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A new relation between bond valence and bond distance

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A new empirical relationship $s = s_0(R^0 - \lambda)^3/(R - \lambda)^3$ between bond distances and bond valences is proposed, where s is the bond valence for the bond distance R, s_0 is the reference bond valence for the reference system with the reference bond distance R^0 and λ is the sum of the cation radii of bonding atoms defined by Pauling. Since λ is the size of the inner electron region, $R - \lambda$ represents the valence electron region between bonding atoms. The new relationship was derived based on the following three hypotheses. (i) The number of electrons (p) in the volumes of $(R - \lambda)^3$ in a coordination polyhedron are equal, even if the bond distances are not equal to each other. (ii) The average electron density $p/(R - \lambda)^3$ is a measure of covalent bond strength. (iii) The sum of the average electron densities around the central atom is conserved, even if the coordination number changes. The new relationship is applicable not only to polyhedra with one type of ligand atom, but also to polyhedra with two or more types of ligand atoms and explains why the Brown–Shannon formula [Brown & Shannon (1973). *Acta Cryst.* A**29**, 266–282] and the Brown–Altermatt formula [Brown & Altermatt (1985). *Acta Cryst.* B**41**, 244–247] work well. The new relationship was applied to a penta-coordinated silicon compound, strong hydrogen-bond systems and some organic compounds with carbon–carbon bonds.

1. Introduction

Bond valence s is defined as the classical valence shared with each bond (throughout this paper, the term 'classical valence' represents the 'valence' proposed in the 19th century). The bond-valence sum rule requires that the sum of the bond valences around a given atom j should be equal to the classical valence of the atom, Z_j

$$Z_j = \sum_i^{n_j} s_{ij}, \tag{1}$$

where i represents an atom bonded to atom j and n_j is the number of atoms bonded to j. Atom i is usually chosen as an electropositive atom and atom j an electronegative atom such as oxygen. Equation (1) shows that Z_j is conserved to be the classical valence of atom j, even if the number of atom i is beyond the classical valence of atom j. O atoms in minerals, for example, are often bonded to three or four electropositive atoms, but their bond-valence sums should be two. Since Pauling's (1929) pioneering work, considerable attention has been attracted to the bond-valence sum rule (Bragg, 1931; Brown, 1978, 1992, and references cited therein; Burdett, 1995; Rutherford, 1998), because of its remarkable usefulness for inorganic structural chemistry. To calculate s_{ij} for a given atom pair, several empirical formulae associating the bond valence with bond distance were proposed (Donnay & Allmann, 1970; Brown & Shannon, 1973; Brown & Altermatt, 1985; Brese & O'Keeffe, 1991; Naskar *et al.*, 1997). Especially, the Brown–Shannon (1973) and Brown–Altermatt (1985) formulae are widely applicable. However, the following essential questions still remain. Why do both the power forms of the Brown–Shannon formula $(R^0/R)^N$ and the exponential form of the Brown–Altermatt formula $\exp[(r_0 - r)/B]$ work so well? Does the bond-valence sum rule always hold good? If the sum of s_{ij} is largely deviated from Z_j, what does the deviation imply? It is considered that the bond-valence sum rule should be interpreted by chemical bond theory and nowadays the chemical bond is usually analysed with molecular orbital theory or ligand field theory. What molecular orbital quantity corresponds to bond valence s_{ij}? In order to answer these questions, the physical background of the bond-valence sum rule should be taken into account.

Brown & Shannon (1973) pointed out that the bond valence is directly related to the covalent character of metal–oxygen bonds. Moreover, Brown (1978, 1992) proposed that the bond-valance sum rule is an extended form of the 'ball and stick' model used for organic compounds and referred to the relation between the bond-valence model and the Lewis electron-pair bond model. The author infers further that if the bond valence is a measure of covalent bond strength, it should be closely related to the electron density distributed in the region between the two atoms bonded together. On the basis of this inference, not using any curve- and parameter-fitting, a new bond-valence–bond-distance formula was searched. The purpose of the present paper is to present the new empirical relation on bond valences and other related new findings.

Urusov (1991) derived the Brown–Shannon and Brown–Altermatt formulae using the Born–Mayer's lattice energy formula and the modified Morse potential function. The present work gives different derivations for the Brown–Shannon and Brown–Altermatt formulae. Molecular orbital studies on the bond-valence sum rule were performed (Burdett & McLarnan, 1984; Burdett & Hawthorne, 1993) and an explanation for the rule was given (Burdett & Hawthorne, 1993; Burdett, 1995). However, the viewpoint of the present work is different from that of Burdett and co-workers.

In order to test the third power relation in the new bond-distance–bond-valence formula, bond distances of many coordination polyhedra, MX_ν, were collected, where M is the central atom coordinated by ligand atoms X and ν is the coordination number. The collected bond distances are listed in Table 1 (in this study the term 'coordination polyhedra' has a wide sense so that chemical species which are usually not regarded as coordination compounds are included. Such examples are BF_3, CO_2, SO_4^{2-} and $NaCl_6$ octahedra in the NaCl crystal). From Table 1, we can easily see the respective bond distances of polyhedra $MX_{\nu1}$ and $MX_{\nu2}$ ($\nu_1 \neq \nu_2$) for many combinations of M and X. In this table the 'bond distance' is the average bond distance for each 'polyhedron' found in the 'compound'; the symbols such as 'LiO4' express the central atom, the ligand atoms and the coordination number. The symbols do not distinguish isolated molecules from bounded ions or moieties in solids. When two or more polyhedra of the same type are present in a compound and the difference between average bond distances of the two poly-

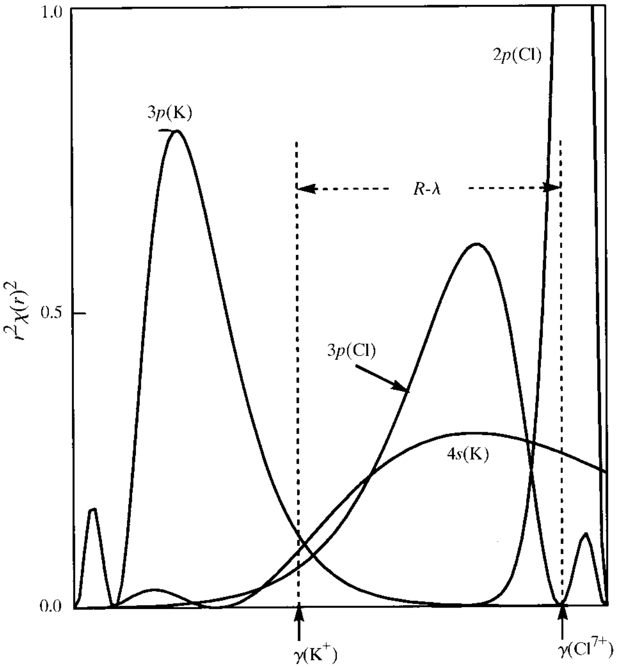


Figure 1
Radial distribution functions for the $3p$ and $4s$ orbitals of the K atom, and the $2p$ and $3p$ orbitals of the Cl atom. The left side is K and the right side Cl with K—Cl 3.146 Å.

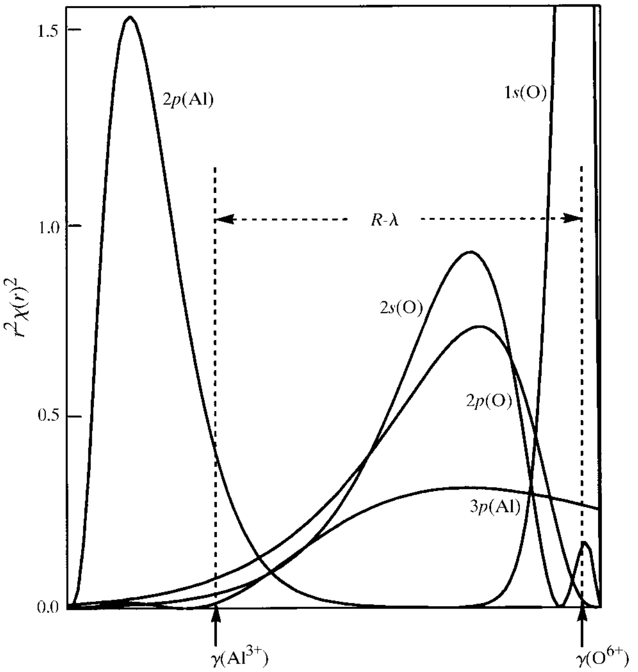


Figure 2
Radial distribution functions for the $2p$ and $3p$ orbitals of the Al atom, and the $1s$, $2s$ and $2p$ orbitals of the O atom. The left side is Al and the right side O with Al—O 1.91 Å.

hedra is more than 2%, both average distances are listed in the table. The reason why the average distance is used as the 'proper distance' of a polyhedron originates from the empirical fact that the average $M-X$ distance in a coordination polyhedron MX_ν is virtually constant, even if the environment around MX_ν changes (Cruickshank, 1961; Burdett, 1995). This is termed the 'averaging effect' for bond distance in this study.

When corrected bond distances for thermal motion are available, the corrected values are used. For molecules in the gas phase, two types of bond distance are measured: r_e and r_g (Kuchitsu, 1968, 1971). r_g is a more suitable measure for the 'chemical bond distance' rather than r_e. However, the difference between r_g and r_e is usually small, *i.e.* $r_g > r_e$ by ~0.01 Å, while the accuracy of the average bond distances for the same type of MX_ν polyhedra is ~0.01 Å. r_e rather than r_g is used when r_g data are not available.

2. Derivation of the new relation

The bond distance R is divided into two parts: valence-electron part and inner-electron part. The valence-electron part is expressed as $R - \lambda$. λ is taken as the sum of the cation radii of M and X, since the cation radius is regarded as the region in which most of the inner electrons are localized. For example, the cation radii of Al and O atoms are in the localization region of $1s^22s^22p^6$ and $1s^2$ electrons, respectively. The cation radius of the Cl atom is the radius of Cl^{7+} with $1s^22s^22p^6$, whereas the cation radius of the H atom is taken to be zero. As the bond-valence value from the new relation is insensitive to the accuracy of the cation radii, both

Table 1
Source data of bond distances collected for this study.

