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# Oxidation states and ionicity

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The concepts of oxidation state and atomic charge are entangled in modern materials science. We distinguish between these quantities and consider their fundamental limitations and utility for understanding material properties. We discuss the nature of bonding between atoms and the techniques that have been developed for partitioning electron density. While formal oxidation states help us count electrons (in ions, bonds, lone pairs), variously defined atomic charges are usefully employed in the description of physical processes including dielectric response and electronic spectroscopies. Such partial charges are introduced as quantitative measures in simple mechanistic models of a more complex reality, and therefore may not be comparable or transferable. In contrast, oxidation states are defined to be universal, with deviations constituting exciting challenges as evidenced in mixed-valence compounds, electrified and highly correlated systems. This Perspective covers how these concepts have evolved in recent years, our current understanding and their significance.

The concept of *oxydationsstufe* was developed over two centuries ago to describe the observed reactions of elements with oxygen<sup>1</sup>. Such chemical reactions are quantized, with distinct changes in structure and properties as more oxygen is bound by an element (for example,  $6\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + 2\text{O}_2$  or  $3\text{Fe}_2\text{O}_3$ ). The modern oxidation state is defined as “the degree of oxidation of an atom in terms of counting electrons”, where the nominal counting of electrons is performed following an agreed set of rules.

This Perspective focuses on chemical bonding in solids, where discussion almost invariably makes reference to oxidation states, ionicity, covalency and charge distributions, which are indeed powerful concepts across the chemical sciences. Despite their widespread use, however, there are uncertainties and ambiguities about these concepts and their interrelationships. The debate became so heated in the 1960s that there was a sequence of three publications in *Nature* on this topic arguing different perspectives: Goodman discussed the role of atomic electronegativity in the distribution of electrons in solids<sup>2</sup>, Mooser and Pearson emphasized that bond ionicity is a theoretical concept that depends on the approximation employed<sup>3</sup>, while Cochran focused on what can and cannot be measured in practice<sup>4</sup>.

As argued previously, the concept of ionicity in solids remains intrinsically ambiguous<sup>5</sup>: charge distributions can be calculated and measured with growing accuracy, but there are several different plausible schemes for their partition between the component atoms. Alternative definitions and measures of ionicity are necessary to describe other properties—for example, dielectric response—which depend on charge distribution. Further difficulties arise when the equilibrium charge distribution is linked to oxidation state. We may agree that a molecule or solid has a metal in its highest accessible oxidation state, but experiment and theory will often reveal significant electron density in its valence shell orbitals.

Debate continues on the topic and is indeed very much alive<sup>7–10</sup>. We attempt to address these problems and show how charge distribution and oxidation state interrelate and can be meaningfully used. We further discuss cases where genuine ambiguities and challenges exist for mixed-valence compounds, as well as new generations of quantum materials at the frontier of materials science.

## Utility of formal oxidation states

Electron counting is at the heart of our understanding of, and approach to, chemical bonding<sup>11</sup>. In the simplest example, two hydrogen atoms (one-electron species) interact through a two-electron covalent bond formed by filled bonding and empty antibonding orbitals. In the solid state, a similar case would be crystalline silicon, where two-electron two-centre covalent bonds are formed between nearest-neighbour silicon atoms in a periodic structure. In both cases, effective charges are usually assumed to be zero. The valence number can, however, be defined as I (hydrogen) and IV (silicon), which represents the number of electrons involved in (or available for) chemical bonding.

The combination of a metal with a more electronegative element can be described by the formation of an ionic (or heteropolar) bond. One such case is LiF, where one-electron transfer from Li ( $1s^2 2s^1$ ) to F ( $2s^2 2p^5$ ) results in closed-shell  $\text{Li}^+$  ( $1s^2 2s^0$ ) and  $\text{F}^-$  ( $2s^2 2p^6$ ) electronic configurations. While one can assign different effective charges to Li and F, the formation of a complete closed shell around F and the depletion of the valence charge density around Li are unambiguously detected by experiment and electronic structure calculations. Perhaps the most important observation here is that the electron associated with Li and all of the originally five *p* electrons of F take part in the resulting valence shell of the compound. Following simple octet rules for forming a closed-shell (diamagnetic) compound, the outcome we described can trivially be predicted for more complex chemical compounds.

