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Charge Concepts

A Piece of the Picture—Misunderstanding of Chemical Concepts

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1. Prologue

"*What is the relationship between static electric charges and oxidation states? None.*" This striking claim can be found in a recent issue of one of the most attractive scientific journals[1] and stems from a series of first-principle calculations on the charges of individual transition-metal atoms embedded within an extended solid-state matrix; ionic, covalent, and intermediate bonding situations were considered.[2] A change in the total electron count of the system (compensated for by a universal background charge) is equated with a change in the oxidation state of the transition-metal atom. It is found that the effective local charge changes only slightly; hence, the usefulness of the term "oxidation state" is called into question.

Informed chemists will rub their eyes in astonishment; apparently even in today's world great attention can be attracted when preaching to the saved. At the same time, however, it is particularly strange that the line of argument with which the term "oxidation state" is questioned also rests on somewhat shaky foundations. How could it even come to this? As all so often, there are many reasons. To begin with, the scope of definition of the widely used and well-defined term "oxidation state"[3] is disregarded. However, in this case, the misconception has much deeper roots. It assumes that quantum mechanical calculations (first principle) of the electronic structures of chemical compounds can be transferred to common chemical concepts without bias. Yet such a strategy appears inevitable; a mathematical description or simulation of a natural phenomenon does not automatically give rise to a conceptual structure, nor does it establish "understanding".[4] Nevertheless, the price to be paid for a conceptual description of the "real" world is high; at the very least, it entails a loss of accuracy and detail; in more extreme situations, it may involve a complete distortion of the subject matter. To minimize these risks, the concepts need to be defined as precisely as possible, and these definitions must always be kept in mind during applications.

2. Heuristic Concepts in Chemistry

The atomic model of the structure of matter, the discovery of numerous chemical elements and their grouping into the periodic table, the formulation of chemical thermodynamics and kinetics, and the development of basic concepts of chemical bonding and the rationalization of chemical constitution form the foundation of modern-day chemistry. In fact, the principles underlying these concepts were already being unlocked in the 19th century. A laudable accomplishment in all these endeavors was the manner in which conclusions drawn about the microscopic (atomic) world rested upon experimental observations made at the macroscopic scale, which were often inaccurate or incomplete. Thus, the approach was inductive; that is, facts were collected and grouped according to certain criteria (which were not necessarily based on causal relationships), and general conclusions were drawn. Only now is this very successful approach being complemented by the deductive method.[5]

Many of the ordering principles and concepts employed in chemistry today can be traced to the early stages of the field, notwithstanding the significant developments, refinements, and extensions made during the following century. These include concepts relating to various kinds of atomic increments, for example, electronegativity, effective radii, volume increments, coordination numbers, and several definitions of atomic charge. These concepts remain invaluable when it comes to mastering the sheer complexity of chemical matter, for example, in the structuring of current knowledge, consideration of new observations, and finally as pedagogic instruments. They have been compared to unicorns,[6] which, although they belong to the realm of fantasy, are considered symbols of law, order, health, and fortune in an otherwise chaotic world. Yet inasmuch as these heuristic concepts of chemistry are useful for the specialist, a great deal of confusion can result when they are used in the wrong context or beyond their proper scope. A good example is the superficial manner in which the various definitions of atomic charge are sometimes handled.

We ordinarily distinguish between ionic charge, oxidation state (synonymous with oxidation number), formal charge, and effective charge, the last of which can be determined in a number of different ways.[7] The *ionic charge* is the

