

The Use of Bond Valence Sums in EXAFS Analysis

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- The Bond Valence Model
 - Bond Valence Sums as a check of EXAFS results
 - Can Bond Valence Sums be used in EXAFS Fits?
 - Restraints v. Constraints in EXAFS Analysis
 - *a priori* knowledge
-

Are there simple rules of chemical bonding that
can complement or even assist EXAFS analysis?

Bond Distances and Formal Valence

For inorganic solid-state chemistry:

- **there are nearly universal ionic sizes.**
- **Bond lengths between atoms are correlated with formal valences of the species.**

Pauling's "2nd Rule" of electrostatic valence (Pauling, 1929) gives a common sense view of charge balance at the atomic scale:

The total strength of the valency bonds which reach an ion from all neighboring atoms is equal to the charge of the ion.

This works well for ionic and covalent bonds, and considers only the *near neighbors*.

How can we use this information in EXAFS analysis?

L. Pauling, *J. Am. Chem. Soc.*, 51, pp 1010 (1929)

L. Pauling, *J. Am. Chem. Soc.*, 69, pp 542–553 (1947).

A. Byström and K. A. Wilhelmi, *Acta Chem. Scand.*, 5, pp 1003-1010 (1953).

W. H. Zachariasn, *Acta Cryst.*, 16, pp 385–389 (1963).

I. D. Brown, *Chem. Soc. Rev.* 7, pp.359–376 (1978).

The Bond Valence Model

Following the description of I. D. Brown and D. Altermatt:

1. For inorganic structures, “bond” means all neighboring cation-anion distances (a local structural view).
2. The oxidation state of a cation i can be written as

$$V_i = \sum_j s_{ij}$$

where the sum is over neighboring atoms j , with each bond between atoms i and j having **bond valence** s_{ij} .

3. This **bond valence** is most commonly parameterized as

$$s_{ij} = \exp[(R'_{ij} - R_{ij})/b]$$

where R_{ij} is the bond distance between atoms i and j and

4. R'_{ij} and b are parameters to be determined empirically.

D. Altermatt and I. D. Brown, *Acta Cryst.* B41, pp.240-244 (1985).

I. D. Brown and D. Altermatt, *Acta Cryst.* B41, pp.244-247 (1985).

N. E. Brese and M. O'Keefe *Acta Cryst.* B47, pp.192-197 (1991).

The Bond Valence Model

Brown and Altermatt considered other functional forms, such as

$$s_{ij} = (R_{ij}/R'_{ij})^N$$

but preferred the exponential form, because there seemed to be a **universal value for the empirical parameter b** :

$$b = 0.37 \text{ \AA}$$

Which makes a **One-Parameter Model** relating Formal Valence V , coordination number N , and bond distance R :

$$v_i = \sum_{j=1}^N \exp[(R'_{ij} - R_{ij})/0.37]$$

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Bond Valence Parameters

Altermatt and Brown (1985) analyzed ~ 15000 cation environments from the Inorganic Crystal Structure Database, and determined reliable bond valence parameters R' for ~ 150 bonds, mostly metal-oxygen, and metal-sulfur.

Some Typical Bond Valence Parameters R' (in Å) for metal-oxides from Altermatt and Brown:

Bond	R' (Å)	Bond	R' (Å)
Cu(I)-O	1.593	Cu(II)-O	1.679
Fe(II)-O	1.734	Fe(III)-O	1.759
Mn(II)-O	1.790	Mn(III)-O	1.760
Mn(IV)-O	1.753		

Brese and O'Keefe (1991) and others have tabulated additional bond valence parameters for more anions (F, Cl, Br, Se, H ...).

Bond Valence Examples: Does it work?

$$V_{\text{sum}} = \sum_{j=1}^N \exp[(R'_{ij} - R_{ij})/0.37]$$

Mineral/Site	Oxygen Coordination	V_{sum}	V_{formal}
Cu₂O (cuprite)			
Cu(I)	2 @ 1.849Å	1.002	1
CuO (tenorite)			
Cu(II)	2 @ 1.951Å, 2 @ 1.961Å, 2 @ 2.784Å.	1.993	2
FeO (ferrous oxide)			
Fe(II)	6 @ 2.1387Å	2.010	2
Fe₂O₃ (hematite)			
Fe(III)	3 @ 1.946Å, 3 @ 2.226Å.	2.955	3
CuFeO₂ (cuprous ferrite)			
Cu(I)	2 @ 1.898Å	0.877	1
Fe(III)	6 @ 1.982Å	3.284	3

