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. Whilst formal oxidation states help us count electrons (in ions, bonds, lone pairs, etc.), 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, electrides, 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[1]. Such chemical reactions are quantised, with distinct changes in structure and properties as more oxygen is bound by an element (e.g. $6\mathrm{Fe} + 3\mathrm{O}_2 \rightarrow 6\mathrm{FeO} + \mathrm{O}_2 \rightarrow 2\mathrm{Fe}_3\mathrm{O}_4 + \frac{1}{2}\mathrm{O}_2 \rightarrow 3\mathrm{Fe}_2\mathrm{O}_3$). 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-upon set of rules[2].

This Perspective focusses on chemical bonding in solids, where discussion almost invariably makes reference to oxidation states, ionicities, covalency, and charge distributions, which are indeed powerful concepts across the chemical sciences. Despite their widespread use, however, there are uncertainties and ambiguities about the 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[3]; Mooser and Pearson emphasised that bond ionicity is a theoretical concept that depends on the approximation employed[4]; while Cochran focused on what can and cannot be measured in practice[5].

As argued previously, the concept of ionicity in solids remains intrinsically ambiguous[6]: 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[7–10]. We attempt to address these problems and to show how ionicity, 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[11]. In one trivial example, two hydrogen atoms (one-electron species) interact through a two-electron covalent bond formed by filled bonding and empty anti-bonding 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 Li^+ ($1s^2 2s^0$) and 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 (see Box 1), e.g. the oxidation state of an atom in its elemental standard state is 0. A less trivial example is a multi-component solid such as the high-temperature superconductor $YBa_2Cu_3O_7$. Here, the oxidation state of O is -2, which means that the sum of oxidation states for Y + 2Ba + 3Cu = 14 to provide the electrons involved in the bonding with oxygen. The common oxidation state of Y is +3, 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 cupric oxide (CuO) and +1 in cuprous oxide (Cu_2O). The unusual electron count in $YBa_2Cu_3O_7$ requires either an additional electron (oxidation) from Cu to the +3 state or a hole stabilised on oxygen – often described as a polaron – which leads to its exotic condensed matter physics[12]. 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[13], 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_3Si_4, discrete Si_4^{6-} polyanions are formed with internal Si-Si bonds, which ensures charge neutrality when combined with thee Ba +2 cations. There have been recent applications of such Zintl compounds in the field of thermoelectrics[14,15].

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[16], and ligand and crystal field theory for predicting structure and spectroscopic response, in particular of transitional metal complexes and materials[17]. 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 Mn(II) ($3d^5$), where the high spin state of 5/2ħ is observed, while MnO_2 contains Mn(IV) ($3d^3$), with a corresponding high spin state of 3/2ħ. The intermediate case of Mn_2O_3 contains Mn(III) ($3d^4$), which is Jahn-Teller active and results in a frustrated magnetic interactions in its ground state bixbyite crystal structure[18]. Each of these oxidation states of Mn can be easily distinguished from their distinct spectroscopic and magnetic signatures[19].

Assigning formal oxidation states allows us to understand and rationalise key properties of the materials, but it is not a statement about effective charge: assigning an oxidation state of +7 to Mn in, for example, the compound $KMnO_4$ 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_2 as explored in Figure 1; although, there is again appreciable electron density in the Ti 3d orbitals due to bond polarisation and weak orbital hybridisation 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; however, practical treatments require simplification[20]. 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 delocalised in real space and cannot be easily interpreted in terms of individual chemical interactions (covalent bonds, lone pairs, etc.).

The link to chemical intuition can be recovered by employing one-electron *localised* orbitals (e.g. obtained with Foster-Boys and Pipek-Mezey schemes in molecules and Wannier orbitals in solids, as discussed further below)[21]. However, the complexity of chemical bonding in many compounds necessities going beyond a one-electron picture, *e.g.* 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[22,23].

Both experiment and electronic structure based 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[6], 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.

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 visualise 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 amongst 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[24], 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[25]; these are Fourier transforms of Bloch wavefunctions onto discrete centres[26]. 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 polarisation due to electrostatic fields is zero. Partial charges of real materials vary with the method employed and the values are difficult to rationalise in terms of integral electron transfer. A range of such approaches are illustrated in Figure 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 localised, atom-centred basis functions. Through a linear combination of atomic orbitals (LCAO) approach, Mulliken's analysis[27] 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[28] employing molecular orbitals and Hirshfeld[29] using the charge density, which take into account to some degree 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 localisation function (ELF, see Figure 2c)[30], 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 localised close to atomic centres[31]. 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 function and with the method used to determine interactions between atoms, whether through LCAO parameterised tight-binding methods or *ab initio* techniques.

