

Charge Distribution and Effective Coordination Number as a tool to investigate structural details



Nancy-Université
 Université
Henri Poincaré

Prof. Massimo Nespolo

CRM2 Université Henri Poincaré Nancy 1 – France
Chair, Commission on Mathematical and Theoretical
Crystallography, International Union of Crystallography

“Charge”? Did I say “Charge”?

Charge Distribution “dictionary”

- ✧ **Charge** = formal oxidation number
- ✧ **PC atom** = an atom sitting at the centre of a coordination polyhedron (**P**olyhedron-**C**entring atom: **red** hereafter)
- ✧ **V atom** = an atom sitting at the corner of a coordination polyhedron (**V**ertex atom: **blue** hereafter)
- ✧ The CD method works in the framework of a Madelung description of the structure (**PC-V** bonds but not **PC-PC** or **V-V** bonds). However, it does not depend on the type of chemical bond.
- ✧ ECoN is instead defined also for homo-nuclear bonds.

Historical background

1929 Birth of the concepts of Bond Strength (**BS**)
(Linus Pauling)



1960~ Introduction of the dependence of the BS from the bond length (**BL**)
(Evans, 1960; Zachariasen, 1963; Clark, Appleman e Papike, 1969; *Baur*, 1970)



1970~The R-s curves – birth of the Bond Valence (**BV**) method - are introduced
(I.D. Brown et al., 1973; 1976; 1985)



1979 ECoN (**E**ffective **C**oordination **N**umber) (Rudolf Hoppe)



1989 Charge Distribution (**CD**) (R. Hoppe et al)



1999 Extension of the applicability of the CD method
(M. Nespolo et al)

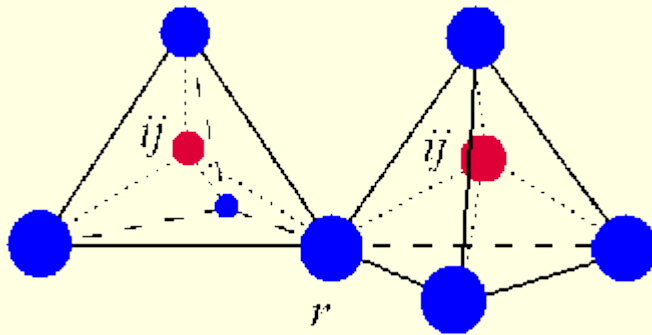


2001 Extension of the CD method by introduction of the recursive formulas and refined exponent for hydrogen bonds
(M. Nespolo et al)

Notation

- *i-th* chemical species of the **PC** atom (different by atomic number AND formal oxidation number)
- *j-th* crystallographic type of **PC** atom (different by Wyckoff position)
- *r-th* chemical species of **V** atom (different by atomic number AND formal oxidation number)
- *s-th* crystallographic type of **V** atom (different by Wyckoff position)
- *ij* → *rs* : the bond (or non-bond!) between the *ij*-th **PC** atom and the *rs* **V** atom
- **PC-V** distances ordered increasingly → minimal distance = d_1

Definition of Pauling's bond strength



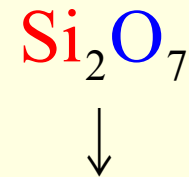
$s(ij)$ = bond strength

$q(ij)$, $q(rs)$ = formal oxidation number (“charge”) of the cation (ij) / anion (rs)

$N(ij)$: (classical) coordination number of the cation

$$s(ij \rightarrow rs) = \frac{q(ij)}{N(ij)}$$

$$-\sum_{ij} s(ij \rightarrow rs) = q(rs)$$



$$s[\text{Si}(ij) \rightarrow \text{O}(rs)] = \frac{4}{4} = 1$$

$$-\sum_1^2 s[\text{Si}(ij) \rightarrow \text{O}(rs)] = -2$$

Definition of bond strength according to the Bond Valence concept

$$s(ij \rightarrow rs) = f[d(ij \rightarrow rs), \mathbf{p}]$$

Brown-Shannon, Brown-Wu

$$s(ij \rightarrow rs) = s_0 \left[d(ij \rightarrow rs) / R_0 \right]^{-N}$$

Brown-Altermatt

$$s(ij \rightarrow rs) = s_0 \exp\left\{ \left[R_0 - d(ij \rightarrow rs) \right] / B \right\}$$

and several other curves...