Bond Valence: Mn-oxides

Mineral/Site	Oxygen Coordination	V_{sum}	V_{formal}
MnO (manganese oxide)			
Mn(II)	6 @ 2.222Å	1.876	2
MnO₂ (pyrolusite)			
Mn(IV)	2 @ 1.878Å, 4 @ 1.891Å	4.181	4
Mn₂O₃ (cubic bixbyite)			
Mn(III)	6 @ 1.993Å	3.196	3
Mn(III)	2 @ 1.899Å, 2 @ 1.985Å, 2 @ 2.248Å	2.997	3
Mn₃O₄ (hausmannite) [tetragonal]			
Mn(II)	4 @ 2.044Å	2.013	2
Mn(III)	4 @ 1.932Å, 2 @ 2.283Å	3.000	3
Mn₃O₄ (makorite) high-pressure phase [orthorhombic]			
Mn(II)	8 between 2.12Å and 2.60Å	1.997	2
Mn(III)	6 between 1.91Å and 2.32Å	3.007	3

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Bond Valence Sums: Two Final Interesting Cases

Mineral/Site	Oxygen Coordination	V_{sum}	V_{formal}
Mn₃O₄ (hausmannite): Wyckoff's description			
Mn(II)	4 @ 1.858Å	3.327	2
Mn(III)	4 @ 2.033Å, 2 @ 2.355Å	2.313	3
Mn₃O₄ (hausmannite): Baron, <i>et al.</i>, <i>Am. Min.</i> 83 (1998)			
Mn(II)	4 @ 2.044Å	2.013	2
Mn(III)	4 @ 1.932Å, 2 @ 2.283Å	3.000	3
Fe₃O₄ (magnetite)			
Fe(III)	4 O at 1.886Å	3.196	3
Fe(II,III)	6 O at 2.060Å	(2.49,2.66)	(2,3)

Part of Brown and Altermatt's motivation was to use bond valence sums and *local coordination* to assess the crystallographic literature.

Conclusion #1:

The Bond Valence Model works remarkably well at relating Formal Valence, Coordination Number, and Bond Length.

Using Bond Valence Sums in EXAFS Analysis

Several groups (G. E. Brown, *et al.*) have used Bond Valence Sums as an *a posteriori* check on results of EXAFS analysis:

1. Do EXAFS Analysis.
2. Do Bond Valence Sum on Resulting Local Structure.
3. Check for “Reasonableness”.

This has proven successful and useful for several real experimental systems (Pb-O, Ti glasses, . . .)

Conclusion #2:

Bond Valence Sums provide a simple, independent check on the Formal Valence, Coordination Number, and Bond Lengths determined from EXAFS analysis.

F. Farges, G. E. Brown, Jr., A. Navrotsky, H. Gao, J. J. Rehr, *Geochim. Cosmochim. Acta* 60, pp.3039–3053 (1996).

J. R. Bargar, G. E. Brown, Jr., and G. A. Parks, *Geochim. Cosmochim. Acta* 61, pp.2617–2637 (1997).

K. Xia, W. Bleam, P. A. Helmke, *Geochim. Cosmochim. Acta* 61, pp.2223–2235 (1997).

F. Farges, D. Neuville, G. E. Brown, Jr., *Am. Mineralogist* 84, pp.1562–1568 (1999).

M. I. Davis, *et al.*, *Inorg. Chem.* 38, pp.3676–3683 (1999).

Bond Valence Sums as a Fitting Constraint

Can we use the connection between R , N , and V in the fit itself?

If we assume we know the Valence State (say from the XANES), we can constraint N and average bond-length $\langle R \rangle$:

$$\langle R \rangle = R' + 0.37 \log(N/V)$$

```
guess e0      = 1.0 # e0 shift
guess sig2    = 0.02 # sigma2
set   s02     = 0.7 # Amp factor

guess N       = 6.0 # Coord. Number
set   bv      = 1.79 # B.V. for Mn(II)
set   V       = 2.0 # Formal Valence

      R       = bv + 0.37*(log(N/V))

path(index    = 1, degen = 1,
      label   = 'Mn-O for MnO',
      feff    = feff0001.dat,
      delr    = (R - reff),
      amp     = s02 * N,
      e0      = e0,      sigma2 = sig2 )
```

Configuration file **constraining** N and R to the Bond Valence R' and Formal Valence V for a fit of the 1st shell of MnO.

