

The bond-valence method

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The bond-valence method expresses the concept that bond lengths and bond valences (or bond order, e.g. 2 for a double bond) are related, and that the sum of the bond valences s_{ij} to an atom j is equal to its valency V_j (or unsigned oxidation state, e.g. 4 for carbon). For an atom symmetrically coordinated by M similar atoms:

$$s_{ij} = V_j / M$$

No distinction is made between ionic and covalent bonds! If the bonds are not equal, we also need a relation between bond length and bond order, e.g.

$$s_{ij} = (d_{ij}/d_0)^{-N} \quad \text{or} \quad s_{ij} = \exp[(d_0 - d_{ij}) / b]$$

where d_0 is the length of a single bond between atom j and atom i and d_{ij} is the actual distance (Pauling, Zachariasen, Baur, and especially I. D. Brown). In practice the second formula is usually used, because b (unlike N) can be assumed to be constant (0.37 Å).

Example: the lead oxides

PbO₂ has the [6]:[3] rutile structure. The lead atom is octahedrally coordinated with Pb—O 2.18 Å. The bond order is then:

$$s_{\text{Pb—O}} = \text{Valency} / (\text{Coordination number}) = 4 / 6 = 0.6667$$

From which we can estimate d_0 for Pb—O:

$$s_{ij} = \exp[(d_0 - d_{ij}) / b] \text{ is rearranged to give } d_{ij} = d_0 - b \ln(s_{ij})$$

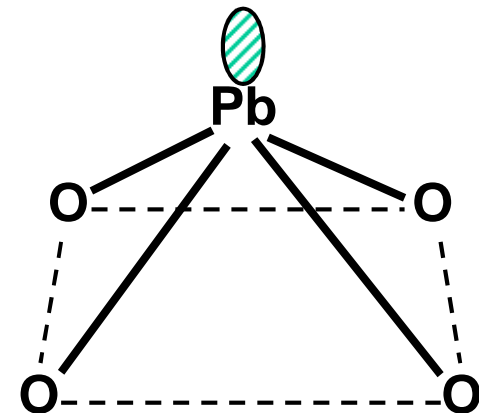
so
$$d_0 = d_{ij} + b \ln(s_{ij}) = 2.18 + 0.37 \ln(0.6667) = 2.03 \text{ \AA}$$

As a test we can use this to find the Pb—O distance in [4]:[4] PbO:

$$s = 2/4 = 0.5$$

$$d = d_0 - b \ln(s) = 2.03 - 0.37 \ln(0.5) = 2.29 \text{ \AA}$$

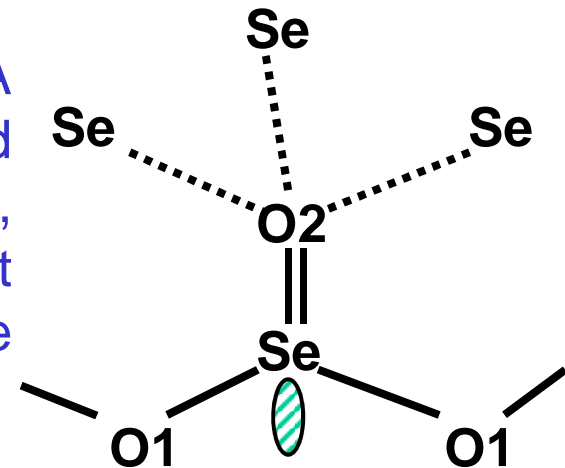
in reasonable agreement with the experimental value of 2.30 Å, despite different coordination numbers, oxidation states and the presence of the lone pair!



Further examples

Pb₃O₄ contains Pb^{IV}[6] and 2Pb^{II}[3] with Pb[6]—O 2×2.13 + 4×2.21 Å and Pb[3]—O 2×2.21 + 1×2.34 Å. It is clear that the [6] atom has the +4 and the [3] atom the +2 oxidation state, because only then would all Pb—O valencies be 2/3 and so all Pb—O distances ca. 2.18 Å as in PbO₂.

SeO₂ has a polymeric structure with Se—O1 1.77 Å and Se—O2 1.61 Å. $d_0(\text{SeO}) = 1.80$ Å gives bond orders s_{ij} of 1.08 and 1.67 and valencies of 2.16 (O1), 1.67 (O2) und 3.83 (Se). If we take into account that O2 also interacts with 3 Se at about 2.8 Å, the valencies increase to 4.03 für Se und 1.87 für O2.



