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WADD TR 61-84

PART II

AD0426135

EMPIRICAL METHODS FOR CALCULATION OF
BOND ENERGIES

TECHNICAL REPORT NO. WADD TR 61-84, PART II
September 1963

AF Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7342, Task No. 734203

(Prepared under Contract No. AF33(616)-6900
by the University of Cincinnati, Cincinnati, Ohio;
H. H. Jaffe, Author.)

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FOREWORD

This report was prepared by the University of Cincinnati, Cincinnati, Ohio, under USAF Contract No. AF33(616)-6900. This contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules". The work was administered under the direction of the Nonmetallic Materials Laboratory, Air Force Materials Laboratory, Research and Technology Division, with Dr. I. J. Goldfarb as project engineer.

This report covers work conducted from January 1961 to June 1962.

ABSTRACT

The attempted computation of bond energies using the Mulliken magic formula was expanded in several directions. Workable approximations to the Y_{ke} term were thought. The dependence of electronegativity on valence state was needed, and this was worked out in great detail. In the process a new and expanded definition of electronegativity was proposed. This definition was tried out in the interpretation of NQR spectra of a series of halogen compounds.

This technical documentary report has been reviewed and is approved.

William F. Gibbs

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I. INTRODUCTION

The present work, aimed at developing semi-empirical methods for estimating bond energies, is a continuation of work initiated by Jaffe' and Doak (3). This work was based on an approximate application of Mulliken's "Magic Formula" (6) to estimate carbon-metal bond energies in symmetrical metal alkyls.

The "Magic Formula" is an empirical equation, based on a combination of the essential features of both molecular orbital and valence bond theory, expressing the atomization energy of a compound in terms of a series of terms which can either be estimated theoretically or semiempirically. It has the form

$$D_0 = \sum X_{ij} - \frac{1}{2} \sum Y_{kl} - \frac{1}{2} \sum K_{mn} - PE - RE$$

where the X_{ij} term is the energy resulting from the interaction of bonding electrons and is assumed to be expressed as

$$X_{ij} = A S_{ij} I_{ij} / (1 + S_{ij})$$

A is an empirical coefficient, adjusted by Mulliken from work on some selected compounds of first row elements, and has a value of 1.16. The I_{ij} are the mean valence state ionization potentials of atoms i and j, and the S_{ij} are overlap integrals.

The Y_{kl} and K_{mn} are electron repulsion energies, which have been neglected in the early work, but the importance of which has been further investigated in the present work.

The promotion energy, PE, is defined as the energy required to promote the atoms to their respective valence states. The resonance energy, RE, is intended to account for all resonance terms of the valence bond theory, not included in the other terms.

In the original work (3), a long series of approximations were made. Y_{kl} and K_{mn} terms were neglected. In the evaluation of X_{ij} , normal ionization potentials were used instead of valence state ionization potentials. Only a single hybridization was considered and promotion energies were neglected.

Manuscript released by author March 1962 for publication as an ASD Technical Documentary Report.

Resonance energies were assumed to involve only ionic resonance energies, and were evaluated from electronegativities of the atoms.

Goldfarb (1) has started an investigation aimed at a removal of some of these drastic assumptions. The present work is intended to continue this process. The most important step which needs to be taken is the calculation of the required promotion energies and valence state ionization potentials for a variety of possible hybrid states of the atoms concerned. Attempts at estimation of the Y_{kl} and K_{mn} have been undertaken, and the electronegativities have been investigated thoroughly.

