Electronegativity and its multiple faces: persistence and measurement

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Abstract Electronegativity is a quantified, typical chemical concept, which correlates the ability of chemical species (atoms, molecules, ions, radicals, elements) to attract electrons during their contact with other species with measurable quantities such as dissociation energies, dipole moments, ionic radii, ionization potentials, electron affinities and spectroscopic data. It is applied to the description and explanation of chemical polarity, reaction mechanisms, other concepts such as acidity and oxidation, the estimation of types of chemical compounds and periodicity. Although this concept is very successful and widely used, and in spite of the fact that it is still subject to scientific investigations, neither a more than intuitive definition nor a generally accepted, logically clear and standardized quantification model has been developed. In the present work, electronegativity is presented and discussed with respect to its main conceptual and operational continuities and discontinuities. We try to analyze the epistemological status of electronegativity, conceived as a typical notion of chemical sciences. Under 'epistemological status' we subsume the issues of its reference, its historical persistence, and the relationship between its measurement and quantification.

Keywords Electronegativity · Chemical properties · Measurement scales · Reactivity · Property quantification, reference

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Introduction

Electronegativity is a concept widely used in modern chemistry to describe the behavior of substances when they encounter other substances. In its common version, it is supposed to address the ability of chemical species to attract bonding electrons. It is used to describe and explain reaction mechanisms and periodicity trends, and as a heuristic tool to predict the chemical kind of compounds for polarity estimations, for the explanation of hydrogen bonds, etc. Modern chemists usually take electronegativity as a concept that denotes a property: "The electronegativity, (χ), of an element is the power of its atoms to draw electrons to itself [sic] when it [sic] is part of a compound, so we can expect the polarity of a bond to depend on the relative electronegativities of the elements." (Atkins and de Paula 2013, p. 363). Empirically, however, electronegativity cannot be directly measured: its value must be determined by indirect means. There are at least three different quantification approaches: the thermochemical, the spectroscopic, and—what we here call—the electrostatic. This plurality adds difficulties to the understanding of the concept.

In the present article, we will try to analyze the epistemological status of electronegativity, conceived as a typical notion of chemical sciences. Under 'epistemological status' we subsume the issues of its reference, its historical persistence, and the relationship between measurement and theoretical quantification.

Quantifying electronegativity: the thermo-chemical approach

In 1932, Linus Pauling pioneered the use of calculations based on the heats of dissociation or formation of A_nB_m-type substances.[1] According to him, electronegativities are "numbers representing their [the elements'] power of attraction for the electrons in a covalent bond, by means of which the amount of partial ionic character of the bond may be estimated. This power of attraction for the electrons in a covalent bond is called the *electronegativity* of the element" (Pauling 1950, p. 236). In this qualitative definition, Pauling clarifies that the concept is applicable only to covalent bonds, and that electronegativity is a property of elements related to the attraction of electrons in that kind of bonding situations. The difference between the actual and the purely covalent bond between atoms A and B is a measure of the *partial ionic energy* (Δ) in the AB bond:

$$\Delta = E_{AB} - 1/2[E_{AA} + E_{BB}] \tag{1}$$

Then Δ is related to the different ways in which bonding electrons are shared in substances A and B, and thus it is a measure of electronegativity χ:

$$\Delta_{AB} = (\chi_A - \chi_B)^2 \tag{2}$$

This description gives only differences of electronegativity. To obtain the absolute values it is necessary to postulate one element as the reference element. For this purpose, Pauling endowed hydrogen with $\chi = 0$ (later, with $\chi = 2.2$, in order to avoid negative values of χ for most metals). In 1961, Allred updated Pauling's scale by means of more accurate thermodynamic measurements.

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[1] Jensen (2012) claims that the first qualitative description of electronegativity was due to the American physical chemist Worth H. Rodebush in 1925.

As the above explanation shows, in the context of the thermochemical approach, electronegativity is a relational property of elements in substances. Calculations are based on the idea of subtracting, from the empirically measured bonding energy, its entire covalent fraction, in order to recover what is considered the "ionic character" of that bond. According to this approach, each specific chemical kind is the result of the electronegativity differences between elements: we obtain salts as one of these kinds, if we bring together typical metals and typical non-metals. The micro-physical description of this kind refers to charged particles, such as Na^+ and Cl^- for NaCl. As a borderline case, which forms a second class of substances, we have the structures consisting of non-metals only. Because of their closeness, the differences of electronegativity in those cases are small, and vanish for homopolar entities such as Cl_2. The second borderline case (third kind) consists of combinations of metallic elements: according to the prevailing modern theoretical description, these substances, whether elementary or combined, gain their internal stability by forming a specific type of bonding, namely, the *electron gas*. These freely swaying electrons hold together the charged metal cones. Since the resulting state cannot be described by the same tools as the other more or less defined entities, a comparative application of the concept of electronegativity is hardly possible (*cf.* Table 1).

