A Simple Model for Vibrational Force Constants

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Abstract: A model is presented for diatomic molecules in which the force field is generated by nuclear charges partially screened by the electrons. The empirical equation for the force constant is $k = 2z_A z_B/R_0^3$, where z_A and z_B are the effective charges on each atom, and R_0 is the equilibrium separation. Effective charges, z, are found for a number of elements from experimental data, including compressibilities of solids. A chart of such values is given. The z values form a very regular pattern and can be interpreted as the effective number of bonding electrons per atom. The z values for the elements can be transferred to heteronuclear molecules with good success. However, some correction must be made for extreme ionic character and for π bonding not possible in the homonuclear cases. The extension of the model to polyatomic molecules is considered, leading to the central force field. As shown by earlier work, this force field when properly used is equivalent to the general valence force field.

The computation of force constants by ab initio quantum mechanical methods has become both straightforward and reliable in recent years.[1] However these methods are still not practical for most molecules. In spite of a great deal of effort, there is still no simple model for molecular force fields which enable good estimates of vibrational frequencies to be made in advance.[2] The well-known Badger rules work well in some cases but are restricted to stretching force constants and do not apply to bending constants.[3] Also there does not seem to be a theoretical basis for the rules.

On the positive side it should be mentioned that the simple ionic model (hard sphere) works very well for the alkali halides.[4] Extension of this model to more complex molecules has met with mixed success and is still controversial.[5] Also for many hydride molecules the Platt model works quite well for both bending and stretching modes.[6] In this model the hydrogen atom is considered to be a bare proton buried in an electron cloud centered on a heavier atom. Such a model has also been extended to general diatomic molecules with some success.[2b]

The same ionic model that works well for diatomic alkali halide molecules also successfully predicts many properties of these substances in the solid state.[7] This includes lattice energies, compressibilities and other elastic constants, infrared absorption, lattice vibrations, and heat capacities. It is well known that compressibilities of solids can be used to calculate force constants for bonds between neighboring atoms.[8] These force constants can then be used to calculate other solid state properties.

For many molecules there is a rough correlation between bond stretching force constants and bond dissociation energies. However, only similar molecules can be compared in this way. Also bond deformation constants are roughly related to the energies needed to twist a molecule into a new shape, or into a conformational isomer. Hopefully a good model for force constants would also throw more light on the energy require-

ments for larger changes in nuclear positions which are chemically significant.

The present paper is an attempt to find a simple, general model for force constants which predicts vibrational frequencies to perhaps 5% and which reveals in a useful way the factors which determine the force constants.

Diatomic Molecules

Starting with the simplest case of two atoms, A and B, bonded together, an exact expression for the quadratic force constant can be derived from perturbation theory.[9]

$$k = \left(\frac{\partial^2 E}{\partial R^2}\right)_{R_0} = \frac{2Z_A Z_B}{R_0^3}(1 - f) \tag{1}$$

$$f = R_0^3 \sum_k \frac{\left\langle \rho_{0k}\dfrac{\cos\theta_A}{r_A^2}\right\rangle \left\langle \rho_{0k}\dfrac{\cos\theta_B}{r_B^2}\right\rangle}{E_k - E_0} \tag{2}$$

Z_A and Z_B are the nuclear charges, R_0 is the equilibrium internuclear separation, and f is a shielding factor due to the relaxation of the electron cloud following a small change in R_0. The relaxation is represented by mixing of excited state wave functions, ψ_k, into the ground state wave function, ψ_0. The transition density, ρ_{0k}, results from this mixing. The brackets indicate integration over the electronic coordinates with respect to each nucleus, $\cos\theta_A$, r_A, and $\cos\theta_B$, r_B.

Since an infinite sum of excited states must be taken, the evaluation of these integrals is not practical. However, an empirical approach can be used. The relaxation of the inner-shell electrons of each atom simply causes these electrons to follow the nuclei so that the wave functions continue to be centered on the nuclei.[10] The effect is to reduce the nuclear charges, Z_A and Z_B, down to essentially the core charges, Z_A' and Z_B', since the inner-shell electrons efficiently shield the nuclei from each other. The result is a large reduction in the energy needed for displacement.