E_0 , σ^2 , and N are varied.
 S_0^2 , V and R' are fixed.

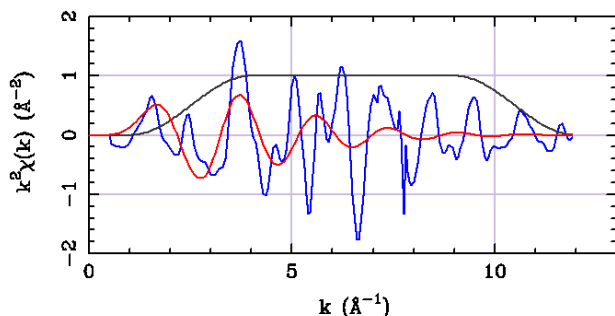
Fits were done in R -space, using FEFF calculation for Mn-O, with k -weight = 2.0 and fit ranges:

$$k = [2.50, 10.50] \text{ \AA}^{-1}$$

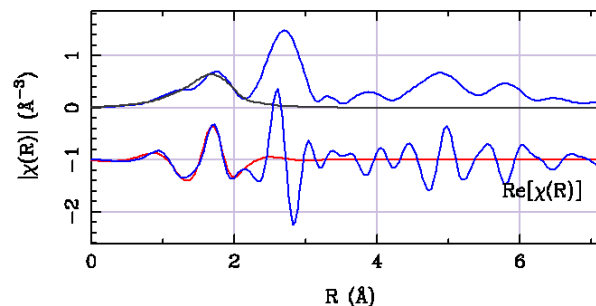
$$R = [1.15, 2.20] \text{ \AA}$$

Constraining N and R for MnO

For MnO, with only one site and one Mn-O distance, the simple constraint works well:



Mn-O EXAFS $k^2\chi(k)$ and 1st shell fit with Bond-Valence Constraint. **Data** (From Lytle) and **Fit**.



$|\chi(R)|$ and $\text{Re}[\chi(R)]$ for 1st shell fit with Bond-Valence Constraint. **Data** and **Fit**.

Fit Variable	Best-Fit Value	
N	6.45	(0.7)
E_0	1.1	(2.1)
σ^2	0.015	(0.004)
R	2.22	[0.02]

\mathcal{R} -factor = 0.045, $\chi^2 = 29.8$,
 $2\Delta k\Delta R/\pi = 5.12$.

We get values very close to crystallography: $N = 6$, $R = 2.22\text{\AA}$.

Using Bond Valence Sum to constrain N , R , and V works well for **one coordination shell**.

Will it work for a shell with more than one distance?

Bond Valence Constraints for Mn_2O_3 and Mn_3O_4 ?

Mn_2O_3 has 2 sites and 4 Mn-O distances between 1.90 and 2.25Å, so an average like $\langle R \rangle$

$$\langle R \rangle = R' + 0.37 \log(N/V)$$

may not work. We're near the limit of available data ($\approx 2\Delta k \Delta R / \pi$) to see all those distances well enough for the B.V. sum to be accurate.

For Mn_3O_4 , with 2 sites, a wider range of distances, and 2 *valence states*, the situation is hopeless.

If the Bond Valence sum is only good to 10%, do we really want to impose it as a constraint?

Conclusion #3:

Bond Valence Sums can be used to constraint R , and N , and V in EXAFS analysis for some cases, but not all cases.

Fitting Restraints

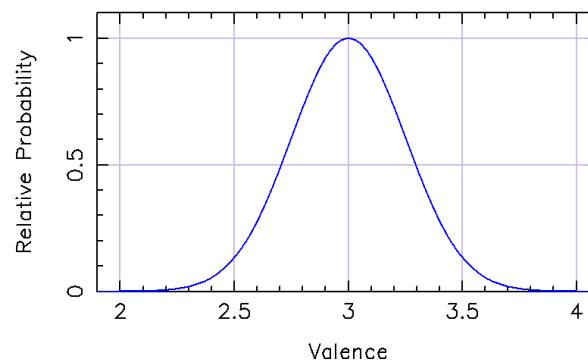
We'd like the valence for Mn_2O_3 to be close to 3, but don't want to force it to be exactly 3. That is, we want a *statistical preference* not a *exact mathematical constraint* for a Bond Valence value.

