively charged hydrogen atoms form intermolecular H-bonds with negatively charged oxygen atoms. But in methoxymethane, all hydrogen is of neutral charge, so that no H-bonding occurs. The additional intermolecular bonds present in a measure of ethanol, but not methoxymethane, explains ethanol's significantly higher boiling point. Simply, there are more bonds in a measure of ethanol than there are in an equivalent measure of methoxymethane, and hence more heat-energy is required to break these bonds and induce boiling.⁶

What does nuclear charge explain?

In the above, we have a causal explanation for at least one of the distinct chemical properties of ethanol and methoxymethane. The distribution of charge within their respective molecules, assessed by way of bond polarity, lead to intermolecular H-bonding in ethanol but not methoxymethane, resulting in significant disparity in their respective boiling points. And this poses a problem for anyone looking to assert the reducibility of atomic species: if nuclear charge can causally explain the chemical properties of substances, then it surely ought to explain bond polarity. But this is not the case. Bond polarity cannot be predicted by, derived from, or explained in reference to the nuclear charges of a molecule's constituent elements, nor by the known causal dependents of nuclear charge, including electronic structure (Gillespie and Robinson 2005; Raub and Jensen 2001).⁷

Recall Hendry's (2006: 869) claim, that "it is nuclear charge... that overwhelmingly determines the chemical behaviour of... compounds, via the electronic structure of free and bound atoms." But what can nuclear charge actually *explain* about the respective properties of ethanol and methoxymethane? The most that nuclear charge can offer us appears to be a descriptive assertion: that a compound of chemical formula C_2H_6O will determinately exhibit the chemical properties of either ethanol or methoxymethane. Nuclear charge seems, as a contemporaneous empirical fact, unable to provide an explanation of the chemical properties of substances.⁸

The obvious rejoinder is that I have developed this claim in specific reference to *isomers*—those molecular species that are already often taken to support emergence. But I have employed ethanol and methoxymethane only in order to utilise a rhetorically useful contrast, and there is nothing particular to their status as isomers that facilitates my

⁶ The reality of intermolecular interaction within substances gives rise to plausible arguments that, e.g., H_2O is not an accurate description of water (Häggqvist 2022; cf. Chang 2012). A convincing equivalent argument could be made on the basis of intermolecular H-bonding for ethanol, so that chemical formula C_2H_6O does not meaningfully describe the substance. But, given that this does not preclude bond polarity as an at-least partial explanation of chemical properties, I leave this possibility aside here.

⁷ Of course, no chemical properties could occur lacking the electronic structure of atoms. But all this establishes is a weak existential dependence. Specific chemical properties are underdetermined by electronic structure, and no causal explanation from electronic structure to the properties of most substances is forthcoming.

⁸ The case of monatomic substances provides an interesting confounding example to this claim. The chemical properties of, e.g., argon in gaseous form, are generally understood as the direct result of the constituent atoms' full valence shells. Thus, one could quite clearly argue that in the case of these monatomic substances, electronic structure provides direct causal explanation for chemical properties. But this is a special example, and the vast majority of chemical substances are molecular, ionic, or metallic. Thus, I leave this issue aside: suffice it to say that my arguments stand at least for these other substances.

claim that nuclear charge is unable to provide an explanation of chemical properties. For example, water, with chemical formula H_2O and no known isomers, has—comparative to similarly constituted compounds—the anomalously high boiling point of $100\text{ }^\circ\text{C}$. How is this explained in chemical theory? On the basis that the bond polarities of H_2O molecules lead to intermolecular H-bonding, just as in the case of ethanol. And just as in the case of ethanol, there is no explanation from the fundamental constituents of atoms for this state of affairs.