- Parameters ($R_0, N; R_0, B$) fitted on structures refined at **ambient temperature and pressure** → method **hardly applicable** to structures studied at **high pressure/temperature**
- Parameters depend on the **cation-anion pair**
- BV-BL curves do not apply well to polyhedra which span a wide range of distances → curves with **3 parameters** have been introduced

Generalization of the concept of coordination number

The **PC** atom at the centre of a regular polyhedron with N **V**-atoms as vertices has coordination number N

What is the coordination number of the PC atom when the polyhedron is not regular?

How to calculate the mean **PC-V** distance for a general polyhedron?

Answer: use a weighted mean

$$d_{mean} = \frac{\sum_N d_j w_j}{\sum_N w_j} \xrightarrow[\substack{\text{regular} \\ \text{polyhedron} \\ w_j = 1, \forall j}]{\text{regular polyhedron}} d_{mean} = \frac{\sum_N d_j}{\sum_N 1} = N$$

ECoN: Effective Coordination Number

Weighted mean **PC-V** distance $d_{mean} = \frac{\sum d_j w_j}{\sum w_j}$

$$d(ij \rightarrow r) = \frac{\sum_s \sum_L d(ij \rightarrow rs)_L \times \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{d(ij \rightarrow rs)_1} \right]^6 \right\}}{\sum_s \sum_L \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{d(ij \rightarrow rs)_1} \right]^6 \right\}}$$

Bond weight (“geometrical bond strength”)

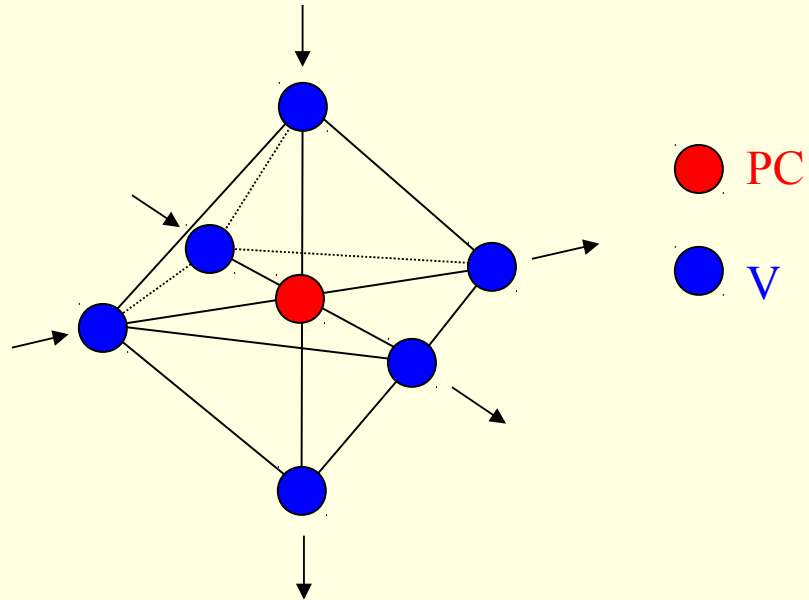
$$BW(ij \rightarrow rs)_L = \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{d(ij \rightarrow r)} \right]^6 \right\}$$