Table I. Effective Charges, z, for Homonuclear Diatomic Molecules from $k = 2z^2/R_0^3$ [a]

Molecule	z	Molecule	z
H_2	0.71	K_2	1.13
Li_2	1.01	Cu_2	1.77
B_2	1.77	As_2	2.82
C_2	2.15	Se_2	2.77
N_2	2.57	Br_2	2.50
O_2	2.13	Rb_2	1.14
F_2	1.68	Ag_2	1.97
Na_2	1.03	Sb_2	2.94
Al_2	1.88	Te_2	2.84
Si_2	2.29	I_2	2.66
P_2	2.86	Cs_2	1.20
S_2	2.69	Au_2	2.62
Cl_2	2.36	Bi_2	2.77

[a] Experimental values of k and R_0 from G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed., Van Nostrand, New York, N.Y., 1950, and from "Données Spectroscopiques Relative aux Molécules Diatomiques", Pergamon Press, Oxford, 1970.

The valence shell electrons cannot adjust their positions in such a favorable way. A pair of electrons in a σ bond, for example, will still be concentrated in the region between the nuclei, even if the atoms approach or recede from each other by small amounts. Thus the bonding electrons have no easy way to lower the energy. This shows up as inefficient screening of the nuclei from each other in terms of eq 1.

Other valence shell electrons will exhibit some screening. Nonbonding σ electrons will behave somewhat like inner-shell electrons. When both bonding and antibonding π orbitals are filled, the π electrons are essentially lone pairs on each atom and will also be shielding. The conclusion is that the core charges will be reduced even further due to some shielding by the valence shell electrons to effective charges z_A and z_B. The condition on these effective charges, for a neutral molecule, will be

$$0 < z_A < Z_A'$$

$$0 < z_B < Z_B' \tag{3}$$

The force constant will be given by the empirical equation

$$k = 2z_A z_B / R_0^3 \tag{4}$$

Homonuclear Diatomics

When both A and B are the same atom, $z_A = z_B = z$, and experimental values of k and R_0 can be used to evaluate the effective charges. Table I shows the results of such an evaluation for a number of molecules where the data are available. The working equation is

$$k = 4.61 z^2 / R_0^3 \tag{5}$$

where k is in mdyn/Å, R_0 is in Å, and z is in positive electronic units.

The results in Table I are quite reasonable in that they all lie within the mandatory limits $0 < z < Z'$. Also they vary with the elements in a reasonable way, as one goes across any row of the periodic table. For the alkali metals z is about unity, then it rises to a maximum value of 2.5–3.0 for the fifth group, falling for the chalcogens and still more for the halogens. This closely parallels the number of electrons that are capable of forming chemical bonds in each molecule. The maximum of three electrons per atom comes at group 5. In groups 6 and 7 the additional electrons go into antibonding orbitals and become shielding. Electrons in a chemical bond have almost no shielding capability. This effect has already been noticed for the alkali metal diatomics.[12]

The variations between the elements have also been discussed by Parr and Borkman.[13] These authors have given a model for force constants in which an effective number of electrons, q, balanced by an equal number of positive charges on the nuclei, generate the potential energy function for the molecule. The model leads to the simple result,

$$k = 7e^2 q^2 / 4R_0^3 \tag{6}$$

so that z and q are almost equal numbers for homonuclear diatomic molecules.

Accordingly z has a dual interpretation in a neutral molecule. It is the amount of unshielded positive charge on each nucleus, and it is also the number of electrons in each atom which are actively bonding. This is not necessarily an integral number. In the halogen molecules, for example, z increases in the order 1.68, 2.36, 2.50, and 2.66 for F_2, Cl_2, Br_2, and I_2. The larger values for the heavy halogens may be due to increased bonding such as π bonding between filled p orbitals and empty d orbitals. Such extra bonding has been suggested to explain the anomalous order of bond strengths, that for F_2 being unusually small.[14,15]

Other factors probably make z larger for heavier atoms, independent of the bonding. For example in Table I, it can be seen that z increases in general as one goes down a column in the periodic table. Cesium has $z = 1.20$, even though there is certainly only one valence electron. However, in such a heavy atom some of the inner-shell electrons are in orbitals that are quite diffuse. They also will be somewhat inefficient in shielding the nucleus. In general only electron density on atom A which is at a distance r_A less than R_0 will exert good screening. This is easily seen for a spherical charge distribution. Alternatively one can argue that weakly held inner-shell electrons contribute some bonding because they are easily polarized, or because they lead to large van der Waals' energies between the two bonded atoms.

Compressibilities

Some homonuclear diatomic molecules such as Be_2 or Mg_2 do not exist. Others have not yet been studied spectroscopically. Force constants can still be obtained for these elements from the solid state compressibilities, providing the crystal structure is cubic. The procedure is to equate pressure–volume work with the energy needed to compress the presumed bonds between neighboring atoms. The result for a cubic crystal is that[8]

$$k_n = 9V_0/nR_0^2\beta \tag{7}$$

where V_0 is the volume holding two atoms, R_0 is the distance between nearest neighbors, β is the compressibility, and n is the number of nearest neighbors.