These examples of both covalent and ionic interactions can be conveniently described using formal oxidation states. The value of oxidation state for each atom in a solid can be assigned following a set of rules (Box 1)—for example, the oxidation state of an atom in its elemental standard state is 0. A less trivial example is a multicomponent solid such as the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Here, the oxidation state of O is  $-2$ , which means that the sum of oxidation states for  $\text{Y} + 2\text{Ba} + 3\text{Cu} = 14$  to provide the electrons involved in the bonding with oxygen. The common oxidation state of Y is  $+3$  and that of Ba is  $+2$ , so seven electrons need to be donated by three Cu atoms (assuming complete reduction of oxygen). The common oxidation states of Cu are  $+2$  as in

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## Box 1 | Assigning formal oxidation states

The oxidation state represents “the degree of oxidation of an atom in terms of counting electrons”<sup>2</sup>. For the simplest cases, the octet (eight-electron) rule is sufficient for electron counting, where atoms are assigned octets in order of decreasing electronegativity until all valence electrons are distributed. The resulting atom charge then represents the oxidation state. For example, when Zn ( $3d_{10}4s_2$ ) and O ( $2s_22p_4$ ) are brought into contact to form ZnO, the octet of O is completed ( $2s_22p_6$ ) with oxidation state  $-2$ , while Zn adopts a  $3d_{10}4s_0$  configuration with oxidation state  $+2$ .

A set of more general rules for determining oxidation states are provided in undergraduate chemistry textbooks. For example, following those given in ref. 55:

1. The sum of oxidation states for all atoms in the species is zero to ensure electroneutrality
2. Atoms in their elemental form: 0
3. The available valence electrons follow the group in the periodic table. For example, atoms of group 1:  $+1$ . Atoms of group 2:  $+2$ . Atoms of group 3:  $+3$ . Atoms of group 13:  $+1$  (lled  $s_2$  lone pair) or  $+3$ .

cupric oxide (CuO) and  $+1$  in cuprous oxide (Cu<sub>2</sub>O). The unusual electron count in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> requires either an additional electron removed from Cu (oxidation) to the  $+3$  state or a hole stabilized on oxygen—often described as a polaron—which leads to its exotic condensed matter physics<sup>12</sup>. This conclusion is made in the absence of any substantial input from theory or experiment, but is crucial in understanding the properties of the material, and demonstrates the importance and power of these simple approaches.

While these concepts are easily transferable to the important area of mixed-anion compounds<sup>13</sup>, more involved consideration of the structure and bonding is required for the cases of polyion systems, where groups of atoms form sub-units that carry a formal charge. In BaSi, the usual oxidation states of Ba  $+2$  and Si  $-4$  fail to deliver a charge-neutral stoichiometric unit; however, the structure contains chains of covalent Si–Si bonds, where each Si adopts a  $-2$  oxidation state. For Ba<sub>3</sub>Si<sub>4</sub>, discrete Si<sub>4</sub><sup>6-</sup> polyanions are formed with internal Si–Si bonds, which ensures charge neutrality when combined with three Ba  $+2$  cations. There have been recent applications of such Zintl compounds in the field of thermoelectrics<sup>14,15</sup>.

Beyond predicting the outcomes of chemical reactions and the stoichiometry of compounds, oxidation states also have a utility in the description of physical properties. Oxidation states underpin a number of successful heuristic tools in molecular and solid-state chemistry, including the valence-shell electron-pair repulsion (VSEPR) theory for predicting structure<sup>16</sup>, and ligand and crystal field theory for predicting structure and spectroscopic response, in particular of transitional metal complexes and materials<sup>17</sup>. One example is Mn, of which there are seven positive oxidation states, where Mn(VII) corresponds to the removal of all of the valence electrons and formal configuration of  $3d_0$ . In the solid state, MnO corresponds to Mn(II) ( $3d_5$ ), where the high spin state of  $5/2\hbar$  is observed, while MnO<sub>2</sub> contains Mn(IV) ( $3d_3$ ), with a corresponding high spin state of  $3/2\hbar$ . The intermediate case of Mn<sub>2</sub>O<sub>3</sub> contains Mn(III) ( $3d_4$ ), which is Jahn–Teller active and results in a frustrated magnetic interactions in its ground state bixbyite crystal structure<sup>18</sup>. Each of these oxidation states of Mn can be distinguished from their distinct spectroscopic and magnetic signatures<sup>19</sup>.

Assigning formal oxidation states allows us to understand and rationalize key properties of the materials, but it is not a statement about effective charge: assigning an oxidation state of  $+7$  to Mn

4. Hydrogen in compounds with non-metals:  $+1$  (hydron) and with metals:  $-1$  (hydride)
5. Fluorine:  $-1$
6. Oxygen:  $-2$  unless combined with fluorine,  $-1$  in peroxides ( $O_2^{2-}$ ),  $-1/2$  in superoxides ( $O_2^-$ ) and  $-1/3$  in ozonides ( $O_3^-$ )
7. Halogens:  $-1$  unless other elements include O or more electronegative halogens

These rules are sufficient for assigning oxidation states of most solids, but there are caveats and a number of interesting exceptions are discussed in the main text such as in polyion and mixed-valence compounds. Many elements, in particular the transition metals, can exist in a variety of oxidation states.

Beyond assignment based on composition alone, as part of crystal structure determination it is common to use knowledge of the local structure (bond lengths and angles) to assign oxidation states based on a valence bond analysis<sup>56</sup>. One assignment algorithm involving analysis of nearest-neighbour coordination environments is implemented in the open-source PYMATGEN package (<http://pymatgen.org>).