$$ECoN(ij \rightarrow r) = \sum_s \sum_L BW(ij \rightarrow rs)_L$$

$$ECoN(ij) = \sum_r ECoN(ij \rightarrow r)$$

6: ECoN = classical coordination number for regular polyhedra

Example of computation of ECoN



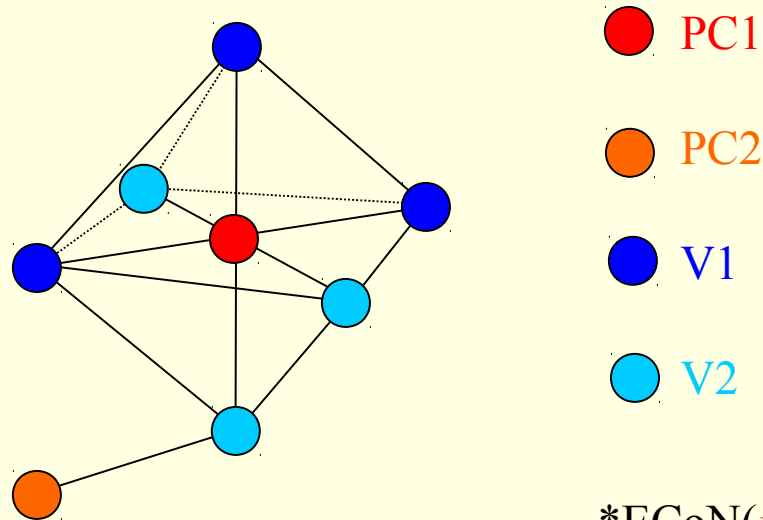
Example of computation of ECoN

PC-V(1) : $d(11 \rightarrow 11)_1$	2.00	1.95	1.89	1.80
BW[$d(11 \rightarrow 11)_1$]	1.00	1.14	1.28	1.36
PC-V(2) : $d(11 \rightarrow 11)_2$	2.00	1.97	1.94	1.87
BW[$d(11 \rightarrow 11)_3$]	1.00	1.08	1.13	1.13
PC-V(3) : $d(11 \rightarrow 11)_3$	2.00	1.99	1.97	1.92
BW[$d(11 \rightarrow 11)_3$]	1.00	1.02	1.03	0.98
PC-V(4) : $d(11 \rightarrow 11)_4$	2.00	2.00	2.02	1.99
BW[$d(11 \rightarrow 11)_4$]	1.00	0.99	0.88	0.76
PC-V(5) : $d(11 \rightarrow 11)_5$	2.00	2.04	2.07	2.18
BW[$d(11 \rightarrow 11)_5$]	1.00	0.87	0.74	0.30
PC-V(6) : $d(11 \rightarrow 11)_6$	2.00	2.05	2.11	2.24
BW[$d(11 \rightarrow 11)_6$]	1.00	0.84	0.63	0.20
Arithmetic mean	2.00	2.00	2.00	2.00
$d(ij \rightarrow r)$	2.00	2.00	1.98	1.91
ECoN(ij)	6.00	5.93	5.69	4.73

“Partial” ECoN

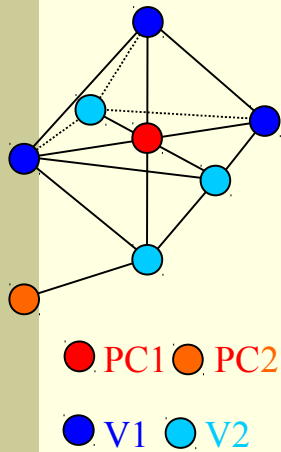
fractional contribution to ECoN of the $PC(ij)$ by $V(rs)$

$$\Delta \text{ECoN}(ij \rightarrow rs) = \frac{\sum_L \text{BW}(ij \rightarrow rs)_L}{\text{ECoN}(ij \rightarrow r)}$$



$$*\text{ECoN}(ij \rightarrow r) = S_{s,L} \text{BW}(ij \rightarrow rs)_L$$

Distribution of the formal oxidation number



$q(ij)$, $q(rs)$ = formal oxidation number of the PC, V $Q(ij)$, $Q(rs)$ = “charge” of the PC, V as obtained from the distribution of $q(ij)$, $q(rs)$

$$Q(rs) = - \sum_{i,j} q(ij) \times \Delta \text{ ECoN}(ij \rightarrow rs) \frac{h(ij)}{h(rs)}$$

$Q(rs) \rightarrow$ structure “balance”: OUB (Over-Under Bonding) effect

$$Q(ij) = q(ij) \times \sum_{r,s} \left[q(rs) / Q(rs) \times \Delta \text{ ECoN}(ij \rightarrow rs) \right]$$

$Q(ij)$ calculated as a function of the “unbalance” $q(rs)$ vs. $Q(rs)$
 \rightarrow structure validation

One more remark on the “charges”

- The computed “charges” Q come from the **distributions of ECoN**, and the formal oxidation numbers q play the role of a **multiplicative factor**.
- Q can be read as true **charges** only in a **pure ionic bond** and in the approximation of **point charges**
- The CD method is a **geometrical analysis**, whose results are read in term of *so-called* “charges” Q

Comparative table of the methods based on the Bond Strength concept

BS method

The Bond Strength is simply the **formal oxidation number divided by the coordination number**. In principle, the method applies only to regular polyhedra

BV method

The Bond Strength is computed from the bond lengths through an empirical curve fitted on a large number of known structures. **Q(PC)** and **Q(V)** convey essentially the **same information**.