The calculation of the needed valence state ionization potentials and promotion energies is based on calculation of the energies of valence states. Two methods are available for such calculations. One, due to Mulliken (7), is based on Slater's treatment of the complex atom (8). It involves expression of the valence state energy in terms of certain integrals over the radial atomic wave functions $F_{1,1}^k$ and $G_{1,1}^k$, the so-called Slater parameters. The other, proposed by Moffitt (4), expands the energy of valence states directly in terms of energies of spectroscopic (stationary) states of the atom (5). If the Slater treatment of the complex atom involved no assumptions, and hence, no approximations, the two methods would be equivalent. Unfortunately, however, considerable approximations are involved in the Slater method; the worst of these are probably the neglect of configuration interaction and of spin-orbit coupling, and the assumption of perfect Russell-Saunders coupling. We believe that the Mulliken method, by averaging over more states tends to minimize these approximations. Also, this method appears to lend itself more readily to machine calculation, and hence we have chosen this method. Consequently, Slater parameters were needed for all elements of interest,

II. WORK PERFORMED

Goldfarb (1) has started an investigation aimed at the removal of some of these drastic assumptions. The present work was aimed at continuing this process. Zung (9) and Hinze (2) have calculated the required promotion energies and valence state ionization potentials for a wide variety of possible hybrid states of the elements of interest. In order to provide better estimates of ionic resonance energies, these data were used to calculate electronegativities as a function of valence states. The results of these calculations were published in three papers, appended hereto as Appendixes I, III, and IV. The Slater-Condon parameters also required as a step in these calculations are being published in a paper appended as Appendix V.

In connection with these electronegativity calculations, the entire concept was critically reexamined. This process led to a redefinition of electronegativity in a generalized manner in such a way that the Mulliken definition is a special case. This work has been published, and a copy of this paper is joined hereto as Appendix II.

In connection with the development of new and modified orbital electronegativity concepts, it appeared extremely desirable to test these concepts in connection with some basic chemical property generally believed closely related to this quantity. This was achieved by relating experimental nuclear quadrupole coupling constants with electronegativities. The results of these efforts are detailed in a series of papers which are appended as Appendixes VI-IX.

Further, it was attempted to calculate the Y_{kl} and K_{mn} terms of the Mulliken "Magic Formula". First, the attempt to use the Mulliken approximation to Y_{kl} in terms of the overlap integral S_{kl} failed. It was found that S for the 3d, 4s and 4p orbitals of transition metals and the sp^3 hybrid orbital of carbon were surprisingly small. In particular, it was found that the 2p orbital of carbon overlapped negligibly with the metal orbitals. This was rationalized on the basis of the realization that the entire p orbital of carbon, i.e. both positive and negative lobes, was almost completely buried in a single lobe of the metal orbital, and consequently almost complete cancellation occurred. This type of problem cannot arise with the s orbitals, to which the Mulliken approximation had been predominantly applied previously, but appears to make this approximation completely useless for higher orbitals, particularly when these are of considerably different size.

Next, in order to avoid the complication of cancellation on integration, an attempt was made to use a new integral, the coincidence integral,

$$C = \int Y_1 Y_2 dt, \text{ or}$$

$$C^1 = \int Y_1^2 Y_2^2 dt$$

where C^2 or C^1 would have been used to replace S^2 in the Mulliken approximation. Both of these formulations turned out quite difficult to evaluate numerically. Finally, it was decided to attempt to evaluate the Coulomb repulsion integral, and to use it to take the place of both the Y_{kl} and K_{mn} terms. A program for these integrals was written, and considerable numerical calculations were performed.

Final analysis of the data obtained, however, indicates that this approach also does not help in reducing the divergences between experimental stabilities and calculated energies. In particular, the contribution of Coulomb repulsion integral to the bond strength (a negative term) rises steeply in going from left to right through the periodic system, exactly contrary to the observed trends. The explanation of this phenomenon seems to lie in the circumstances that a major portion of the Coulomb repulsions is already included in other terms of the magic formula.

Another attempt was made to evaluate a measure of the bond energy of a complete series of carbon metal bonds across the periodic table. Using the alkyl derivatives of Zn, Ga, and As, it was attempted to determine the empirical proportionality parameters of the "Magic Formula". Ignoring the Y_{kl} and K_{mn} terms, for which no workable approximation has been found to date, no single set of empirical parameters could be found which permitted the expression of the desired bond energies in terms of the "Magic Formula".