Pauling and Waser have calculated k_n values for a number of metallic elements. By analogy with the diatomic case, $k_n = 2z_n^2/R_0^3$, where z_n is the effective nuclear charge, or number of valence electrons, in the case where n neighbors exist. Table II gives a number of z_n values found in this way. For hexagonal close packing and face centered cubic, $n = 12$. For body centered cubic, n has also been set equal to 12, instead of the 8 used by Pauling and Waser. This allows for the 6 next-nearest neighbors in the bccub case. The larger value of R_0^3 for these 6 atoms reduces their effect to that of 4 atoms at the shorter distance. More distant atoms are ignored. The implicit assumption is that their displacements will be effectively screened for the central atom.

The values of z_n for an element are not the same as for the diatomic molecule, nor are they expected to be. For example, the alkali metals now have z_n equal to about 0.5 instead of 1.0. The interpretation is as follows: There is still one valence electron per atom. It spends $\frac{1}{12}$ of its time in a bond to any one neighbor and $\frac{11}{12}$ of its time in bonds which are adjacent. The

Table II. Effective Charges, z_n, for Solid State Elements from Compressibilities

Element	z_n	z	Element	z_n	z
Li	0.50		Ti	1.44	2.3
Na	0.56		V	1.39	2.2
K	0.56		Cr	1.35	2.1
Rb	0.52		Fe	1.26	2.0
Cs	0.52		Co	1.28	2.0
Be	0.88	1.6	Ni	1.27	2.0
Mg	0.89	1.6	Cu	1.15	
Ca	0.98	1.8	Zr	1.46	2.4
Sr	0.98	1.9	Nb	1.69	2.7
Ba	0.93	1.8	Mo	1.93	3.0
Al	1.04		Ru	1.83	2.9
Sc	1.07	2.0	Rh	1.79	2.8
La	1.12	2.1	Pd	1.55	2.5
Nd	1.10	2.0	Ag	1.26	
Pr	1.10	2.0	Hf	1.59	2.5
Tl	1.05	1.9	Ta	1.86	2.9
C	2.20[a]		W	2.01	3.2
Si	1.99[a]		Re	2.19	3.5
Ge	1.93[a]		Ir	2.13	3.5
Sn	2.19[a]		Pt	2.39	3.8
			Au	1.64	
			Pb	1.18	2.2
			Th	1.48	2.7

[a] Diamond structure, $n = 4$. Data from ref 8 and from "Constantes Selectionnées Metaux", Pergamon Press, Oxford, 1969.

Table III. Values of $z_A z_B$ for Heteronuclear Diatomic Molecules

Molecule	$z_A z_B$(exptl)[a]	$z_A z_B$(calcd)[b]
CN	5.70	5.47
CO	5.95	4.58
CF	3.30	3.61
NO	5.26	5.47
CP	6.52	6.14
CS	6.71	5.78
CCl	3.72	5.07
PO	6.23	6.04
ClF	4.27	3.96
PN	7.36	7.35
SiN	5.87	5.88
SiO	6.90	4.88
SiF	4.12	3.86
SiCl	5.97	5.40
SiS	7.11	6.16
ClO	3.92	5.02
NS	6.21	6.91
SO	5.74	5.73
SeO	5.95	5.91
CSe	6.55	5.96
BrF	4.83	4.20
ICl	6.50	6.28
IBr	6.47	6.55
IO	5.53	5.74
AsO	6.74	6.01
AsN	6.92	7.25
TeO	7.04	6.05

[a] Calculated from experimental results given in references at end of Table I. [b] Calculated from z values in Table 1, assuming transferability.

shielding is near zero for $^1/_{12}$ of an electron and about one half for $^{11}/_{12}$ of an electron. That is, an electron which is bonding between atoms A and B is still partly shielding for an atom C, also bonded to B, but not to A.

This seems like a reasonable result and is obviously of great importance in extending the model to polyatomic molecules. As an example, consider the tetrahedral P_4 molecule. All four atoms are singly bonded to each other. The vibrational spectrum is almost entirely determined by a single force constant, k, for the P–P stretch.[16] This constant is 2.19 mdyn/Å and R_0 is 2.21 Å which leads to a calculated z_n value of 2.26. This may be compared to $z = 2.86$ for the P_2 molecule.