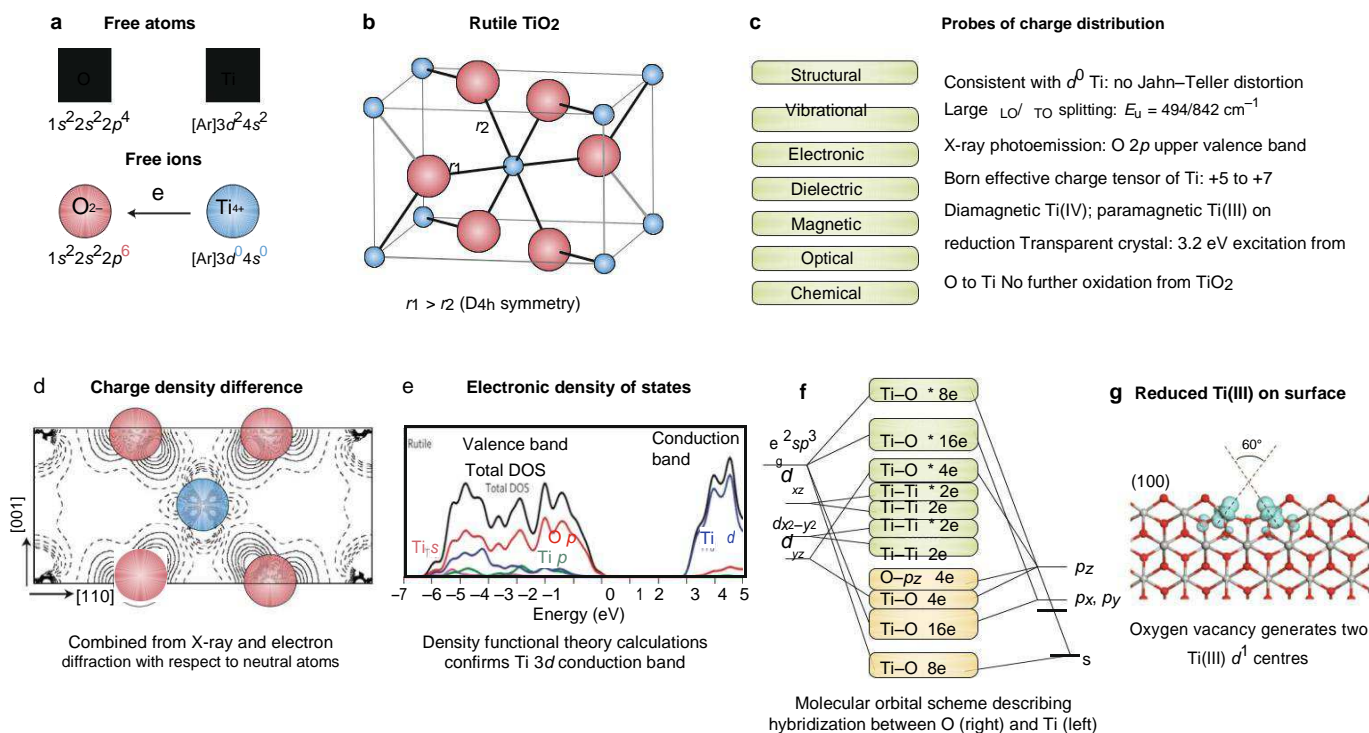
in, for example, the compound KMnO<sub>4</sub> does not imply, as argued above, that a calculated or experimentally measured charge density analysis will find zero charge density in the  $3d$  orbitals; but it does indicate that all the  $3d$  electrons are directly involved in bonding (interaction) with oxygen. Similarly, Ti is in oxidation state  $+4$  in TiO<sub>2</sub> as explored in Fig. 1; although there is again appreciable electron density in the Ti  $3d$  orbitals due to bond polarization and weak orbital hybridization as observed in the electronic density of states. The next section will explore these ideas in greater depth.

## Determining and understanding partial charges

The historical description of chemical interactions, or bonding, involving the sharing and transfer of integral numbers of electrons was challenged following the development of quantum mechanics. The distribution of electrons in chemical systems is described by the many-electron Dirac equation (or Schrödinger equation in the non-relativistic limit); however, practical treatments require simplification<sup>20</sup>. Techniques employing one-electron wavefunctions are ubiquitous in quantum chemistry, and for solids these take the form of periodic (Bloch) functions. By their nature, these functions are delocalized in real space and cannot be easily interpreted in terms of individual chemical interactions (for example, covalent bonds and lone pairs).

The link to chemical intuition can be recovered by employing one-electron localized orbitals (for example, obtained with Foster–Boys and Pipek–Mezey schemes in molecules and Wannier orbitals in solids, as discussed further below)<sup>21</sup>. However, the complexity of chemical bonding in many compounds necessitates going beyond a one-electron picture—for example, in the chemistry of radicals with multi-centre multi-electron interactions. More generally, electrons can be separated into groups, with strong correlation within a single group, and weak correlation between them<sup>22,23</sup>.