III. DISCUSSION AND CONCLUSIONS

A. Bond Energies

No workable approximation to the Y_{kl} and K_{mn} terms in Mulliken's "Magic Formula" could be developed. No choices of the empirical parameters of the "Magic Formula" permitted a satisfactory expression of bond energies. The qualitative differences between transition metals and Group A metal carbon bonds, persisted in the data obtained for transition metals in their lowest and probably most logical valence or hybridization state. However, "higher" states of these metals gave apparent bond strengths larger than would be in accord with the known chemistry of these compounds.

From these results it appears necessary to conclude that the Mulliken "Magic Formula" is probably incapable of providing a theoretical estimate of bond energies in large compounds of heavy elements. This find is another example of the commonly encountered observation in theoretical chemistry that an initial very crude approximation loses in precision when refined. In the light of these observations it is suggested that further work along these lines be abandoned.

B. Electronegativities

In contrast to the negative results of this work, the work on electronegativities, which was stimulated by the need for these values in calculation of ionic resonance energies, has been highly productive.

Electronegativities for all elements of the A Groups of the periodic system, for the elements of the first transition series, and for certain positive ions have become available, many of these for the first time. All these values are, for the first time, available as a function of hybridization of the elements. The intermediate data and methods developed permit ready calculation of any additional values.

In addition, the redefinition of the electronegativity concept has opened up a completely new field of investigation. The usefulness of this concept has been demonstrated in the correlation of Taft ρ^* - values and in the applications to NQR frequencies. Further applications are planned.

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APPENDIX I

Electronegativity. I.

Orbital Electronegativity of Neutral Atoms

By Jurgen Hinze and H. H. Jaffe

Electronegativity is discussed on the basis of Mulliken's definition ($\chi = E_v + I_v$), which leads to the conclusion, that it is not a property of atoms in their ground state, but of atoms in the same conditions in which they are found in molecules, the valence state. Valence state promotion energies are calculated and reported for a large variety of states of the atoms and ions of the first and second period. Combining these promotion energies with ionization potentials and electron affinities yields the electronegativities of a number of valence states. It is found that electronegativity can be defined in this way only for bonding orbitals, and the term "orbital electronegativity" is suggested for the values listed. The calculated orbital electronegativities for σ orbitals are found to be higher in every case than for π orbitals, and to be linearly related to the amount of s character in the hybrid orbitals. As expected, the electronegativity increases with increasing s character of the orbital considered.

Electronegativity is a measure of the power of a chemically bonded atom to attract electrons to itself. This concept, first introduced by Pauling, (22) was rapidly accepted and many applications have been found in all fields of chemistry. Pauling set up a scale of electronegativities of the elements, by comparing the energy of the heteronuclear bond A-B with the average, arithmetic (21) or geometric, (23) of the homonuclear bond energies of the molecules A-A and B-B. With this method, no absolute values can be obtained, and because of the inherent uncertainties in thermochemical data this relative scale is somewhat indefinite. Despite these inadequacies, a wide variety of chemical phenomena have been reasonably explained by use of electronegativities.

The degree of electron transfer in the bond A-B toward the negative atom may be regarded as good measure of electronegativity difference. Unfortunately, such electron transfer is not directly observable and calculations of electron distribution for any molecule is an involved problem in itself, even for simple molecules, and not a suitable method to use as a base for an electronegativity scale.

Since such exact results are not available, several alternate scales of electronegativity have been proposed, based on various observable properties of molecules which are related to the electron distribution. Such properties are dipole moments, (15) force constants (9) and nuclear quadrupole resonance frequencies (10). The accomplishments in this field have been carefully reviewed by Pritchard and Skinner (25).