A crucial consideration when modelling atomic charge is the polarisability 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 polarisation can be accounted for in a simple manner, to describe

the response to applied electric fields, 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[5]. 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 often 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 polarisability of the constituent ions than are the lattice vibrational properties. 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 polarisable ions in materials modelling, e.g. described with the shell model[32].

Taking into account the electronic polarisability 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 polarisability 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 polarisation 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 polarisation is the aim of the 'modern theory of polarisation'[27], in which the electron clouds associated with ions are represented by Wannier functions. The polarisation difference is usually calculated through topological analysis of the electron distribution via the Berry phase formalism, from which the number of Wannier centres (i.e. electrons) that move with a particular atomic displacement can be derived[33,34]. 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.[35] obtained ionic partial charges from first-principles calculations that recovered formal oxidation states for each species in a diverse set of systems (LiH, water, $BaBiO_3$ and Sr_2FeWO_6). This approach highlights the link between changes in polarisation and oxidation states that is intuitively satisfying; nevertheless, it remains one amongst 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. 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 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[19].

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 recognised, it is nevertheless a very useful concept and recent approaches to assigning 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 straightforward to assign in systems where atoms display a single oxidation state, but they can start to blur in polyion 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 $M_X^A M_Y^B$ and $M_X^B M_Y^A$ will be controlled by how distinguishable the two crystallographic sites are[36]. Robin and Day categorised these systems into three classes[37]: (i) Class 1, where the sites are very different and the electrons are completely trapped, (ii) Class 3, where the sites are indistinguishable and the system has a genuine non-integral oxidation state, and (iii) Class 2, where the sites are distinguishable, however, not very different, and so a range of intermediate oxidation state behaviours can be observed.

Class 1 compounds should be the easiest to understand; however, the assignment in some systems still promotes debate. Silver monoxide, (AgO or Ag_2O_2) is one such example, where Ag exists in the +1 and +3 oxidation states, with Ag(I) in a linear coordination between two oxygen, 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 localised hole polarons on oxygen. This controversy was solved using electronic structure calculations in tandem with X-ray photoemission and fine-structure analysis[38]. Another Class 1 system, covelite (CuS) 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_2^{2-} 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[39].

Temperature can conspire to make the analysis of oxidation states in mixed valence systems difficult. At room temperature, magnetite (Fe_3O_4) crystallises in a cubic AB_2O_4 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 Attfield and co-workers revealed the presence of localised electrons which are distributed over three linear Fe-site units, termed trimerons[40]. This breakthrough was enabled by large 40-micrometre 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 quite 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_{12} clusters that feature metallic-like three-centre bonds within each icosohedron, 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_{12} clusters and B_2 pairs[41]. The resultant structure is a "boron boride", perhaps best characterised by the formula $(B_2)^{\delta+}(B_{12})^{\delta-}$.

Highly-correlated systems can also present a challenge to our understanding of oxidation states. Plutonium – important as a nuclear fuel – is situated amongst the actinides in the periodic table. In the early actinides (Th to Np), the 5f electrons are delocalised, 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[42]. The ground state has only recently been conclusively revealed to be a quantum mechanical admixture of localised and itinerant electronic configurations, with the charge fluctuating between distinct Pu(IV) ($5f^4$), Pu(III) ($5f^5$) and Pu(II) ($5f^6$) electronic configurations[43].

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 have been shown to be the origin of divergent spin behaviours in $YbRh_2Si_2$ and β-$YbAlB_4$, $YbAgCu_4$, and $YbIr_2Zn_{20}$,[44] and similarly the valence fluctuations of Ce in $CeIrIn_5$.[45] In superconductivity, nearly critical valence fluctuations has been reported to mediate Cooper pairing in $CeCu_2Ge_2$ and $CeCu_2Si_2$ under high pressure[46].

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 of (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-*T* superconductors[47], boron compounds[48], supported metal and semiconductor nanoclusters[49], layered MXenes[50] and beyond. The key concepts in electron group theory, the theory of polarisation, supercritical behaviour, and

the integral view of microscopic and mesoscopic behaviour of solids including charge and spin fluctuations are all essential ingredients to the future application and utility of the oxidation state.