No.	Polyhedron	Bond distance	Reference			Compound
1	LiO4	1.95	68 JSPSA6	48	5561	$LiSO_4\cdot H_2O$
2		1.948	72 ACBCAR	29	682	$LiHCOO\cdot H_2O$
3		1.952	75 ACBCAR	31	1946	$LiHCOO\cdot H_2O$
4		1.967	78 ACBCAR	34	741	$LiGaO_2\cdot 6H_2O$
5	LiO5	2.092	72 ACBCAR	28	2037	$LiHC_2O_4\cdot H_2O$
6		2.057	76 ACBCAR	32	2381	$LiC_4H_5O_5$
7	LiO6	2.133	75 ACBCAR	31	1735	$LiClO_4\cdot H_2O$
8	LiF4	1.883	74 ACBCAR	30	2678	$Na_3Li(BeF_4)_2$
9		1.85	76 ACBCAR	32	1356	$RbLi_2Be_2F_7$
10	LiF6	2.009	71 ZAACAB	386	335	$LiCaAlF_6$
11	BeF4	1.552	74 ACBCAR	30	2678	$Na_3Li(BeF_4)_2$
12		1.545	75 ACBCAR	31	1895	$Co(NH_4)_2(BeF_4)_2\cdot 6H_2O$
13		1.55	76 ACBCAR	32	1356	$RbLi_2Be_2F_7$
14	BeO3	1.52	77 ACBCAR	33	381	Y_2BeO_4
15	BeO4	1.618	69 ACBCAR	25	310	$Be(SO_4)_2\cdot 4H_2O$
16		1.630 (riding)	69 ACBCAR	25	310	$Be(SO_4)_2\cdot 4H_2O$
17		1.653	72 ACBCAR	28	1899	$Al_2Be_3(SiO_3)_6$
18		1.627	77 ACBCAR	33	203	$NH_4P_3Be_2O_{10}$
19		1.622	78 ACBCAR	34	429	$K_2[Be(C_2O_4)_2]$
20	BO3	1.36	56 MJTOAS	2	1	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$
21		1.360	66 CJCHAG	44	3083	$CaB_3O_4(OH)_3\cdot H_2O$
22		1.365	75 ACBCAR	31	2405	$Na_2[B_3O_8(OH)]\cdot 2H_2O$
23		1.373	77 ACBCAR	33	2767	$Li_4B_7O_{12}Cl$
24	BO4	1.48	56 MJTOAS	2	1	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$
25		1.476	66 CJCHAG	44	3083	$CaB_3O_4(OH)_3\cdot H_2O$
26		1.479	69 ACBCAR	25	1811	$Ba[B(OH)_4]_2\cdot H_2O$
27		1.475	75 ACBCAR	31	2405	$Na_2[B_5O_8(OH)]\cdot 2H_2O$
28	BF3	1.313 (ED)	66 JCPSPA6	45	4341	BF_3 (gas)
29	BF4	1.386	69 ACBCAR	25	2161	KBF_4
30		1.382	71 ACBCAR	27	1102	NH_4BF_4
31		1.406 (rigid)	71 ACBCAR	27	1102	NH_4BF_4
32	CO2	1.16 (re)	84 KBCSJP	3	II 650	CO_2 (gas)
33	CO3	1.280	75 ACBCAR	31	890	$Na_2CO_3\cdot H_2O$
34		1.278	77 ACBCAR	33	1273	$Mg(CO_3)_4(OH)_2(H_2O)_3$
35	CS2	1.553 (re)	84 KBCSJP	3	II 650	CS2 (gas)
36	CS3	1.712	70 ACBCAR	26	877	$K_2CS_3\cdot H_2O$
37	NO3	1.250	67 ACCRA9	22	699	$Ni(NO_3)_2\cdot 4H_2O$
38		1.256	73 ZEKGAX	137	290	$Mg(NO_3)_2\cdot 6H_2O$
39		1.253	75 ACBCAR	31	1486	$HNO_3\cdot H_2O$
40	NaO5	2.383	68 ACBCAR	24	13	α-$Na_2Si_2O_5$
41	NaO6	2.453	67 ACCRA9	22	182	$NaAl(SO_4)_2\cdot 12H_2O$
42		2.424	71 ACBCAR	27	2269	$Na_2[H_2SiO_4]\cdot 5H_2O$
43		2.497	71 ACBCAR	27	2269	$Na_2[H_2SiO_4]\cdot 5H_2O$
44		2.438	77 ACBCAR	31	21	$Na_3[Ce(C_4H_4O_5)_3]\cdot 2NaClO_4$
45	NaO8	2.637	75 ACBCAR	31	2405	$Na_2[B_5O_8(OH)]\cdot 2H_2O$
46		2.598	75 ACBCAR	31	2405	$Na_2[B_5O_8(OH)]\cdot 2H_2O$
47	MgO4	1.901	73 ACBCAR	29	1398	$Mg[PO_2(OC_2H_5)_2]_2$
48	MgO6	2.062	66 ACCRA9	20	875	$MgCl_2\cdot 12H_2O$
49		2.098	70 ACBCAR	26	1075	$Mg[H_3IO_6]\cdot 6H_2O$
50		2.072	73 JCDTB1		816	$MgSO_4\cdot 7H_2O$
51		2.06	77 ACAPCT	31	37	$Mg(C_6H_4O_2N_2)\cdot 6H_2O$
52	AlC4	2.09	53 JCPSA6	21	986	$Al_2(CH_3)_6$
53	AlO4	1.741	64 CSMBC		309	$KAlSi_3O_8$
54		1.740	64 CSMBC		315	$NaAlSi_3O_8$
55		1.749	64 CSMBC		325	$CaAl_2Si_2O_8$
56		1.75	70 ACBCAR	26	1686	α-$Ba[AlO(OH)_2]_2$
57		1.77	72 ACBCAR	28	760	γ-$Ba[AlO(OH)_2]_2$
58		1.753	75 ACBCAR	31	689	$Ca_3Al_2O_6$
59	AlO6	1.91	64 CSMBC		195	Kyanite, siliminate
60		1.915 (ND)	58 ACCRA9	11	798	AlOOH
61		1.881	67 ACCRA9	22	182	$NaAl(SO_4)_2\cdot 12H_2O$
62		1.908	67 ACCRA9	22	793	$KAl(SO_4)_2\cdot 12H_2O$
63		1.923	67 ACCRA9	22	793	$RbAl(SO_4)_2\cdot 12H_2O$
64		1.916	67 ACCRA9	22	793	$NH_4Al(SO_4)_2\cdot 12H_2O$
65		1.92	67 ZEKGAX	125	317	$Al(OH)_3$
66		1.904	72 ACBCAR	28	1899	$Al_2Be_3(SiO_3)_6$
67		1.92	72 ACBCAR	28	519	α-$Ba_2[Al_4(OH)_{16}]$
68		1.897	77 ACBCAR	33	263	$AlPO_4\cdot 2H_2O$
69	AlF4	1.69	69 INOCAJ	14	332	$NaAlF_4$

Table 1 (continued)

No.	Polyhedron	Bond distance	Reference			Compound
70		1.65	71 ZAACAB	380	212	$LiAlF_4$ (gas)
71	AlF6	1.801	67 ACCRA9	23	162	$NaCaAlF_6 \cdot H_2O$
72		1.801	71 ZAACAB	386	335	$LiCaAlF_6$
73		1.800	76 ACBCAR	32	3190	$Cs_2NaAl_3F_{12}$
74	AlCl4	2.13	71 ACBCAR	27	386	$AlSeCl_7$
75		2.126	72 ACBCAR	28	1421	$AlCl_4{}^- \cdot CH_3COO^+$
76		2.129	78 ACBCAR	34	1328	$KAlCl_4$
77	AlBr4	2.300	75 ACBCAR	31	2177	$NH_4Al_2Br_7$
78	SiC4	1.878	76 ACBCAR	32	2025	$C_{20}H_{27}NSi \cdot HCl \cdot H_2O$
79	SiN4	1.739	69 ACBCAR	25	2160	α-Si_3N_4
80	SiF4	1.552	73 JCPSA6	59	1549	SiF_4 (gas)
81		1.555	73 JMOSB4	18	337	SiF_4 (gas)
82	SiF6	1.677	64 ACCRA9	17	1408	Na_2SiF_6
83		1.694 (riding)	64 ACCRA9	17	1408	Na_2SiF_6
84		1.677	73 ACBCAR	29	2741	MSiF$_6 \cdot 6H_2O$ (M = Co, Ni, Zn)
85		1.697 (riding)	73 ACBCAR	29	2741	MSiF$_6 \cdot 6H_2O$ (M = Co, Ni, Zn)
86	SiO4	1.62	64 CSMBC		195	Kyanite
87		1.63	64 CSMBC		195	Andulsite
88		1.63	64 CSMBC		195	Siliminate
89		1.617	68 ACBCAR	24	13	α-$Na_2Si_2O_5$
90		1.636	71 ACBCAR	27	2269	$Na_2[H_2SiO_4] \cdot 5H_2O$
91		1.636	74 ACBCAR	30	2434	High(γ)-Li_2BeSiO_4
92		1.644	76 AMMIAY	61	831	$CaAl(OH)SiO_4$
93	SiO6	1.763	70 ACBCAR	26	233	SiP_2O_7
94		1.783	71 ACBCAR	27	594	$[Ca_3Si(OH)_6 \cdot 12H_2O](SO_4)(CO_3)$
95		1.778	76 ACBCAR	32	3200	Rutile type SiO_2
96	PC4	1.801	76 ACAPCT	30	157	$[P(C_6H_5)_4]_2[Ni(MoS_2)]$
97	PN4	1.614	71 ACBCAR	27	51	$N_3P_3Cl_2(NHPr^i)_4 \cdot HCl$
98	PO4	1.54	66 JCPSA6	44	2230	$Fe_3(PO_4)_2 \cdot 4H_2O$
99		1.535	71 ACBCAR	27	2247	$Ca(H_2PO_4)_2 \cdot H_2O$
100		1.537	75 ACBCAR	31	2026	$Zn_3(PO_4)_2 \cdot 4H_2O$
101		1.542	76 ACBCAR	32	2842	$Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$
102		1.536	77 ACBCAR	33	263	$AlPO_4 \cdot 2H_2O$
103	PO5	1.63	78 ACBCAR	34	629	$P[\{(CH_3)_2CO\}_2(C_6H_5COCN)_2 \cdot OCH_3]$
104	PS4	2.07	69 ACBCAR	25	1229	P_4S_9
105		2.07	71 JSSCB1	3	300	$Pd_3(PS_4)_3$
106		2.05	73 ACBCAR	29	1864	$GaPS_4$
107		2.058	78 ACBCAR	34	384	$Zn_4(P_2S_6)_3$
108	PCl4	1.93	71 ACBCAR	10	122	$[PCl_4]_2[Ti_2Cl_{10}]$
109		1.942 (riding)	71 ACBCAR	10	122	$[PCl_4]_2[Ti_2Cl_{10}]$
110		1.926	71 ACBCAR	10	122	$[PCl_4][Ti_2Cl_9]$
111		1.944 (riding)	71 ACBCAR	10	122	$[PCl_4][Ti_2Cl_9]$
112		1.90	71 ZAACAB	380	51	$[PCl_4][PCl_6]$
113		1.91	71 ZAACAB	380	56	PCl_5TaCl_5, PCl_5NbCl_5
114	PCl6	2.13	71 ZAACAB	380	51	$[PCl_4][PCl_6]$
115	PBr4	2.15	70 ACBCAR	26	443	$PBr_4{}^+ \cdot Br^-$
116	SO4	1.474	68 ACBCAR	24	1176	$K_2Mn(SO_4)_2 \cdot 4H_2O$
117		1.474	69 JCPSA6	51	4213	$H_2SO_4 \cdot 2H_2O$
118		1.464	69 ACBCAR	25	310	$BeSO_4 \cdot 4H_2O$
119		1.481 (riding)	69 ACBCAR	25	310	$BeSO_4 \cdot 4H_2O$
120		1.471	73 JCDTB1		816	$MgSO_4 \cdot 7H_2O$
121		1.486 (riding)	73 JCDTB1		816	$MgSO_4 \cdot 7H_2O$
122	ClO4	1.438	68 ACSAA4	49	1063	$H_5O_2{}^+ \cdot ClO_4$
123		1.437	71 ACBCAR	27	898	$HClO_4 \cdot (5/2)H_2O$
124	KO5	2.65	73 ACBCAR	29	1035	$KBC_8H_8O_{10} \cdot 10H_2O$
125	KO6	2.80	74 ACBCAR	30	6	$K_3(NSeO_2)_3$
126		2.88	74 ACBCAR	30	6	$K_3(NSeO_2)_3$
127		2.80	75 ACBCAR	31	1361	$K_4Th(C_2O_4)_2 \cdot 4H_2O$
128	KO7	2.90	75 ACBCAR	31	1361	$K_4Th(C_2O_4)_2 \cdot 4H_2O$
129	KO8	2.81	75 ACBCAR	31	1361	$K_4Th(C_2O_4)_2 \cdot 4H_2O$
130		2.816	78 ACBCAR	34	429	$K_2[Be(C_2O_4)]$
131	KO9	2.95	75 ACBCAR	31	1361	$K_4Th(C_2O_4)_2 \cdot 4H_2O$
132	CaO6	2.346	75 ACBCAR	31	689	$Ca_3Al_2O_6$
133		2.391	75 ACBCAR	31	689	$Ca_3Al_2O_6$
134	CaO7	2.37	72 ACBCAR	28	1182	$CaCu_4(OH)_6(SO_4)_2 \cdot 3H_2O$
135		2.44	72 ACBCAR	28	1182	$CaCu_4(OH)_6(SO_4)_2 \cdot 3H_2O$
136		2.576	75 ACBCAR	31	689	$Ca_3Al_2O_6$
137		2.525	75 ACBCAR	31	689	$Ca_3Al_2O_6$
138		2.439	76 ZEKGAX	144	S 82	$CaGe_2O_5$
139	CaO8	2.453	71 ACBCAR	27	594	$[Ca_3Si(OH)_6 \cdot 12H_2O](SO_4)(CO_3)$

Pauling's (1960) ionic radii, termed 'crystal radii', and Shannon's effective ionic radii (Shannon, 1976) can be used to determine λ. Since the ionic radius table, including the cation radii of electronegative atoms, is only deduced by Pauling (1960), Pauling's ionic radii are used to determine λ. The coordination number dependence of the cation radius can be neglected so that the radii for coordination number 6 can be usually used for every M and X.