The best theoretical definition of electronegativity is given by Mulliken, (18) based on the concept that the energy expended in going from the covalent molecule A-B to the ionic states $A - B^-$ and A^-B is equal if A and B have the same electronegativity. Thence, he concludes (19) that the electronegativity of A is proportional to

$$\chi^A = I_V^A + E_V^A \quad (1)$$

where I_V^A and E_V^A are the appropriate valence state ionization potential and electron affinity, respectively. Electronegativities obtained from equation 1 are, to a good approximation, proportional to Pauling's values. (28)

Pauling (22) defined electronegativity as an atomic property and believes (23) that it is virtually constant, even for different oxidation states of any one element. Thus, he quotes electronegativities of iron as, 1.8 (Fe^{2+}) or 1.9 (Fe^{3+}); of copper as 1.9 (Cu^+) or 2.0 (Cu^{2+}); and of tin as, 1.8 (Sn^{2+}) or 1.9 (Sn^{4+}). (11) This conclusion seems somewhat surprising on the basis of the Mulliken definition, since one hardly expects ionization potential and electron affinity, or even their sum, to be the same for different oxidation states, and, hence, demands closer examination, particularly because differences of electronegativities have been noted by many authors.

Belluge and Daudel (1) and Sanderson (27) have discussed electronegativities for different oxidation states, but their approaches were hampered by lack of data. The distinct but related problem of the dependence of electronegativities on valence states of neutral atoms has been considered by Walsh, (32) who concluded that the electronegativity of carbon increases in the order tetrahedral < trigonal < diagonal. Similarly, Wilmhurst (34) inferred from n.q.r. frequencies that the electronegativity of halogens increases with increasing s character in its bonding orbital.

This concept has been generalized by Bent (2) and needs careful examination, as already pointed out by Pritchard and Skinner (25); this need has become even more urgent in view of the renewed interest in electronegativities. (34,33) A start in this direction has already been made by Mulliken (18) and Skinner, (28) but the range of the valence states considered was insufficient to permit recognition of over-all trends.

Theoretical Background - Since the electronegativity is a property of atoms in a molecule, the ionization potentials and electron affinities in equation 1 are not the values of the atoms in their ground states but of the same condition in which the atoms are in a molecule. The "atom in molecule" was defined by Van Vleck (31) as valence state. It is not a stationary state nor even a non-stationary state but a statistical average of stationary stages (35) chosen so as to have as nearly as possible the same interaction of the electrons of the atom with one another, as they have when the atom is part of a molecule. The valence state can be considered as formed from a molecule by removing from one atom all the other atoms with their electrons in an adiabatic manner, i.e. without allowing any electronic rearrangement. This state has been discussed in many places in the literature (18), (12), (6) and needs no further explanation.

Two useful methods have been suggested for the calculation of valence state energies, one by Moffitt, (16) extended by Companion, (4) and the other by Van Vleck (31) and Mulliken. (18) Moffitt expresses the valence state energy as an appropriate linear combination of spectroscopic state energies. Mulliken's method is based on Slater's (30) treatment of the many electron atom, in which the energy W of any spectroscopic state is given by

$$W = \sum_i I_i + \sum_{i>j} \sum_k (a_{ij}^k F_{ij}^k - \delta_{ij} b_{ij}^k G_{ij}^k) \quad (2)$$

For the energy of a valence state, use of equation 2 is quite analogous to its more general application for spectroscopic states. In both cases the same integrals over the radial part of the wave function, I , F^k , and G^k , arise, while the a 's and b 's are easily evaluated and δ_{ij} the Kronecker δ is 0 when the spins of i and j are unequal and 1 when they are equal. Since the valence state is an average of these two alternatives, δ_{ij} is $\frac{1}{2}$. The two methods (Moffitt and Mulliken) are identical, provided just those spectroscopic states used in the Moffitt method are employed to evaluate the F 's and G 's in the Mulliken expression.