The smaller values of z_n, compared to z for a diatomic molecule, can be interpreted by a general formula,

$$z_n = z \left(\frac{1}{n} - \frac{(n-1)}{n} \sigma \right) \tag{8}$$

where σ is the shielding deficiency for the electrons in the $(n - 1)$ adjacent bonds. In P_4 there would be one electron which is not shielding at all (the bonding electron) and two electrons which have $\sigma = 0.70$, or 30% shielding.

While this view is oversimplified, eq 8 can be used to calculate z values for diatomic molecules from z_n values for solids. The shielding deficiency, σ, averages 0.50 for the alkali metals and aluminum and 0.60 for the copper, silver, and gold. The former value may be considered characteristic for the representative metals and the latter value for the transition metals. This enables a number of new z values to be found, as shown in Table II.

The results are entirely reasonable. For the metals of groups 2 and 3 the new results fall nicely into place with the results of Table I. The transition metals of the first series have z equal to about 2.0 but definitely falling off at the end of the series. The second transition series has somewhat larger z values, and the third series has larger values still. This is the same pattern shown in Table I as the total number of electrons increases. On the average, the transition metals behave as if they had more bonding electrons than the trivalent metals. This is consistent with the d electrons acting as valence electrons, in part.

However, as the d shell fills up, there is a drop in the bonding ability of the d electrons. It can be anticipated that zinc, cadmium, and mercury will show reduced z values.

The group 4 elements, C, Si, Ge, and Sn, which have the diamond structure, give z_n values of about 2. From eq 8, z is calculated to be 3.2, if σ is taken as 0.5. This is the expected z value for a diatomic molecule with four bonds. Of course C_2 and Si_2 have only two bonds and z is correspondingly less.

Heteronuclear Diatomic Molecules

There is a large amount of data available for diatomic molecules with two different atoms. Using eq 4 and experimental results for k and R_0, values of $z_A z_B$ can be found. Separation of this product function into its two parts is not obvious. However, as a start one can try to simply transfer the z values from the homonuclear case. Table III shows the comparison of results for a number of molecules formed between two different nonmetallic elements, where covalency is expected to dominate the bonding. Also the z_A and z_B values are known from Table I in a straightforward way.

The agreement between experimental values and calculated values is surprisingly good, considering that transfer of z values assumes a constancy in the number of bonding electrons. Furthermore, the major deviations are rapidly explained by expected changes in the bonding situation. For example, CO has an experimental value of $z_A z_B$ equal to 5.95, whereas the geometric mean of C_2 and O_2 is only 4.58. But it is well known that CO behaves very much like N_2 in being nearly triply bonded, whereas both C_2 and O_2 are only doubly bonded.

The triple bonding in CO results because the $(p)^4$ configuration of an oxygen atom can combine with the $(p)^2$ configuration of a carbon atom to behave like two $(p)^3$ atoms. It is expected that all combinations of a group 4 atom with a group 6 atom will show extra bonding in this way. Indeed Table III bears this out in that $z_A z_B$(exptl) is always considerably larger than $z_A z_B$(calcd) for such molecules.

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Table IV. Values of $z_A z_B$ for Diatomic Hydrides[a]

Molecule	$z_A z_B$(exptl)	$z_A z_B$(calcd)
LiH	0.90	0.72
BeH	1.19	0.99
BH	1.24	1.26
CH	1.38	1.53
NH	1.45	1.82
OH	1.54	1.62
FH	1.62	1.19
NaH	1.13	0.73
MgH	1.44	1.14
AlH	1.57	1.33
SiH	2.26	1.63
PH	2.08	2.03
SH	2.19	1.91
ClH	2.31	1.68
KH	1.37	0.80
CaH	1.72	1.28
MnH	1.46	
NiH	1.51	1.42
CuH	1.50	1.26
ZnH	1.38	
GaH	1.51	
GeH	2.07	1.88
AsH	2.07	2.31
BrH	2.55	1.77
RbH	1.46	0.81
SiH	1.81	1.35
PdH	1.89	1.78
AgH	1.67	1.40
CdH	1.43	
InH	1.73	
IH	2.80	1.89
CsH	1.57	0.85
BaH	1.93	1.42
PtH	2.39	2.63
AuH	2.42	1.86
HgH	1.30	
TlH	1.61	
PbH	1.95	1.56
BiH	2.19	1.97

[a] Data from references at end of Table 1.