The Sb—Br distance in **SbBr₃** is 2.50 Å. Taking this as d_0 , we can estimate:

$$[\text{SbBr}_6]^- \quad d(\text{Sb—Br}) = 2.50 - 0.37 \ln(5/6) = 2.57 \text{ (observed 2.56 Å)}$$

$$[\text{SbBr}_6]^{3-} \quad d(\text{Sb—Br}) = 2.50 - 0.37 \ln(3/6) = 2.76 \text{ (observed 2.79 Å)}$$

Standard d_0 -values (\AA ; $b = 0.37 \text{\AA}$)

See also www.iucr.org/resources/data/datasets/bond-valence-parameters/

	Li	Na	Mg	Al	Si	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
N	1.61	1.93	1.85	1.79	1.77	2.26	2.14	1.93	1.86	1.85	1.87	1.86	1.84	1.75	1.72	1.72
O	1.47	1.76	1.69	1.62	1.62	2.13	1.97	1.81	1.79	1.79	1.75	1.75	1.69	1.68	1.66	1.69
F	1.36	1.68	1.58	1.55	1.58	1.99	1.84	1.76	1.70	1.64	1.70	1.67	1.62	1.59	1.59	1.62
S	1.94	2.28	2.18	2.13	2.13	2.59	2.45	2.24	2.23	2.18	2.20	2.16	2.06	2.04	2.02	2.09
Cl	1.91	2.15	2.08	2.03	2.03	2.52	2.37	2.19	2.16	2.08	2.13	2.09	2.04	2.04	2.00	2.01
Se	2.09	2.41	2.32	2.27	2.26	2.72	2.56	2.38	2.33	2.29	2.32	2.28	2.24	2.14	2.12	2.22
Br	2.02	2.33	2.28	2.20	2.20	2.66	2.49	2.32	2.30	2.26	2.26	2.26	2.18	2.16	2.13	2.15
I	2.22	2.56	2.46	2.41	2.41	2.88	2.72	2.54	2.51	2.45	2.49	2.47	2.37	2.34	2.36	2.36

$d_0(\text{M}-\text{O})$ is almost equal (1.62\AA) for $\text{M} = \text{Al}, \text{Si}, \text{P}, \text{S}$ and Cl . In a structure determined by direct methods, if one of these atoms is coordinated by O in a way that does not allow space for a lone pair or H-atom, $V_j = \sum_i s_{ij}$ should be 3(Al), 4(Si), 5(P), 6(S) or 7(Cl) and the element can be assigned. *In contrast it can be difficult to distinguish between different transition metals in the same oxidation state in proteins, where also the distances may be less accurate.*

Is d_0 independent of the oxidation state?

Manganese compounds are a good test of the bond-valence method, because many different oxidation states, electronic configurations and coordination geometries are possible, involving 15 rather different ionic radii. We will assume $d_0(\text{MnO}) = 1.75 \text{ \AA}$ and $b = 0.37 \text{ \AA}$ throughout. The presumed correct oxidation states are given in square brackets.

MnO: Mn1 [6] 2.223 Å. $V = 6 \times \exp((1.75 - 2.223)/0.37) = 1.67 [2.0]$

Mn₃O₄: 1Mn1 [4] 2.040 Å. $V = 1.83 [2.0]$
2Mn2 [4] 1.930 + [2] 2.282. $V = 2.93 [3.0]$