Despite the widespread use of Pauling's scale and its subsequent improvement by Allred, a major difficulty in developing a thermodynamic scale of electronegativities is the lack of measured values for many single bonds and especially for metallic bonds. However, the thermodynamic scale is one of the most used, and generally serves as a point of reference for other electronegativity scales.

The spectroscopic approach

The second measurement domain that has been used to build a scale of electronegativity is a spectroscopic one. In turn, in this domain two main fields can be distinguished: one that uses the atomic radius and the effective nuclear charge as a geometric relationship between the valence electrons and the nuclei, and the other that uses the ionization potential and the electron affinity.

The scales of Gordy (1946) and Allred and Rochow (1958) belong to the first field. So, the atomic electronegativity is calculated as:

$$\chi = aZ_{eff}/r^n + b \tag{3}$$

where r is the atomic radius, Z_{eff} is the effective nuclear charge, and a and b are the linear coefficients that relate this electronegativity values with those of thermo-chemical measurements. The resulting concept is also called *geometrical electronegativity*, because it relates the geometrical disposition of the nuclei with the valence electrons. We call it

Table 1 Applicability of electronegativity differences ($\Delta\chi$) with respect to the differentiation general substance classes (kinds)

Type of substance	Example	$\Delta\chi$	Bonding pairs	Predictability of chemical kind
Homopolar	Chlorine, $Cl_{2(g)}$	0	Yes	Yes
Heteropolar	Hydrogen chlorine, $HCl_{(g)}$	0.9	Yes	Yes
Ionic	Sodium chloride, $NaCl_{(s)}$	2.1	No	Yes
Metallic	Sodium, $Na_{(s)}$	0	No	No

'spectroscopic quantification' because it uses the empirically determined values of r and Z_{eff}.

The differences between the approaches of Allred and Rochow and of Gordy are based on how the values of Z_{eff} are obtained. According to Gordy (1946), the value of the effective charge of the nucleus can be obtained by the difference between the valence electrons (n) and the shielding constant of the valence shell (s):

$$Z_{eff} = n - s(n - 1) \tag{4}$$

By contrast, Allred and Rochow (1958) built their value for n in Eq. 3 by means of values obtained empirically with X-ray spectroscopy or by using Slater's rules.[2] These two scales were the first to introduce the concept of force for the quantification of electronegativities, and so made possible the development of electronegativity values for elements that had not been determined so far. Gordy also developed a useful relational strategy to obtain electronegativities for metals by relating Eq. 3 with the bond-stretching force constant k measured in radio frequency spectroscopy, the bond length d and the bond order N:

$$k = aN\left(\chi_A \chi_B / d^2\right)^{3/4} + b \tag{5}$$

Another method that uses the covalent radius to develop a scale was developed by Sanderson (1951). According to this author, electronegativity is associated with the average electron density of the atoms (ED), which represents the average degree of compactness of the electronic sphere around the atomic nucleus. This number is a measure associated with each atom and can be calculated by means of the number of electrons Z (not the atomic number) and of either the covalent or the ionic radius r as follows:

$$ED - Z/4.19i^3 \tag{6}$$

On this basis, the electronegativity of an atom can be calculated through a stability radius, obtained in terms of the ratio ED/ED_i, where ED_i is the electron density value of an inert isoelectronic atom. In order to calculate ED_i it is necessary to obtain a covalent radius that is not accessible empirically and, therefore, is interpolated from known values; thus, it is a fictional value. Sanderson claims that the stability radius is a measure of the degree of compactness of electrons and a measure of the force of attraction to the nucleus, thus a measure of electronegativity.

The second subgroup of spectroscopic measurements was developed by Robert Mulliken (1934). According to this approach, electronegativity is measured as the average of the sum of the electron affinity (A) and the ionization potential (I):

$$\chi_A = 1/2(I_A + \mathcal{A}_A) \tag{7}$$

This relation allows for obtaining values for isolated atoms. However, the lack of empirical measurements for ionization potentials and electron affinities has been a serious obstacle to the construction of a complete scale. Despite the lack of empirical data, this approach was considered to be of reasonable theoretical value: "Mulliken's method has much greater theoretical support" (Mullay 1987, p. 4). Intuitively, this approach describes

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[2] According to this set of rules, the electron shells have their own values of $n1$, the sum of which determines the shielding constant of the atoms n. Within this scale the value of n in Eq. 3 is 2, whereas in Gordy's scale the value is 1.