CD method

The Bond Strength depends on the geometry (shape, volume, distortion etc.) of each coordination polyhedra. **Q(PC)** **validates the structure**, **Q(A)** **evaluates its balance**.

Comparison of BV and CD

	BV	CD
Bond strength	Depends on the chemical species in the coordination polyhedra (cations)	Depends only on the geometry of the coordination polyhedra
Temperature, pressure	Limitations on the range of T,p	No limitations
Chemical type of cations	Not suitable to the investigation study of isomorphic replacements	Suitable to the investigation study of isomorphic replacements
Evaluation of the applicability of the method	Not included (no internal evaluation criterion)	Included [the <i>internal criterion</i> is Q(M)]
Computation method	Pocket calculator	Computer program※

※ (<http://www.crm2.uhp-nancy.fr/crm2/en/labo/staff/Nespolo/CD.php>) - not the last version!

Example : hedenbergite (1)

p (GPa)	PC	V	$d(ij \rightarrow rs)_l$	d(PC-V) _{av}	$d(ij \rightarrow r)$	BW($ij \rightarrow rs$) _l	ECoN (ij)
0	Ca	O4	2.334 (x2)	2.509	2.429	1.24	6.89
		O1	2.352 (x2)			1.19	
		O3	2.632 (x2)			0.54	
		O3	2.721 (x2)			0.38	
	Fe	O2	2.085 (x2)	2.128	2.125	1.11	5.95
		O1	2.136 (x2)			0.97	
		O1	2.162 (x2)			0.90	
	Si	O2	1.584	1.634	1.627	1.16	3.90
		O1	1.600			1.10	
		O3	1.667			0.86	
		O3	1.685			0.79	

Example : hedenbergite (2)

p (GPa)	PC	V	$d(ij \rightarrow rs)_l$	d(PC-V)av	$d(ij \rightarrow r)$	BW($ij \rightarrow rs$) _l	ECoN (<i>ij</i>)
9.9	Ca	O4	2.296 (x2)	2.429	2.382	1.22	7.20
		O1	2.306 (x2)			1.2	
		O3	2.536 (x2)			0.64	
		O3	2.577 (x2)			0.55	
	Fe	O2	2.036 (x2)	2.079	2.076	1.12	5.95
		O1	2.094 (x2)			0.95	
		O1	2.107 (x2)			0.91	
	Si	O2	1.567	1.618	1.61	1.15	3.88
		O1	1.575			1.13	
		O3	1.654			0.84	
		O3	1.675			0.76	

Example : hedenbergite (3)

p (Gpa)	site	q	Q (CD)	Q (BV [1])	Q (BV [2])	
0	Ca	2.00	2.00	1.97	1.87	
	Fe	2.00	1.96	2.15	2.08	
	Si	4.00	4.02	3.91	3.92	
	σ		0.03	0.13	0.08	
	O1	-2.00	-2.11	-2.06	-2.07	
	O2	-2.00	-1.93	-1.84	-1.87	
	O3	-2.00	-1.96	-2.06	-2.04	
	σ		0.10	0.13	0.11	
	9.9	Ca	2.00	2.00	2.29	2.44
		Fe	2.00	1.97	2.44	2.37
Si		4.00	4.01	4.08	4.09	
σ			0.03	0.38	0.41	
O1		-2.00	-2.13	-2.27	-2.29	
O2		-2.00	-1.89	-1.97	-2.00	
O3		-2.00	-1.98	-2.20	-2.20	
σ			0.12	0.24	0.25	

Structures with deformed polyhedra

Introduction of a **recursive formula** in the computation of $d(\text{mean})$, BW and ECoN

$${}^n d(ij \rightarrow r) = \frac{\sum_s \sum_L d(ij \rightarrow rs)_L \times \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{{}^{n-1} d(ij \rightarrow r)} \right]^6 \right\}}{\sum_s \sum_L \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{{}^{n-1} d(ij \rightarrow r)} \right]^6 \right\}}$$