Thus, there has been no successful intertheoretic reduction from chemical explanations about chemical properties to physical explanations on the basis of nuclear charge. But microstructuralism appears to claim that the causal powers of the elements *are* explained by nuclear charge. To affirm such a view in light of the preceding would be to suggest that the causal powers of atomic species do not extend to the properties of the substances they constitute. Thus, for example, the causal powers of oxygen could not be held to directly contribute to the boiling point of water. But this would upset a crucial claim of microstructuralism itself—that “the presence of an element in a compound explain[s] the chemical properties of the compound” (Hendry 2006: 869). Moreover, this would be to deprive atomic species of the causal powers we expect of them.

As it stands, then, it seems reasonable to reject the claim that the causal powers of atomic species can be explained in exclusive reference to their constituent fundamental particles. My goal now is to elaborate this conclusion, while also making a case for the specific consideration of emergence for atomic species. I accomplish this through a discussion of the chemical concept of *electronegativity*.

Electronegativity and a new case for emergence

An elemental property to explain bond polarity

Electronegativity is ordinarily defined in accord with Linus Pauling’s (1960: 88) formulation as “the power of an atom in a molecule to attract electrons.” Pauling (1932) developed the first quantitative measure of electronegativity, a relative value derived from the heat-energy produced when thermochemically dissociating diatomic molecules of identical atoms, with hydrogen as a reference point. Thus quantified, electronegativity values are discrete numbers associated with discrete elements that indicate relative propensity to transfer or receive electrons when part of a bonded pair.

On this basis, respective electronegativities can provide causal explanations of bond polarity. In H_2O molecules, for instance, the bonds between hydrogen and oxygen are predictably polar covalent on the basis of oxygen’s significantly greater electronegativity. That oxygen is the receiver in this unequal electron-sharing is also thereby predictable, so that oxygen’s overall negative charge and its bonded hydrogens’ overall positive charge in an H_2O molecule (and thus, water’s intermolecular H-bonding and anomalously high boiling point) is explainable via oxygen and hydrogen’s respective electronegativities.⁹

⁹ More generally, the bond polarities in a molecule correlate to specific properties in compound substances. “Covalent, ionic, and metallic bonds are... very different entities used to distinguish between molecular, ionic, and metallic substances” (Hurst 2002: 763). In turn, a substance’s being molecular, ionic, or metallic explains many macroscopic properties, including melting and boiling points, conductivity, hardness, brittleness, and so on.

Given that electronegativity both (a) seems sufficient to causally explain bond polarity and consequent chemical properties, and (b) is a discrete value associated with discrete elements, this might all look promising for the potential reducibility of atomic species. If electronegativity could be explained via an atom's constitutive fundamental particles, then this would render my above critique moot. But, as it turns out, such an explanation does not seem plausibly forthcoming.

Which electronegativity?

The propensity of an atom to transfer or receive electrons under bonding conditions is not a physically observable property. “The capability of atomic entities to attract electrons is a highly abstracted instance” (Ruthenberg and Mets 2020: 415), the notion of which initially emerged from Pauling's (1932: 3570) difficulties “in the application of quantum mechanics to problems of molecular [configuration]” regarding corollaries between bond-energy, geometrical molecular characteristics, and the elemental participants of a given molecule. Pauling's approach could associate a value to discrete atomic species that indicated the bond-energy they exhibited under non-polar covalent conditions and, normalised to hydrogen, thereby reliably indicate the energy-distribution for atoms under bonding conditions via electronegativity difference. But note that electronegativity so determined is derived from *molecules*. Thermochemical dissociation of more complex molecules can provide, on this basis, distinct molecular ‘electronegativities’ that are not generalisable to their elemental constituents. This raises the question—is electronegativity a molecular or atomic property?

This was not a question that went contemporaneously unaddressed. Shortly after Pauling's initial quantification, Mulliken (1934: 782, emphasis added) proposed a new measure of electronegativity, writing: “one of the most familiar and useful chemical concepts is that of *relative* electronegativity. The physical basis of this has remained obscure. In the present paper, a possible... *absolute* scale is discussed.” Mulliken goes on to develop an electronegativity scale derived from the averages of electron affinity and ionisation potential, with the explicit goal of establishing electronegativity as an atomic property. But Mulliken's approach is not a truly absolute measure, in that electron affinity is only determinable through the energy differential between an uncharged atom and its anion. This raises a related but distinct question to that posed by Pauling's approach: is electronegativity a property to be associated with isolated atoms, or only atoms in relational contexts?