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least ambiguous; it defines the charge of an ion as observed in electrical transport experiments; it can only take on an integral multiple of the elementary charge. The term *oxidation state*, as the name suggests, is derived from the differing number of oxygen equivalents that an element can bind to; this early definition was given by F. Wöhler.[8] There are now strict rules for the calculation of oxidation states.[3] It is a purely formal concept; nowhere within the definition is it claimed that a particular oxidation state can be associated with a real charge. Nevertheless, the term is certainly useful, since a specific oxidation state can be correlated to real properties. Thus, it is possible to determine differences in oxidation states as whole numbers through redox titrations. A particular oxidation state of a transition metal can be attributed a specific number of unpaired electrons. Moreover, typical values of effective atomic radii and preferred coordination numbers, as well as characteristic coordination polyhedra, are coupled to the oxidation state of an element. Finally, oxidation states are commonly used in the balancing of chemical equations. The term *effective charge* creates the impression of a physically well-defined value; however the opposite is true, as it is impossible to objectively state the true charge of an atom embedded within a particular chemical environment. To do so would require the nuclear charge to be balanced against the number of electrons belonging to the respective atom, and this is only possible if a well-defined portion of space (along with the electrons inside it) can be attributed to the atom in consideration. However, defining such boundaries between atoms in a chemical compound is prone to bias, since there are no objective criteria available by which to do this. In fact, the same dilemma also arises during the experimental determination of effective charges, as the characteristic ranges of the various experimental probes vary, and each delineates a particular volume by chance. Lastly, the term *formal charge* is used in the representation of molecular structures in the Lewis convention for the purposes of electron bookkeeping; the term does not carry any physical meaning.

3. Quantum Mechanical Descriptions of Chemical Systems and their Interpretation

The heuristic concepts described above were established without fully understanding the physical principles underlying the interactions between electrons and atomic nuclei. This understanding would have to wait until the development of quantum mechanics, which led to the Schrödinger equation.[9] This equation is the basis for a first-principle description of chemical systems. Nevertheless, the pre-quantum-mechanical concepts have survived. The first reason is the fact that the exact wavefunction as a solution to the Schrödinger equation is practically impossible to determine for multielectron systems. The development of the approximation methods that are necessary to address this problem was inspired by these pre-quantum-mechanical concepts;[10] for example, the notion of the electron-pair bond was used during the development of the "valence bond" method.

However, the second reason is more important. With the Schrödinger equation, chemistry becomes structureless; each chemical system is described by its own wavefunction. In fact, the calculation of a wavefunction does not automatically allow for the molecule or solid to be attributed to a specific category, such as polar, nonpolar, saturated, unsaturated, electron-deficient, and so forth. For such an assignment, some sort of mapping of the relevant wavefunction must be made for the corresponding chemical concept. On the other hand, the validity of a concept can be assessed by checking whether this map is realistic and makes sense. Which procedure should be used to obtain the corresponding map is, however, a matter of dispute. The *Faraday Discussions 135*,[11] which took place in September 2006 in Manchester, suggested a number of methods (*Chemical Concepts from Quantum Mechanics*) without laying an end to the debate. Moreover, many concepts cannot be derived from theory reduction from the principles of quantum mechanics (e.g. Ref. [12]), because they were introduced heuristically as ordering criteria.

In this Essay, the main focus will be on oxidation states, which also belong to the category of heuristic ordering criteria and thus cannot be derived directly from the wavefunction. At best, specific numbers can be obtained through quantum chemical calculations by defined procedures; these values are related to charge and can thus be correlated to the oxidation state. In this case it is pointless to think too much about the physical meaning; it suffices to consider pragmatically the usefulness of the correlation. However, pragmatism is always a bit arbitrary!

A large number of different methods is available by which atomic charges can be determined, and it is beyond the scope of this Essay to discuss them all here. A comprehensive overview is given in the work of Meister and Schwarz.[7] For the sake of argument, we will only consider two methods by which atomic charges may be derived from quantum chemical calculations. The first of these is based on the LCAO (linear combination of atomic orbitals) method and can be traced back to Mulliken.[13] The charges are determined by analysis of the occupancies of atomic orbitals (population analysis). The extent to which this approach depends on the choice of basis set can be reduced by a projection onto a minimal set of modified atomic orbitals (MAO).[14]

An alternative strategy is the division of position space into regions that are allocated to individual atoms. The charge of the atoms is determined by integration of the electron density within their respective regions. Topological analysis of the electron density (atoms in molecules,[15,16] AIM) ensures that the regions are non-overlapping and space-filling. This method is not only useful for quantum chemical calculations but also for analysis of experimentally determined electron densities (c.f. Ref. [17]).