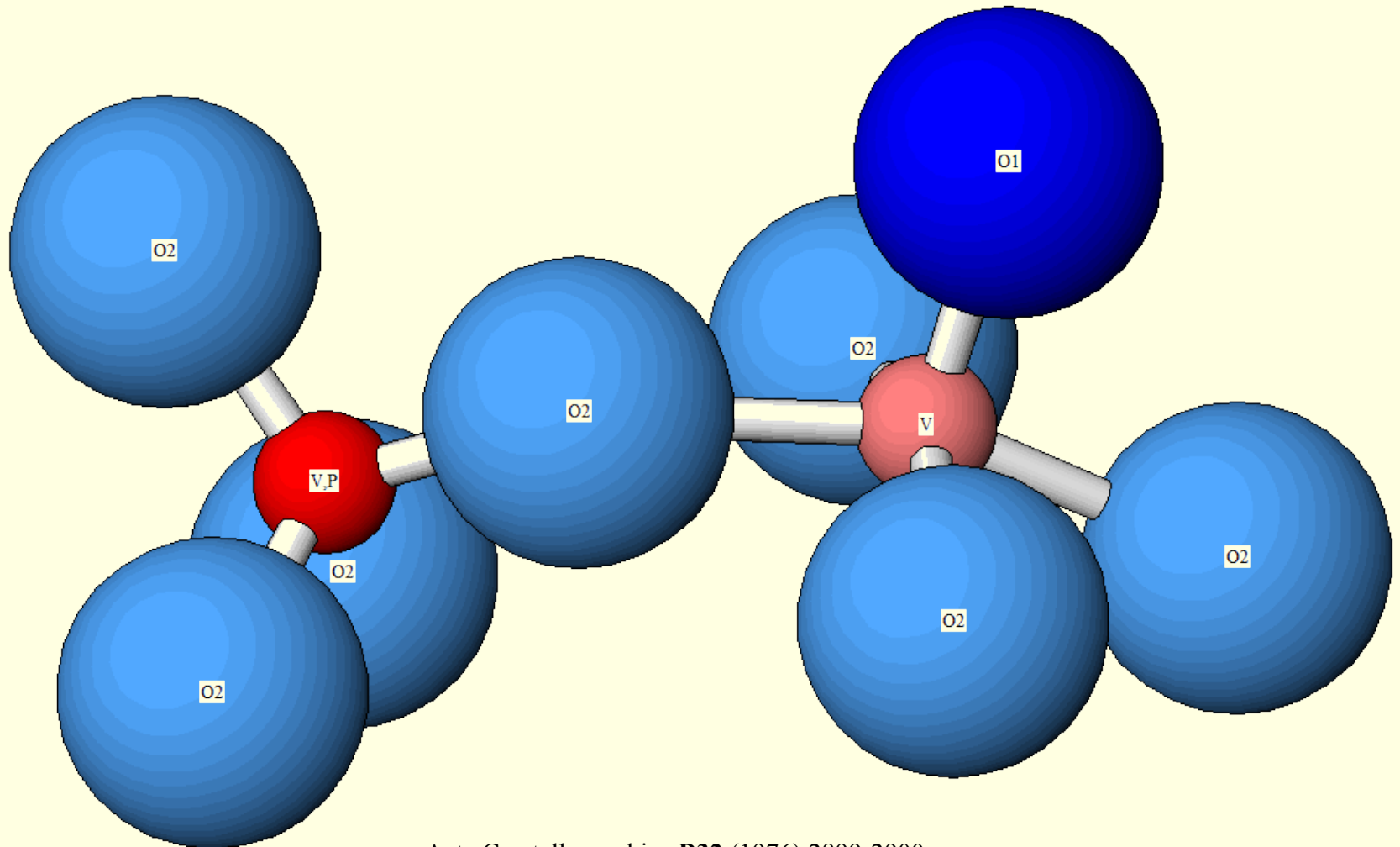
$${}^0 d(ij \rightarrow r) = d(ij \rightarrow rs)_1$$

$${}^n \text{BW}(ij \rightarrow rs)_L = \exp \left\{ 1 - \left[\frac{d(ij \rightarrow rs)_L}{{}^n d(ij \rightarrow r)} \right]^6 \right\}$$

$${}^n \text{ECoN}(ij \rightarrow r) = \sum_s \sum_L {}^n \text{BW}(ij \rightarrow rs)_L$$

$${}^n \text{ECoN}(ij) = \sum_r {}^n \text{ECoN}(ij \rightarrow r)$$

Example : $\text{V}_{1.08}\text{P}_{0.92}\text{O}_5$ (1)