The Mulliken method was chosen for all our calculations for a number of reasons. (1) It lends itself much better to routine computation. (2) If one of the spectroscopic states needed to express the valence state energy is not observed, Moffitt's method fails. (3) Configuration interaction is ignored in both methods; however, use of the largest possible number of states in the determination of the F's and G's is most likely to minimize the effect of configuration interaction. (29) (4) Although the Moffitt method is reasonably straightforward for some simple valence states, it becomes very complex when hybrid orbitals are involved.

For the calculation of valence state ionization potentials I_v and valence state electron affinities E_v , we require the corresponding values for the atomic ground states, I_g and E_g , respectively. The ground state ionization potentials I_g , usually obtained by extrapolation from spectral data, are listed by Moore (17) (see Table I) and may be considered to be accurately known. Unfortunately, the ground states electron affinities, E_g , are not as readily obtainable, (24) The best values were chosen by Edlen, (8) and Cubicciotti (7) (see Table I). These electron affinities probably represent the most important source of inaccuracy in our calculations (≈ 0.3 eV.). Such absolute errors, however, do not affect the valence state dependence of the calculated electronegativities.

The valence state ionization potentials and electron affinities are obtained by combining the valence state promotion energies of the atom, P_0 , and of the positive and negative ion P^+ and P^- , respectively, with the ground state potentials

$$I_v = I_g + P^- - P_0$$

$$E_v = E_g + P_0 - P^-$$

Since I_v is the energy necessary to remove an electron from the valence state, and E_v the energy released by addition of an electron to this state while the remaining electrons are not permitted to rearrange, the following transitions must be considered, using carbon as an example (36)

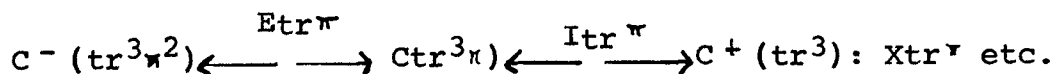
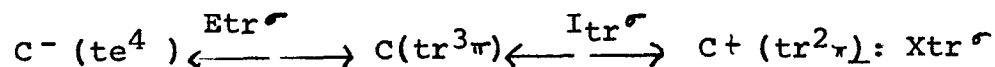
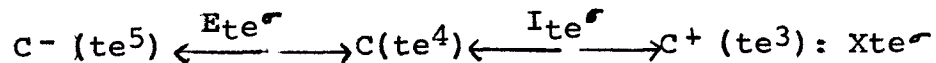


TABLE I

GROUND STATE IONIZATION POTENTIALS I_g AND ELECTRON
AFFINITIES E_g (IN eV.)

	E_g	Ref.	I_g
H	.747	28	13.595
Li	.82	28	5.390
Be	- .19	28	9.320
B	.33	28	8.296
C	1.12	29	11.256 ^a
N	.05	28	14.535 ^a
O	1.465	29	13.614
F	3.48	30	17.418
Ne	- .57	28	21.559
Na	.47	28	5.138
Mg	- .32	28	7.644
Al	.52	28	5.984
Si	1.46	28	8.149
P	.77	28	10.977
S	2.07	29	10.357
Cl	3.69	30	12.974 ^a

^a Private communication from Dr. Ch. E. Moore, National Bureau of Standards

All combinations needed are shown in Figure 1. The possibilities are considerably more varied and complex for many other elements, such as nitrogen, as shown in Figure 2.