$R - \lambda$ can be associated with the radial distribution function $4\pi r^2 \chi(r)^2$ of the outermost shell of an atom, where χ (r) is the radial part of an atomic orbital. Slater (1964) pointed out that the radial distribution function plays an essentially important role for bond distance determination. Using SCF (self-consistent field) atomic orbitals of ground state neutral atoms proposed by Clementi (1965), the radial distribution functions (without 4π) of K—Cl, Al—O, K—K and Si—Si were drawn as Figs. 1–4. In Fig. 1 the width of the horizontal axis is equal to the observed K—Cl distance (3.15 Å) in KCl crystals. The radial distribution functions of the 3p and 4s orbitals of K are drawn from left to right, those of 2p and 3p of Cl from right to left. The other figures are drawn in the same way with Al—O 1.91 (sixfold coordination), K—K 4.54 (in a b.c.c. lattice, body-centered cubic) and Si—Si 2.35 Å (in a diamond structure). The symbols $\gamma(K^+)$ and $\gamma(Cl^{7+})$ *etc.* denote the Pauling' cationic radii. In these figures, we can see that almost all the inner electrons are localized in the region within the cationic radii and the valence electrons are distributed in the region of $R - \lambda$. This justifies the use of $R - \lambda$. In addition, we can see that at the observed bond distances the maximum points of the outermost radial distribution functions of two bonded atoms almost overlap each other, as Slater emphasized (1964). Note that this holds for all types of chemical bonds: the ionic bond of KCl, the covalent bond of Si—Si, the metallic bond of K—K and the covalent–ionic bond of Al—O. This indicates that the 'maximum overlap principle' holds for all types of chemical bond. In other words, this principle holds not only for covalent compounds, but also for ionic compounds. With respect to this fact, Slater (1964) stated that even in the typical ionic compounds the covalent contribution to the wave function is large enough to be a determining factor in fixing bond distances and atoms tend to be much more nearly neutral than a straight ionic interpretation would indicate.

Bond distances in the coordination polyhedron are lengthened with an increase in coordination number generally. This should decrease the electronic densities around the *M*—*X* bonds. Thus, the sum of the electronic densities of the *M*—*X* bonds is expected to be conserved. This is the basic idea which leads to the new bond-valence–bond-distance relation.

Let us consider the volume of the cube region $(R - \lambda)^3$ lying along the *M*—*X* axis and denote the number of electrons found in the volume as *p*. Here three assumptions are introduced:

(i) The number of electrons found in the volumes of the cube regions for *M*—*X* bonds in a coordination polyhedron are equal, even if the bond distances are not equal to each other.

(ii) The average electron density $p/(R - \lambda)^3$ is a measure of covalent bond strength.

(iii) The sum of those around the central atom *M* is conserved, even if the coordination number of *M* changes.

Table 1 (continued)

No.	Polyhedron	Bond distance	Reference			Compound
140		2.432	76 AMMIAY	61	831	$CaAl(OH)SiO_4$
141	CaO9	2.693	75 ACBCAR	31	689	$Ca_3Al_2O_6$
142		2.54	77 ACBCAR	33	2938	$CaCl_2{\cdot}8H_2O$
143	Ti$^{(IV)}$O4	1.808	73 ACBCAR	29	2009	β-Ba_2TiO_4
144	Ti$^{(IV)}$O5	1.89	68 ACBCAR	24	1327	Y_2TiO_5
145	Ti$^{(IV)}$O6	1.961	75 ACBCAR	48	1981	$TiO_{2\,-\,\alpha}$
146		1.967	76 ACBCAR	32	1756	$Ga_4Ti_{21}O_{48}$
147		1.961	76 ACBCAR	32	2200	TiO_2
148	Ti$^{(IV)}$Cl4	2.170 (ED)	84 KBCSJP	3	II 653	$TiCl_4$ (gas)
149	Ti$^{(IV)}$Cl6	2.349	71 INOCAJ	10	122	$[PCl_4]_2[Ti_2Cl_{10}]$
150		2.352	71 INOCAJ	10	122	$[PCl_4][Ti_2Cl_9]$
151	Mn$^{(II)}$O6	2.20	67 ACCRA9	23	630	$Mn(CH_3COO)_2{\cdot}4H_2O$
152		2.19	68 ACBCAR	24	1176	$K_2Mn(SO_4)_2{\cdot}1.5H_2O$
153		2.23	72 ACBCAR	28	2687	$MnK_2(SO_4){\cdot}4H_2O$
154	Mn$^{(II)}$Cl4	2.365	76 ACBCAR	32	1371	$2[C_5H_5NH]^+{\cdot}[MnCl_4]^{2-}$
155	Mn$^{(II)}$Cl6	2.56	67 ACCRA9	23	766	$(CH_3)_4NMnCl_3$
156		2.546	73 ACBCAR	29	744	$CsMnCl_3$
157	Mn$^{(II)}$Br4	2.451	70 ACBCAR	28	1231	$CsMnBr_3$
158		2.504	76 ACBCAR	32	1371	$2[C_5H_5NH]^+{\cdot}[MnBr_4]^{2-}$
159	Mn$^{(II)}$Br6	2.687	70 ACBCAR	28	1640	$CsMnBr_3$
160	Fe$^{(III)}$O4	1.88	68 ZEKGAX	127	S137	$Bi_2Fe_4O_9$
161	Fe$^{(III)}$O6	2.016	70 ACBCAR	26	1469	Ca_2FeO_5
162		1.998	70 AMMIAY	55	78	$Fe(H_2O)_6[Fe(H_2O)_4(SO_4)_2]_2$
163		2.01	75 ACBCAR	31	322	$FeAsO_4{\cdot}2H_2O$
164	Fe$^{(II)}$O6	2.129	64 ACCRA9	17	1167	$FeSO_4{\cdot}7H_2O$
165	Co$^{(III)}$C6	1.894	73 ACBCAR	29	822	$[Co(NH_3)_6][Co(CN)_6]$
166	Co$^{(III)}$N6	1.967	70 ACBCAR	9	465	$[Co(NH_3)_6][ZnCl_4]_2$
167		1.972	73 ACBCAR	29	822	$[Co(NH_3)_6][Co(CN)_6]$
168	Co$^{(II)}$O4	1.95	75 ACBCAR	31	2487	$Co_2Mn_3O_8$
169	Co$^{(II)}$O6	2.14	75 ACBCAR	31	2487	$Co_2Mn_3O_8$
170	Co$^{(III)}$S6	2.322	72 ACBCAR	28	1550	$Co[(CH_3O)_2PS_2]_3$
171	Co$^{(II)}$Cl4	2.28	67 ACCRA9	23	563	$[N(CH_3)_4]_2.CoCl_4$
172	Co$^{(II)}$Cl6	2.447	68 ACSAA4	22	2793	$CsCoCl_3$
173	Ni$^{(II)}$N6	2.12	60 ACCRA9	13	639	$[Ni(en)_3](NO_3)_2$
174		2.123	75 ACBCAR	31	2736	$Ni(C_3N_2H_4)_6(BF_4)_2$
175		2.089	76 ACBCAR	32	1121	$[Ni(bipy)_3]SO_4{\cdot}7.5H_2O$
176	Ni$^{(II)}$N4 (sq)	1.90	65 JCSOA9		5801	$K_2[Ni(C_6H_{12}N_8O_8)]{\cdot}4H_2O$
177		1.897	68 ACBCAR	24	754	$Ni(C_7H_9N)_4(ClO_4)_2$
178	Ni$^{(II)}$O6	2.065	67 ACCAR9	22	699	$Ni(NO_3)_2{\cdot}4H_2O$
179		2.06	70 ZAACAB	379	204	$NiSeO_4{\cdot}6H_2O$
180		2.062	71 ACBCAR	27	1427	$Ni(NO_3)_2{\cdot}6H_2O$
181		2.047	73 ACBCAR	29	2741	$NiSiF_6{\cdot}6H_2O$
182	Ni$^{(II)}$S4 (tetr)	2.179	68 CJCAHG	22	3463	$NiCo_2S_4$
183	Ni$^{(II)}$S6	2.401	69 ACSAA4	23	2325	NiS_2
184		2.394	70 PLRBAQ	5	2552	NiS (300 K)
185		2.407	70 PLRBAQ	5	2552	NiS (77 K)
186	Ni$^{(II)}$Cl4 (tetr)	2.273	67 ACCRA9	23	563	$[Ni(CH_3)_4]_2{\cdot}NiCl_3$
187	Ni$^{(II)}$Cl6	2.408	68 ACBCAR	24	330	$(CH_3)_4NNiCl_3$
188		2.396	69 ACSAA4	23	14	$RbNiCl_3$
189	ZnN4	2.01	66 ACCRA9	21	901	$Zn(imidazole)_2Cl_2$
190		2.00	75 ACBCAR	31	2713	$Zn(imidazole)_4(ClO_4)_2$
191	ZnN6	2.16	67 ACSAA4	21	993	$Zn(imidazole)_6Cl_2{\cdot}4H_2O$
192	ZnO4	1.947	70 ACBCAR	26	860	$Zn(OH)_8(NO_3)_2{\cdot}2H_2O$
193		1.962	75 ACBCAR	31	2026	$Zn_3(PO_4)_2{\cdot}4H_2O$
194	ZnO6	2.096	67 ACCRA9	22	240	$Zn(NO_3)_2{\cdot}6H_2O$
195		2.129	70 ACBCAR	26	860	$Zn(OH)_8(NO_3)_2{\cdot}2H_2O$
196		2.112	75 ACBCAR	31	2026	$Zn_3(PO_4)_2{\cdot}4H_2O$
197		2.106	76 ACBCAR	32	753	$Zn[Pb(IO_3)_6]{\cdot}6H_2O$
198	ZnCl4	2.287	66 ACCRA9	23	563	$[N(CH_3)_4]_2{\cdot}ZnCl_4$
199		2.277	75 ACBCAR	34	1330	$(H_5O_2){\cdot}Zn_2Cl_5$
200	GaO4	1.83	60 JCPSA6	33	676	β-Ga_2O_3
201		1.848	65 ACCRA9	18	481	$LiGaO_2$
202		1.83	71 ACBCAR	27	621	α-Li_5GaO_4
203		1.829	76 ACBCAR	32	1196	$SrGa_2Ge_2O_8$
204		1.82	76 ACBCAR	32	1196	$BaGa_2Ge_2O_8$
205		1.841	76 ACBCAR	32	1756	$Ga_4Ti_2O_{48}$
206		1.826	78 ACBCAR	34	741	$LiGaO_2{\cdot}6H_2O$
207	GaO5	1.94	68 JINCAO	30	1389	$InGaO_3$
208	GaO6	2.01	60 JCPSA6	33	676	β-Ga_2O_3