Table V. Values of $z_A z_B$ for Alkali Halide Molecules

Molecules	$z_A z_B$(exptl)	$z_A z_B$(calcd)
LiF	2.05	1.70
LiCl	2.53	2.38
LiBr	2.64	2.52
LiI	2.73	2.69
NaF	2.75	1.70
NaCl	3.14	2.43
NaBr	3.16	2.53
NaI	3.29	2.69
KF	3.04	1.90
KCl	3.50	2.67
KBr	3.61	2.82
KI	3.76	3.00
RbP	3.23	1.91
RbCl	3.63	2.69
RbBr	3.70	2.85
RbI	3.50	3.03
CsF	3.42	2.02
CsCl	4.07	2.83
CsBr	4.08	3.00
CsI	4.38	3.19

z_B values of the halogens from Table I reproduce the experimental results remarkably well.

One would also expect the effective charge for hydrogen to be unity in a number of other cases, such as CH, NH, and OH. In these molecules a second factor must be considered. The proton has no π type orbitals that can be used to accept the π bonding electrons of C, N, or O. Hence the z_B values of 2.15, 2.57, and 2.13 for these atoms are too high, since electrons formerly bonding now become isolated on the electronegative atom. The net result is a near cancellation of errors, as seen in Table IV.

The transition metal hydrides and other nonionic metal hydrides show fairly good agreement between $z_A z_B$(exptl) and $z_A z_B$(calcd). This offers another possible way to find z values for the elements. For example, it seems clear that zinc, cadmium, and mercury have smaller z values than their neighbors on either side in the periodic table. That for mercury is unusually small, consistent with its high compressibility in the solid state.

The Alkali Halides

The diatomic alkali halides offer the extreme examples of ionic bonding. Table V shows the experimental values of the product $z_A z_B$ compared with the calculated product from the z values of Table I. Only lithium gives good agreement between the two sets of numbers. Lithium forms the most covalent bonds of any of the alkali metals and also has the fewest inner-shell electrons. The deviations between the experimental and calculated results increase with increasing size of the alkali metal and decreasing size of the halogen atom.

CsF shows the largest discrepancy of 41% and is also the most ionic of these molecules. The observed value of 3.42 for $z_A z_B$ is difficult to rationalize in terms of bonding electrons or unshielded nuclei. Instead it is useful to use the ionic model to understand the force constant. Write the potential energy function for the diatomic molecule as

$$F = -\frac{e^2}{R} + \frac{B}{R^m} \qquad (9)$$

whence

$$k = \frac{e^2}{R_0{}^3}(m - 1) \qquad (10)$$

Accordingly the experimental values of $z_A z_B$ in Table V are equal to $(m - 1)/2$.[17]

If these cases are excluded, the remaining entries of Table III show agreement to better than 10% (CCl is an exception). The vibrational frequencies, which depend on the square root of the force constant, would be predicted to within 5%. An arbitrary correction could also be made for the group 4–group 6 combinations to bring them into line.

Table IV gives experimental values of $z_A z_B$ for diatomic hydride molecules, calculated from force constants and bond distances, and also the values found from $z_A = 0.71$ for hydrogen and z_B equal to its values from Tables I and II. The experimental values are all in the range of 1 to 3 as expected from the fact that the effective charge of hydrogen has a maximum value of unity. On a percentage basis, there are some fairly large discrepancies, the calculated values being too low. The largest errors are for the alkali and alkaline earth hydrides and for the halogen hydrides. The first group consists of molecules which are quite ionic in their bonding. These will be discussed later, together with the alkali halides.

The hydrogen halides show deviations which can be ascribed to electron transfer from hydrogen to halogen and penetration of the hydrogen into the electron cloud of the halogen atom. It may be recalled that the covalent radius of hydrogen (0.30 Å) is considerably less than half the bond distance in H_2 (0.37 Å). This illustrates the penetration phenomenon. In fact the Platt model works well for the hydrogen halides.[6] If the charge, z_A, on hydrogen is taken to be unity (the bare proton) then the

The repulsive exponent, m, is not known theoretically, but it can be found from the compressibility of the solid salt.[7] The potential energy function for the solid is given by

$$E = -\frac{Ae^2}{R} + \frac{nB}{R^m} \qquad (11)$$

where A is the Madelung constant and n is the number of nearest neighbors of opposite charge. Equation 11 leads to

$$k_n = \frac{1.748(m-1)}{6} \frac{e^2}{R_0^3} = 0.291k \qquad \text{(NaCl structure)}$$

$$k_n = \frac{1.763(m-1)}{8} \frac{e^2}{R_0^3} = 0.220k \qquad \text{(CsCl structure)}$$

$$(12)$$

Equation 7 is used to find k_n from the compressibility of the solid.