Both experiment and computational techniques are widely used to obtain electron density maps in solids, with a variety of procedures used to interpret them in terms of atomic charges. However, individual atomic charges in a multi-electron compound are not a quantum mechanical observable and there is a high degree of ambiguity both in their definition and in the approaches to calculating them, in contrast to the simpler and heuristic oxidation state. Nevertheless, the concept of partial (atomic) charges is a useful one and we consider briefly the ways in which it has been formulated and applied.



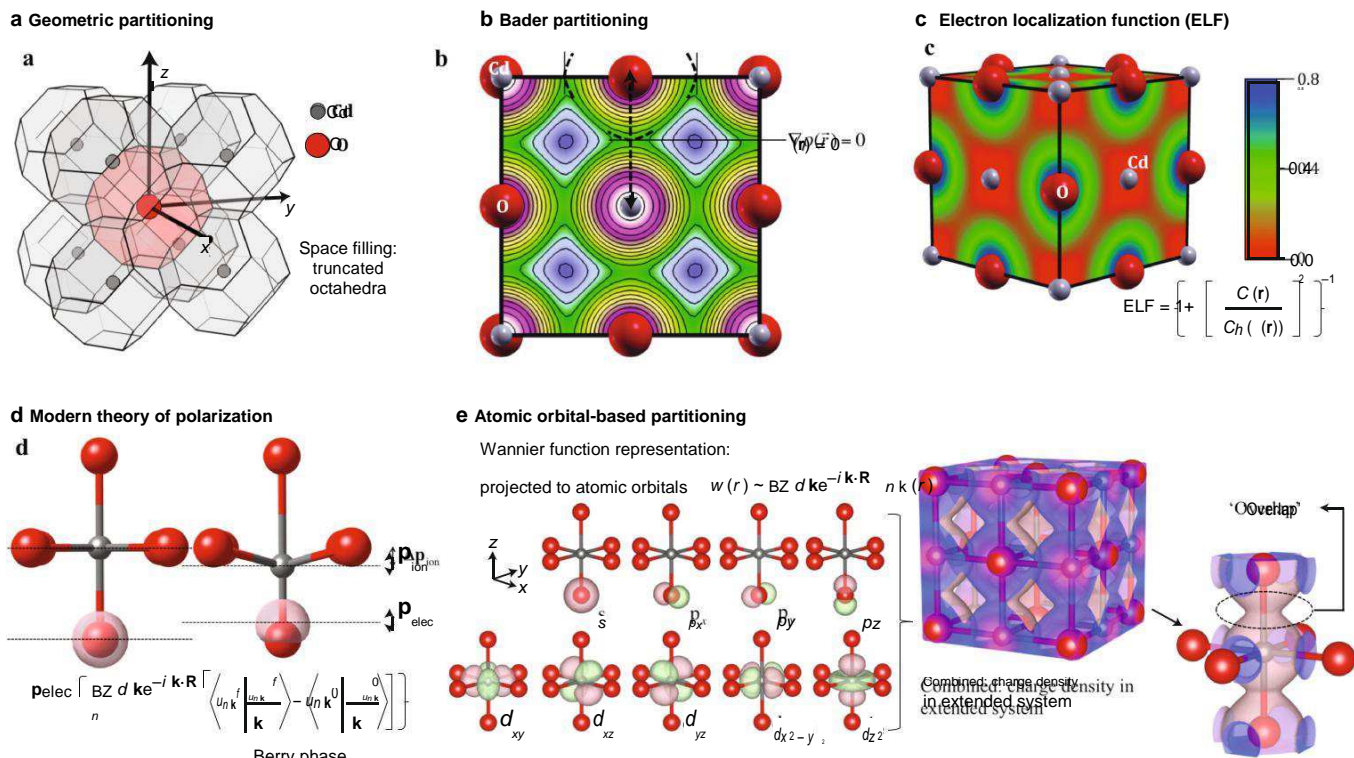
**Fig. 1 | Charge distribution in TiO<sub>2</sub>.** **a**, The formal oxidation states are +4 for Ti and –2 for oxygen. **b**, The material adopts a range of polymorphs, but here we focus on rutile, which is one of the most stable. **c**, Various experimental probes that relate to the charge density and oxidation states are available. **d**, the measured charge density difference confirms a depletion of *d*-orbital density from Ti and a transfer to O. **e,f**, The first-principles electronic density of states demonstrates a conduction band formed of Ti *d* orbitals (**e**), with hybridization in the valence band that can be described by a simple molecular orbital scheme<sup>51,52</sup> where the filled combinations are shaded yellow (**f**). **g**, Finally, when excess electrons are added to the material or formed via charged point defects, they localize to give paramagnetic Ti(III) *d*<sup>1</sup> centres as calculated from first-principles and observed in surface measurements. Adapted from ref. 51, International Union of Crystallography (**d,f**); ref. 53, Springer Nature Ltd (**e**); and ref. 54, American Chemical Society (**g**).