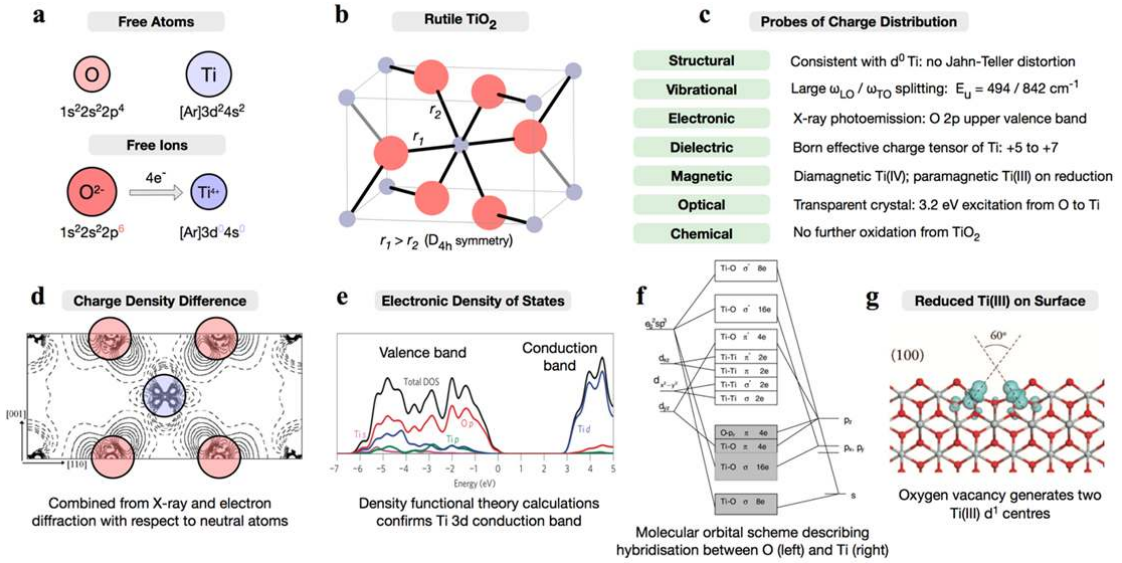


Figure 1 Charge distribution in TiO_2. (a) The formal oxidations states are +4 for Ti and -2 for oxygen. (b) The material adopts a range of polymorphs, but here we focus on rutile, which is one of the most stable. (c) Various experimental probes of the charge density are available; (d) the measured charge density difference confirms a depletion of d orbital density from Ti and a transfer to O [Reproduced from Ref. [51]]. (e) The first-principles electronic density of states demonstrates a conduction band formed of Ti d [Reproduced from Ref. [52]], with hybridisation in the valence band that can be described by (f) a simple molecular orbital scheme[51,53]. (g) Finally, when excess electrons are added to the material or formed via charged point defects, they localise to give paramagnetic Ti(III) d^1 centres as calculated from first-principles and observed in surface measurements [Reproduced from Ref. [54]].