Table 1 (continued)

No.	Polyhedron	Bond distance	Reference			Compound
209	GeO4	1.77	69 ZEKGAX	128	66	Li_4GeO_4
210		1.756	69 ZEXGAX	130	S 82	$CaGe_2O_5$
211		1.748	76 ACBCAR	32	1196	$SrGa_2Ge_2O_8$
212		1.753	76 ACBCAR	32	1196	$BaGa_2Ge_2O_8$
213	GeO6	1.908	76 ZEXGAX	144	S 82	$CaGe_2O_5$
214		1.884	76 ACBCAR	32	2200	Rutile-type GeO_2
215	AsO4	1.683	66 ACCRA9	21	437	$Cu_2(AsO_4)(OH)\cdot 3H_2O$
216		1.688	70 ACBCAR	26	1574	$Na_2HAsO_4\cdot 7H_2O$
217		1.691	72 ACBCAR	28	3056	$CaKAsO_4\cdot 8H_2O$
218		1.679	75 ACBCAR	31	322	$FeAsO_4\cdot 2H_2O$
219	AsO6	1.84	70 CJCHAG	48	3124	$Co_8As_3O_{16}$
220	ZrF6	1.996	73 ACBCAR	29	1955	$CuZrF_6\cdot 4H_2O$
221		2.000	60 NATWAY	47	397	$LiZrF_6$
222	ZrF7	2.063	72 ACBCAR	27	1958	$K_2Cu(ZrF_6)_2\cdot 6H_2O$
223	ZrF8	2.109	73 ACBCAR	27	1967	$Cu_3(ZrF_7)_2\cdot 16H_2O$
224	ZrO6	2.09	67 MNLMBB	36	233	$Na_2ZrSi_4O_{11}$
225	ZrO8	2.22	58 ACCRA9	11	896	$ZrSiO_4$
226		2.20	63 INOCAJ	2	243	$C_{20}H_{28}O_8Zr$
227	Mo$^{(VI)}$O4	1.77	71 ACBCAR	27	2066	$Cu_3Mo_2O_9$
228		1.755	72 ACBCAR	28	60	$Gd_2(MoO_4)_3$
229	CdCl2	2.24	84 KBCSJP	3	II 650	$CdCl_2$ (gas)
230	CdCl5	2.547	71 JCSIAP		3628	$[Co(NH_3)_6][CdCl_5]$
231	CdCl6	2.62	64 ACCRA9	17	790	$CsCdCl_3$
232		2.61	64 ACCRA9	17	790	Cs_2CdCl_4
233	InS4	2.46	77 ACBCAR	33	1163	$Tb_3In_5S_{12}$
234	InS6	2.64	77 ACBCAR	33	1163	$Tb_3In_5S_{12}$
235	Sn$^{(IV)}$C4	2.147	75 ACBCAR	31	705	$(4\text{-}CH_3C_6H_4)Sn$
236	Sn$^{(IV)}$N6	2.183	77 ACBCAR	33	1076	$RbSn(NH_2)_6$
237	Sn$^{(IV)}$O4	1.955	75 ACBCAR	31	511	K_4SnO_4
238	Sn$^{(IV)}$O6	2.063	67 JCSIAP		1949	$Sn(NO_3)_4$
239		2.057	68 CJCHAG	46	857	$M_2Sn_2O_7$ (M = Y, Sm, La)
240		2.10	69 ACAPCT	23	1219	$MnSn(OH)_6$
241		2.054	76 ACBCAR	32	2200	SnO_2
242	Sn$^{(IV)}$O8	2.161	67 JCSIAP		1949	$Sn(NO_3)_4$
243	Sn$^{(IV)}$Cl4	2.28	84 KBCSJP	3	II 650	$SnCl_4$ (gas)
244	Sn$^{(IV)}$Cl6	2.42	74 JOMRA4	13	27	M_2SnCl_6 (M = K, NH_4, Rb,...)
245	Sb$^{(V)}$O6	1.987	77 ACBCAR	33	1271	α-Sb_2O_4
246	Sb$^{(V)}$Cl6	2.353	70 ACBCAR	26	1671	$[C(N_3)_3]SbCl_6$
247		2.364	72 ACBCAR	28	1421	$SbCl_6^-\cdot CH_3CO^+$
248		2.37	72 ACBCAR	28	1430	$SbCl_6^-\cdot (CH_3)_2CHCO^+$
249	Te$^{(IV)}$Cl6	2.528	66 ACSAA4	20	165	$(NH_4)_2TeCl_6$
250		2.541 (riding)	66 ACSAA4	20	165	$(NH_4)_2TeCl_6$
251	Te$^{(IV)}$Br6	2.695	66 CJCHAG	44	939	Cs_2TeBr_6
252		2.693	76 ACBCAR	32	2859	$[CH_3CHCHNH_3COOH]_2\cdot TeBr_6$
253		2.713	76 ACBCAR	32	2863	$[(CONH_2)_2(CH_2)_2]_2H_2TeBr_6$
254	Te$^{(IV)}$I6	2.93	72 JINCAO	8	184	K_2TeI_6
255	I$^{(VII)}$O4	1.769	70 ACBCAR	26	1782	$NaIO_4$
256	I$^{(VII)}$O6	1.91	70 ACBCAR	26	1069	$Mg[H_3IO_6]\cdot 6H_2O$
257		1.92	70 ACBCAR	26	1075	$Cd[H_3IO_6]\cdot 3H_2O$
258	BaO7	2.888	73 ACBCAR	29	2009	β-Ba_2TiO_4
259	BaO8	2.89	72 ACBCAR	28	760	γ-$Ba[AlO(OH)_2]_2$
260		2.81	73 ACBCAR	29	2009	β-Ba_2TiO_4
261	BaO10	2.875	72 ACBCAR	28	519	α-$Ba_2[Al_4(OH)]_{16}$
262	La$^{(III)}$O9	2.538	77 JSSCB1	19	271	$La_2(SO_4)_3\cdot 9H_2O$
263	La$^{(III)}$O12	2.686	77 JSSCB1	19	271	$La_2(SO_4)_3\cdot 9H_2O$
264	Tb$^{(III)}$S7	2.78	77 ACBCAR	33	1163	$Tb_3In_5S_{15}$
265	Tb$^{(III)}$S8	2.88	77 ACBCAR	33	1163	$Tb_3In_5S_{15}$
266	Re$^{(VII)}$O4	1.74	69 INOCAJ	8	436	Re_2O_7
267		1.72	76 ACBCAR	32	1334	Re_2O_7
268	Re$^{(VII)}$O6	1.90	69 INOCAJ	8	436	$KReO_4$

Riding: riding correction; rigid: rigid body correction; ED: electron diffraction; ND: neutron diffraction; *tert*: tetrahedral; sq: square planar; re: distance for equilibrium structure; gas: gas phase. The references are given as the year, journal coden, volume number and page. The journal and other reference codens are: ACAPCT, *Acta Chem. Scand. A*; ACBCAR: *Acta Cryst. Section B*; ACCRA9: *Acta Cryst.*; ACSAA4: *Acta Chem. Scand.*; AMMIAY: *Am. Mineral.*; CJCHAG: *Can. J. Chem.*; CSMBC: *Crystal Structures of Minerals* (Bragg & Claringbull, 1965); INOCAJ: *Inorg. Chem.*; JCDTB1: *J. Chem. Soc. Dalton Trans.*; JCPSA6: *J. Chem. Phys.*; JCSIAP: *J. Chem. Soc. A*; JCSOA9: *J. Chem. Soc.*; JINCAO: *J. Inorg. Nucl. Chem.*; JMOSB4: *J. Mol. Struct.*; JOMRA4: *J. Magn. Reson.*; JSSCB1: *J. Solid State. Chem.*; KBCSJP: *Kagaku Binran* (*Chemistry data*) (The Chemical Society of Japan, 1984); MJTOAS: *Mineral. J.*; MNLMBB: *Miner. Mag.*; NATWAY: *Naturwissenschaften*; PLRBAQ: *Phys. Rev. B*; ZAACAB: *Z. Anorg. Allg. Chem.*; ZEKGAX: *Z. Kristallogr.*

Thus, if these assumptions are applicable to the two regular polyhedra $MX_{\nu 1}$ and $MX_{\nu 2}$, the following relation should hold

$$\frac{p\nu_1}{(R^0_{\nu 1}-\lambda)^3}=\frac{p\nu_2}{(R^0_{\nu 2}-\lambda)^3}, \qquad (2)$$

where $R^0_{\nu 1}$ and $R^0_{\nu 2}$ are $M-X$ distances in $MX_{\nu 1}$ and $MX_{\nu 2}$, respectively. Equation (2) is equivalent to the following relation

$$\frac{1}{\nu_2}=\frac{1}{\nu_1}\frac{(R^0_{\nu 1}-\lambda)^3}{(R^0_{\nu 2}-\lambda)^3}. \qquad (3)$$

Multiplying Z_M (the oxidation number of the central atom M) to both sides of (3) creates the following relation

$$\frac{Z_M}{\nu_2}=\frac{Z_M}{\nu_1}\frac{(R^0_{\nu 1}-\lambda)^3}{(R^0_{\nu 2}-\lambda)^3}. \qquad (4)$$

Since Z_M/ν is the bond valence for a regular polyhedron, (4) is interpreted as the coordination number dependence of bond valence. Thus, (4) exhibits the bond distance dependence of the bond valence. Replacing Z_M/ν for s and removing suffixes ν_1 and ν_2 from the bond distance symbols we obtain

$$s=s_0\frac{(R^0-\lambda)^3}{(R-\lambda)^3}, \qquad (5)$$

where s is the bond valence, R is the bond distance between atoms M and X, and s_0 is the reference bond valence for the 'reference system' with the reference bond distance R^0. The definition of s_0 and R^0 is essentially the same as in the Brown–Shannon (1973) formula. Usually, regular polyhedra are taken as the reference systems. s_0 is taken as Z_M/ν, where Z_M is the positive oxidation number of M (usually a metal cation such as Al^{3+}). When no regular polyhedron is available, the reference bond distance is taken as the average distance in a deformed $M-X$ coordination polyhedron. Equation (5) gives a new interpretation that the

Table 2
Examination of (12): the coordination number dependence of the bond distance.

'sq' represents square-planar coordination and 'tetr' tetrahedral coordination.