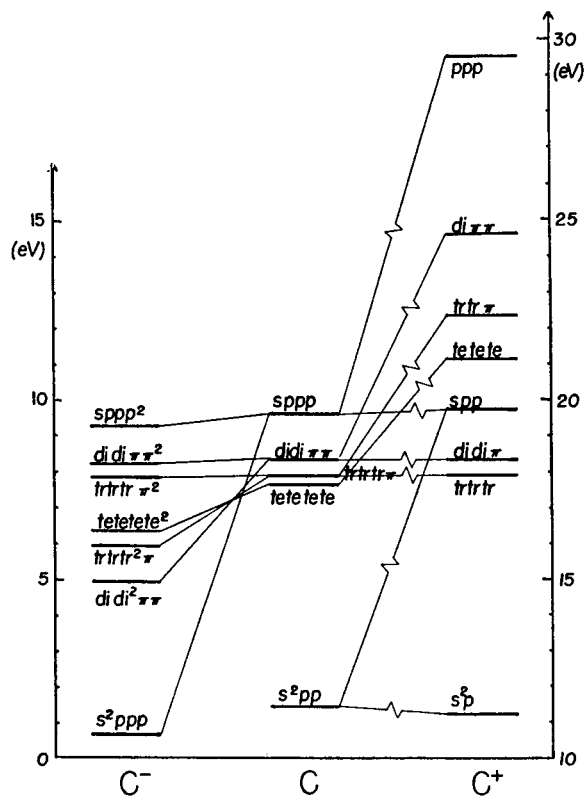


Fig. 1.—Valence state term system of C, C⁻ and C⁺ with possible connections.

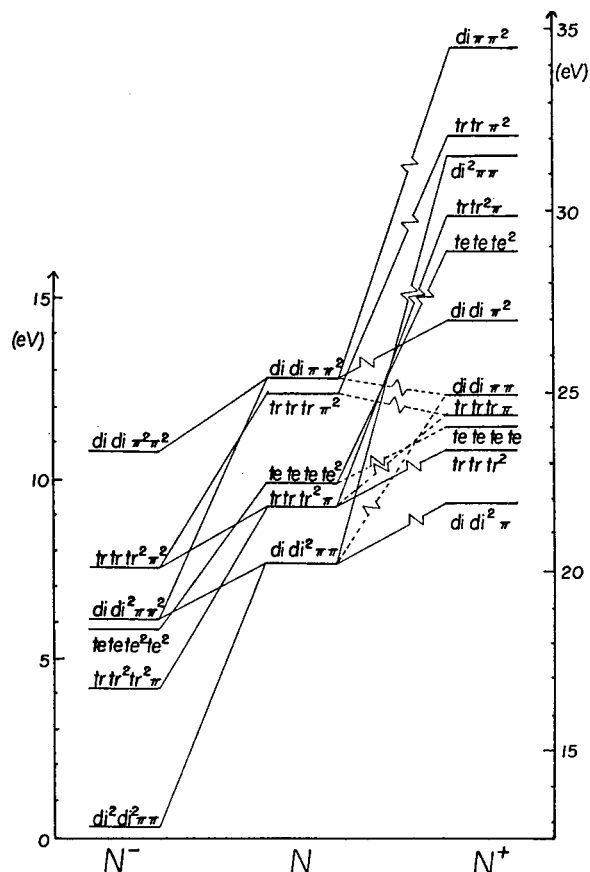


Fig. 2.—Valence state term system of N, N⁻ and N⁺ with possible connections. Ionization of lone pair electrons indicated with dotted line.

Procedure

Determination of the Slater-Condon Parameters. - In principal it is possible to evaluate the Slater-Condon parameter from equation 2 by integration. This calculation is very time consuming and cumbersome, especially since good Hartree-Fock functions are frequently not available. An alternate method was used to obtain the parameters semiempirically by fitting this equation to spectroscopic energy levels.