In this way m is found to be 7.7 for NaCl. This leads to a calculated value of k for the diatomic molecule of 1.18 mdyn/Å, compared to the experimental value of 1.10. The relationships $k_n = 0.291k$ or $0.220k$ are obeyed fairly well for all the alkali halides, except those of lithium.

The important conclusion from the ionic model is that the force constant comes largely from the repulsive part of the potential. That is, the value of m determines the force constant. But the repulsive term is considered as arising from the interpenetration of the electron clouds surrounding each ion and not from the nuclear repulsion. The energy is raised by virtue of the operation of the Pauli exclusion principle. This effect is presumably included in the exact eq 11, but it is well camouflaged. It is not clear how it can be interpreted as a simple failure of electrons to screen the nucleus.

Accordingly if the empirical eq 4 is used for very ionic molecules, the values of $z_A z_B$ that result will be too large. There will be an increment arising from the interpenetration of filled electron shells. Apparently the increment can be small in some cases, such as the lithium halides, because lithium ion has only two inner-shell electrons.

Other Diatomic Molecules

Table VI has $z_A z_B$ from experimental data for a number of other metal halides. The $z_A z_B$ products calculated from previously derived z values for the elements are also included. The metal fluorides behave like the alkali halides in that the experimental values are 25–30% higher than the calculated values. The other halides give surprisingly good agreement (within 10%, on the average) between the two sets of numbers. These diatomic halides are expected to show smaller errors due to inner-shell electron overlaps. The reason is that there are valence shell electrons in antibonding orbitals which increase R_0 somewhat.

Because of the greater electronegativity of the metals in Table VI compared to the alkali metals, another factor must be considered. There will be π bonding between the filled p orbitals of the halogen atoms and the partly empty p orbitals of the metals. This is similar to the situation in carbon monoxide. The effect is to raise the value of $z_A z_B$(exptl) since a greater number of electrons are bonding electrons. Such π bonding should be more important for fluorine than for the other halogens, because double bonding is more effective for first row elements than for later ones. As the size of the metal atom increases, π bonding will diminish because of poor overlap. This will be compensated by a larger error due to overlap of the electron clouds.

Table VII has experimental and calculated $z_A z_B$ values for a number of metal oxides, sulfides, and others. The results are quite consistent with errors expected from ionic character and π bonding. For example, oxides show the greatest deviation

Table VI. Values of $z_A z_B$ for Diatomic Metal Halides[a]

Molecules	$z_A z_B$(exptl)	$z_A z_B$(calcd)
BeF	3.15	2.52
BF	3.50	2.97
MgF	3.75	2.69
AlF	4.09	3.16
CaF	4.09	2.86
CuP	3.90	2.97
GaF	4.14	
GeF	4.55	3.36
SnF	4.66	
SnF	5.26	4.60
TlF	4.54	
PbF	5.00	3.70
BiF	5.25	4.65
BeCl	3.24	3.54
BCl	3.82	4.18
MgCl	4.21	3.78
AlCl	4.37	4.43
CaCl	4.74	4.25
ScCl	5.61	4.72
CuCl	4.31	4.18
GaCl	4.26	
GeCl	4.54	4.72
AgCl	4.72	4.65
InCl	4.78	
SnCl	5.38	5.19
HgCl	3.62	
TlCl	4.81	
BBr	3.90	4.47
MgBr	4.31	4.00
AlBr	4.47	4.71
CuBr	4.51	4.43
AgBr	4.98	4.93
TlBr	4.84	5.00
AlI	4.61	5.00
CuI	4.78	4.71
AgI	5.17	5.24
InI	4.87	
TlI	5.03	

[a] See references at end of Table 1.

between the two sets of numbers, with the experimental values being too large. This results from errors due to both ionicity and π bonding. In comparison, the sulfides show somewhat smaller deviations, and the carbides give good agreement with calculated $z_A z_B$ values.

For the three carbide molecules ionicity is expected to be small, because of nearly equal electronegativities of carbon and of rhodium, iridium, and platinum. It may be noted that CuO, AgO, and PtO show an inversion in that their calculated $z_A z_B$ values are larger than the experimental ones. This may result from reduced ionicity, in part, because of the high electronegativity of these metals. A second factor lies in the filled, or nearly filled, shells of d orbitals. These are expected to inhibit oxygen to metal π bonding.