No.	Polyhedron 1	Polyhedron 2	λ	R_1(obs)	R_2(cal)	R_2(obs)
1	LiO_4	LiO_6	0.69	1.97	2.16	2.13
2	BeO_4	BeO_3	0.40	1.63	1.55	1.52
3	BF_3	BF_4	0.29	1.31	1.42	1.41
4	BO_3	BO_4	0.31	1.37	1.47	1.48
5	CO_2	CO_3	0.24	1.16	1.29	1.28
6	CS_2	CS_3	0.44	1.56	1.72	1.71
7	NaO_6	NaO_8	1.04	2.45	2.59	2.59
8	MgO_6	MgO_4	0.74	2.09	1.92	1.90
9	AlO_6	AlO_4	0.59	1.91	1.74	1.75
10	AlF_6	AlF_4	0.57	1.80	1.65	1.67
11	SiF_4	SiF_6	0.48	1.55	1.71	1.69
12	SiO_4	SiO_6	0.50	1.63	1.79	1.77
13	PO_4	PO_5	0.43	1.54	1.63	1.63
14	PCl4	PCl6	0.60	1.94	2.14	2.15
15	TiO_6	TiO_4	0.77	1.96	1.81	1.81
16	TiO_6	TiO_5	0.77	1.96	1.89	1.89
17	$TiCl_6$	$TiCl_4$	0.94	2.35	2.17	2.17
19	$MnCl_4$	$MnCl_6$	1.09	2.37	2.56	2.55
20	$MnBr_4$	$MnBr_6$	1.19	2.48	2.67	2.69
21	FeO_6	FeO_4	0.73	2.01	1.85	1.88
22	CoO_6	CoO_4	0.72	2.14	1.96	1.95
23	$CoCl_6$	$CoCl_4$	0.98	2.45	2.26	2.28
24	NiN_6	NiN_4(sq)	0.80	2.11	1.94	1.90
25	NiS_4(tetr)	NiS_6	0.98	2.18	2.35	2.40
26	$NiCl_6$	$NiCl_4$(tetr)	0.95	2.40	2.22	2.27
27	ZnN_4	ZnN_6	0.85	2.00	2.17	2.17
28	ZnO_6	ZnO_4	0.83	2.11	1.95	1.96
29	ZnO_6	ZnO_5	0.83	2.11	2.02	2.03
30	GaO_4	GaO_5	0.71	1.84	1.93	1.94
31	GaO_4	GaO_6	0.71	1.84	2.00	2.00
32	GeO_4	GeO_6	0.62	1.75	1.91	1.90
33	AsO_4	AsO_6	0.53	1.69	1.85	1.84
34	ZrO_8	ZrO_6	0.89	2.21	2.09	2.09
35	ZrF_8	ZrF_6	0.87	2.11	2.00	2.00
36	$CdCl_6$	$CdCl_5$	1.23	2.61	2.53	2.55
37	InS_4	InS_6	1.10	2.46	2.66	2.64
38	SnO_6	SnO_4	0.80	2.06	1.90	1.96
39	SnO_6	SnO_8	0.80	2.06	2.19	2.16
40	SnS_4	SnS_6	1.00	2.40	2.60	2.57
41	$SnCl_4$	$SnCl_6$	0.97	2.28	2.47	2.43
42	LaO_9	LaO_{12}	1.24	2.54	2.73	2.69
43	TbS_7	TbS_8	1.22	2.78	2.86	2.89
44	ReO_6	ReO_4	0.65	1.90	1.73	1.74

ratio of bond valences is equal to the ratio of the average electron densities distributed in the bonding region $R - \lambda$.

According to the above description, the cube $(R - \lambda)^3$ seems to have a particular significance. However, any region with the volume proportional to $(R - \lambda)^3$ satisfies (5). Hence, there is an ambiguity in the choice of the volume which justifies (5).

3. Extension to hetero-ligand polyhedra

Equation (5) seems to be applicable only to a polyhedron with one type of ligand (hereafter known as the 'homo-ligand polyhedron'), since its derivation procedure should be valid for a homo-ligand polyhedron. Nevertheless, it has been found that (5) is also applicable to a polyhedron with two or more types of ligand atoms (hereafter termed a 'hetero-ligand polyhedron'), as described below. The new relation for a polyhedron MX_nY_m ($n + m = \nu$) is proposed below, which is tested from empirical results in §4.4

$$\frac{1}{\nu}\left\{\sum_i^n \frac{(R^0_{MX}-\lambda_{MX})^3}{(R_{MX_i}-\lambda_{MX})^3}+\sum_j^m \frac{(R^0_{MY}-\lambda_{MY})^3}{(R_{MY_j}-\lambda_{MY})^3}\right\}=1. \tag{6}$$

Here R^0_{MX} and R^0_{MY} are the reference bond distances for MX_ν and MY_ν, respectively. Multiplying Z_M to both sides of (6) leads to

$$\frac{Z_M}{\nu}\left\{\sum_i^n \frac{(R^0_{MX}-\lambda_{MX})^3}{(R_{MX_i}-\lambda_{MX})^3}+\sum_j^m \frac{(R^0_{MY}-\lambda_{MY})^3}{(R_{MY_j}-\lambda_{MY})^3}\right\}=Z_M. \tag{7}$$

Using (5), (7) can be expressed as $\sum_i^n s_{MX_i} + \sum_j^m s_{MY_j} = Z_M$. This means that (5) is also applicable to a hetero-ligand polyhedron. According to the assumption leading to (3), the $(R - \lambda)^3$ factor originates from the average electron density defined as $\bar{\rho} = p/(R - \lambda)^3$. Replacing $(R - \lambda)^3$ factors in (6) with $p/\bar{\rho}$ leads to the following expression

$$\frac{1}{\nu}\left\{\sum_i^n \frac{\bar{\rho}_{MX_i}}{\bar{\rho}^0_{MX}}+\sum_j^m \frac{\bar{\rho}_{MY_i}}{\bar{\rho}^0_{MY}}\right\}=1. \tag{8}$$

This equation is readily transformed to the following form.

$$\sum_i^n(\Delta\bar{\rho}_{MXi}/\bar{\rho}^0_{MX})+\sum_j^m(\Delta\bar{\rho}_{MYj}/\bar{\rho}^0_{MY})=0, \tag{9}$$

where $\Delta\bar{\rho} \equiv \bar{\rho} - \bar{\rho}^0$. This expresses the 'compensation of the average electron density change ratio'. Equation (8) indicates that the new relation (5) can be tested empirically by counting the number of valence electrons (p) found in the volume $(R - \lambda)^3$ [or in another volume proportional to $(R - \lambda)^3$] around each bond axis in MX_ν, MY_ν and MX_nY_m ($n + m = \nu$). This is feasible in principle by both accurate X-ray electron density analysis and computational chemistry methods.

In addition, the following relation has also been found.

$$\frac{1}{\nu}\left\{\sum_i^n\left(\frac{R_{MX_i}}{R^0_{MX}}\right)+\sum_j^m\left(\frac{R_{MY_j}}{R^0_{MY}}\right)\right\}=1. \tag{10}$$

This new equation is the generalized form of the averaging effect for bond distance and will be tested in §4.4. The relation between (6) and (10) is not known at present. Equation (10) also implies compensation of the bond distance change ratio.

$$\sum_i^n(\Delta R_{MXi}/R^0_{MXi})+\sum_j^m(\Delta R_{MYj}/R^0_{MYj})=0. \tag{11}$$

4. Discussion

4.1. Coordination number dependence of bond distance

In this section, we examine (2) which is the original relation for (5). Equation (2) is transformed into

$$R^0_{\nu 2}=\left(\frac{\nu_2}{\nu_1}\right)^{1/3}(R^0_{\nu 1}-\lambda)+\lambda. \tag{12}$$

We tested (12) for Al—O (λ = 0.59 Å). From Nos. 59 to 68 in Table 1 we obtain the average Al—O distances of AlO_6 as 1.91 ± 0.01 Å. We also calculated the bond distance in AlO_4 from (12): $R_4^0 = (4/6)^{1/3}(1.91 - 0.59) + 0.59 = 1.74$. This is in good agreement with the actual value of 1.75 ± 0.01 Å (Nos. 53–58 in Table 1). Other examples are listed in Table 2, using R_1^0(obs) and R_2^0(obs) values in Table 1. In Table 2 we can see that (12) reproduces the bond distance $R_2{}^0$ within an error of 1.5% on the whole. Note that for almost all the data in Table 2, the coordination number difference is within 2. When the coordination number difference is large, the differences R_2 become large, as seen in KCl (gas) and KCl (solid).

Here we predict the K—Cl distance for the gas phase molecule of KCl, using R_1 = 3.15 Å for the crystal (Wells, 1984) and $\lambda = \gamma(K^+) + \gamma(Cl^{7+}) = 1.33 + 0.26 = 1.59$ Å, $\nu_1 = 6$ and $\nu_2 = 1$. Thus, the K—Cl distance for the molecule is expected to be $(1/6)^{1/3}(3.15 - 1.33) + 1.33 = 2.33$ Å. This largely deviates from the observed value (2.667 Å) by 13%. The K—Cl distance in crystals is 3.146 Å. If Fig. 1 is drawn with K—Cl 2.667 Å, the maximum points of the radial distribution functions of the 4*s*(K) and 3*p*(Cl) orbitals should not overlap each other. Thus, the electronic states of KCl(gas) and KCl(solid) should be significantly different from each other. This may be the cause of the large discrepancy. In Fig. 2 the maximum region in the 3*p* radial distribution function of Al is fairly broad. Thus, even if the Al—O distance changes from 1.91 to 1.75 Å, the maximum overlapping is still kept. This may be an important factor for (5) to hold good for Al—O bonds. This should be adopted to many other MX_ν polyhedra, because the outermost orbitals of metal atoms are generally broad.

4.2. Comparison with the Brown–Shannon formula

This section shows that the new relation (5) explains why Brown–Shannon's (1973) formula, $s = s_0(R_0/R)^N$, holds. The constant R_0 is the same as the average bond distance of the metal–oxygen polyhedron. For example, the R_0 values of Li^+ (fourfold coordination), Be^{2+}(4), B^{3+}(3), Al^{3+}(6) and Si^{4+}(4) are 1.954, 1.639, 1.375, 1.909 and 1.625 Å, respectively. The corresponding values in Table 1 are 1.95, 1.63, 1.37, 1.91 and 1.63, respectively.

The power number N is obtained from the equation of $(R^0 - \lambda)^3/(R - \lambda)^3 = (R^0/R)^N$. However, the N value from this formula depends on R, while N from the Brown–Shannon formula is independent of R. Hence, N is considered to have the following limit value

$$N = \lim_{R\to R^0} \frac{3\ln\left(\frac{R^0-\lambda}{R-\lambda}\right)}{\ln\left(\frac{R^0}{R}\right)} = \frac{3R^0}{R^0 - \lambda}. \qquad (13)$$

Now let us compare N from (13) with N given in Table 1 in the paper of Brown & Shannon (1973). Hereafter the former N is termed N (cubic) ['cubic' is after the third power of (5)] and the latter N(BS) (BS: Brown–Shannon, 1973). Table 1 gives the optimized N values of the M—O bonds, where M = H^+, Li^+, Be^{2+}, B^{3+}, Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, P^{+5}, S^{+6}, K^+, Ca^{2+}, Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+}, Ge^{4+} and As^{5+}. Using the Brown–Shannon R_0 values and Pauling's (1960) cationic radii, N (cubic) were calculated from (13) and are shown in Fig. 5 with those from Brown & Shannon's N(BS). Fig. 6 compares the bond valences from (5) with those from the Brown–Shannon formula, using selected M—O values. Although there are discrepancies between N(BS) and

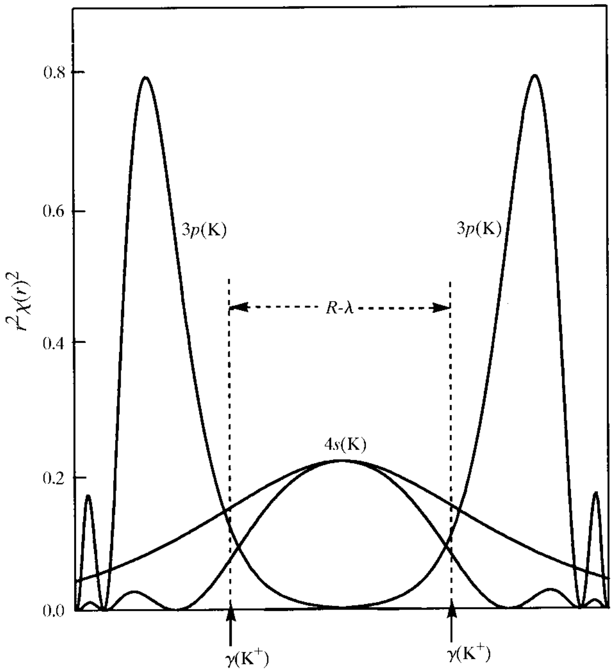


Figure 3
Radial distribution functions for the 3*p* and 4*s* orbitals of two K atoms in the b.c.c. structure with K—K 4.52 Å.