the tension of one atom between the tendencies to lose or to gain electrons. Mulliken calls this tendency '*electroaffinity*', and assumes that both I and A can be a correct measure of that property. As the ionization potential can be inferred for different valence states, Hinze and Jaffe (1962) developed the concept of *orbital electronegativity.*

Allen (1989) developed another scale of electronegativity that uses the ionization potential. According to him, electronegativity should be considered the "third dimension" of the periodic table: "It is most likely that this new third dimension is an energy because the Schrödinger equation itself identifies energy as the central parameter for describing the structure of matter" (Allen 1989, p. 9003). Allen's argument is that the periodic table itself is reducible to the foundations of quantum mechanics.[3] On this basis, he proposes:

$$\chi_{spec} = m\varepsilon_p + m\varepsilon_s/m + n \qquad (8)$$

The variables m and n are the numbers of the valence electrons of the p and the s orbitals; and are the one-electron energies obtained as the difference between the ground state and the first ionized state.

The electrostatic approach

The third empirical quantification domain for electronegativity is the electrostatic, which actually drew upon the thermochemical approach very early. Because the heats of dissociation of two-atomic compounds are used as a basis of Pauling's scale of electronegativity, this is a relational model that requires a kind of normalization (as the mentioned setting of hydrogen). Accordingly, Pauling's scale is generally restricted to those elements which form two-atomic compounds (*cf.* Table 1), and it excludes the noble gases (no compounds of the noble gases were known at the time Pauling published his original work). Although it was some time before noble gases were added to any electronegativity scale at all, progress was made with metals in the discussion of the dipole moment as a reference. This development supplemented the data published by Pauling since, as mentioned above, he only considered covalent compounds in his original work (Pauling 1932).

The American chemist Malone—who, as it were, was the very first to react to Pauling's concept—chose the dipole moment (electric moment) of two-atomic and more-atomic molecular substances in a short article on *The Electric Moment as a Measure of the Ionic Nature of Covalent Bonds* (Malone 1933).[4] Dipole moments are inferred from the measurement of dielectric constants (permittivity) of substances. Malone intends to offer another measure for electronegativity: "The perfection of two independent measures of electronegativity, one based on thermal and one on dipole moment data, would be of considerable value." (Malone 1933, p. 199). Malone mentions two aspects of this value: the supplementary aspect of differently incomplete scales, and the perspective to calculate "bond angles in polyatomic atoms". However, "Before this can be done, a clearer definition of electronegativity must be given." (Malone 1933, p. 199) Unfortunately, he did not

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[3] Eric Scerri has reacted to the scale of Allen and his argument about the reducibility of the periodic table to the Schrödinger's equation, and claims that "…the success of the periodic table does not rest on accepting a reductionist account of chemical phenomena and the structure of matter in terms of quantum mechanics and electronic configurations. I do not think I am alone in claiming that modern physics has not altered the periodic system in any fundamental way" (Scerri 1993, p. 5786).

[4] Because his calculations referred to more-atomic substances, Malone had to assume bond angles, like the following: NH_3/100°; PH_3/98°; AsH_3/96°; SbH_3/94°.

elaborate on what he meant by a "clearer definition" in that article. On the contrary, he seemed to follow the Pauling concept without any reasonable criticism. He even revised his first approach (which he began to develop before Pauling's paper appeared) when he recognized that Pauling had used hydrogen as the reference for his scale. What might be a critical statement can be found in the very first paragraph of Malone's paper: "The idea that the electric moment bears some relation to the ionic quality of the two-electron type of bond has been known for a number of years. It is true that the terms used in describing a bond have been loosely applied, and it is uncertain in some cases just what meaning has been intended." (Malone 1933, p. 197).

Table 2 compares electronegativity values of the main approaches.[5] Estimated over all values for each element, standard variations only rarely exceed 5%. With only few exceptions, the entries are in good accordance. Taking into account that the most customary applications of electronegativity (that is, estimations with respect to reactivity, polarity and chemical kind; see Table 1) are relational and qualitative, the claimed accuracy is more than adventurous. This only apparent accuracy indicates a somewhat vaulting ambition with respect to quantification or mathematization of the postulated "property".

What is electronegativity?

There are various reviews about electronegativity from the viewpoint of theoretical chemistry (e.g., Pritchard and Skinner 1955; Ferreira 1967; Batsanov 1968; Mullay 1987), but more general issues and questions referred to the history and philosophy of chemistry have rarely been raised (e.g., Jensen 1996, 2003, 2012). We shall discuss three crucial issues in order to clarify the definition of electronegativity and its epistemic status: *reference, stability*, and *experimentation*. Regarding reference, we address the problem of the ontological denotation of the word 'electronegativity' in expressions like '*a* is more electronegative than *b*'. By stability we mean the historical persistence of the concept and the reasons for that. And with experimentation we refer to the role of measurement in the building of the concept. Although there is some overlap between these issues, we separate them in an attempt to gain more clarity.