In Table 1, calculated atomic charges for simple compounds obtained through both Mulliken and AIM methods are compared with the oxidation states. Of course these numbers are nothing new; they are only given to illustrate the points made herein. As expected, neither of the methods gives the correct oxidation state, and no mathematical relationship between the calculated charge distributions and oxidation states is found. Even a mere correlation be-

Table 1: Oxidation states and calculated atomic charges of various molecules and of MgO as an example of a solid. Details of the calculations are given in the Supporting Information.

Basis		Oxidation state	Calculated atomic charges Mulliken[13] Minimal	 Mulliken Extended	 AIM[15] Extended
SF_6	S	+6	+1.02	+1.21	+3.89
	F	−1	−0.17	−0.20	−0.65
SO_2	S	+4	+0.53	+0.68	+2.38
	O	−2	−0.27	−0.34	−1.18
H_2S	S	−2	+0.04	−0.20	+0.05
	H	+1	−0.02	+0.10	−0.02
CO_2	C	+4	+0.28	+0.37	+2.25
	O	−2	−0.14	−0.18	−1.12
CO	C	+2	+0.12	−0.03	+1.18
	O	−2	−0.12	+0.03	−1.17
CH_4	C	−4	−0.31	−0.41	−0.07
	H	+1	+0.08	+0.10	+0.02
MgO(f)	Mg	+2	+0.62	+1.80	+1.73
	O	−2	−0.62	−1.80	−1.73

comes progressively less meaningful as the bonding in the molecule or solid becomes less polar. At least for polar cases, Mulliken population analysis yields charges that are proportional to the oxidation states, despite the fact that the absolute values are much too small. In the case of the AIM method the calculated charges are larger and thus give rise to greater charge separation, a trend which is also confirmed by a factor analysis of a wide range of reference materials.[7]

In light of the poor agreement, the question naturally emerges: does it even make sense to correlate atomic charges with oxidation states? Our answer here is that yes, it does! There are a series of well-known relationships between oxidation states and specific physical quantities. If new compounds in which the oxidation states of the components are not apparent are to be described using such a scheme, the determination of atomic charges and a correlation with oxidation states would be very helpful. An example of this approach would be the shift of the Pt($4f_{7/2}$) band in the ESCA (electron spectroscopy for chemical analysis) spectrum of a compound in comparison to elemental platinum. In the case of positive oxidation states of platinum, a shift of approximately 1.2 eV per step is observed.[18,19,20] However, a series of new binary platinum compounds Cs_2Pt,[21] BaPt,[22] Ba_3Pt_2[23] and Ba_2Pt[24] exhibit platinum in a negative oxidation state, and in these Ba–Pt compounds, a shift of the $4f_{7/2}$ band to smaller energy values was in fact measured;[25] this shift correlates well with the calculated AIM atomic charges (Figure 1). Yet the actual oxidation states of the elements in these compounds are not at all intuitive; only a precise analysis of the bands at the Fermi surface (e.g. delocalized electrons in the interlayer region in Ba_2Pt) and the covalent interactions between Pt atoms (one-dimensional chains in BaPt, Pt_2 dumbbells in Ba_3Pt_2) leads to a consistent formal description: $[\mathrm{Ba}(2+)\cdot e^{-}]\cdot\mathrm{Pt}(-)$, $[\mathrm{Ba}(2+)_{1.5}\cdot 1.5e^{-}]\cdot\mathrm{Pt}(1.5-)$, and $[\mathrm{Ba}(2+)_2\cdot 2e^{-}]\cdot\mathrm{Pt}(2-)$. These examples highlight the need for factors other than calculated charges to be taken into consideration in order to obtain a meaningful connection with oxidation states.