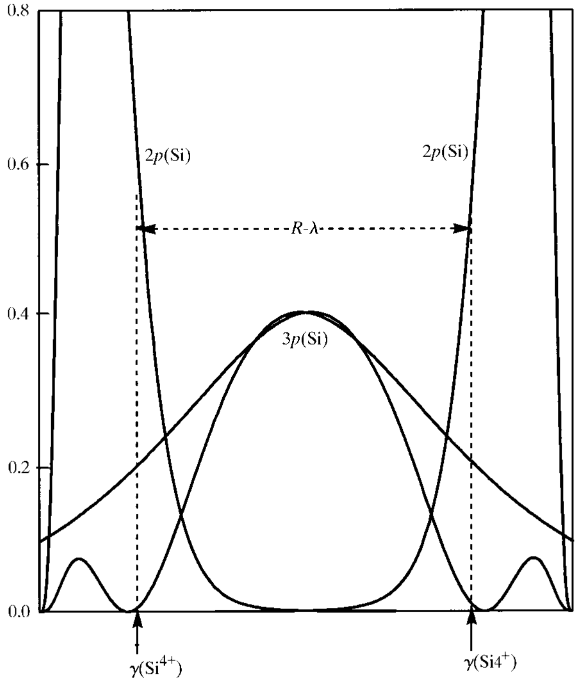


Figure 4
Radial distribution functions for the 2*p* and 3*p* orbitals of two Si atoms in the diamond structure with Si—Si 2.35 Å.

Table 3
Parameters for the Brown–Altermatt (1985) formula.

	Brown–Altermatt		The present work				
	r_0 (Å)	B (Å)	r_0 (Å)	B (Å)	R_0 (Å)	λ (Å)	Z_M/ν
H1O−2	0.882	0.37	0.97	0.293	0.97	0.09	1.000
Li1O−2	1.466	0.37	1.49	0.267	1.96	0.69	0.250
Be2O−2	1.381	0.37	1.38	0.327	1.63	0.40	0.500
B3O−2	1.371	0.37	1.37	0.360	1.37	0.29	1.000
C4O−2	1.390	0.37	1.38	0.380	1.28	0.24	1.333
Na1O−2	1.803	0.37	1.82	0.259	2.45	1.04	0.167
Mg2O−2	1.693	0.37	1.67	0.310	2.08	0.74	0.333
Al3O−2	1.651	0.37	1.64	0.350	1.75	0.59	0.750
Al3Cl−1	2.032	0.37	2.00	0.413	2.13	0.76	0.750
Si4O−2	1.624	0.37	1.63	0.377	1.63	0.50	1.000
P5O−2	1.617	0.37	1.63	0.400	1.54	0.43	1.250
P5S−2	2.145	0.37	2.17	0.513	2.06	0.63	1.250
S6O−2	1.624	0.37	1.64	0.420	1.48	0.38	1.500
Ti4O−2	1.815	0.37	1.81	0.347	1.96	0.77	0.667
Mn2Cl−1	2.133	0.37	2.10	0.347	2.56	1.06	0.333
Fe3O−2	1.759	0.37	1.74	0.337	2.00	0.73	0.500
Zn2Cl−1	2.027	0.37	2.02	0.339	2.28	1.00	0.500
Zr4O−2	1.928	0.37	1.94	0.352	2.21	0.88	0.500
Sn4O−2	1.905	0.37	1.91	0.370	2.07	0.80	0.667
Sn4Cl−1	2.276	0.37	2.24	0.420	2.42	0.97	0.667

N(cubic) values, their tendencies are the same on the whole. Moreover, both *N* values show no significantly different bond valence values, as shown in Fig. 6. Thus, we can conclude that both *N* values are essentially the same.

4.3. Derivation of the Brown–Altermatt formula

This section states that the Brown–Altermatt formula (1985), $s = \exp\left[(r_0 - r)/B\right]$ (B is set to 0.37 for every atom pair), can be derived from (5). First the right side of (5) is altered to its inverse form: $s = s_0(R-\lambda)^{-3}/(R^0-\lambda)^{-3}$. Taking the logarithm of both sides of this equation leads to the following relation

$$\ln\left(\frac{s}{s_0}\right) = -3\ln\left(\frac{R-\lambda}{R^0-\lambda}\right) = -3\ln\left(1+\frac{R-R^0}{R^0-\lambda}\right). \tag{14}$$

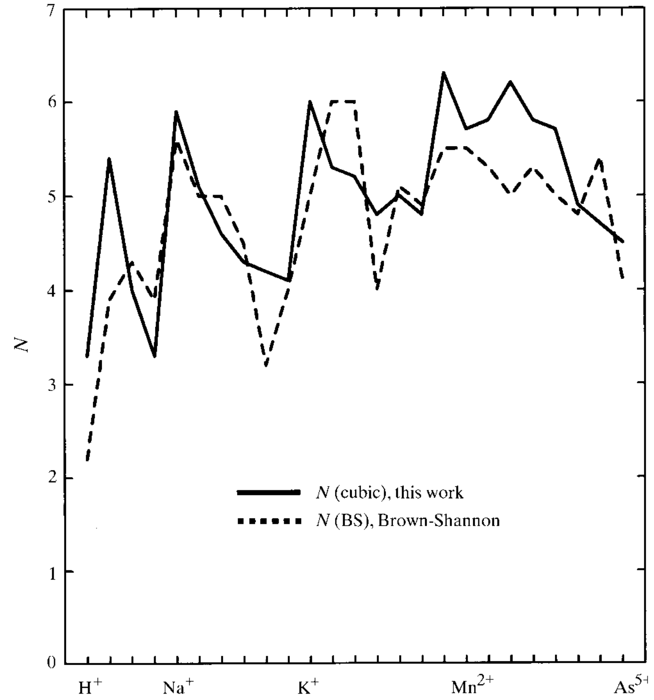


Figure 5
Comparison of the power number *N*(cubic) with *N*(BS).

For the usual variation range in the bond distance R, the inequality $R^0 - \lambda > |R^0 - R|$ holds well. Equation (14) can be approximated as $\ln(s/s_0) = 3(R^0 - R)/(R^0 - \lambda)$. From this relation, we obtain

$$s = s_0 \exp\left[(R^0 - R)/\beta\right] \tag{15}$$

$$\beta \equiv (R^0 - \lambda)/3. \tag{16}$$

Equation (15) is essentially the same as the Brown–Altermatt formula. β corresponds to the parameter B. In the actual Brown–Altermatt formula, the reference system is taken as that where $s_0 = 1$. Therefore, the parameter r_0 is calculated from (15) by setting $s = 1$ and $s_0 = Z_M/\nu$, where Z_M/ν is the value of the reference system of MX_ν with the distance R^0. The parameter B is calculated by replacing R^0 in (16) by r_0. Thus, both parameters are obtained as follows

$$r_0 = (Z_M/\nu)^{1/3}(R^0 - \lambda) + \lambda \tag{17}$$

$$B = (r_0 - \lambda)/3 \tag{18}$$

Calculated r_0 and B values for 20 atom pairs extracted from 141 atom pairs in the paper of Brown & Altermatt (1985) are listed in Table 3. The symbol Al3O–2, for example, represents the pair Al^{3+} and O^{2-}. Values of R^0 and Z_M/ν were taken from Table 1. r_0 and B values by Brown &Altermatt are also listed in Table 3. This table shows that all r_0 values defined in (17) are very close to the r_0 values in the Brown–Altermatt formula, except for H—O. Moreover, most of the B values in the present work fall between 0.33 and 0.42, close to 0.37. From this result it is expected that if parameter B is treated as a constant, as Brown & Altermatt (1985) did, its optimized value for 141 atom pairs should be approximately equal to 0.37. With respect to the relation between Brown–Shannon's power number N and Brown–Altermatt's B parameter, Brown & Wu (1976) found the relation $N \cong R^0/B$ and Urusov (1991) gave a derivation for this relation. Here another derivation is given, *i.e.* this relation can be easily derived from (13) and (16).

In addition, the alternative approximate formula which is also derived from (5) was considered. Taking the logarithm of both sides of (5) itself leads to the following equation: $\ln(s/s_0) = 3\ln\left[1 + (R^0 - R)/(R - \lambda)\right]$. Through the same procedure as described above, we obtain $s = s_0\exp\left[(R^0 - R)/B'\right]$, where $B' = (R - \lambda)/3$. These equations can also be used as an approximation for (5). However, B' depends on R, while the B parameter of the Brown–Altermatt formula is constant. Hence, this alternative does not correspond to the Brown–Altermatt formula.

Table 4
Examination of the new relations for hetero-ligand polyhedra.