Reference

Many chemists consider electronegativity to be a molecular concept: "Electronegativity is an important part of the intuitive approach to understanding nature that sets chemists off from other physical scientists [...]. The reason for the sustained interest appears to lie in the fact that the idea of electronegativity is practically a direct consequence of foundation concepts of modern chemistry, specifically the following three:

1. Molecules are made up of atoms held together by chemical bonds.
2. Chemical bonds involve a sharing of electrons between the atoms.
3. The electrons are not always shared equally." (Mullay 1987, p. 2)

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[5] Different bonding states of the same elemental kind, expressed as orbitals (s, p, sp, sp^2, sp^3) have different values of electronegativity. That means, for example, that the electronegativity of carbon atoms in diamond differs from that in graphite.

Table 2 Selected electronegativity values from different scales (Mullay 1987). Values of the last column are taken from Allen (1989)

Element	Pauling	Mulliken and Jaffe	Allred and Rochow	Gordy	Sanderson	Allen
H	2.2	2.1 (*s*)	2.20	2.17	2.31	2.3
Li	0.98	0.84 (*s*)	0.97	0.96	0.86	0.912
Be	1.57	1.40 (*sp*)	1.47	1.38	1.61	1.576
B	2.04	1.93 (*sp*^{2})	2.01	1.91	1.88	2.051
C	2.55	2.48 (*sp*^{3})	2.50	2.52	2.47	2.544
N	3.04	2.28 (*p*)	3.07	3.01	2.93	3.066
O	3.44	3.04 (*p*)	3.50	3.47	3.46	3.610
F	3.98	3.90 (*p*)	4.10	3.94	3.92	4.193

Although these three statements are correct, the claim that the molecular picture is central for the "idea of electronegativity" is hardly comprehensible. To illustrate this systematic incorrectness, let us take a closer look at the electronegativity of metals. Because metals do not form covalent bonds under normal circumstances, Pauling's theoretical approach of the extra energy in an atomic bond is not applicable to them (see Eq. 1). According to modern chemical knowledge, the model of a bonding electron pair make no sense regarding the "ionic" state, be it salt or metal; that is, using the concept of molecule in these cases is senseless. Although we find electronegativity values (see Table 2) for metals in both "absolute" scales and "relational" scales, electronegativity is not applicable to the metallic state (bond) with respect to taxonomic or classificatory purposes. Electronegativity differences of zero (as for sodium in Table 1) do not refer to a molecular state of the reaction partners. Consequently, Pauling's first scale did not contain metals. Nevertheless, Pauling's scale can be easily accommodated to yield a fuller picture because the analysis of thermochemical data is independent of any particle-centred interpretation. Hence, in a preliminary attempt, we can conclude that electronegativity is an elementary property. However, if it is considered to be a natural property of bonds, it is not one that is a necessary condition for all possible "chemical" bonding types.

As we stressed above, there is not one uniform definition of electronegativity up to the present day. By contrast, with the development of both semi-empirical calculations and the so-called ab initio quantum chemistry, we witness a proliferation of a variety of *electronegativities*. Nevertheless, most results of this variety of approaches seem to converge or, in other words, seem to represent something reasonably similar. All these different physical descriptions, such as *covalent radius*, *ionization potential*, *electron affinity*, *dipole moment*, *dissociation energy*, and *spectroscopical data* can be interpreted as having something in common if the "curve-fitting", that is, the choice of algorithms, is performed properly.

As to the interpretation of this puzzling situation, two aspects should be taken into account. Firstly, the quantification concepts mentioned above conceptually refer—directly or indirectly—to *atoms* (although, nevertheless, empirically they operate with stuff samples). Because of this strong restriction, the obtained data address processes very close to each other: adjoining or removing outer shell electrons is the basis for ionizations, and the same electrons do have a crucial impact with respect to spectroscopy and atomic radii measurements. Thermochemical descriptions indirectly refer to more simplified systems, too: dissociation of diatomic molecules leads to atoms, and during that process again the

outer electrons are involved.[6] From that point of view, it is not surprising that there is a certain convergence between the different scales, to the extent that the behavior of outer shell electrons obviously strongly correlates with the tendency of atoms to take up or give away these electrons during chemical processes.

