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ATOMIC SHIELDING CONSTANTS

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Abstract

In analogy with the method of Zener for the atoms from Li to F, simple rules are set up giving approximate analytic atomic wave functions for all the atoms, in any stage of ionization. These are applied to x-ray levels, sizes of atoms and ions, diamagnetic susceptibility, etc. In connection with ferromagnetism it is shown that if this really depends on the existence of incomplete shells within the atoms, rather far apart in the crystal, then the metals most likely to show it would be Fe, Co, Ni, and alloys of Mn and Cu (Heusler alloys).

IT IS often extremely useful to have simple approximations to the wave functions and energy levels of atoms and ions. Zener[1] has derived such functions for the atoms up to F, fixing the values of his parameters by variation methods. In the present paper, the functions are tentatively extended to the other atoms. The shielding constants and other parameters are not fixed by variation methods, but adjusted merely to get agreement with empirical values of stripped atom and x-ray energy levels, sizes, etc., so that the values do not have the certainty of Zener's calculations. It is to be hoped that eventually a variation calculation can be made here too; but we may anticipate that the figures given in this paper will be substantially verified, and in the meantime, an approximate set of functions is much better than none. The principal set of shielding constants which now exists is that of Pauling,[2] and it is believed that the present set is simpler, more general, and more accurate. The density functions derived from the present shielding constants agree fairly well with those found by Hartree's method, in cases where that has been carried out.

THE WAVE FUNCTIONS

The nodes in the wave function are found by Zener to be unimportant, and a glance at Hartree's distribution, say for Rb^+, shows that they come much nearer the nucleus than for hydrogen wave functions, and are therefore less important. Consequently we neglect them entirely, taking as the radial part of the wave function of one electron simply

$$r^{n^*-1}e^{-((Z-s)/n^*r)},$$

the asymptotic form at large distances for a hydrogen-like wave function of quantum number n^* in the field of a nuclear charge $(Z-s)$. Here Z is sup-

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[1] C. Zener, Phys. Rev. **36**, 51 (1930); Guillemin and Zener, Zeits. f. Physik **61**, 199 (1930).

[2] Linus Pauling, Proc. Roy. Soc. **A114**, 181 (1927).

posed to be the actual charge on the nucleus, and s is a screening constant. We assign values of n^*, the effective quantum number, and $Z-s$, by simple rules, to the electrons in each shell in each atom or ion, and so have a complete set of one-electron wave functions. The method of combining such one-electron wave functions into functions for the whole atom has been described elsewhere.[3]

The values of n^* and $(Z-s)$ are given by the following rules:

(1) n^* is assigned by the following table, in terms of the real principal quantum number n:

for $n=1, 2, 3, 4, 5, 6$
$n^*=1, 2, 3, 3.7, 4.0, 4.2$

(2) For determining $Z-s$, the electrons are divided into the following groups, each having a different shielding constant: $1s$; $2s$, p; $3s$, p; $3d$; $4s$, p; $4d$; $4f$; $5s$, p; $5d$; etc. That is, the s and p of a given n are grouped together (as Zener has done), but the d and f are separated. The shells are considered to be arranged from inside out in the order named.

(3) The shielding constant s is formed, for any group of electrons, from the following contributions:

(a) Nothing from any shell outside the one considered.

(b) An amount 0.35 from each other electron in the group considered (except in the $1s$ group, where 0.30 is used instead).

(c) If the shell considered is an s, p shell, an amount 0.85 from each electron with total quantum number less by one, and an amount 1.00 from each electron still further in; but if the shell is a d or f, an amount 1.00 from every electron inside it.

As a first example, we take C, $Z=6$. Here we have two $1s$ electrons, four $2s$, p electrons. For effective nuclear charge, $Z-s$, we have

$1s$: $6-0.30=5.70$ (Zener has 5.6875)
$2s$, p: $6-3(0.35)-2(0.85)=3.25$ (Zener has $1.59\times 2=3.18$)

As a second example, we take Fe, $Z=26$. There are two $(1s)$'s, eight $(2s, p)$, eight $(3s, p)$, six $(4d)$, two $(4s)$. The effective nuclear charges are

$1s$: $26-0.30=25.70$
$2s$, p: $26-7(0.35)-2(0.85)=21.85$
$3s$, p: $26-7(0.35)-8(0.85)-2(1.00)=14.75$
$3d$: $26-5(0.35)-18(1.00)=6.25$
$4s$: $26-1(0.35)-14(0.85)-10(1.00)=3.75$.