Molecular Ions

In the previous discussion the parameter z has been described both as an effective positive charge on the nucleus and as an effective number of bonding electrons for each atom. The two descriptions are complementary and do not conflict with each other. However, removal of an electron to form a positive molecular ion leads to different predictions as to how z should be affected. In the effective charge picture, z should increase for such ionization, since there is one electron less to shield the nucleus. The nature of the electron removed must also be considered. If it is a bonding electron, there should be little change in z, since such electrons have little shielding power in

Figure 1. Chart of effective nuclear charges for the elements.

1 H 0.71																	2 He
3 Li 1.01	4 Be 1.6											5 B 1.77	6 C 2.15	7 N 2.57	8 O 2.13	9 F 1.68	10 Ne
11 Na 1.03	12 Mg 1.6											13 Al 1.88	14 Si 2.29	15 P 2.86	16 S 2.69	17 Cl 2.36	18 Ar
19 K 1.13	20 Ca 1.7	21 Sc 2.0	22 Ti 2.3	23 V 2.2	24 Cr 2.2	25 Mn 1.9	26 Fe	27 Co 2.0	28 Ni 2.0	29 Cu 1.77	30 Zn 1.7	31 Ga 1.9	32 Ge 2.2	33 As 2.82	34 Se 2.77	35 Br 2.50	36 Kr
37 Rb 1.14	38 Sr 1.9	39 Y	40 Zr 2.5	41 Nb 2.7	42 Mo 3.0	43 Tc	44 Ru 2.9	45 Rh 2.8	46 Pd	47 Ag 1.97	48 Cd 1.8	49 In 2.0	50 Sn 2.2	51 Sb 2.94	52 Te 2.84	53 I 2.66	54 Xe
55 Cs 1.20	56 Ba 1.9	57 La 2.0	72 Hf 2.6	73 Ta 2.9	74 W 3.2	75 Re 3.5	76 Os	77 Ir 3.6	78 Pt 3.6	79 Au 2.62	80 Hg 1.5	81 Tl 2.0	82 Pb 2.2	83 Bi 2.77	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104														

58 Ce	59 Pr 1.9	60 Nd 1.9	61 Pm	62 Sm
90 Th 2.7	91 Pa	92 U	93 Np	94 Pu

Table VII. Values of $z_A z_B$ for Diatomic Oxides and Others[a]

Molecule	$z_A z_B$(exptl)	$z_A z_B$(calcd)
BeO	3.85	3.20
BO	5.21	3.77
MgO	4.07	3.41
AlO	5.68	3.97
CaO	4.73	3.83
ScO	6.53	5.06
TiO	6.65	4.90
VO	6.41	4.69
CrO	5.47	4.69
FeO	5.31	4.26
CuO	3.74	3.77
GaO	5.24	
GeO	7.34	4.69
SrO	5.23	4.05
ZrO	8.21?	5.32
RuO	6.75	6.20
AgO	3.44	4.20
SnO	7.58	4.69
SbO	7.62	6.35
BaO	6.01	4.05
LaO	7.40	4.26
PtO	7.05	7.67
PbO	7.03	4.69
BeS	4.73	4.04
BS	5.99	4.76
CaS	6.12	4.84
PbS	7.93	5.92
RhC	6.38	6.02
IrC	7.72	7.74
PtC	7.54	7.74
BN	3.84	4.55

[a] The experimental values are from force constants and internuclear distances. See references at the end of Table 1. The calculated values are from z_A and z_B values obtained from Tables 1 and 11.

Table VIII. Experimental Values of z or $z_A z_B$ for Some Diatomic Molecules and Their Ions[a]

Molecule	z	Ion	z
H_2	0.71	H_2^+	0.63
N_2	2.57	N_2^+	2.48
O_2	2.13	O_2^+	2.25
Cl_2	2.36	Cl_2^+	2.52
C_2	2.15	C_2^-	2.22
	$z_A z_B$		$z_A z_B$
BeH	1.19	BeH$^+$	1.29
CH	1.53	CH$^+$	1.29
OH	1.62	OH$^+$	1.16
FH	1.62	FH$^+$	1.36
MgH	1.44	MgH$^+$	1.60
AlH	1.57	AlH$^+$	1.53
PH	2.08	PH$^+$	1.89
ClH	2.31	ClH$^+$	2.06
ZnH	1.38	ZnH$^+$	1.62
CdH	1.43	CdH$^+$	1.86
HgH	1.30	HgH$^+$	2.14
CO	5.96	CO$^+$	4.43
NO	5.26	NO$^+$	6.46
AsO	6.74	AsO$^+$	7.92

[a] Data for hydride ions from ref 18. Other data from references at end of Table I.

any case. Removal of an antibonding or a nonbonding electron should cause a larger increase in z.