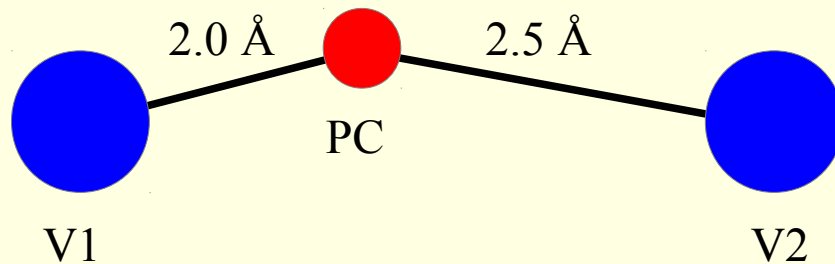


Example : $V_{1.08}P_{0.92}O_5$ (2)

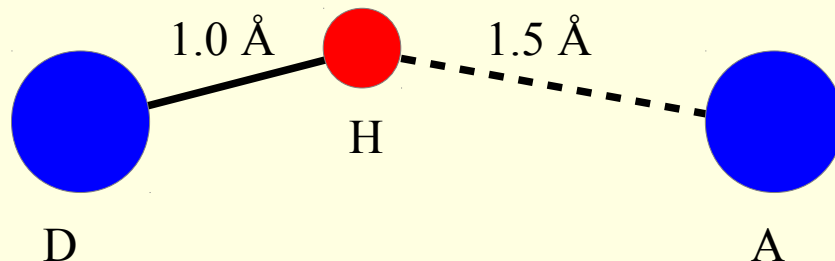
PC atoms	q	distances	${}^1\text{ECoN}$	Q	n	${}^n\text{ECoN}$	Q
V	5.00	O1 : 1.578 O2 : 4×1.897	2.86	4.71	10	3.81	4.94
0.92P+0.08V	5.00	O2 : 4×1.514	4.00	5.29	1	4.00	5.06
σ				0.41			0.10
V atoms	q			Q			Q
O1	-2.00			-2.44			-2.10
O2	-2.00			-1.89			-1.98
σ				0.46			0.10

Hydrogen bonds

Specificity of hydrogen bonds: short bonds with huge (relative) difference between the D-H and H...A bond distances



$$\begin{aligned} 2.5/2.0 &= 1.25 \\ \exp\{1 - [1.25]^6\} &= \exp\{1 - 3.81\} \\ &= \exp\{-2.81\} = 0.06 \end{aligned}$$