Finally we take Fe, lacking a K electron, so that there is only one $(1s)$, but otherwise it is as before. Then

$1s$: 26.00
$2s$, p: $26-7(0.35)-1(0.85)=22.70$
$3s$, p: $26-7(0.35)-8(0.85)-1(1.00)=15.75$
$3d$: $26-5(0.35)-17(1.00)=7.25$
$4s$: $26-1(0.35)-14(0.85)-9(1.00)=4.75$.

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[3] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

THE ENERGY VALUES

The total energy of an atom or ion—the negative of the energy required to remove all electrons from the nucleus to an infinite distance—is found by Zener to be accurately given by the sum of the quantities $-((Z-s)/n^*)^2$ for all electrons of the atom (This is the significance of his connection of the shielding constant with the empirical "mean effective charge"). This is very reasonable. If we take as an atomic wave function a product of one-electron wave functions of our type, for each electron, then allow the energy operator to act on it, the result will consist of several parts, as one can readily verify: (1) the sum of $-((Z-s)/n^*)^2$ for each electron, times the function, coming from the second derivative in the Laplacian operator; (2) terms in $1/r$, and higher powers, times the function, coming from the Laplacian; (3) terms in $1/r$, times the function, coming from the potential energy. For the correct wave function, (2) and (3) will cancel each other, leaving just terms (1), a constant times the function, so that Schrödinger's equation will be satisfied. It seems very reasonable that, in a wave function which is a good approximation, this will be nearly the case too. But this leaves as the energy just the sum which we have mentioned. We therefore take that as giving the energy of an atom or ion, saving ourselves by this simple rule from the necessity of computing the energy by the usual method of integrating H. This of course gives the energy in terms of the Rydberg energy.

As a first example, we take the energy required to remove all the L electrons from C. We have

normal atom: $-2(5.70)^2-4(3.25/2)^2=-64.98-10.56=-75.54$
atom with L electrons stripped off: $-2(5.70)^2=-64.98$
Difference = energy of removal $=10.56=10.56\times 13.56$ volts
$=143.2$ volts (correct, 145.2; Zener has 142.7)

As a second example, we take the energy required to remove any electron from the Fe atom, We have

normal atom: $-2(25.70)^2-8(21.85/2)^2-8(14.75/3)^2-6(6.25/3)^2-2(3.75/3.7)^2$ $=-2497.2$

atom lacking one $1s$ electron: $-1(26.00)^2-8(22.70/2)^2-8(15.75/3)^2$ $-6(7.25/3)^2-2(4.75/3.7)^2=-1964.6$. Difference $=532.6$; observed K absorption limit $=524.0$

atom lacking one $2s$, p electron: $-2(25.70)^2-7(22.20/2)^2-8(15.60/3)^2$ $-6(7.25/3)^2-2(4.75/3.7)^2=-2437.7$. Difference $=59.4$; observed L absorption limits, $L_{11}=61.9$, $L_{21}=53.4$, $L_{22}=52.4$

atom lacking one $3s$, p electron: -2491.1; difference $=6.1$; observed M_{11} $=7.07$; M_{21}, $M_{22}=4.2$

atom lacking one $3d$ electron: 2496.4; difference $=0.8$; observed energy of removal of $3d$ electron from Fe atom, by Moseley law in optical spectra, 0.8

atom lacking one $4s$ electron: 2496.3; difference $=0.9$; observed energy of removal of $4s$ electron $=0.58$

It is interesting to notice in this example how the so-called "outer shielding" of the x-ray terms comes about, by the decrease of the shielding constants of the outer electrons when an inner electron is removed. It is also interesting to see how this rearrangement of shielding constants brings it about that the 3*d* electrons, although much further in than the 4*s*, still require about the same energy for their removal.

As a final example, we take the ionization potential of the alkalies:

normal Li: energy of K shell $-(1.30/2)^2=$ energy of K shell -0.423
ionized Li: energy of K shell; difference $=0.423$; observed ionization potential $=0.397$.

We observe that we can get these ionization potentials directly, without considering the inner shells. Thus we have for the ionization potentials:

Na $(2.20/3\ )^2=0.537$, observed $=0.378$
K $(2.20/3.7)^2=0.354$, observed $=0.319$
Rb $(2.20/4.0)^2=0.302$, observed $=0.307$
Cs $(2.20/4.2)^2=0.274$, observed $=0.287$

The examples which we have worked out are a fair sample of the energies obtained in general from the scheme; one sees that they are qualitatively accurate, though by no means to be trusted in detail. The principal criterion used in setting up the rules for the shielding constants has been to make the energy check fairly well with experiment.