Consider a Gaussian distribution for “Valence”:

We could choose the ideal valence (centroid), the “*uncertainty*” in that valence (FWHM), and the relative importance of this term (Height) compared to our EXAFS data.

We'd do the bond valence sum based on our EXAFS data, and try to persuade it toward the expected Valence without forcing it.

This is called a fitting *restraint*.



A typical Gaussian “expected distribution” for Bond Valence Sum of a coordination shell.

Fitting Restraints vs. Fitting Constraints

While a **constraint** is an exact mathematical relationship between variables in the fitting model, a **restraint** is a *statistical preference* for a value or set of values.

Restraints have been used in other fields (say, x-ray diffraction analysis with SHELX), and have been discussed for EXAFS analysis by Binsted, *et al.* for EXCURVE98.

The idea is similar to the classic approach of

“Fit, Calculate the Bond Valence, Check Result”

but we’ll put the sum and “check” right into the fit, and steer the Valence toward a preferred value statistically.

When refining local structures from XAFS data, it may be useful to give some statistical preference to the expected Bond Valence Sum around the central atom.

How to Impose a Restraint:

A “normal” fit minimizes a χ^2 statistic by adjusting variables \vec{x} :

$$\chi^2 \sim \sum_i^N \left[\frac{\tilde{\chi}_i^{\text{data}} - \tilde{\chi}_i^{\text{model}}(\vec{x})}{\epsilon_i} \right]^2$$

A **restraint** is just another term, λ , added to the function to minimize:

$$\chi^2 \sim \sum_i^N \left[\frac{\tilde{\chi}_i^{\text{data}} - \tilde{\chi}_i^{\text{model}}(\vec{x})}{\epsilon_i} \right]^2 + \lambda(\vec{x}, \vec{b})$$

λ depends on the fit variables \vec{x} (set of R , N , and E_0) and on parameters \vec{b} (our Gaussian centroid and FWHM!). Consider

$$\lambda(\vec{x}) = \left[(V(\vec{x}) - V_0) / \delta V \right]^2$$

where V_0 is the “Expected Formal Valence”, and δV measures our confidence in that V_0 relative to our confidence in our data.

Fitting Restraints:

With restraint $\lambda(\vec{x}) = ([V(\vec{x}) - V_0]/\delta V)^2$, our χ^2 becomes

$$\chi^2 \sim \sum_i^N \left[\frac{\tilde{\chi}_i^{\text{data}} - \tilde{\chi}_i^{\text{model}}(\vec{x})}{\epsilon_i} \right]^2 + \left[\frac{V(\vec{x}) - V_0}{\delta V} \right]^2$$

The restraint adds another “data point” to our fit, with “data” $V(\vec{x})$ and “model” V_0 , and uncertainty δV .

$\delta V \rightarrow 0$	Force $V(\vec{x}) = V_0$	constraint
$\delta V \rightarrow \infty$	$V(\vec{x})$ determined by our data alone	no prior knowledge
Finite δV	$V(\vec{x})$ influenced by our data <i>and</i> V_0	restraint!

δV lets us “**numerically tune**” our belief in the Bond Valence Sum.

A restraint gives a Gaussian distribution for V around V_0 , and allows us to quantify our *prior knowledge* of our system.

Bond Valence Restraint for MnO

Recall that ideally for MnO, $N = 6$, $R = 2.222\text{\AA}$. Varying N , R , E_0 , and σ^2 , and changing the Restraint Weight δV for the Bond Valence Sum shows:

δV	0.01	0.1	1.0	10.0	100.0
	Constrained		→	Free	
R (Å)	2.223(.05)	2.223(.04)	2.226(.04)	2.229(.03)	2.229(.03)
N	6.4(0.8)	6.4(0.8)	5.6(1.0)	4.7(1.4)	4.7(1.5)
V_{sum}	1.999	1.983	1.718	1.437	1.439
E_0	1.2(2.6)	1.2(2.8)	0.6(3.3)	0.1(3.1)	0.1(3.2)
σ^2 (Å ²)	0.0158(4)	0.0157(4)	0.0131(4)	0.0100(5)	0.0102(6)
\mathcal{R}	0.035	0.035	0.025	0.021	0.021
χ^2	21.4	21.1	16.4	12.7	12.7
Correlations					
$C(N, R)$	1.00	0.97	0.28	-0.02	-0.02
$C(N, \sigma^2)$	0.57	0.56	0.80	0.89	0.90
$C(R, E_0)$	0.92	0.92	0.90	0.90	0.90