As Leach (2013: 25) indicates, “dozens of quantitative electronegativity scales have been suggested, using physical parameters including: enthalpy data, ionisation potential and electron affinity, effective nuclear charge and covalent radius, stretching force constants, average electron density, dielectric properties, the work function, relative compactness, configuration energy, polarizability, number of valence electrons, pseudopotentials, NMR chemical shifts and isomer shifts in Mössbauer spectroscopy.” New measures are regularly proposed.¹⁰ But it is broadly accepted that all such measures fall under the two broad categories: thermochemical measures (including Pauling's approach) and atomic or spectroscopic measures (including Mulliken's approach).¹¹ In differentiating these, we can

¹⁰ Some contemporary examples include: Rahm et al. (2019), Tantardini and Oganov (2021) and Kumari et al. (2022).

¹¹ It has on occasion being proposed that a third category of electrostatic measures be acknowledged [see e.g. Ruthenberg and González (2017)]. But these electrostatic measures are feasibly accounted for as a

Table 1 Electronegativity values for selected chemical elements from several electronegativity scales

	Hydrogen	Boron	Oxygen	Fluorine
Pauling (1932)	2.2	2.04	3.44	3.98
Mulliken (1934)	2.1	1.93	3.04	3.9
Allred-Rochow (1958)	2.2	2.01	3.5	4.1
Gordy (1946)	2.17	1.91	3.47	3.94
Sanderson (1955)	2.31	1.88	3.46	3.92
Allen (1989)	2.3	2.051	3.61	4.193
Rahm et al. (2019)	2.266	1.9	3.1	3.883
Max Deviation	0.21	0.171	0.57	0.31

Maximum deviation given in bottom row. Table adapted and extended from Ruthenberg and González 2017

say that “in the [thermochemical] case, the [electronegativity] concept is associated with an energy difference between two interacting species, while in the [spectroscopic] case it is associated with a response function of an isolated [atom]” (Franco-Pérez and Gázquez 2019: 10,069).

Thus far, philosophical treatments of electronegativity have tended to emphasise that thermochemical and spectroscopic ‘electronegativities’ are ontologically inconsistent, often to evince the reality or usefulness of pluralism in chemistry (see e.g. Ruthenberg and Mets 2020; Accorinti and Labarca 2020). As per Accorinti (2019: 74), “Pauling’s [electronegativity] is an external property... defined in terms of the relation between two substances. If a value of [electronegativity] is assigned to the elements it is only because hydrogen is conventionally taken as a reference. Mulliken’s [electronegativity] is an intrinsic property of atoms, as long as it depends on the non-relational tendencies of each atom to gain or lose electrons.”¹²

This concern is not, however, recognised by practicing chemists. The view that thermochemical measures of electronegativity articulate an external property is typically evidenced via Pauling’s (1960: 88) formulation of electronegativity as “the power of an atom in a molecule to attract electrons.” This is tenuous, however, given that Pauling’s (1960: 88–9) *next sentence* affirms Mulliken’s view that electronegativity is an absolute property of atoms. Contemporary scientific accounts ordinarily refer to electronegativity as a property or descriptor of atoms in isolation [see e.g. Rahm et al. (2019), Tantardini and Oganov (2021) and Kumari et al. (2022)].

But operational recourses say something important about concepts even if the implications of such are overlooked. What the preceding has demonstrated is that we have, essentially, no notion of what the physical basis of electronegativity could be. That is, there is *no aspect of physical systems that appears uniquely tied to electronegativity*.

This brings us to the actual results of the diverse array of operations employed to derive electronegativity scales. Table 1 collates the values of several prominent scales for a few indicative elements. Immediately apparent is that while these scales are approximately

Footnote 11 (continued)

branch of thermochemical measures, and in keeping with the bulk of scientific literature on the topic, I treat them as such here.