This leads to the second important aspect, which refers to *periodicity*. We know various means to reveal systematic and periodic trends of the properties (propensities, dispositions) of chemical elements with respect to the customary framework of the periodic system, particularly if main-block elements are taken into account. Among those are atomic radii, ionization potentials, and electrical conductivity. Hence, to represent the trends of elemental behavior it is not necessary to use electronegativity as a derived and only indirectly quantifiable concept. Periodicity is addressed significantly more easily using direct measurements rather than electronegativity. A closer look at the ionization potentials of elements reveals that metals have relatively low values and non-metals relatively high values. The very old experiences regarding, for example, the building of salts by reactions of typical metals and typical non-metals (such as CsF from Caesium and Fluorine) might be represented easily by the difference of the ionization potentials alone. As to other cases, for example arsenic iodide, AsI_3, predictions with respect to polarities and bonding states are much more complicated. Electronegativity, however, does not offer more—or more accurate—information (see Table 2).[7] However, the combination of measures obtained for different purposes might open up new perspectives. Mulliken's approach (Eq. 7), for example, follows exactly that strategy. In this approach, the electron affinities provide a kind of corrective, particularly for those elements that show "anomalies" when only the ionization potentials are applied.[8]

More recent approaches seem to suggest that the more abstract[9] the approach, the more "pure" is the access to electronegativity (see, for example, the concept of orbital electronegativity, and Allen's pure quantum-chemical approach, Eq. 8). If we consider the obtained measures superficially (Table 4), it indeed looks as if *absolute* (non-relational) electronegativity values exist. However, a closer look reveals that all relevant empirical descriptions and theoretical calculations actually do compare (at least) two states. This is obvious regarding Pauling's calculations, which refer to a substance and its dissociated parts; this is perhaps less obvious with respect to the atomic physical measures, but here as well two states are compared, for example, the uncharged particle and the anion, if electron affinity is to be investigated. Even less obvious, but still in force, is this *relationality* if a

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[6] The situation with respect to the use of dipole moments as a starting point is slightly more complicated, as the work of Malone (1933) has shown. In order to obtain Δ-measures from dipole moments of hydrides, he had to assume molecule bond angles. The dipole moment is a resultant of the electrical impact of the constituents. There are heteropolar substances with a dipole moment of zero (*e.g.*, CCl_4), and homopolar substances with a dipole moment different from zero (*e.g.*, O_3).

[7] Even hydrogen does not fit into group one of the periodic table with respect to its electronegativity values.

[8] Note that, e.g., the ionization potentials do not follow a steady trend within the periods. There are small breaks between the s^2-elements and the p^1-elements, and between the p^3-elements and the p^4-elements, respectively. Thus, a linear and direct transformation of ionization potentials into electronegativity is not possible (see our discussion of the noble gases and Table 4).

[9] Here we adopt the mainstream interpretation of "abstraction" by Hasok Chang, according to whom abstraction is "the act of removing certain properties from the description of an entity; the result is a conception that can correspond to actual entities but cannot be a full description of them." (Chang 2004, p. 202). Abstraction, reduction, and modelling are related notions. Among them, modelling seems to be the most neutral, reduction has always an abstracting character, but abstraction must not at all purpose reduction.

concept such as *electron density* is applied and *covalent radii* are needed for calculations (*cf*. Sanderson 1951, and Table 2).

In this case, atoms and their electronic shells are separated conceptually from their environment, that is, from their chemical vicinity. Since the measurement of electron affinities and ionization potentials requires isolated atoms, it becomes possible—through Eq. (7), for example—to derive electronegativities even for noble gases. On the one hand, this might be considered an advantageous achievement as far as atomic physics is concerned, because it expands the set of actual measures and closes a perhaps unattractive gap in the periodic table. On the other hand, this extreme abstraction could as well be regarded as a theoretical weakness, as far as chemistry and the reactivity of substances are concerned.

As is well known, the lower atomic number noble gases do not form compounds (the heavier ones do, but only very few and under extremely artificial conditions). For those elements, even simplified calculations of "electronegativities" (like those we inferred from ionization energies only, "abstracting" from electron affinities) yield reasonable results in comparison with more sophisticated approaches (see Table 3). The deviation range is not significantly different from those found in Table 2. Moreover, we actually do not have a rigid criterion to decide which of the two approaches might give the "true" values. However, the electron affinity values do indicate that noble gas atoms show just the opposite behavior than that expected for entities of that high electronegativity, because they do not tend to take up additional electrons at all. Hence, if electronegativity is considered the property of atoms to attract electrons during chemical interactions, then the removal of the "interactive" part of this concept distorts the original intention.