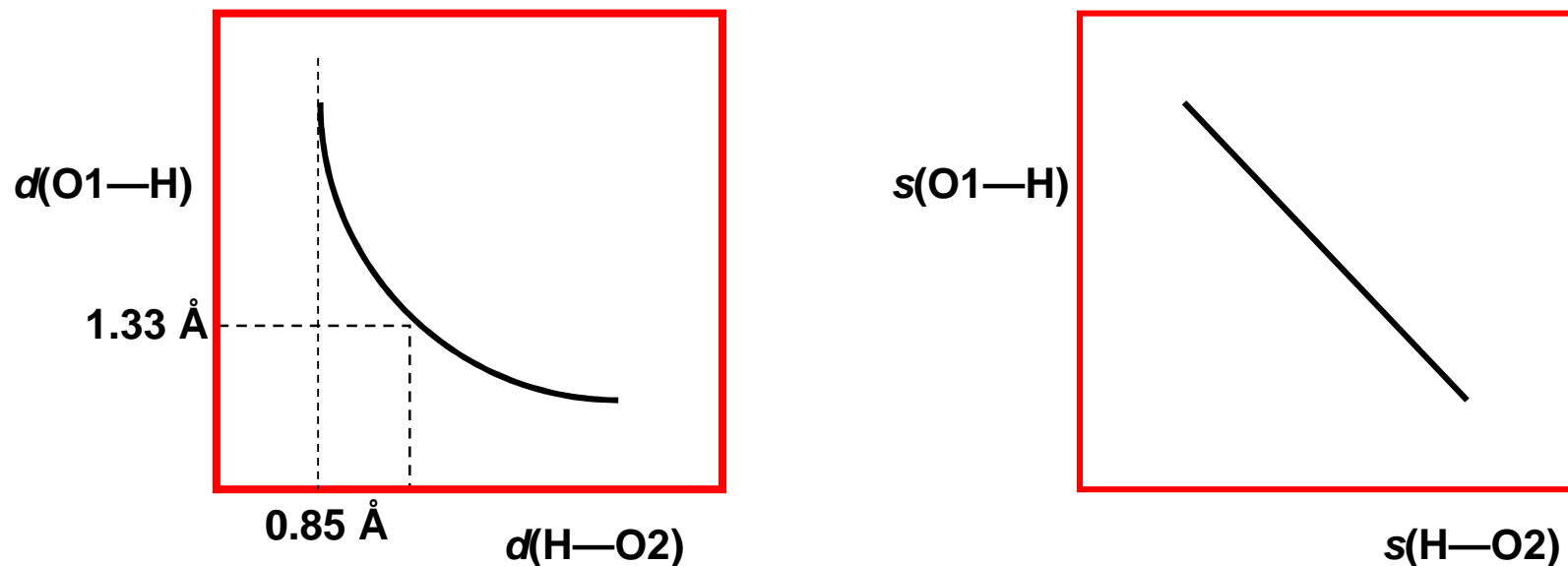
Mn₂O₃: 1Mn1 [2] 1.962 + [2] 1.997 + [2] 2.050. $V = 3.04 [3.0]$
(1Mn2 has a very similar environment).

Mn₅O₈: 1Mn1 [4] 1.853 + [2] 1.879 Å. $V = 4.44 [4.0]$
2Mn2 [2] 1.849 + [2] 1.893 + [2] 1.919 Å. $V = 4.16 [4.0]$
2Mn3 [1] 2.047 + [2] 2.167 + [2] 2.314 + [1] 2.283 Å. $V = 1.77 [2.0]$

MnO₂: Mn1 [2] 1.889 + [1] 1.901 + [1] 1.902 + [2] 1.905 Å. $V = 4.02 [4.0]$

Mn₂O₇: 1Mn [1] 1.574 + [2] 1.588 + [1] 1.762 Å. $V = 5.68 [7.0]$

O1—H...O2 Hydrogen bonds



This relationship becomes linear when the bond valences are plotted instead of distances. $d_0 = 0.85$, $s(\text{OH}) = 0.5$ and a bond length of 1.33 \AA for the symmetric case imply $b \approx 0.7$, appreciably more than the usual 0.37 \AA .

Similar plots can be made for $[\text{I}_3]^-$ anions and SN_2 -reactions.

Uses and limitations of the BV-method

1. The method is good at assigning oxidation states, but elements close in the periodic table can only be distinguished if they must have different oxidation states (e.g. Al and Si in zeolites, or phosphate and sulfate).
 2. O^{2-} , OH^- and OH_2 can be distinguished in minerals, even if the H-atoms cannot be seen in the electron density.
 3. Possible H and Li positions can be predicted (e.g. in structures from powder data).
 4. Conduction pathways may be predicted in ionic conductors.
 5. The lengthening of O–H and N–H bonds involved in hydrogen bonding may be predicted accurately.
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6. The method fails completely for structures with appreciable π -back-bonding such as metal carbonyls in low oxidation states, metal cluster compounds with some metal-metal bonding, as well as for structures that do not have closed shell electronic configurations (e.g. carbenes).