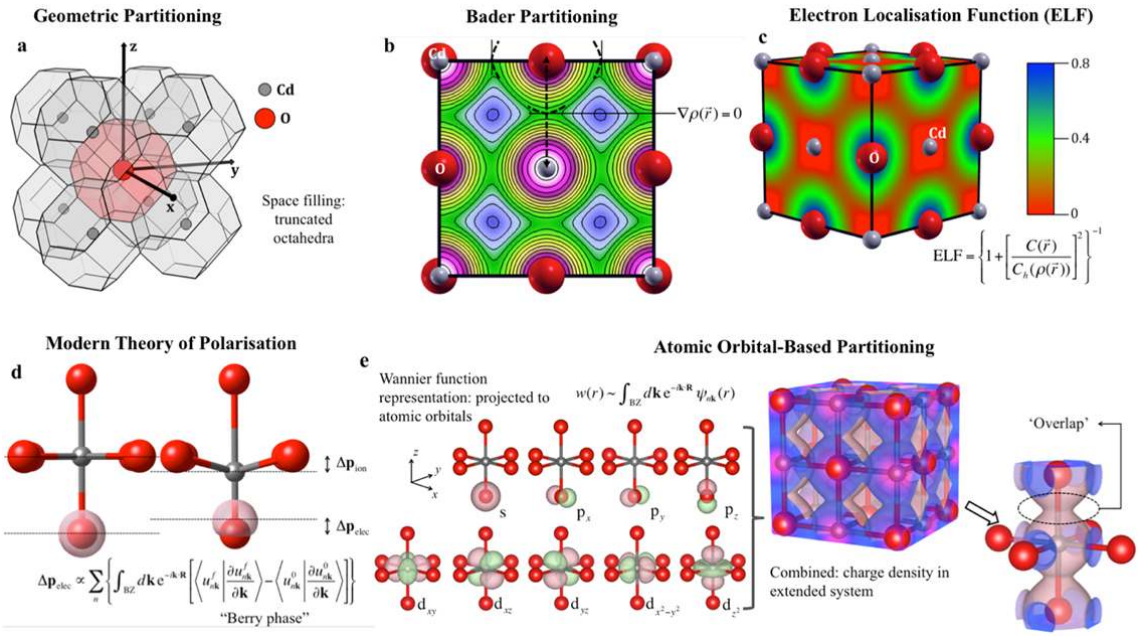


Figure 2 Illustration of five approaches for partitioning electron density between atomic centres in chemical systems. We use the case of CdO, in which Cd has a formal +2 and O has a -2 oxidation state. (a) Geometric partitioning based on space filling for a Wigner-Seitz polyhedral decomposition of CdO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

Box 1 Assigning formal oxidation states

The oxidation state represents "the degree of oxidation of an atom in terms of counting electrons" [IUPAC, 2018]. 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 ($2s^2p^6$) 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 “Inorganic Chemistry” [Mark Weller, Tina Overton, Jonathan Rourke, and Fraser Armstrong, OUP, 6th Edition, 2014.]:

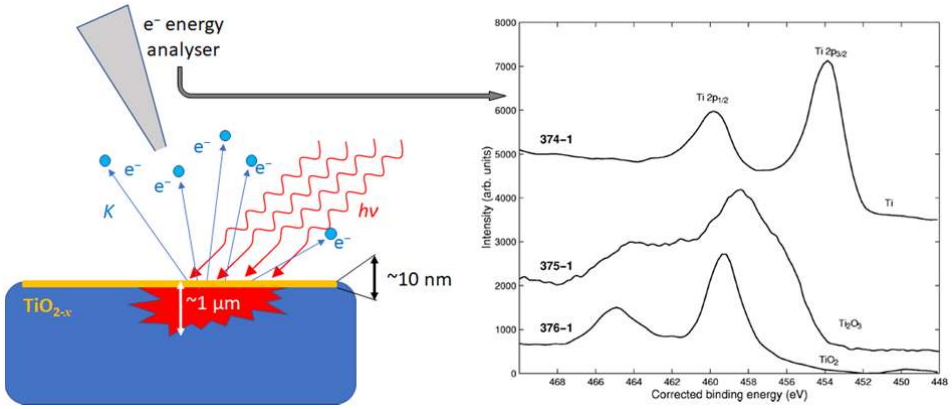
1. The sum of oxidation states for all atoms in the species is zero to ensure electroneutrality
2. Atoms in their elemental form: 0
3. The available valence electrons follow the Group in the Periodic Table, e.g.
    - Atoms of Group 1: +1
    - Atoms of Group 2: +2
    - Atoms of Group 3: +3
    - Atoms of Group 13: +1 (filled s^2 lone pair) or +3
4. Hydrogen in compounds with nonmetals: +1 (hydron)
    - in compounds 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^-)
    - -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[55]. One assignment algorithm involving analysis of nearest-neighbour coordination environments is implemented in the open-source PYMATGEN package [http://pymatgen.org].

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, which is widely used to assign atomic oxidation states. Based on the photoelectric effect discovered by H. R. Hertz in 1887 and explained by A. Einstein in 1905, it allows one to probe a range of electronic states in atoms comprising materials or molecules. The basic process is shown in the schematic below. A source provides a beam of X-rays of frequency ν which 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 Einstein's formula: $E_\mathrm{b} = K - h\nu - \Phi$, where Φ 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. It is therefore possible, by varying the frequency, to probe states varying 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 K. Siegbahn considers the effect of both the initial and final state of the excited electron, and relates the quantised 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 detectors 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 oxidised form of 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. [56]. The XPS measurements employed to distinguish chemical elements and their electronic states are often referred to as Electron Spectroscopy for Chemical Analysis, or ESCA.