	R	R^0	R/R^0	λ	$R-\lambda$	$R^0-\lambda$	$(R^0-\lambda)^3/(R-\lambda)^3$
(1) $AlOCl_3$							
Al—O	1.85	1.75	1.057	0.59	1.26	1.16	0.780
Al—Cl	2.09	2.13	0.981	0.76	1.33	1.37	1.093
Al—Cl	2.09	2.13	0.981	0.76	1.33	1.37	1.093
Al—Cl	2.09	2.13	0.981	0.76	1.33	1.37	1.093
	2.03	2.03	1.000		1.31	1.31	1.015
(2) $POCl_3$							
P—O	1.45	1.54	0.942	0.43	1.02	1.11	1.289
P—Cl	1.99	1.94	1.024	0.60	1.39	1.34	0.896
P—Cl	1.99	1.94	1.024	0.60	1.39	1.34	0.896
P—Cl	1.99	1.94	1.024	0.60	1.39	1.34	0.896
	1.84	1.83	1.003		1.29	1.28	0.994
(3) PON_2S							
P—N(1)	1.66	1.61	1.031	0.45	1.21	1.16	0.881
P—N(2)	1.66	1.61	1.031	0.45	1.21	1.16	0.881
P—O	1.60	1.54	1.039	0.43	1.17	1.11	0.854
P—S	1.91	2.06	0.927	0.63	1.28	1.43	1.394
	1.70	1.69	1.007		1.22	1.21	1.003
(4) PCN_2S							
P—N(1)	1.68	1.61	1.043	0.45	1.23	1.16	0.839
P—N(2)	1.70	1.61	1.056	0.45	1.25	1.16	0.799
P—C	1.77	1.80	0.983	0.49	1.28	1.31	1.072
P—S	1.94	2.06	0.942	0.63	1.31	1.43	1.301
	1.77	1.76	1.006		1.27	1.26	1.003
(5) $Mn^{II}O_2Cl_4$							
Mn—O	2.15	2.20	0.977	0.89	1.26	1.31	1.124
Mn—O	2.15	2.20	0.977	0.89	1.26	1.31	1.124
Mn—Cl(1)	2.52	2.55	0.988	1.06	1.46	1.49	1.063
Mn—Cl(1′)	2.52	2.55	0.988	1.06	1.46	1.49	1.063
Mn—Cl(2)	2.59	2.55	1.016	1.06	1.53	1.49	0.924
Mn—Cl(2′)	2.59	2.55	1.016	1.06	1.53	1.49	0.924
	2.42	2.43	0.994		1.41	1.43	1.037
(6) $Ni^{II}N_2O_4$							
Ni—N(1)	1.97	2.11	0.933	0.80	1.17	1.31	1.404
Ni—N(2)	1.98	2.11	0.938	0.80	1.18	1.31	1.404
Ni—O(1)	2.11	2.06	1.024	0.78	1.33	1.28	0.891
Ni—O(3)	2.17	2.06	1.053	0.78	1.39	1.28	0.781
Ni—O(5)	2.21	2.06	1.073	0.78	1.43	1.28	0.717
Ni—O(7)	2.10	2.06	1.019	0.78	1.32	1.28	0.758
	2.09	2.08	1.007		1.30	1.29	0.993
(7) $Sb^{VI}Cl_5O$							
Sb—Cl(2)	2.33	2.36	0.987	0.88	1.45	1.48	1.063
Sb—Cl(3)	2.34	2.36	0.992	0.88	1.46	1.48	1.042
Sb—Cl(3′)	2.34	2.36	0.992	0.88	1.46	1.48	1.042
Sb—Cl(4)	2.35	2.36	0.996	0.88	1.47	1.48	1.021
Sb—Cl(5)	2.33	2.36	0.987	0.88	1.45	1.48	1.063
Sb—O	2.05	1.99	1.030	0.71	1.34	1.28	0.872
	2.29	2.29	0.997		1.44	1.44	1.017
(8) $Sb^{VI}Cl_5O$							
Sb—Cl(1)	2.30	2.36	0.975	0.88	1.42	1.48	1.132
Sb—Cl(2)	2.32	2.36	0.983	0.88	1.44	1.48	1.086
Sb—Cl(3)	2.32	2.36	0.983	0.88	1.44	1.48	1.086
Sb—Cl(4)	2.33	2.36	0.987	0.88	1.45	1.48	1.063
Sb—Cl(5)	2.30	2.36	0.975	0.88	1.42	1.48	1.132
Sb—O	2.43	1.99	1.221	0.71	1.72	1.28	0.412
	2.33	2.29	1.021		1.48	1.44	0.985
(9) $Sn^{IV}Cl_3O_3$							
Sn—Cl(1)	2.32	2.42	0.959	0.97	1.35	1.45	1.239
Sn—Cl(2)	2.35	2.42	0.971	0.97	1.38	1.45	1.160
Sn—Cl(3)	2.34	2.42	0.967	0.97	1.37	1.45	1.186
Sn—O(1)	2.15	2.06	1.044	0.80	1.35	1.26	0.813
Sn—O(2)	2.12	2.06	1.029	0.80	1.32	1.26	0.870
Sn—O(3)	2.12	2.06	1.029	0.80	1.32	1.26	0.870
	2.23	2.23	1.000	0.80	1.35	1.35	1.023

The references are given as in Table 1. (1) $AlOCl_3$ 72 ACBCAR 28 1437 $AlCl_3\cdot CH_3CH_2COCl$; (2) $POCl_3$ 71 INOCAJ 10 344 $POCl_3$ (gas); (3) PON_2S 75 ACBCAR 34 2098 $(N_2H_2)_2P(SOC_6H_5)$; (4) PCN_2S 75 ACBCAR 31 2333 $C_{12}H_{16}N_2P_2S_2$; (5) $Mn^{II}O_2Cl_4$ 67 ACCRA9 23 630 $MnCl_2\cdot 2H_2O$; (6) $Ni^{II}N_2O_4$ 72 ACBCAR 28 2583 $Ni[C_5H_3N(COO)-COOH]_2\cdot 3H_2O$; (7) $Sb^{VI}Cl_5O$ 66 ACCRA9 20 749 $SbCl_5\cdot HCON(CH_3)_3$; (8) $Sb^{VI}Cl_5O$ 69 ACBCAR 28 1442 $2SbCl_5\cdot COClCH_2CH_2COCl$; (9) $Sn^{IV}Cl_3O_3$ 69 ACBCAR 25 1720 $[SnCl_3POCl_3]^+[(PO_2Cl_2)^-]_2$.

4.4. Application to hetero-ligand polyhedra

Since (6) and (10) exhibit similar behaviour and the form of (10) is simple, (10) is first tested. $PSCl_3$ is almost tetrahedral with P—S 1.885 and P—Cl 2.011 Å (×3), see Moritani *et al.* (1971). The average P—S distance of the PS4 tetrahedron is 2.06 (Nos. 104–107 in Table 1) and the average P—Cl distance of the PCl4 tetrahedron (Nos. 109 and 111 in Table 1) is 1.94 Å. Thus, the left side of (10) is $(1/4)(2.06/1.89 + 3 \times 1.94/2.01) = 0.996 \simeq 1$. Compensation for the ratio of bond distance change is $(2.06-1.89)/2.06 + 3 \times (1.94-2.01)/1.94 = 0.083-0.108 = -0.025 \cong 0$. Other examples are listed in Table 4. The last-row values in the column of R, R^0 and R/R^0 are arithmetic averages of these values. The averages of R/R^0 values correspond to the left-side values of (10).

In (10), bond distance changes of $M-X$ and $M-Y$ in MX_nY_m start at the reference distances R^0_{MX} in MX_ν and R^0_{MY} in MY_ν. However, it is considered that (10) also applies to the case where the bond distance changes start at the existing distances in MX_nY_m. For example, suppose that a $PSCl_3$ molecule with P—S 1.89 and P—Cl 2.01 (× 3) Å (not the reference distances) is placed in an environment with $C_{3\nu}$ symmetry and then the P—S distance is lengthened by 6% to 2.00 Å. In this case, each P—Cl distance is expected to be shortened by 2% to 1.97 Å. From this consideration, we obtain the following equation by replacing R^0 by R in (10)

$$\frac{1}{\nu}\left\{\sum_i^n \frac{dR_{MX_i}}{R_{MX_i}} + \sum_j^m \frac{dR_{MY_j}}{R_{MY_j}}\right\} = 0. \tag{19}$$

The integral form of (19) leads to the following relation (note $\int dx/x = \ln x + \text{const.}$)

$$\left\{(R_{MX_1}\cdot R_{MX_2}\cdots R_{MX_n})(R_{MY_1}\cdot R_{MY_2}\cdots R_{MY_m})\right\}^{1/\nu} = \text{const.} \tag{20}$$

It is considered that the constant can be taken as the value calculated with the bond distances of the homo-ligand polyhedra MX_ν and MY_ν. Thus, we obtain

$$\left\{(R_{MX_1}\cdot R_{MX_2}\cdots R_{MX_n})(R_{MY_1}\cdot R_{MY_2}\cdots R_{MY_m})\right\}^{1/\nu} = \left\{\left(R^0_{MX}\right)^n\left(R^0_{MY}\right)^m\right\}^{1/\nu}. \tag{21}$$

Equation (21) represents the 'conservation of the geometrical average' of the bond distances in a hetero-ligand coordination polyhedron with coordination number ν.

Here we test (21). For the $PSCl_3$ molecule, the left side of (21) is $(1.885 \times 2.011 \times 2.011 \times 2.011)^{1/4} = 1.979$ and the right side $(2.063 \times 1.944 \times 1.944 \times 1.944)^{1/4} = 1.973$ Å.

Next, we examine (6). For $PSCl_3$ the left side of (6) is $(1/4)\{(2.06–0.63)^3/(1.89–0.63)^3 + 3(1.94–0.60)^3/(2.01–0.60)^3\} = 1.009$. Other examples are shown in Table 4 on the last row in the column of $(R^0 - \lambda)^3/(R - \lambda)^3$. The last row in the columns of $R - \lambda$ and $R^0 - \lambda$ are the geometrical averages of these values. The corresponding equation to (21) in terms of $\bar{\rho}$ is as follows

$$\left\{(\bar{\rho}_{MX_1}\cdot\bar{\rho}_{MX_2}\cdots\bar{\rho}_{MX_n})(\bar{\rho}_{MY_1}\cdot\bar{\rho}_{MY_2}\cdots\bar{\rho}_{MY_m})\right\}^{1/\nu} = \left\{\left(\bar{\rho}^0_{MX}\right)^n\left(\bar{\rho}^0_{MY}\right)^m\right\}^{1/\nu}. \qquad (22)$$

Here we consider the physical meaning of (22). The principle of minimizing electron–electron repulsion states that the valence electrons arrange themselves as symmetrically as possible so that the molecular shape tends to be symmetric (Gillespie & Nyholm, 1957). $\bar{\rho}^0_{MX}$ and $\bar{\rho}^0_{MY}$ should originate from the electron density distribution, which minimizes the electron–electron repulsion around M in MX_ν and MY_ν, because both MX_ν and MY_ν are regular in shape. From this fact it is inferred that (22) is related to the minimum electron pair repulsion principle, although multiplication of the average electron densities is not directly connected with the electron–electron repulsion energy.

To show an example of the bond-valence sum for a hetero-ligand polyhedron we take penta-coordinate silicon, because whether the valence of such a Si atom is 4 or 5 is an interesting question. Boer *et al.* (1968) reported the crystal structure of tetramethylammonium bis(*o*-phenylenedioxy)phenylsiliconate, $C_6H_5Si(O_2C_6H_4)_2^-N(CH_3)_4^+$. This is an organosilicon compound containing penta-coordinate silicon. The structure of the $C_6H_5Si(O_2C_6H_4)_2^-$ ion is shown in Fig. 7. The parameters R^0, λ and s_0 for SiC_4 are 1.88 and 0.56 Å and 1, and for SiO_4 1.63, 0.50 Å and 1. Equation (5) gives the following bond-valence sum of the Si atom

$$1\cdot\frac{(1.88-0.56)^3}{(1.89-0.56)^3} + 2\cdot 1\cdot\frac{(1.63-0.50)^3}{(1.79-0.50)^3} + 2\cdot 1\cdot\frac{(1.63-0.50)^3}{(1.70-0.50)^3} = 0.978 + 2\cdot 0.672 + 2\cdot 0.835 = 3.992 \simeq 4.$$

Thus, the bond-valence sum of this Si atom is conserved as 4, although the number of atoms bonding to silicon is 5. This conservation is realised by the change in Si—O bond distance (1.63 → 1.70, 1.79 Å). This does not only apply to penta-coordinate silicon compounds; also strong hydrogen-bond systems in the next section and bridge-bonded compounds

Table 5
Prediction of $X\cdots X$ (Å) distances of symmetric hydrogen-bond systems $X—H—X$.

$X—H—X$	R^0_{XH}	λ	$R_{X\cdots X}$(cal)	$R_{X\cdots X}$(obs)
O—H—O	0.957 (r_e)	0.09	2.36	2.42–2.44†
	0.974 (r_g)	0.09	2.41	2.42–2.44†
F—H—F	0.92	0.07	2.27	2.25–2.29‡
Cl—H—Cl	1.27	0.26	3.07	3.14§
Br—H—Br	1.41	0.39	3.35	3.38§

† $Ca(H_2PO_4)_2$ (Dickens *et al.*, 1973); $H_5O_2^+$ in yttrium oxalate trihydrate (Brunton & Johnson, 1975); $N_2H_5C_2O_4$ (Nilsson *et al.*, 1968). ‡ $NaHF_2$ (McGaw & Ibers, 1963); KHF_2 (Carrel & Donohue, 1972); $K_2[Ta(O_2)F_5]\cdot KHF_2$ (Ružic Toroš & Kojić Prodić, 1976). § $CsX\cdot 1/3(H_3O\cdot HCX_2)$ (X = Cl, Br; Schroeder & Ibers, 1968).