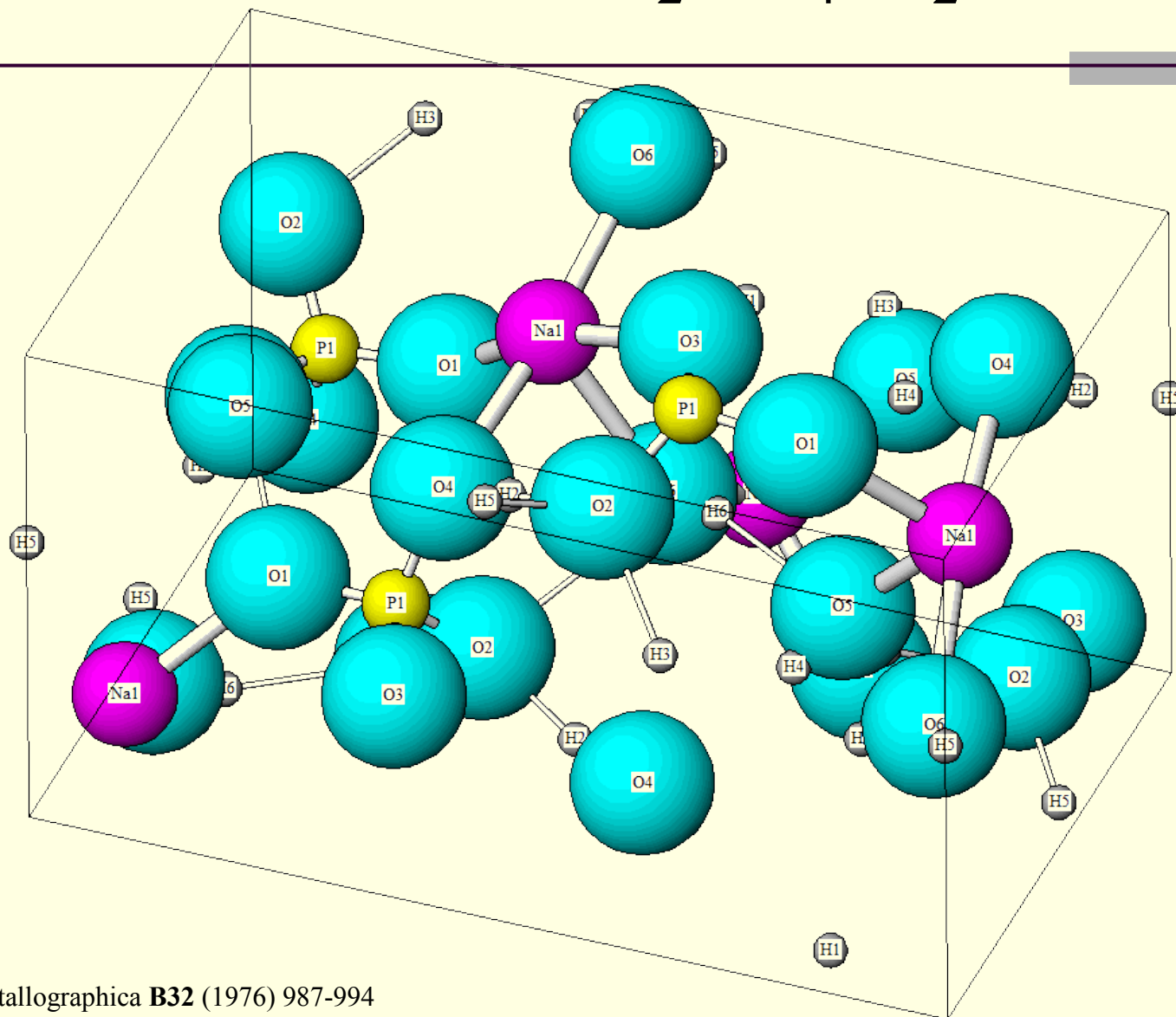
$$\begin{aligned} 1.5/1.0 &= 1.5 \\ \exp\{1 - [1.5]^6\} &= \exp\{1 - 11.39\} \\ &= \exp\{-10.39\} = 3.07 \times 10^{-5} \end{aligned}$$

Hydrogen bonds

- When $PC = H$, re-refinement of the exponent on the basis of a set of structures solved and refined by single-crystal neutron diffraction

$${}^n d(\mathbf{H} \rightarrow r) = \frac{\sum_s \sum_L d(\mathbf{H} \rightarrow rs)_L \exp \left\{ 1 - \left[\frac{d(\mathbf{H} \rightarrow rs)_L}{n^{-1} d(\mathbf{H} \rightarrow r)} \right]^{1.6} \right\}}{\sum_s \sum_L \exp \left\{ 1 - \left[\frac{d(\mathbf{H} \rightarrow rs)_L}{n^{-1} d(\mathbf{H} \rightarrow r)} \right]^{1.6} \right\}}$$

Example : $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (1)



Example : $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (2)