Care should be taken in the experimental setup 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,

437 the electronic state of an atom/ion in the material may experience fluctuations, and will do
438 so necessarily in metals either intrinsically or upon a local photoexcitation during the
439 measurement. If the time of fluctuation is small, (for example in intra-ionic processes) only
440 the line shape will change. For long times (characteristic of inter-ionic charge transfer
441 processes), however, the XPS measurement can resolve different oxidation states and
442 involved electronic terms.
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a

Free Atoms

O — $1s^2 2s^2 2p^4$

Ti — $[Ar]3d^2 4s^2$

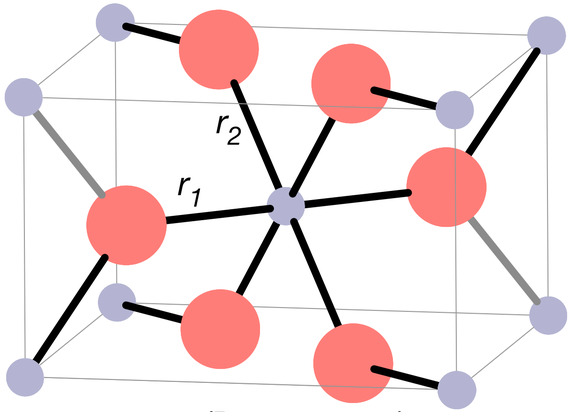
Free Ions

O^{2-} —4e⁻→ Ti^{4+}

$1s^2 2s^2 2p^6$ → $[Ar]3d^0 4s^0$

b

Rutile TiO_2



$r_1 > r_2$ (D_{4h} symmetry)

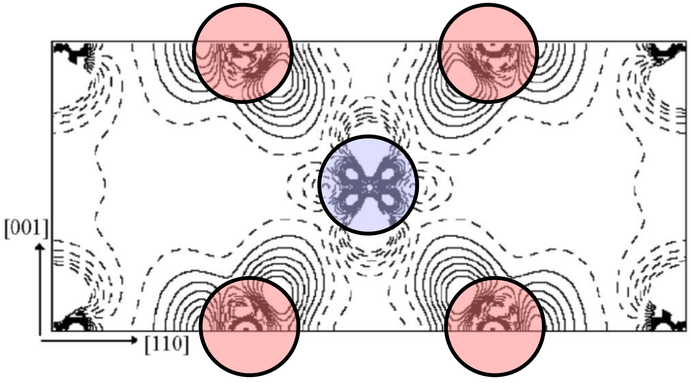
c

Probes of Charge Distribution

Structural	Consistent with d^0 Ti: no Jahn-Teller distortion
Vibrational	Large ω_{LO} / ω_{TO} splitting: E_u = 494 / 842 cm^{-1}
Electronic	X-ray photoemission: O 2p upper valence band
Dielectric	Born effective charge tensor of Ti: +5 to +7
Magnetic	Diamagnetic Ti(IV); paramagnetic Ti(III) on reduction
Optical	Transparent crystal: 3.2 eV excitation from O to Ti
Chemical	No further oxidation from TiO_2