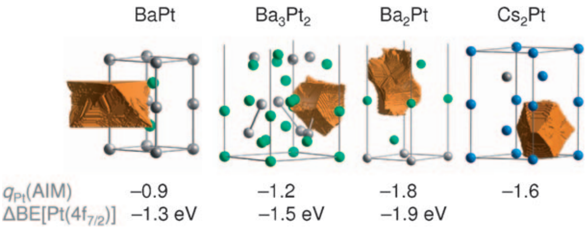

Figure 1. Atomic basins (AIM)[15] of platinum, AIM atomic charges q_{Pt}(AIM), and shifts ΔBE in the Pt($4f_{7/2}$) band relative to elemental platinum for four different binary platinum compounds.[21–25]

4. "Charge self-regulation upon changing the oxidation state of transition metals in insulators"[2]

The authors of the cited work[2] investigated semiconducting and insulating host lattices, such as GaAs, Cu_2O, and MgO, with transition metals as defect atoms. They first present a qualitative molecular-orbital picture. The states of the whole system are characterized in different ways. Those in which the contributions of the transition-metal atoms dominate are denoted CFR (crystal field resonance), while those for which the contribution of orbitals from host-lattice atoms dominate are denoted DBH (dangling bond hybrid). The authors assume that a variation in the occupancy of transition-metal orbitals also changes the character of the bonding and antibonding states of the whole system. With increasing occupancy of the atomic orbitals of the transition metal, the DBH states become bonding (and thus increasingly occupied) while CFR states become antibonding (and occupancy decreases). They call this effect the *self-regulated response*, which essentially keeps the local charge at the transition-metal atom constant.

These qualitative considerations are plausible, and the associated charge balancing is confirmed by DFT calculations. The calculations were performed for supercells of the host compounds containing 64 to 128 atoms in which one of the cations is replaced with a transition-metal atom. Variable electron counts in the entire system were compensated by a universal background charge to maintain charge neutrality. These calculations are fine, but the way in which the atomic charge of the transition metal is derived is questionable, as it involves integration of the electron density in a sphere with an arbitrary radius of 1.3 Å. The "effective range" of the dopant atoms will vary from one transition metal to another and will also vary as a function of the host compound used and of the total electron count for the system. From Figure 5 of the work it can be seen that the differences in electron density for a system with varying electron counts will give positive and negative values at the transition-metal center, and the integral value will certainly depend on the choice of radius. To what extent the choice of the radius influences the results is not clarified.

Although the work of Raebiger et al. is certainly interesting, what does it actually have to do with the term oxidation state that appears in the title? By definition, the oxidation state depends on all of the atoms in a system. In the case considered, the system is defined by the atoms of the host crystal, the dopant atom, the total electron count, and the compensatory background charge. So how do these various factors influence the choice of oxidation state that is attributed to the transition-metal atom? For a given structure the atom types remain the same, independent of the charge of the whole system; thus, by definition, the oxidation states must remain unchanged by this factor. The background charge likewise does not change the oxidation states, since it is not localized and cannot be attributed to a single atom. The only factor, then, that could lead to a change in oxidation state is the total electron count, provided that the effect is localized on individual atoms. This, however, is not the case, as Figure 5 in the work shows. The electron density differences make it clear that the distinction between CFR und DBH states, as laid out in the formal considerations at the outset, is not possible in real systems. Therefore, the allocation of different oxidation states for the transition-metal atoms upon variation of the total electron count is highly questionable. Our criticism of the work discussed is thus based around exactly the two points (determination of atomic charges and allocation of oxidation states) that Resta[1] highlights in his commentary, in which he tries to make us rethink this matter.

5. Concluding Remarks

An ensemble of atoms, be they discrete molecules or extended solids, always reacts collectively. Although we can attempt to describe the role of an individual atom, the degree of incrementalization required is always going to be somewhat arbitrary. Certainly objective methods for the derivation of increments, such as the allocation of charges or coordination numbers, are helpful, providing that dissimilar compounds are compared in an unbiased manner. But even here there are limits on the extent to which comparisons can be drawn, and these should always be kept in mind.

The values obtained for atomic charges from quantum chemical calculations vary strongly, depending on the method. It depends on the method, along with the nature of the system in consideration, whether a correlation of the obtained values with oxidation states makes any sense. This is a well-established fact, and it is illustrated by the values in Table 1. The results presented in the work of Raebiger et al. do not contradict this fact; however, the conclusion they present about the relationship between charge and oxidation state ignores the definition of the latter term and thus is less than convincing. Therefore, the response to the work,[1] which encourages us to reform our way of thinking and throw our basic school education out the window, is rather far-fetched.

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