Besides the classical *object-related* point of view discussed here, there is a *quality-related* perspective. According to Hasok Chang: "A *quality* is *observable* if it can be registered by human sensation and the claim of registering that quality is not destroyed by the withdrawal of *optional interpretations*. *Observation* is an act of gathering information by human sensation without optional interpretations." (Chang 2005, p. 879; emphases in the original). Which are the qualities connected to electronegativity? Is electronegativity a quality in its own right? By contrast to other paradigmatic examples such as temperature, acidity, hardness and laminarity (in streaming liquids), there is no manifest correlate here (Table 4). Moreover, electronegativity is non-observable because we need interpretations to characterize it both qualitatively and quantitatively. Additionally, it is not directly measurable. Hence, electronegativity is *derived* theoretically from sophisticated measurement results (which may carry their own specific issues with respect to the theory of measurement and operations, see below).

Table 3 Noble gas electronegativity values according to Mulliken (Eq. 7), and calculated from ionization potentials alone (reference assumption: $\chi_{Fluorine} = 4.0$), and electron affinities (E_{ea})

Element	"χ" (ionization potential only)	χ (Mulliken)	Electron affinity (E_{ea}/kJ/mol)
He	5.65	–	−21
Ne	4.95	4.60	−29
Ar	3.62	3.36	−35
Kr	3.21	2.98	−39
Xe	2.79	2.59	−41

Note that the latter have to be read conversely to the common convention for energy measures: negative values mean endothermic processes (values from Atkins and de Paula 2013)

Table 4 Qualitative comparison of selected quantified scientific concepts

	"Direct" measurement	Clear definition	Level of abstraction	Manifest correlate
Electronegativity	No	No	High	No
Temperature	Yes	Yes	Low	Yes
Acidity	Yes	Yes	Low/High	Yes
Hardness	Yes	Yes	Low	Yes
Laminarity	No	Yes	Medium	Yes

Of course, observability is not a necessary condition for a phenomenon to be characterized as a proper chemical property (like, for example, the oxidation number). Nevertheless, for the sake of a better understanding and differentiation of scientific concepts, we follow Chang's characterization and consider electronegativity a non-observable quality. Summing up, we conclude that electronegativity makes reference particularly to the disposition of atoms to attract bonding electrons. On the one hand, this atomistic description shows a tendency to be overdone, in that it leads to an *absolute* and purely physical account, which is more easily available by other means and makes no sense with respect to *relational* chemical purposes (noble gases). On the other hand, its results can be transferred to depict higher class entities (elements), as well.

Historical stability

Electronegativity is a very persistent chemical concept: "…its modern history spans about 50 years. But even to this day there is no definite answer to the question, what is electronegativity? Why electronegativity is so useful to chemist? And why has it had such a long existence?" (Mullay 1987, p. 2). Hence, taking into account that basic relational behavior of chemical kinds can be explained in roughly the same way by another, simpler, and more direct means, the widespread acceptance as a reasonable, quantified, and unified chemical concept and the ongoing interest in theoretical chemistry are quite surprising. There is a pragmatic value on the one hand, and a strong theoretical belief in a fundamental property on the other, which might explain the persistence of electronegativity.

The pragmatic value of electronegativity unfolds in the educational realm—where only the relational scales are used—and in the description and explanation of reaction mechanisms. The concept is supported and stabilized particularly by the construction of easy algorithms to refer to relational matters, and by the obviously easy way to accommodate it to periodicity trends.

Certainly, the applicability of the concept of electronegativity to a multifarious bunch of reference items—substances, elements, molecules, atoms, radicals, ions and orbitals—and the diverse ways to obtain at least roughly similar numbers are very fascinating. The continuing and uninterrupted interest in electronegativity in theoretical chemistry is driven by the intention of improving the value standards reached so far. As the definitions of chemistry in textbooks of the last centuries indicate, the trend goes from stuff-related via element-related to particle-centred descriptions. With the advent of quantum chemistry in the second and third decade of the 20th century, the notion of substance (stuff) increasingly has been neglected and the interest in microstructures, electronic functions, and calculational methods has come to the fore (cf. Ruthenberg and van Brakel 2008). Following that

trend, today many chemists take an essentialist point of view with respect to the sub-microscopic entities and properties debated in chemistry. From this viewpoint, electronegativity is a constant and intrinsic property of natural kinds and thus something natural in its own right (Leach 2013). This common belief and the pragmatic strength in the classificatory and taxonomic fields stabilize the concept.