Determining the electronic density associated with a particular atom or ion in a solid-state material is in some ways a natural choice to calculate the atomic charges. Indeed, experimental techniques such as X-ray diffraction (XRD) allow one to measure such densities, and visualize them in real space via a Fourier transform. Information obtained from local surface probes including scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), while limited, can also be used to reconstruct charge density distributions. At the same time, theoretical techniques provide increasingly accurate electron density maps in solids. The crucial question then remains: how are these electronic densities, which are continuous functions through the unit cell of a crystal, partitioned among the constituent atoms? In the vast majority of cases, there is overlap in density between atoms, making the partitioning a non-trivial problem.

A simple approach is to use geometric partitioning, where the charge within a certain radius or polyhedron, or, in the analysis of Bader<sup>24</sup>, within a contour of zero density gradient is computed and associated with an atom. An alternative approach is to construct a set of Wannier functions to associate electrons with each atom<sup>25</sup>; these are Fourier transforms of Bloch wavefunctions onto discrete centres<sup>26</sup>. These sets of Wannier functions are then assigned to ionic cores via their spatial proximity. Unfortunately, such methods only provide a unique and unambiguous definition of atomic charge when both the orbital overlap and polarization due to electrostatic fields is zero. Partial charges of real materials vary with the method employed and the values are difficult to rationalize in terms of integral electron transfer. A range of such approaches are illustrated in Fig. 2 for the case of CdO.

The overlap in electron density between atoms can be accounted for through analysis of the electronic wavefunctions in terms of localized, atom-centred basis functions. Through a linear combination of atomic orbitals (LCAO) approach, Mulliken's and the alternative Löwdin analysis<sup>27</sup> represented the atomic charge in terms of populations of atomic orbitals. Each pair of atoms has a gross, net and overlap population, given in terms of the atomic orbital basis set. Originally the overlap population was divided equally between the interacting ions, but subsequent improvements on this method have been applied including those of Christoffersen<sup>28</sup> employing molecular orbitals and Hirshfeld<sup>29</sup> using the charge density, which take into account the polarity of the bond between the atoms. Wavefunction-derived properties, such as the single and pair electron densities, have been incorporated in the electron localization function (ELF, see Fig. 2c)<sup>30</sup>, which describes the probability of finding an electron close to another in the same spin state and allows one to determine regions where electrons are localized close to atomic centres<sup>31</sup>. Electronic wavefunction analysis, however useful, cannot solve the fundamental problem that atomic charge in compounds is not an observable. Results from such analyses vary strongly with the choice of basis functions and with the method used to determine interactions between atoms, whether through LCAO parameterized tight-binding methods or ab initio techniques.

A crucial consideration when modelling atomic charge is the polarizability of the ion in question. When an electric field is applied to a material, the ions respond not just by changing their centre of mass coordinates, but also by deformation of their electron clouds. Displacement upon ionic polarization can be accounted for in a simple manner, to describe the response to applied electric fields,



**Fig. 2 | Illustration of five approaches for partitioning electron density between atomic centres in chemical systems.** We use the case of CdO, in which Cd has a formal +2 and O has a -2 oxidation state. **a**, Geometric partitioning based on space filling for a Wigner–Seitz polyhedral decomposition of CdO in a CsCl-like structure. **b**, Topological analysis of the electron density  $\rho(r)$  in rocksalt CdO as shown using Bader’s ‘atoms in molecules’ approach. **c**, Analysis of electron pair probability distribution as determined using the electron localization function (ELF; here the functions  $C$  and  $C_h$  are related to the electron pair density<sup>30</sup>). **d**, Changes in electric polarization  $\mathbf{p}$  from topological analysis of the electron distribution using the Berry phase formalism applied to standard band structure calculations in the Bloch function basis<sup>33,34</sup>. **e**, Projection of extended electronic wavefunctions onto localized orbitals (Wannier functions,  $w(r)$ , defined again using pre-calculated Bloch functions) that combine to reproduce the full electron density of the crystal.

by attributing an effective charge to the ion. Good agreement with experimental measurements that probe the dielectric response of a material can be achieved with this approach<sup>5</sup>. Care must be taken with such effective charges including the frequently used Born charge, however, as their derivation, while useful when modelling the dielectric response of a material, can mask the underlying physics. For example, such charges can be used in a rigid-ion model of a crystal to calculate the vibrational (phonon) modes, but in doing so one is explicitly assuming that the ions are non-deformable, which greatly limits the transferability of these models. Moreover, the cohesive energy of a crystal is much less dependent on the polarizability of the constituent ions than the lattice vibrational properties are. The ionic charge that reproduces cohesive energies will generally be different from the effective charge that reproduces vibrational frequencies accurately. This problem can be overcome by using polarizable ions in materials modelling, for example, described with the shell model<sup>32</sup>.