SIZES OF ATOMS AND IONS

The maximum of the radial charge density for one of our shells comes, as we immediately find by differentiation, at $(n^*)^2/(Z-s)$. Thus our shielding constants permit us to compute the sizes of atoms and ions. For example, the radius, as defined in this way, of the outer, 4*s* shell of Fe is $(3.7)^2/3.75=3.65=1.95$ Angstroms. The radii of the outer shells, defined in this way, can be brought into interesting connection with the internuclear distances in valence compounds and in metals, in which the substances exist in the atomic state. For binding, we should expect that the electrons forming the bond would wish to have the maximum possible overlapping, which would come if the internuclear distance were the sum of the radii so defined, so that the maxima of density lay together. As a matter of fact, this is closely the case, when the valence electrons are *p* electrons; but when both valences are *s* electrons, the distances are smaller, about 2/3 of this. In any case, the correlation is quite good, and should be useful in predicting approximate internuclear distances where they are not known. We give, in Table I, the atomic radii so derived, and in Table II a number of internuclear distances, as observed in band spectra and crystals, together with the sum of the theoretical radii for comparison, and the ratio of the two. These ratios are, as we stated, about 1 when one or both valences are *p* electrons, but about 2/3 when both are *s* electrons. In a few cases, such as the hydrogen halides, where one might suppose the substances to be ionic rather than valence compounds, the excellent agreement with our rule gives us confidence that the valence bond essentially describes the situation.

TABLE I. *Atomic radii (Angstroms).*

(These radii are the radii of the values for maximum radial density in the charge distributions of the outer shells of the neutral atoms, computed from the effective quantum numbers and effective nuclear charges by the formula $(n^*)^2/(Z-s)$.

H	0.53								
Li	1.63	Na	2.17	K	3.32	Rb	3.86	Cs	4.25
Be	1.09	Mg	1.68	Ca	2.56	Sr	3.00	Ba	3.30
B	.82	Al	1.37	Sc	2.43	Y	2.84	La	3.12
C	.65	Si	1.15	Ti	2.32	Zr	2.71	—	—
N	.55	P	1.00	V	2.22	Nb	2.60	Ta	2.86
O	.47	S	.88	Cr	2.12	Mo	2.48	W	2.73
F	.41	Cl	.78	Mn	2.02		2.36		2.60
				Fe	1.95	Ru	2.28	Os	2.51
				Co	1.87	Rh	2.18	Ir	2.40
				Ni	1.80	Pd	2.10	Pt	2.31
				Cu	1.73	Ag	2.02	Au	2.22
				Zn	1.67	Cd	1.95	Hg	2.15
				Ga	1.46	In	1.71	Tl	1.88
				Ge	1.29	Sn	1.51	Pb	1.66
				As	1.16	Sb	1.35	Bi	1.48
				Se	1.05	Te	1.22		
				Br	.96	I	1.12		

TABLE II. *Internuclear distances in valence compounds (Angstroms).*

(Observed internuclear distances, observed from band spectra or crystal structure. Band spectrum data are taken from Report of National Research Council on Molecular Spectra in Gases, pp. 222–232, except for the following: BO, Jenkins, Proc. Nat. Acad. Sci. **13,** 496, (1927); NO, Guillery, Zeits. f. Physik **42,** 121 (1927), recalculated by Birge; OH, Report as above, but corrected by Birge; H_2O, Debye, Polare Molekeln, Hirzel, 1929, p. 85; HI, Czerny, Zeits. f. Physik **44,** 236 (1927), calculated by Birge; H_2, Birge, Proc. Nat. Acad. Sci. **14,** 12 (1928); Na_2, Loomis, Phys. Rev. **32,** 223 (1928); MgH, Watson and Rudnick, Phys. Rev. **29,** 413 (1927). Data on crystal structure are from Landolt-Börnstein, Tables, 5th Ed., Ergänzungsband.

The columns are as follows: (1) substances; (2) observed internuclear distances; (3) sum of atomic radii for outer shell, as given in Table I; (4) ratio of observed distance to sum of radii; (5) sum of atomic radii for inner incompleted shell, in substances which might be ferromagnetic; (6) ratio of observed distance to sum of radii of inner shells. Substances are divided into four classes: (a), molecules with one or both valences p electrons; (b) molecules with both valences s electrons; (c) crystals with one or both valences p electrons; (d) crystals with both valences s electrons.)