¹² It is worth noting that, given that Mulliken’s scale is partially derived from electron affinity, Accorinti is wrong to account for the approach as strictly non-relational.

Table 2 Collation of the scales from which electronegativity values are given, and the method by which electronegativity values are stated to be derived, from several tertiary chemistry textbooks

Textbook	Value	Methodology
Chang and Overby (2021)	Pauling	Mulliken
Silberburg and Amateis (2021)	Pauling	Mulliken
Brown et al. (2021)	Pauling	Mulliken
Reger et al. (2010)	Pauling	Mulliken
Atkins et al. (2013)	Pauling	Pauling/Mulliken
Zumdahl et al. (2013)	Pauling	Pauling
Petrucci et al (2017)	Pauling	Pauling
Robinson et al (1997)	Pauling	None
Kotz et al (2014)	Pauling	None
Umland (2001)	Allred–Rochow	Allred–Rochow

Only Atkins et al. (2013) gives explicit indication that different means of derivation produce different electronegativity values. Table updated from Hurst (2002)

commensurate, there are consistent deviations between scales. That these small deviations give the impression of clustering is obvious, and this might intuitively recommend the view that each method is indirectly tracking some absolute property. But this would be speculative, and the lack of a physical basis for electronegativity recommends a position of agnosticism in this regard.

The problem is compounded in that many electronegativity scales are developed for specific epistemic utilities. Thus, e.g., Martin Rahm's (2019: 342) recent electronegativity scale is intended to permit the discrete electronegativities of elemental constituents to predict overall charge shifts in molecules undergoing chemical reaction. Meanwhile, Varsha Kumari et al's (2022: 360) scale is intended to more-accurately predict bond length in specific molecular species. Both of these scales show similarly small deviations from other measures, yet accomplish specific epistemic goals with different degrees of efficiency. Thus, relative utility or accuracy of prediction provides no means of establishing an ultimately more 'correct' electronegativity scale either. It seems inarguable that "electronegativity is one of the most important elemental descriptors" (Rahm et al. 2019: 342). But the question has become—which electronegativity?

In finalising this point, consider the presentation of electronegativity in science education. Table 2 collates the electronegativity values, and method of derivation, given by ten tertiary chemistry textbooks. The inconsistency evident therein makes it apparent that the uncertain identity of electronegativity is not an issue confined to the frontiers of chemical or theoretical research. Although Pauling's values are clearly favoured, students can encounter different and often contradictory understandings of the concept within their first university-level interactions with molecular structure.

Is electronegativity a physical atomic property?

Despite the many 'electronegativities' indicated in the preceding, it remains a reasonably persuasive intuition that the small deviations across various scales, and electronegativity's significant epistemic utility, indicate some definite physical property to which the general notion corresponds. This has, on occasion, motivated the view that despite the unclear physical identity of electronegativity, we ought nevertheless to endorse the view

that electronegativity constitutes a definite property of atomic species. E.g., Leach (2013: 27) has argued that, since electronegativity can explain various regularities of the periodic table which nuclear charge alone cannot, “electronegativity... should be considered a... property of the basic elemental substance, a component of... the indestructible stuff present in compounds and simple substances.” The argument is essentially that, since electronegativity has such far-reaching explanatory capacity and epistemic utility, we ought to take electronegativity values, as “single dimensionless number[s]” (Leach 2013: 27) associated with discrete elements, to correspond with a physical atomic property regardless of our inability thus far to identify its physical basis.