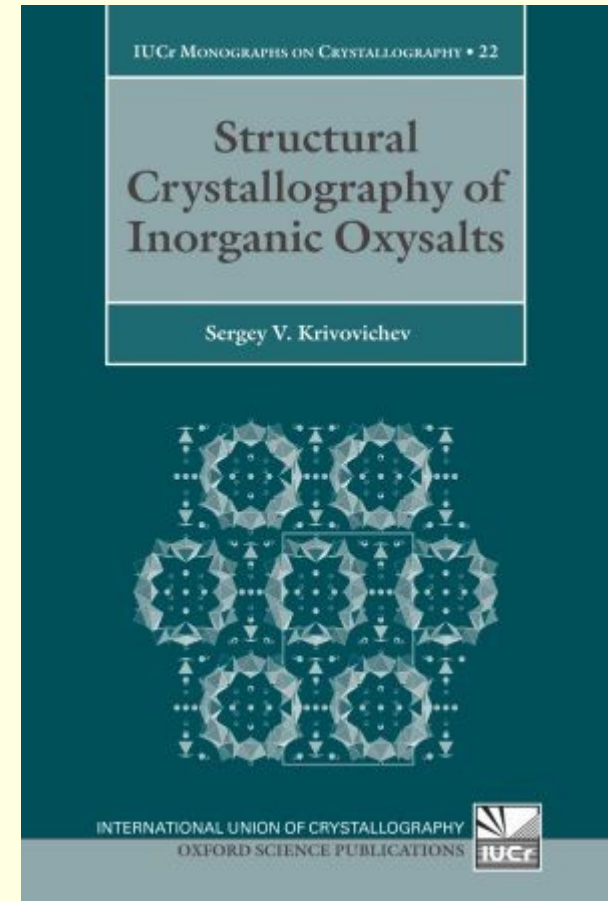
P	Na	H1	H2	H3	H4	H5	H6
1.4970	2.3352	0.8288	0.9580	0.8793	0.9419	1.1145	0.8508
1.5195	2.3776	1.7607	1.5909	1.9746	2.2961	1.7202	2.1109
1.5774	2.4353						
1.5779	2.4608						
	2.4651						
	2.5341						

Example : $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (3)

Atom	q	n	${}^n\text{ECoN}$ (6)	Q (6)	n	${}^n\text{ECoN}$ (1.6)	Q (1.6)
P	5.00	2	3.92	5.70	2	3.92	5.10
Na	1.00	3	5.82	0.95	3	5.82	1.01
H1	1.00	1	1.00	0.90	9	1.39	0.97
H2	1.00	1	1.00	0.91	7	1.74	1.02
H3	1.00	1	1.00	0.92	8	1.30	0.95
H4	1.00	1	1.00	0.92	1	1.00	0.94
H5	1.00	1	1.00	0.85	6	1.81	1.00
H6	1.00	1	1.00	0.85	6	1.17	1.01
σ				0.28			0.05
O1	-2.00			-1.69			-1.82
O2	-2.00			1.36			-2.05
O3	-2.00			-2.23			-2.10
O4	-2.00			-2.21			-1.93
O5	-2.00			-2.17			-2.12
O6	-2.00			-2.34			-1.98
σ				0.39			0.11

“Anion”-centred structures

- Usually, non-molecular structures are described in terms of polyhedra centred on electropositive atoms (“**cations**”) with corners occupied by electronegative atoms (“**anions**”).
- This is mainly because “anions” are usually larger than “cations” and fill most of the crystal space, while “cations” enter the “holes” left by the distribution of “anions” (**Pauling's first rule**)
- An increasing number of structures that are better described by “**anion**”-centred polyhedra is reported in the literature – the current knowledge is summarised in Krivovichev's recent book.



Summary

- **Main applications:** Structure validation, investigation of structural details
- **What else?** Seek for missing atoms through “charge” maps (ex. light atoms in presence of heavy atoms)
Differentiation of the oxidation state of atoms with different “charge” (e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$)
- **Limits:**
 - Simple Madelung-type approach, don't ask for hints about electronic density or other advanced features!
 - When it works, it works pretty well! But it's not a universal panacea for troublesome structures!
 - It doesn't work when only one type of **PC** or **V** atom is present (nothing to “distribute”)
 - In principle, it doesn't work on structures with **PC-PC** / **V-V** bonds – but you can use the barycenter of the bond as “virtual atom” (currently under investigation)
 - “Cation”-centred structured vs. “anion”-centred structures: probably not only a size-effect; the topology of the bond networks is currently investigation in terms of graph theory

Prerequisite: reliable bond distances → **correctly refined structure**