On the other end of the spectrum, on the basis of the ambiguous status of electronegativity, some scientists even deny that it is a proper theoretical achievement: "Interpretative chemistry still operates in terms of empirical concepts such as electronegativity and molecular shape, commonly said to be without theoretical underpinning. Admittedly, there are those who pontificate against the use of such classical concepts, while remaining singularly unsuccessful themselves to account for the predictive powers of these ideas, or to provide alternatives that are theoretically more soundly based" (Boeyens 2003, p. vi). Here, by "empirical concepts" obviously "premature concepts" are addressed. Consistently, the ab initio effort tries to eliminate or replace electronegativity by other—allegedly more mathematized and thus more appropriate—concepts such as chemical potential. As a result of the impossibility to accomplish this deduction, electronegativity for some quantum chemists cannot be a real property: "Purportedly introduced two centuries ago by Berzelius, it still features in many theories, albeit like the concepts valence, bond and structure, without 'first principle underpinning'. This means that they are not represented by quantum–mechanical observables, have served a noble purpose in the past and are now obsolete" (Boeyens and Du Toit 1997, p. 296). Nevertheless, systematically the quantum-related approaches have not yet shown that they are more accurate and applicable than the "classical" approaches without "first principle underpinning". On the contrary, chemical properties do not necessarily need any specific and particular physical certification to acquire scientific and philosophical legitimacy.

Experimentation

How could an ill-defined, unobservable entity like χ be quantified? To begin with, we wish to express our understanding of some pertinent notions: By *quantification* we mean the act of attaching numbers, including or excluding algorithms, to attributes, and by *measurement* we mean the application of instruments in order to correlate at least two attributes of empirical systems.[10] By *direct measurement* we mean one-step operations that aim at an undisturbed translation of one attribute into another. According to this interpretation, for example, melting points, ionization potentials, stuff concentrations, temperature, and hardness are measured directly, whereas quantities of numerical character, as for example electronegativity, are *measured*—better: inferred—indirectly (*cf.* Table 4). The distinction between quantification and measurement makes possible to differentiate between cases in which instrumental devices are applied directly and with the purpose of obtaining or producing knowledge and those cases in which calculations, graphical representations, curve fitting, and the like, prevail. Hence, we consider quantification as theoretical data processing, and measurement as performance of instrumental operations. Customarily, measurement comes first and quantification makes use of its outcomes. According to this

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[10] We borrow the latter part of these attempts to characterize the central expressions from Heidelberger (1994). The author argues in favor of a correlative interpretation of the representational theory of measurement. That correlative interpretation has the advantage that any measurement depends on specific properties of certain representatives.

and with respect to our topic, what is actually measured is not what is listed in χ-scales. What we have here is rather a calculational interpretation of measures obtained for different purposes.

There is another important aspect. Regarding the measurement of temperature and the issue of "making contact between thinking and doing", Chang states: "Operationalizing an abstract theory involves operationalizing certain individual concepts occurring in it, so that they can serve as clear and convenient bridges between the abstract and the concrete." (Chang 2004, p. 197). With respect to the graduation of the temperature scale, Ernst Mach (1900, p. 46) claimed that the number assigned to a state of heat is called temperature; he called the criterion for that assignment *Zuordnungsprinzip* (*principle of coordination*). Whereas there is a manifest—sensible—correlate (heat) for the concept of temperature, such a correlate is missing in the case of electronegativity.

Moreover, there is another general issue here: scientific scales are derived with a certain arbitrariness. Although Chang's view was designed to cover the direct measurement of a physical quantity like temperature, we take it as the suggestion of identifying the mentioned "bridges between the abstract and the concrete." According to these poles, it is clear that there are several layers of abstraction here. In order to gain a richer picture of experimental aspects, it is helpful to take a closer look. One part of the operational side of the derivation of Mulliken's χ-value can be described as follows. If we consider an arbitrary portion of elemental stuff to be the concrete starting point, then the preparation/purification of this portion needs an operational input. After preparation, this portion is brought into a glass apparatus, evaporated (under low pressure, which has to be made sure by some calibration as well), and set under an increasing electric potential (which is the coordinative measure) until dissociation takes place. This dissociation results in free electrons and atomic cations, and causes a jump in the electrical current the serves as an indicator. Since the experiment is performed at high temperatures, the current has to be registered, and the results have to be corrected, usually by calculation, with respect to standard temperature. This is an abbreviated version of the description of only one operational part of what is necessary to infer electronegativity values following Mulliken (the other is electron affinity, see Eq. 7). Considered and interpreted in isolation, we could assign the measuring role to the electric potential, the measured role to the ionization potential, and call the whole process an *operational bridge.* However, there is a very long way from here to an operational bridging between the *abstract* concept of electronegativity and the *concrete* elemental stuff. Mulliken's concept contains the measurement of ionization potentials as one *local* operational bridge, and the measurement of electron affinity as another. Hence, both parts might be describable in the way Chang suggests. How the complete algorithm should be represented operationally, however, is unclear. As far as we can see, there is no obvious and direct path from the abstract idea of "the power of the atoms of an element to draw electrons to itself when it is part of a compound" to the manifest, empirical world. As to electronegativity, van Fraassen's "Clausewitz doctrine" comes to the fore.[11]: It is rather the theorizing that carries constructive aspects to the experimentation than the other way around. Nevertheless, we should keep in mind that "operationalization is the act of creating operational meaning where there was none before." (Chang 2004, p. 197)