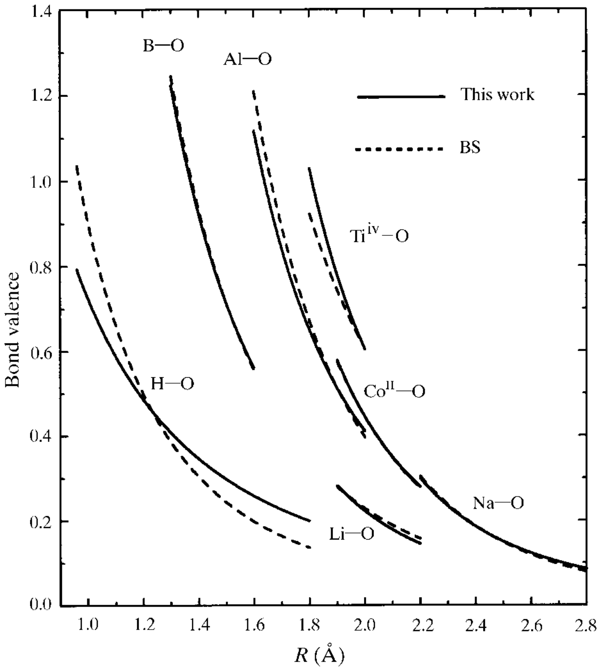


Figure 6
Comparison of the bond valences from (5) with those from the Brown–Shannon formula, BS.

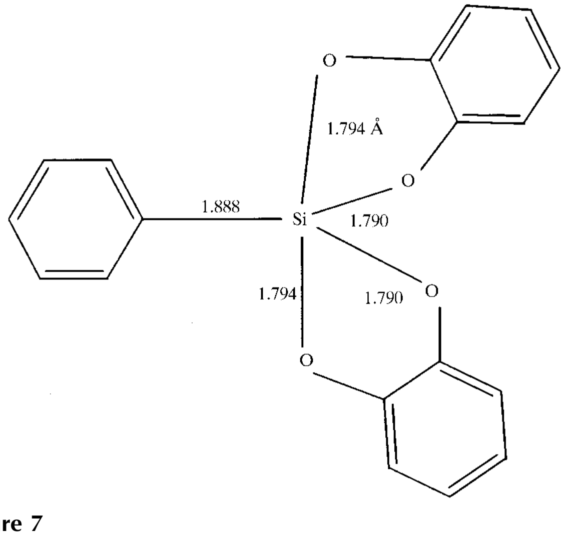


Figure 7
Schematic representation of $[C_6H_5Si(O_2C_6H_4)_2]^-$ (Boer *et al.*, 1968).

such as Al_2Cl_6 and B_2H_6 have been recognized as 'special cases' for their chemical bonds (Coulson, 1961). The author believes that this recognition originates from the unrealistic definition of the classical valence, where bond distance is not taken into account. The above result on the penta-coodinate silicon is an example which suggests that the bond-valence sum is the realistic definition as the 'bonding power' (original sense of the classical valence concept).

4.5. Application to strong hydrogen-bond systems

The application of the bond-valence sum rule to hydrogen-bond systems has often been discussed (Donnay & Donnay, 1973; Brown, 1976, 1978), but their hydrogen-bond systems are limited to O—H··· O. On the other hand, (5) is applicable not only to O—H···O, but also to other types of hydrogen-bond systems, as described below.

First we predict the distances of $X\cdots X$ in symmetric hydrogen-bond systems X—H—X (X = O, F, Cl, Br). The distance $R_{X\ldots X}$(cal) for a linear symmetric hydrogen-bond system can be predicted from (12) with $R_{X\ldots X}(\mathrm{cal}) = 2\{(2/1)^{1/3}(R^0_{XH} - \lambda) + \lambda\}$. The term in curly brackets is obtained from entering $s = 1/2$, $s_o = 1$ and $R^0 = R^0_{XH}$ in (5). The reference X—H distances are r_e values of the reference molecules, H_2O, HF, HCl and HBr. For O—H—O systems, two reference O—H distances were given: r_e and r_g. λ in this equation is equal to the cation radius of X. Table 5 shows that the distances of $R_{X\ldots X}$(cal) are in good agreement with the distances of $R_{X\ldots X}$(obs) on the whole. The r_e and r_g for H—O of H_2O give different values of $R_{\mathrm{O}\ldots\mathrm{O}}$(cal) and this difference may not be small. Thus, when considering the hydrogen-bond distances, it is important to take molecular motion into account, as discussed by Busing & Levy (1958) and Pedersen (1975). An accurate X-ray electron-density analysis on a symmetric hydrogen-bond O—H—O in sodium hydrogen diacetate (Stevens *et al.*, 1977) indicates that this hydrogen bond is essentially the same as an ordinary covalent bond. This fact may assure the success of the above $R_{X\ldots X}$ prediction for symmetric hydrogen-bond systems.

Next, we consider the hydrogen position in asymmetric hydrogen bonds, assuming that $R_{X\ldots X}$ is given and that X—H···X is linear. The bond-valence sum for the H atom is expressed as $s_{X-\mathrm{H}} + s_{\mathrm{H}\ldots X} = 1$. Here we set $R_1 = R_{X-\mathrm{H}}$, $R_2 = R_{\mathrm{H}\ldots X}$ and $L = R_{X\ldots X}$. Entering these quantities into (5) leads to the following simultaneous equations

$$\frac{(R^0-\lambda)^3}{(R_1-\lambda)^3}+\frac{(R^0-\lambda)^3}{(R_2-\lambda)^3}=1 \qquad (23)$$

$$R_1+R_2=L. \qquad (24)$$

Swanson & Williams (1970) determined the crystal structure of $[N(CH_3)_4]HCl_2$ by X-ray diffraction and found that the Cl···Cl distance in HCl_2^- is 3.22 Å, but whether the H atom is midway between the two Cl atoms was questioned. Smith (1974) discussed this problem based on nuclear quadrupole resonance (NQR) studies. This problem is easily resolved by (23) and (24). The given parameters are $L = 3.22$, $R^0 = 1.27$ (HCl molecule) and $\lambda = \gamma(\mathrm{Cl}^{7+}) = 0.26$ Å. The simultaneous equations lead to the solution of asymmetric hydrogen bonds with $R_1 = 1.38$ and $R_2 = 1.84$ Å. These distances are very close to those from neutron diffraction (Williams & Peterson, 1971): R_1 = 1.37 and R_2 = 1.85 Å, as shown in Table 6. This good agreement may be due to the fact that this Cl—H···Cl system is a 'strong' hydrogen-bond system, where the covalent contribution to the H···Cl bond is relatively large and the arrangement of Cl—H···Cl is really linear.

Table 6
Electron populations of the H atoms (q_H) in the hydrogen-bond systems Cl—H···Cl (Smith, 1974).

R denotes distance in Å.

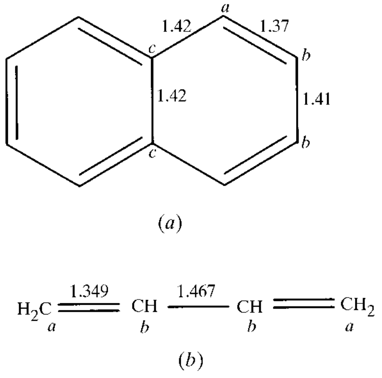
System	R(Cl···Cl)	R(Cl—H)	R(H···Cl)	q_H
HCl molecule		1.27		0.48
Symmetric†	3.14 ± 0.02	1.57	1.57	0.44
Asymmetric ‡	3.22 ± 0.02	1.37	1.85	0.43

† $CsCl\cdot1/3H_3O\cdot HCl_2$ (Schroeder & Ibers, 1968). ‡ $[N(CH_3)_4]HCl_2$ (Swanson & Williams, 1970, for X-ray; Williams & Peterson, 1971, for ND).

Smith (1974) derived the electron populations of the hydrogen atoms in Cl—H···Cl from the NQR frequencies for ^{35}Cl, assuming four-electron, three-centre bonds. The column headed q_H in Table 6 shows the hydrogen atom's electron populations for the hydrogen chloride molecule, the symmetric HCl_2^- ion in $CsCl\cdot1/3\ H_3O\cdot HCl_2$ (Schoroeder & Ibers, 1968) and the asymmetric HCl_2^- ion in $[N(CH_3)_4]HCl_2$. As Smith mentions, the H atom's electron populations in the two hydrogen systems are approximately equal to that in hydrogen chloride. This suggests that the electron population conservation is closely related to the bond-valence sum rule.

4.6. Organic compounds with C—C bonds

Application of the bond-valence sum rule to organic compounds with C—C bonds is an effective way of testing the idea that bond valence is a measure of covalent bond strength. However, until now the bond-valence sum rule has not been applicable to organic compounds with C—C bonds, because the bond valence for an atom pair has been defined in cases



(*a*)

(*b*)

Figure 8
(*a*) Naphthalene and (*b*) 1, 3-butadiene. The numerical figures represent C—C distances in Å.

Table 7
Bond-valence sums (V_c) of C atoms in some organic compounds.

s_{CC} represents the bond valence of each C—C bond.

	R_{cc} (Å)	s_{cc}	V_c
Ethylene	1.34	1.69	3.69
Acethylene	1.20	2.62	3.62
Benzene	1.40	1.43	3.86
Naphthalene	1.37 (*ab*)	1.56 (*ab*)	3.92 (*a*)
	1.41 (*bb*)	1.39 (*bb*)	3.95 (*b*)
	1.42 (*ac*)	1.36 (*ac*)	4.08 (*c*)
	1.42 (*cc*)	1.36 (*cc*)	
1,3-Butadiene	1.35 (*ab*)	1.64 (*ab*)	3.64 (*a*)
	1.47 (*bb*)	1.20 (*bb*)	3.84 (*b*)

where formal positive and negative charges are assigned to each atom (Brown, 1977). This is from the ionic model interpretation (Pauling, 1929). However, as shown below, (5) as well as Brown–Shannon and Brown–Altermatt formulae are also applicable to such organic compounds, *if the bond valence for a pure covalent bond is regarded as the classical bond order* (fractional classical valence shared with each bond). All the structural data used below are taken from *Kagaku-binran* (The Chemical Society of Japan, 1984). The reference system for C—C bonds is taken as ethane C_2H_6 with $R^0_{CC} = 1.54$ Å, $s_0 = 1$, $\lambda_{CC} = 0.30$ Å and thus $s_{CC} = (1.24)^3/(R_{cc} - 0.30)^3$. For the Brown–Shannon formula, the power number N is obtained from (13) as $N = 3 \times 1.54/(1.54 - 0.30) = 3.73$ and thus $s_{cc} = (1.54/R_{cc})^{3.73}$. For the Brown–Altermatt formula, values of $r_0 = 1.54$ and $B = 0.37$ are used and thus $s_{cc} = \exp[(1.54 - R_{cc})/0.37]$. The bond valence for C—H is regarded as unity ($s_{CH} = 1$) for all the compounds considered below, since these C—H distances are approximately constant around 1.09 Å.

Ethylene, C_2H_4, acethylene, C_2H_2, benzene, C_6H_6, naphthalene, $C_{10}H_8$ (see Fig. 8*a*), and 1,3-butadine, $H_2C{=}CH{-}CH{=}CH_2$ (see Fig. 8*b*), are chosen, because their C—C distances are significantly different from that of C_2H_6. The calculated C—C bond valences, s_{cc}, from (5) and the bond-valence sums around the C atoms, V_c, are listed in Table 7. We can confirm that both the Brown–Shannon formula and Brown–Altermatt's formula lead to s_{cc} values close to those from (5). Table 7 shows that the bond-valence sums for the C atoms in the above compounds are 3.6–4.1, which is not far from the carbon's classical valence, 4. This fact suggests that the bond valence is a quantity closely related to the classical bond order, which is regarded as the number of Lewis electron pairs contributing to the covalent bond.

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