d

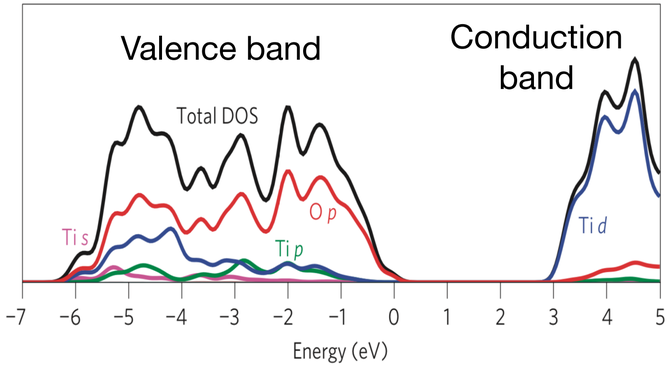
Charge Density Difference



Combined from X-ray and electron diffraction with respect to neutral atoms

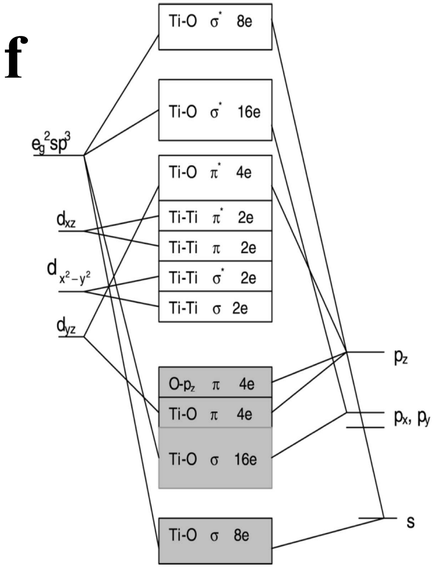
e

Electronic Density of States



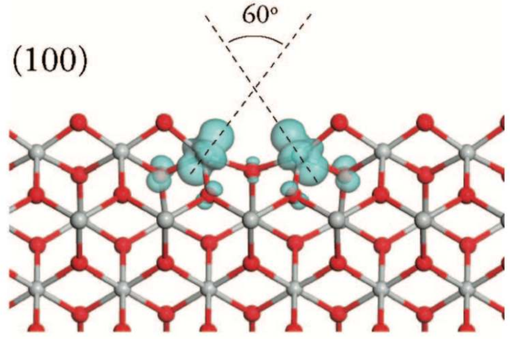
Density functional theory calculations confirms Ti 3d conduction band

f



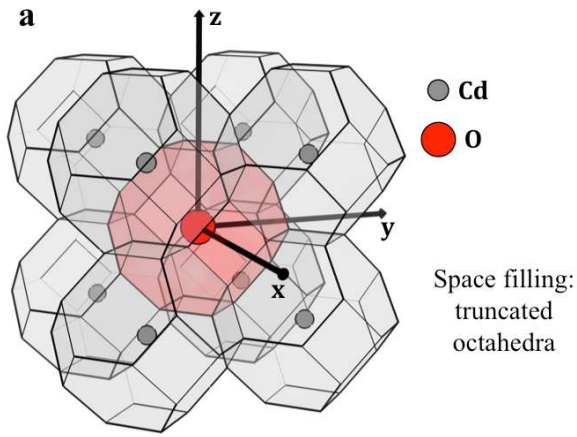
Molecular orbital scheme describing hybridisation between O (left) and Ti (right)

Reduced Ti(III) on Surface

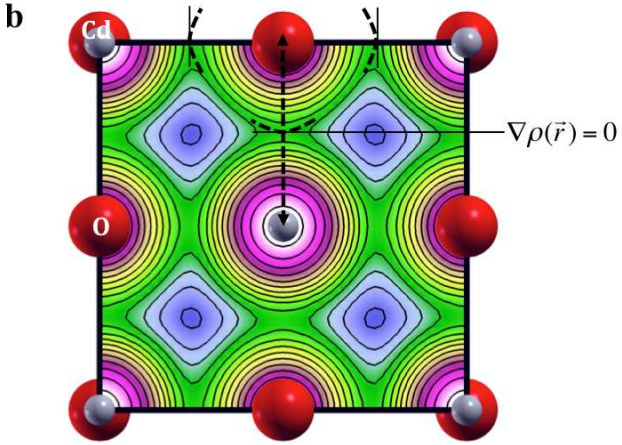


Oxygen vacancy generates two Ti(III) d^1 centres

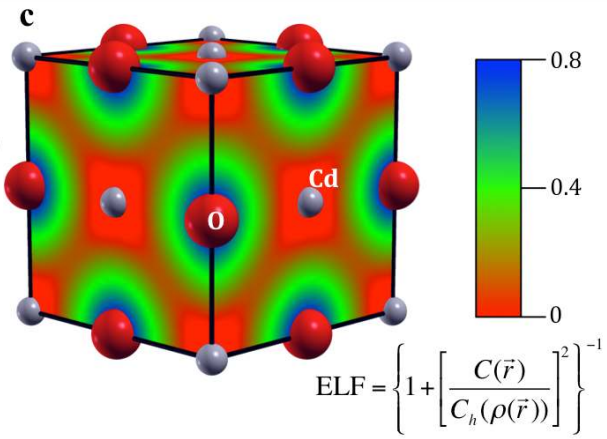
Geometric Partitioning



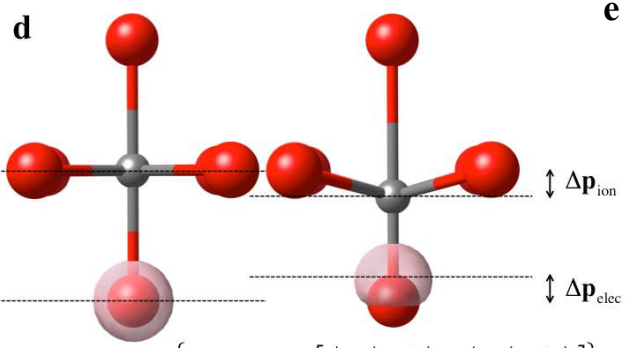
Bader Partitioning



Electron Localisation Function (ELF)



Modern Theory of Polarisation



Atomic Orbital-Based Partitioning