Taking into account the electronic polarizability of an ion in a solid can remove some of the ambiguities with regard to defining atomic charges. Indeed, this outcome is expected, given that the link between polarizability and experimentally observable quantities is far clearer than that between the poorly defined atomic charges and experiment. In a dielectric crystal, the dipole moment within a unit cell cannot be uniquely defined owing to the arbitrary choice in the definition of the unit cell as a result of translation symmetry. However, differences in polarization between displaced (atomic and electronic) configurations, which are the source of experimentally observable quantities, do not depend on the unit-cell choice. The

computation of such differences in polarization is the aim of the ‘modern theory of polarization’<sup>27</sup>, in which the electron clouds associated with ions are represented by Wannier functions. The polarization difference is usually calculated through topological analysis of the electron distribution via the Berry phase formalism, from which the number of Wannier centres (that is, electrons) that move with a particular atomic displacement can be derived<sup>33,34</sup>. Thus a partitioning of electrons is achieved, which is not based on spatial considerations with respect to ion core coordinates, but on the lattice dynamic distribution of the electronic states. Employing this theory, Jiang et al.<sup>35</sup> obtained ionic partial charges from first-principles calculations that recovered formal oxidation states for each species in a diverse set of systems (LiH, water, BaBiO<sub>3</sub> and Sr<sub>2</sub>FeWO<sub>6</sub>). This approach highlights the link between changes in polarization and oxidation states that is intuitively satisfying; nevertheless, it remains one among several approaches.

Experimental techniques that measure electron density suffer from the same ambiguity as electronic structure calculations in partitioning to atomic centres. Alternative techniques can be used to probe atomic charges, beyond those based on measuring the dielectric response of a material already mentioned. In electrochemical processes, ionic charges are exchanged in integer numbers through redox reactions. X-ray photoemission spectroscopy (XPS) is widely used to infer oxidation states via the shifts and splittings of core levels that act as spectral fingerprints (Box 2). Another probe is the absorption edge in ‘X-ray absorption near edge structure’ (XANES) measurements, which increases in energy as the oxidation state of the absorption site increases. Neutron spectroscopy, spin resonance

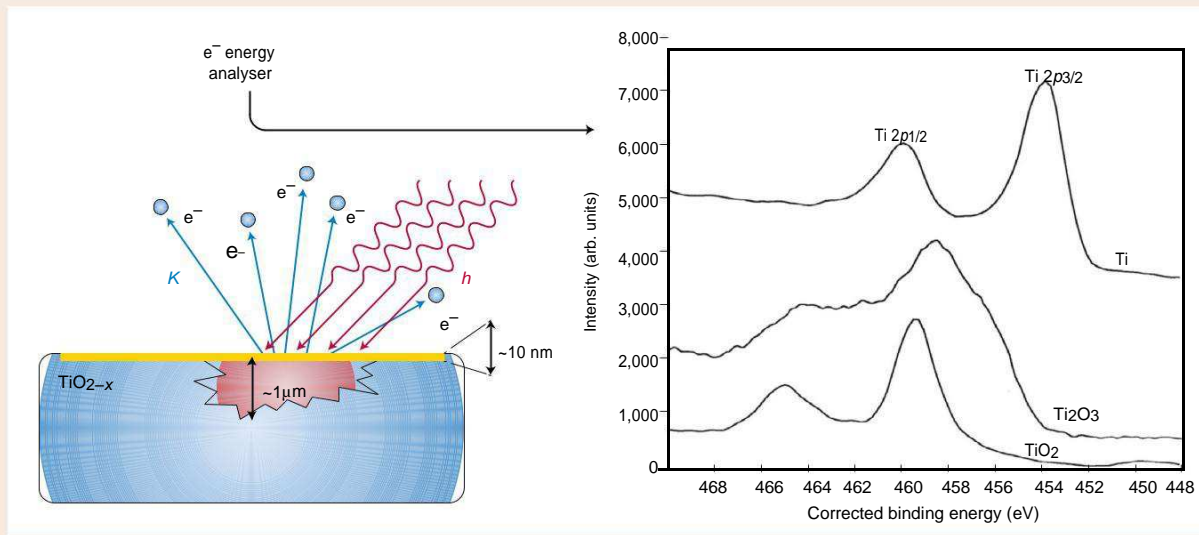
## Box 2 | X-ray photoelectron spectroscopic (XPS) fingerprints of oxidation states

The experimental technique of X-ray photoelectron spectroscopy (XPS) is a crucial analytical tool in materials science that is widely used to assign atomic oxidation states. Based on the photoelectric effect discovered by Hertz in 1887 and explained by Einstein in 1905, it allows one to probe a range of electronic states in atoms comprising molecules or extended solids. The basic process is shown in the schematic below. A source provides a beam of X-rays of frequency  $\nu$  that impinges on the surface of a sample; electrons are subsequently excited from bound to empty states in the system and leave the sample under the influence of an external electric field. By measuring the kinetic energies  $K$  of such photoelectrons, the binding energies  $E_b$  of the initial states are determined via the classical Einstein's formula:  $E_b = K - h\nu - \Phi$ , where  $\Phi$  is the work function of the sample. The frequency of the X-rays determines which electronic states are probed and how deep within the sample the photons can penetrate and emit photoelectrons. It is therefore possible, by varying the frequency, to probe electronic states ranging from the valence band to deep within the atomic core. Moreover, lower frequencies allow one to analyse surface electronic states (so-called soft XPS), while high frequencies are used to probe states within the bulk of the sample (hard XPS).