Given that different electronegativity scales display variable utility depending on epistemic goals and molecular context,¹³ it is difficult to envision how electronegativity as a single dimensionless number could even in principle accurately encapsulate the various atomic behaviours that various electronegativity scales facilitate engagement with. But such an issue could be circumvented if a physical basis for electronegativity could be identified. The most prominent attempt at such comes from Allen (1989: 9003), who argues that “it is most likely that [electronegativity] is an energy, because Schrödinger’s equation identifies energy as the central parameter for describing the structure of matter.” Allen (1989: 9005) proposes that we view electronegativity as the per-electron energy of valence electrons in the *s* and *p* orbitals of an atom, with the goal of producing a quantum-mechanically viable electronegativity (with Murphy et al. 2000). Thus, he proposes equation:

$$\chi_{\text{spec}} = (me_p + ne_s)/(m + n)$$

Where χ_{spec} is electronegativity value, *m* and *n* are the respective numbers of *p* and *s* valence electrons, and e_p and e_s are the per-electron energies for *p* and *s* orbitals obtained via the energy differential between a ground-state neutral atom and its first ionised state. The electronegativities derivable on this basis are in general accord with other scales (Table 1).

There are problems with Allen’s approach that cannot be fully discussed here.¹⁴ But even interpreting the scale as sympathetically as we can for the reductionist, Allen’s approach does not actually facilitate the determination of electronegativity from a purely quantum-mechanical description of an atom. The problem arises from the specification of orbital positions for valence electrons. Doing so requires the independent electron approximation, which presumes that electron-electron interactions are null, since by the strict principles of quantum mechanics only an atom as a whole has a defined stationary quantum state. The specification of orbitals is not possible from physical principles,¹⁵ and its empirical basis lies in its explanatory capacity regarding qualitative analogies made evident by periodicity.

¹³ This is particularly the case for the transition metals, and notably platinum, for which the predictive function of Pauling’s electronegativity and the Allred-Rochow scale entirely depends upon which types of atom a given atom of platinum is engaged in chemical bonding with Raub and Jansen (2001: 223–4).

¹⁴ Most significant are that the scale utilises ionisation potentials calculated for specific orbitals, and therefore relies on relational measures rather than direct measurements, and that it is of limited utility, particularly regarding the transition metals. Interestingly, Allen (1989: 9014) addresses the issue regarding transition metals, and accounts it as a measurement limitation due to the contribution of *d* orbital electrons to the *p* orbital in those elements.

¹⁵ Indeed, assigning definite orbital positioning to electrons violates the Pauli principle, a core tenet of quantum mechanics, by contradicting its entailment that electrons are indistinguishable.

To invoke Hendry's (2017: 154) formulation regarding configurational Hamiltonians, the upshot is that Allen's quantum-mechanical formulation of electronegativity requires putting in *by hand* the parameters by which an electronegativity value can be determined. In that this regards orbital positioning, these parameters are drawn directly from chemical rather than physical theory. Allen's scale is, therefore, no more a true quantum-mechanical description of electronegativity than configurational Hamiltonians are a true quantum-mechanical description of molecules.¹⁶ Electronegativity remains entirely intractable from the sole basis of the mass, charge, and motion of fundamental particles.

A physical basis for electronegativity therefore remains as elusive as it was when Mulliken (1934: 782) noted as much. One response is to argue that since "electronegativity [is] not represented by quantum-mechanical observables, [it has] served a noble purpose in the past and [is] now obsolete" (Boeyens and du Toit 1997: 296). This sentiment is echoed by some philosophers, with e.g. Klaus Ruthenberg and Juan González (2017: 74) arguing that "the persistence of electronegativity rests on the unquestioned—and ill-founded—belief that it is a natural property." In my view, we are left in a position of prudential agnosticism regarding whether or not electronegativity is a physical property (or properties) of atoms.

The case for emergence

Despite this, electronegativity's status as a descriptor of atoms in isolation is often taken for granted within the chemical community, and the concept provides a crucial basis by which chemists explain the properties of substances in reference to their elemental constituents. The upshot is that if microstructuralism-as-reductionism is to maintain the propositions that (a) the causal powers of atomic species are exhausted by those conferred by their physical bases, and (b) the presence of a chemical element in a substance serves to explain the properties of that substance, then regardless of whether or not electronegativity scales are taken to be tracking some physical atomic property, all the various epistemic utilities of the concept will have to be explained in reference only to fundamental particles in interaction with a few fundamental forces. It is impossible to say decisively whether such an undertaking is even theoretically possible. But, given the sheer diversity of the electronegativity concept, it does not seem particularly *plausible*.