Referring to the "measurement" of psychometric constructs, Eran Tal also is critical with respect to the general applicability of an epistemic iteration. Tal raises questions like

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[11] "It makes the language of construction, rather than of discovery, appropriate for experimentation as much as for theorizing" (van Fraassen 2008, p. 112).

"Are the questionnaires measuring what they should?" (Tal 2013, p. 1163), and proceeds: "It is doubtful whether these questions can be answered through a process of iterative stabilization similar to the one encountered in the standardization of physical quantities." We consider that, in the general field of natural sciences, the quantification of concepts might run into similar problems. Thus, regarding electronegativity, we might transfer Tal's question into the following: "Are the approaches represented in the equations discussed here measuring what they should?" Lacking any neutral reference, such a question is not easy to answer. Too quickly we might be satisfied with the tidy and welcome conversion of the χ-values from different scales. It might well be, because we constructed, at least in part, both theories and experiments, that we prepared just those aspects into the whole approach which we now find tidy and welcome. Whether we are in fact addressing "the power in chemically bound atoms to draw electrons" and how this might be done, however, is indeed a process of interplay and negotiation between theoretical and empirical efforts.

Since electronegativity manifestly has at least some typical aspects in common with comparative dimensionless numbers from the applied and engineering sciences, we shall briefly consider these aspects to round up the picture. One example, very well introduced in chemistry, is the pH for the characterization of acidity or basicity of the Brönsted/Arrhenius type in aqueous solutions. Its value is dimensionless because it is defined as the logarithm of the molar concentration of hydrogen ions (times minus one). Hence, although this number is an "observable in disguise", it is derived by a simple algorithm from a direct and intentional determination, and the reset into the measured value and the translation into the corresponding meaning are quite easy. Clearly, pH and electronegativity are different in several systematic respects (see Table 4). First, due to the lack of a clear definition, the derivation of electronegativity as a dimensionless number is not as close to the concrete measurement and not as clear-cut (Eqs. 1–8 and Table 2). Second, the abstraction level for electronegativity goes many steps beyond that for pH-acidity (this is not to claim that the involved measurement processes are simple and clear.[12]) Third, corresponding to that and other abstractions (cf. Chang 2012), we cannot denote any manifest correlate for electronegativity.

Conclusions

The most important points and results of this investigation can be summarized as follows:

- Electronegativity is an extremely successful but ill-defined heuristic concept for the description of central properties of entities in the dappled chemical world.
- It is rather a theoretical construction than a natural property. That is, it is "produced" and can by no means be measured directly.
- Historically, there is a general trend from "relational" to "absolute" methods, that is, towards abstraction, mathematization, and quantum modelling; the more "stuffy" the method is, the more complicated the derivation of electronegativity values, and the more "quantum" the approach, the more remote are quotidian, directly observable stuff properties. This tendency follows the main historical trend in the theoretical sections of the chemical sciences –the main trend for about the last two centuries.
- With respect to the most relevant applications, and in chemical education, the relational models prevail.

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[12] The measurement of acidity has its own problems and peculiarities, cf. Chang (2012).

- With respect to the needs regarding the main concept's applications (description of polarities and bonding modes in substances, depiction of oxidation numbers, explanation of reaction mechanisms and acidity, etc.), the mathematization of electronegativity—particularly in the absolute approaches—is excessive and tends to lead to *apparent scientificity*.
- The extension of electronegativity scales to species without specific chemical behavior (noble gases) is a theoretical exaggeration.
- Electronegativity is a dimensionless number that—like other measures in the applied sciences—has a complex referential background. It is conceptually rooted in the realm of chemical reactivity on the one hand, but it is supplied by the physics of isolated particles on the other.

Despite certain disadvantages of the concept (excessive mathematization, restricted applicability, inadequate extension, unmeasurability), Mullay is right when he states: "Electronegativity is an important part of the intuitive approach to understanding nature that sets chemists off from other physical scientists" (Mullay 1987, p. 2). The persistence of electronegativity rests on the unquestioned—and ill-founded—belief that it is a natural property, and on pragmatic simplifications, which are very helpful in everyday work on chemical *reactivity* in offices, laboratories, and classrooms, and which are typical—if not necessary—for chemists.

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