The theory of the process developed by Siegbahn considers the effect of both the initial and final state of the excited electron, and relates the quantized bands in the observed spectroscopic signatures to the 'true' electron energies in the material, which are characteristic of particular elements in particular chemical states.

By calibrating the experimental set-up against known 'reference' samples, one can determine chemical shifts in certain bands that arise due to changes in the chemical environment. For example, a change in the oxidation state of Ti between that in its metallic phase to the fully oxidized form of  $\text{TiO}_2$  results in an observed shift of 4.6 eV in its  $2p$  core levels, as shown in the schematic, where the data are taken from ref. 57. Due to the capability of XPS measurements to distinguish between chemical elements and their electronic states, the technique is also referred to as electron spectroscopy for chemical analysis, or ESCA.

Care should be taken in the experimental set-up regarding sample preparation, where charging effects will influence the observed work function and where surface inhomogeneity will give rise to specific spectroscopic signatures. As the chemical environment around atoms of interest will affect both the energy and line shapes, and a number of electronic terms may coexist even within one oxidation state, curve-fitting procedures are applied to separate individual contributions. Such analysis yields valuable information about the chemical nature of the material's constituent elements. Moreover, the electronic state of an atom or ion in the material may experience fluctuations, and will do so necessarily in metals either intrinsically or upon a local photoexcitation during the measurement. If the time of fluctuation is short (for example, in intra-ionic processes), only the line shape will change. For long times (characteristic of inter-ionic charge transfer processes), however, the XPS measurement can resolve different oxidation states and involved electronic terms.



techniques, and other spectroscopic or magnetic measurements can be used to probe unpaired spin densities, which can give information on bonding character and from which details on oxidation states can be inferred<sup>19</sup>.

It is useful at this point to draw together the threads of our argument. The concept of oxidation state is a simple but powerful one. It relates to electron count and indicates the number of electrons from component atoms that are involved in chemical bonding. Charge density is a distinctive entity, which is accessible from experiment and theory, but whose partition into atomic charges is intrinsically ambiguous. Provided this crucial factor is recognized, it is nevertheless a very useful concept and recent approaches to assign partial charges tend to align them with oxidation states. Our discussion continues with examples of systems and problems that

pose particular challenges to the twin concepts of atomic charge and oxidation state.

### Challenges for mixed-valence and correlated systems

The ongoing debate on oxidation states in more complex or complicated systems keeps the field open for further refinement. Oxidation states are often straightforward to assign in systems where atoms display a single oxidation state, but they can start to blur in poly-ion and mixed-valence compounds, where elements are present in more than one distinct state. Imagine a system where metal M exists in oxidation states (A and B), occupying two detectable sites in the crystal (labelled X and Y). The degree of mixing between these two Heitler-London configurations  $M^A_X M^B_Y$  and  $M^B_X M^A_Y$  will be controlled by how distinguishable the two crystallographic sites are<sup>36</sup>.

Robin and Day categorized these systems into three classes<sup>37</sup>: class 1, where the sites are very different and the electrons are completely trapped; class 2, where the sites are distinguishable but not very different, and so a range of intermediate oxidation state behaviours can be observed; and class 3, where the sites are indistinguishable and the system has a genuine non-integral oxidation state.

Class 1 compounds should be the easiest to understand; however, the assignment in some systems still promotes debate. Silver monoxide (AgO or Ag<sub>2</sub>O<sub>2</sub>) is one such example, where Ag exists in the +1 and +3 oxidation states, with Ag(I) in a linear coordination between two oxygen ions, and Ag(III) in a distorted square planar coordination. Despite these different crystallographic sites, assignment of the oxidation states present in AgO has been contentious, with some studies favouring an explanation of Ag(I), Ag(II) with localized hole polarons on oxygen. This controversy was solved using electronic structure calculations in tandem with X-ray photoemission and fine-structure analysis<sup>38</sup>. Covellite (CuS), another class 1 system, is a mineral in which Cu is found in two distinct coordination environments (trigonal planar and tetrahedral) and S is also found in different environments, with one third of the S in a trigonal pyramidal coordination and two thirds present in S–S dimers. Counter to chemical intuition, the oxidation state of Cu in CuS is thought to be Cu(I) due to the presence of the S<sub>2</sub><sup>2-</sup> dimers; although debate remains as to whether there is a mixture of oxidation states on the Cu sites, on the S sites or on both<sup>39</sup>.