Part (a): Molecules with one or both valences p electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc
BO	1.21	1.29	0.94
CH	1.13	1.18	.96
CN	1.17	1.20	.98
CO	1.15	1.12	1.02
NO	1.15	1.02	1.12
N_2	1.21	1.10	1.10
O_2	1.20	.94	1.28
OH	.98	1.00	.98
H_2O	1.07	1.00	1.07
AlH	1.66	1.90	.87
AlO	1.62	1.84	.88
SiN	1.56	1.70	.92
I_2	2.66	2.24	1.19
HF	.92	.94	.98
HCl	1.28	1.31	.98
HBr	1.42	1.49	.95
HI	1.62	1.65	.98

Part (b): Molecules with both valences *s* electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc
H_2	.76	1.06	.71
Na_2	3.08	4.34	.71
CuH	1.47	2.26	.65
AgH	1.63	2.55	.64
AuH	1.54	2.75	.56
MgH	1.74	2.21	.79
CaH	2.01	3.09	.65
ZnH	1.61	2.20	.73
CdH	1.78	2.48	.72
HgH	1.76	2.68	.66

Part (c): Crystals with one or both valences *p* electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc
C (diamond)	1.54	1.30	1.18
(graphite)	1.43	1.30	1.10
(ethane C—C)	1.55	1.30	1.19
C—N (KCN)	1.15	1.20	.96
Al	2.86	2.74	1.04
Si	2.35	2.30	1.02
Ge	2.44	2.58	.95
As	2.51	2.32	1.08
Se	2.35	2.10	1.12
In	3.24	3.42	.95
Sn (diamond lattice)	2.80	3.02	.93
Sn (white)	3.02	3.02	1.00
Sb	2.87	2.70	1.06
Te	2.87	2.44	1.18
Tl	3.36	3.76	.89
Pb	3.48	3.32	1.05
Bi	3.10	2.96	1.04

Part (d): Crystals with both valences *s* electrons.

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc	(5) Sum of radii inner shell	(6) Ratio obs/calc inner shell
Li	3.03	3.26	.93		
Be	2.23	2.18	1.02		
Na	3.72	4.34	.86		
Mg	3.22	3.36	.96		
K	4.50	6.64	.68		
Ca	4.97	5.12	.78		
Ti	2.93	4.64	.63	2.62	1.12
V	2.63	4.44	.59	2.22	1.18
Cr	2.51	4.24	.59	1.93	1.30
Mn	2.52	4.04	.62	1.71	1.47
Fe	2.50	3.90	.64	1.53	1.63
Co	2.51	3.74	.67	1.38	1.82
Ni	2.50	3.60	.69	1.27	1.97
Cu	2.54	3.46	.73		
Zn	2.67	3.34	.80		
Zr	3.18	5.43	.59	4.00	.79
Mo	2.72	4.96	.55	2.94	.92
Ru	2.64	4.56	.58	2.33	1.13
Rh	2.70	4.36	.62	2.11	1.28
Pd	2.73	4.20	.65	1.93	1.41

Part (d): Crystals with both valences *s* electrons—*Continued.*

(1) Substance	(2) Distance observed	(3) Sum of radii	(4) Ratio obs/calc	(5) Sum of radii inner shell	(6) Ratio obs/calc inner shell
Ag	2.88	4.04	.71		
Cd	2.96	3.90	.76		
Ta	2.83	5.72	.50	3.95	.72
W	2.73	5.66	.48	3.44	.79
Os	2.71	5.02	.54	2.72	1.02
Ir	2.70	4.80	.56	2.47	1.09
Pt	2.77	4.62	.60	2.25	1.23
Au	2.87	4.44	.65		