$$S_0^2 = 0.70$$

Bond Valence Restraint for Mn_2O_3

Returning to Mn_2O_3 with two Mn(III)-O octahedra and 3 different Mn-O distances

- one regular (6 O @ 1.993Å).
- one distorted (2 O @ 1.985Å, 2 O @ 1.899Å, and 2 O @ 2.248Å).

and data (from Lytle) limited to 12 \AA^{-1} ($2\Delta k\Delta R/\pi \approx 7$), we ask:

Can the Bond Valence Sum help us see the splitting in the Mn-O shell?

We assert the following “prior information” on our data:

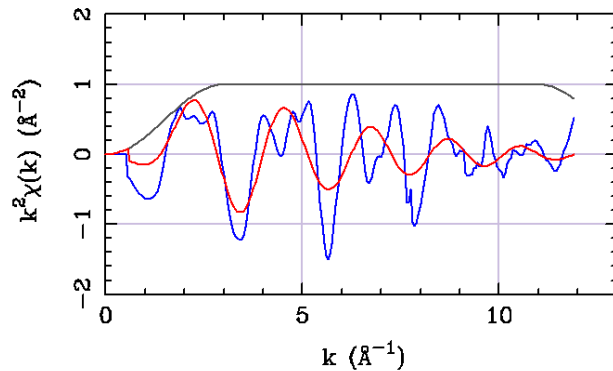
- The Valence for both sites should be close to +3.
- one Mn site has 6 O at one distance
- the other Mn site has 2 bonds that are the same length as the regular octahedron, 2 “short” O bonds, and 2 “long” O bonds.

We'll vary 3 distances, N , E_0 and σ^2 , and set S_0^2 to 0.7 as before (6 variables).

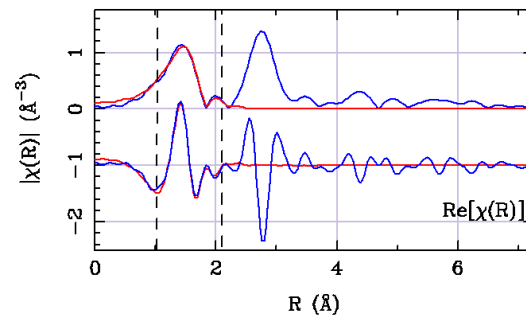
We'll *restrain* both sites to have a Bond Valence Sum near 3:

$$\lambda_1 = \left[(V(R_1) - V_0) / \delta V \right]^2$$
$$\lambda_2 = \left[(V(R_1, R_2, R_3) - V_0) / \delta V \right]^2$$

Bond Valence Restraint for Mn_2O_3



Mn_2O_3 $k^2 \chi(k)$ Data (From Lytle) and Fit with Bond-Valence Restraint.



Mn_2O_3 $\chi(R)$ and $\text{Re}[\chi(R)]$ for Data and Fit with Bond Valence Restraint.

Using $\delta V = 1$:

Parameter	Value	Fit Variable	Best-Fit Value	Predicted
$C(N, R_1)$	0.2	N	5.86 (0.7)	6
V_1 (regular)	3.40	E_0	1.2 (1.9)	
V_2 (distorted)	3.00	σ^2	0.005 (0.004)	
\mathcal{R}	0.007	R_1 ($8x$)	1.96 (0.02)	1.99
χ^2	91.8	R_2 ($2x$)	1.85 (0.09)	1.90
$2\Delta k \Delta R / \pi$	7.2	R_3 ($2x$)	2.28 (0.05)	2.25

Conclusions

- The Bond Valence Model is a simple, powerful way to check the results of XAFS analysis – especially the connection between R , N , and formal valence.
- Bond Valence Sums may be appropriate for hard constraints in some EXAFS analysis, but this is not universal.
- Use of Bond Valence as *a priori* knowledge of bonding environment and as a fitting *restraint* may be appropriate in a much wider range of systems.
- Could there be other *a priori* knowledge to use as a fitting restraints for your system?