It is worth recalling the pragmatic basis upon which emergentists stake their claim. If the explanatory salience of chemical theory over physical theory can be established for some chemical property, then it is equally reasonable to suggest that the property might be an emergent one as it is to infer that it will prove reducible to its constituent fundamental particles (Hendry 2010: 190).

The preceding has established that there has been no intertheoretic reduction of electronegativity by way of physical theory. Moreover, there are no obvious grounds upon which to expect that such will be forthcoming. Allen's scale, arguably the most promising attempt to establish a physical basis for electronegativity, in fact provides an explanation of the concept that crucially relies upon an aspect of chemical theory—the orbital positioning of valence electrons. The variety of deviating electronegativity scales might be leveraged to argue that chemical theory is equally unable to *explain* electronegativity, conceived of as a singular concept. But epistemic utility is in fact better served by referring to a variety of

¹⁶ Elsewhere, Allen (1993: 5787) effectively concedes as much, referring to his approach as a "middle ground" between chemical and physical theory.

electronegativity values as dependent upon investigative context and epistemic goals. The capacity of physical theory to make sense of such is unclear.

On this basis, I submit, it is just as plausible to infer that electronegativity is an emergent property (or properties) of atomic species as it is to assert that its various epistemic utilities will prove reducible to the physical bases of atoms. Admittedly, this is not a positive argument for emergentism. Rather, it is the acknowledgement that evidential recourse neither supports inferring the ontological reducibility of electronegativity nor the causal powers of atomic species.

That said, there are certain conceptual benefits to adopting emergentism in this case. For instance, if we accept that electronegativity just is an emergent property of atomic species, then we can unproblematically allow that the causal powers of oxygen extend to, and can partially explain, the boiling point of water. This by way of the bond polarities in an H₂O molecule facilitating intermolecular H-bonding, increasing the number of bonds in a measure of water and so increasing the amount of energy required to boil it. If the reductionist is to persuasively assert that oxygen plays a similar causal role in the chemical properties of water, this will require an explanation of electronegativity in exclusive reference to the fundamental constituents of atoms. But, as demonstrated, such an intertheoretic reduction is still lacking. Understanding electronegativity as a causal power of atomic species that is not directly conferred by their physical bases—a modest emergentism about electronegativity—can therefore provide intuitive causal explanations from chemical elements to the properties of substances that are not available to the reductionist.

Concluding remarks

I opened my discussion of the emergentist view with the claim that it seems feasible that the causal powers of higher-level chemical entities are not exhausted by those conferred by their physical bases; this on the evidentiary basis of isomerism. I can now make a stronger claim—that it seems feasible that the causal powers of *all* chemical entities, through to atomic species as the smallest instance of such, are not exhausted by those conferred by their physical bases. That electronegativity provides a basis upon which to expand the remit of emergentism encapsulates the crucial philosophical ramification of this paper.

Moreover, the microstructural view of chemical elements, as currently articulated, entails that the causal powers of chemical elements do not extend to the properties of substances so constituted. By contrast, a modest emergentism about electronegativity can provide causal explanations for the properties of substances in reference to their elemental constituents by way of bond polarity.

An indispensable concept in historical and contemporary chemistry, electronegativity has only recently become a focus of philosophical discussion. The arguments presented here suggest a number of additional philosophical avenues to which electronegativity might prove relevant. Most obviously, the consequences of electronegativity for microstructuralism as an essentialist account of natural kinds have yet to be explored. Debates regarding scientific realism more broadly might also benefit from electronegativity's inclusion, particularly regarding the ontological suppositions of the argument from success. Finally, given that chemistry is the most obvious candidate of the special sciences for reducibility to physics, the challenge of electronegativity may have broader ramifications for reductionist claims in other fields, notably the life sciences and theories of mind.

Author contributions MC is the sole author.

Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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