In studying valence, we are interested in the size of the outer shell, but for ferromagnetism the essential, as the writer has shown in an earlier paper,[4] is the existence of an inner shell in process of formation, small enough so that the distance of separation is relatively great compared with the size of the shell. To see what metals should show ferromagnetism, if this idea is correct, we also give in Table II the radii for the *d* shells in process of formation in the transition groups, and the ratio of internuclear distance to twice this radius. This ratio is greater for Fe, Co, and Ni than for any other element, so that these would be most likely to be ferromagnetic. We might suppose that as two such shells were moved apart, the interaction was nonferromagnetic (the terms of lowest multiplicity lying lowest) out to about 1.55 times the sum of the radii; there the interaction would change sign, passing through a critical region (suggesting the fact that Mn sometimes shows magnetic properties, usually not). The first element beyond the critical region, Fe, would show the greatest ferromagnetism. As the internuclear distance still further increased, the exponential dropping off of the wave function would make the interaction less, resulting in weaker effects in Co and Ni. These conclusions are made much more reasonable by considering the Heüsler alloys. Here Cu takes the place of Mn in an alloy with Al or other substance, and the alloy is almost as ferromagnetic as Fe. Now if Cu can replace Mn, it is presumably in a form with two $4s$ electrons, nine $3d$'s so that it has an open shell of *d* electrons, which is even smaller than for Ni (radius = 1.17/2A). This very small radius, added to the large radius of Mn, gives a sum of 1.44A, and a ratio intermediate between Fe and Co, suggesting a strong ferromagnetism, although Mn by itself is too big, Cu too small (and in ordinary Cu undoubtedly the $3d$ shell is closed anyway) to show ferromagnetic properties.

In ionic compounds, the atoms exist as ions, which have closed shells; and the interionic forces are repulsions (except for the electrostatic attractions), and account for the hardness and impenetrability of the structures. These repulsions become large, as has often been shown, as soon as the outer shells begin to overlap, and the internuclear distances in ionic crystals should be the sums of radii representing, not the radius of maximum density in the shell, but a considerably larger radius at which the charge just begins to become

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[4] J. C. Slater, Phys. Rev. **35**, 509 (1930).

appreciable. It appears that the appropriate radius is roughly one at which the radial density becomes 10 percent of its maximum value. By solving the problem numerically, we find that for the density function we have used, this radius is a numerical factor times the radius of maximum density, this factor being 3.38 for $n^*=1$, 2.49 for $n^*=2$, 2.25 for $n^*=3$, 2.01 for $n^*=3.7$, 1.96 for $n^*=4.0$. Thus, finding the radius of maximum density, now for the ion rather than for the atom, and using these factors to get radii of 10 percent density, we get the ionic radii given in Table III. They should be compared with the ionic radii of Wasastjerna, which are to be added to give grating spaces, and which are also tabulated. It is seen that the agreement in general is decidedly good. This renders it highly probable that the atoms really exist in these compounds as ions, as has been supposed. Computed values are included for the inert gases, and these should be the radii of these gases, as derived in the kinetic theory. The latter of course vary over a considerable range, but our values seem to lie well within this range in each case. For example, for He, Jeans in his "Dynamical Theory of Gases" gives values from 0.99A to 1.10A, as determined by various methods: our value is 1.05A.

TABLE III. *Ionic radii (Angstroms).*

(Observed radii as given by Wasastjerna; see for instance W. L. Bragg, Phil. Mag. **2**, 258 (1926); the sum of these radii gives the interionic distance in ionic crystals. Calculated values are for radius where density is 10% of its maximum value. This equals constant times $(n^*)^2/(Z-s)$, where the constant equals 3.38 for $n^*=1$, 2.49 for $n^*=2$, 2.25 for $n^*=3$, 2.01 for $n^*=3.7$, 1.96 for $n^*=4.0$)

Ion	Observed	Calculated	Ion	Observed	Calculated
H^-		2.57	$Se^{=}$		2.34
He		1.05	Br^-	1.92	2.02
Li^+	0.76	.67	Kr		1.77
Be^{++}	(.3)	.49	Rb^+	1.50	1.58
			Sr^{++}	1.20	1.43
$O^{=}$	1.32	1.37			
F^-	1.33	1.09	$Te^{=}$		2.66
Ne		.91	I^-	2.19	2.30
Na^+	1.01	.77	Xe		2.02
Mg^{++}	.75	.67	Cs^+	1.75	1.80
Al^{+++}	(.55)	.60	Ba^{++}	1.40	1.62
Si^{4+}	(.3)	.54			
$S^{=}$	1.69	2.16			
Cl^-	1.72	1.79			
A		1.52			
K^+	1.30	1.33			
Ca^{++}	1.02	1.17			

We can get a valuable check on the size of atoms by using the diamagnetic susceptibility, which is proportional to the mean value of Σr^2. From our wave functions, by integration we find this quantity for one of the electrons to be $(n^*)^2\,(n^*+1/2)\,(n^*+1)/(Z-s)^2$. For the inert gases, we have the following values:

	computed	observed
He	2.07	2.34
Ne	7.08	8.31
A	23.37	22.6