Temperature effects can make the analysis of oxidation states in mixed valence systems difficult. At room temperature, magnetite (Fe<sub>3</sub>O<sub>4</sub>) crystallizes in a cubic AB<sub>2</sub>O<sub>4</sub> spinel structure, in which Fe(III) ions occupy the tetrahedral A sites, and a 50:50 ratio of Fe(II) and Fe(III) ions occupy the octahedral B sites, which can be difficult to distinguish. Below 125 K, the system undergoes what is known as the Verwey transition, a structural distortion to a monoclinic superstructure, and becomes electrically insulating, with the charge ordering of the similarly sized +2 and +3 ions contentious for many years. Recently, an investigation by Atfield and co-workers<sup>40</sup> revealed the presence of localized electrons that are distributed over three linear Fe-site units, termed trimerons. This breakthrough was enabled by the synthesis of large 40- $\mu$ m grains of the low-temperature structure, which allowed the identification of the emergent order.

Similarly, pressure can change the nature of charge distributions in a solid, making the analysis of oxidation states complex. Boron is a metalloid that exists in several well-known allotropes. In nearly all of these allotropes, the structures are made up of icosahedral B<sub>12</sub> clusters that feature metallic-like three-centre bonds within each icosahedron, and covalent two- or three-centre bonds between the icosahedra, satisfying the octet rule and yielding insulating electronic structures. Under pressures exceeding 19 GPa and less than 89 GPa, boron adopts a novel ionic structure, consisting of an NaCl-type arrangement of icosahedral B<sub>12</sub> clusters and B<sub>2</sub> pairs<sup>41</sup>. The resultant structure is a ‘boron boride’, perhaps best characterized by the formula (B<sup>+</sup>)<sub>2</sub>(B<sup>-</sup>)<sub>2</sub>.

Highly correlated systems can also present a challenge to our understanding of oxidation states. Plutonium—important as a nuclear fuel—is situated among the actinides in the periodic table. In the early actinides (Th to Np), the 5f electrons are delocalized, which allows them to take part in bonding within the lattice, similar to the behaviour of the 5d series. For the heavier actinides (above Am), the 5f electrons are localized, and do not take part in bonding. Plutonium is at the cusp of these two behaviours, resulting in one of the most complex electronic structures for an elemental metal<sup>42</sup>. The ground state has only recently been conclusively revealed to be a quantum mechanical admixture of localized and itinerant electronic configurations, with the charge fluctuating between distinct Pu(IV) (5f<sup>4</sup>), Pu(III) (5f<sup>5</sup>) and Pu(II) (5f<sup>6</sup>) electronic configurations<sup>43</sup>.

The breakdown of simple concepts of oxidation state has also been emerging as a key ingredient in many observations of

unconventional critical phenomena, which do not follow standard spin-fluctuation theories. The quantum criticality of Yb-valence fluctuations has been shown to be the origin of divergent spin behaviours in YbRh<sub>2</sub>Si<sub>2</sub> and  $\beta$ -YbAlB<sub>4</sub>, YbAgCu<sub>4</sub>, and YbIr<sub>2</sub>Zn<sub>20</sub> (ref. <sup>44</sup>), and similarly the valence fluctuations of Ce in CeIrIn<sub>5</sub> (ref. <sup>45</sup>). Regarding superconductivity, nearly critical valence fluctuations have been reported to mediate Cooper pairing in CeCu<sub>2</sub>Ge<sub>2</sub> and CeCu<sub>2</sub>Si<sub>2</sub> under high pressure<sup>46</sup>.

These are examples of challenging cases to the oxidation state concept. Situations where the assignments of oxidation states become ill-defined are usually those associated with intriguing new physics that tests our very understanding of chemical bonding in solids.

## Outlook

With the ever-increasing arsenal of advanced theoretical methods and experimental techniques available at present, the misunderstandings (and challenges to our understanding) of oxidation states are slowly decreasing. The related but distinct concepts of oxidation state, atomic charge and ionicity will remain of key importance in understanding and describing chemical bonding in general, but particularly in solids. While modern sophisticated methods may uncover challenges to what are inherently simple and intuitive investigative tools, the concept of oxidation state, which has survived over two centuries of use in the chemical sciences, will stay at the core of our description of the interaction of atoms in molecules and solids, provided the distinctions between it, the atomic charge and ionicity are fully appreciated.

As our understanding of the structure and properties of diverse materials continues to improve, we expect a clearer view to emerge of electronic and ionic interactions in highly challenging systems including new classes of high-temperature superconductors<sup>47</sup>, boron compounds<sup>48</sup>, supported metal and semiconductor nanostructures<sup>49</sup>, layered MXenes<sup>50</sup> and beyond. The key concepts in electron group theory, the theory of polarization, supercritical behaviour, and the integral view of microscopic and mesoscopic behaviour of solids including charge and spin fluctuations are all essential ingredients in the future application and utility of the oxidation state.

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## Competing interests

The authors declare no competing interests.

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