In the effective number of bonding electrons view, removal of a bonding electron should cause a large drop in z, whereas removal of a nonbonding electron should have little effect. If an electron is removed from an antibonding orbital, z should increase. These predictions also follow from simple molecular orbital theory.

Table VIII gives experimental values of z, or of $z_A z_B$, for a number of molecular ions. The corresponding results for their neutral counterparts are also shown. In three cases, H_2, N_2,

and CO, a bonding electron is removed on forming the ion. The change in z or $z_A z_B$ is a compromise between the expectations of the shielding model and the bonding electron model. The magnitude decreases, but by rather small amounts. That is, the decrease in z is not 0.50, corresponding to a loss of one bonding electron between the two atoms.

In the molecules O_2, Cl_2, BeH, MgH, AlH, NO, and AsO, an antibonding electron is removed. The value of z, or $z_A z_B$, increases in all cases (except AlH), as predicted by both models. Again the increases are rather small. In the remaining hydride molecules an essentially nonbonding electron is removed. For the nonmetal hydrides the value of $z_A z_B$ decreases by small amounts. For the metallic hydrides the value of $z_A z_B$ increases by small amounts.

The decrease in $z_A z_B$ for the nonmetallic hydrides is not predicted by either the screening or bonding electron model. However, it has been pointed out above that the better model for these molecules is that due to Platt.[6] The force constant is given by $k = 4\pi\rho e$, where ρ is the electron density at the proton

position. In a positive ion ρ will be diminished and the empirical value of $z_A z_B$ will be less.[18] Obviously the Platt model cannot account for an increase in this parameter, and it has been shown that the model is poor for metallic hydride ions.[18]

Conclusion

Tables IV, VI, and VII contain data for elements whose z values are not given in Tables I or II. From the data, and by comparison to neighboring elements, z values can be estimated for Mn, Zn, Ga, Cd, In, Hg, and Tl. A periodic chart (Figure 1) of the elements can now be shown in which effective nuclear charges, z, are given for 63 of the elements. By interpolation, a number of z values for other elements can be estimated but are not shown in the chart.

Hopefully, the effective charges can be useful in several ways. For example, the vibrational frequencies of diatomic molecules such as Co_2, or even Fe_2, could be predicted. Frequencies for heteronuclear molecules can be predicted, if suitable corrections are made for ionic character and π bonding. Finally, the compressibilities of metals can be estimated, at least for cubic solids.

Since the effective charges are also equal to the number of bonding electrons for the atom, they should be related to bond energies. Indeed, a rough correlation with the heats of atomization of the metals is immediately obvious. However, there are individual variations which show that the relationship is not simple. At the very least, a size factor must also be considered.

The most important use of the z values lies in their possible application to the force constants for polyatomic molecules. A model in which each nucleus is represented by an effective positive charge leads to the central force field. At one time it was thought that such a force field was of limited value. However, more recent work shows that, properly used, the central force field is the same as the general valence force field.[19] For example, in a three-atom case, the three internuclear distances are not independent variables. Instead one must use two of these distances and the included angle.

The screened nucleus model allows all of the constants of the general valence force field to be evaluated quite readily. Unfortunately there is no theoretical reason to believe that a single effective charge for each nucleus will be valid for every set of displacement coordinates. It is quite likely that the bending mode will require a different value of z from stretching modes. Also only positive interaction constants can be calculated from the model, whereas it is known that in some cases such constants are negative.

In spite of these misgivings it seems worthwhile to try to use the screened nucleus model in polyatomic cases. Using an empirical approach, as in this work, the factors which determine z in various cases may become clear.

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A General Analysis of Noncovalent Intermolecular Interactions

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Abstract: We present ab initio calculations on a wide variety of intermolecular complexes, including "van der Waals" molecules, H-bonded complexes of varying strength, "charge-transfer" complexes, ionic associations, radical complexes, and three-body interactions. We use the Morokuma component analysis and electrostatic potentials in order to help us analyze the interaction energy and minimum energy structure of such complexes. We present a simple approach to use the electronic structure of the monomers that make up the complex, in order to predict the structure and interaction energy of the complex in the absence of detailed calculations or experiments.

Attempts to understand intermolecular interactions go back nearly as far as the theories of chemical bonding, the first postulate of the hydrogen bond coming from G. N. Lewis's lab around 1920.[1] Subsequent simple theoretical models by Pauling,[2] among others, showed that electrostatic models could qualitatively reproduce observed H-bond energies. In 1954,