In the use of equation 2 to express the energies of spectroscopic states some integrals, $F_0(ss)F_0(sp)$ and $F_0(pp)$ always appear with the same factors for all states arising out of any one configuration. Hence, it is impossible to obtain values for these integrals separately. By combining all these into one constant term, W_0 , which is characteristic for each configuration and noting that: $F_2(pp) = G_2(pp)$, equation 2 simplifies to

$$W = W_0 + \sum_l c^l M^l \quad (3)$$

The factors c^l have been calculated for all spectroscopic states, which arise from the different combinations of s and p electrons. (37) (38) The M's in equation 3 are integrals over the radial part of the wave function and dependent on n and l only. The Slater functions depend on l only through the effective nuclear charge (Z_{eff}) which does not differ, according to Slater's recipe, for configurations involving only s and p electrons. But, it has been shown that the Slater-Condon parameters are different for different configurations of the same atom. These differences must be ignored here, since it is not possible to obtain enough information from one configuration to calculate all the Slater-Condon parameters necessary to express a valence state energy. Thus, in configuration sp the spectroscopic state depends only on F_{sp}^k and G_{sp}^k , but the energy of the valence state d^2 involves also the integrals F_{ss}^k , F_{pp}^k and G_{pp}^k . Therefore, it was necessary to consider together the configurations s^2p^n , sp^{n-1} and p^{n-2} for the evaluation of the Slater-Condon parameters of one atom or ion. It was found, however, that this procedure does not increase appreciably the uncertainties in the Slater treatment. (34) Under these considerations equation 3 changes to

$$W = W_0 + n \Delta W_{sp} + m \Delta W_p^2 + \sum_l c^l M^l \quad (4)$$

where W_0 is the constant term for configuration s^2p^n , ($W_0 + \Delta W_{sp}$) and ($W_0 + \Delta W_p^2$) are the constant terms for the configurations sp^{n-1} and p^{n+2} , respectively.

Thus, $n = 1$ if data of configuration sp^{n+1} are fitted and $m = 1$ if data of configuration p^{n+2} are fitted, otherwise, n and m are zero.

In Slater's treatment many approximations are made, especially all configuration interaction is neglected. Consequently, equation 4 is not expected to represent the observed energy levels exactly. Since, in most cases, more multiplet levels are known than are needed to estimate the unknowns in equation 4, a least squares multiple regression method was used to obtain the best average values for the Slater parameters. For these elaborate calculations an IBM 650 was used. The energy levels to be fitted in this way have been obtained from Moore's (17) tables. Some of the data not tabulated have been obtained by extrapolation, using the straight line relation of corresponding states in an isoelectronic sequence noted by Rohrlich. (26)

The calculations described have been made for the elements of the first and second period up to their triply positive ions. For some of these elements no multiplet levels for the configuration p^{n+2} have been observed, and consequently ΔWp^2 could not be obtained by the method described. The evaluation of these ΔWp^2 was done by the following procedure. With the known ΔWp^2 and the corresponding ΔWsp a factor k was determined, so that

$$K \Delta Wsp = \Delta Wp^2 \quad (5)$$

This factor k shows little but steady variation in any one period. This permits a reliable extrapolation of the k 's corresponding to the unknown ΔWp^2 values. Having determined the k 's, the Wp^2 's for the configuration $2p^6$; $3p^4$; $3p^5$ and $3p^6$ have been estimated by equation 5.

Evaluation of the Valence State Energy. - For the expression of the valence state energy equation 3 was used. The rather cumbersome evaluation of the factors c^1 for the valence states was performed using an IBM 650. (39) The F_0 's appearing in the valence state equation cannot be obtained explicitly, as shown above. It is, however, always possible to eliminate these F_0 's in terms of the W 's described. The evaluation of the promotion energies involving these eliminations and substitution of the Slater-Condon parameters into the valence state equation was also performed with the IBM 650. (39)

Two methods appear feasible for the treatment of negative ions, for which calculations as described above cannot be done,

since no spectroscopic data are available. One method is to extrapolate along a series of ionization potentials of equivalent valence states of an isoelectronic sequence, using one of the procedures described. (8), (14) The other method involves extrapolation of promotion energies along a series of equivalent valence states of an isoelectronic sequence and combination of the resultant promotion energy of the negative ion with the ground state electron affinity. Rohrllich (26) has shown that the extrapolation involved in the second method is linear and hence the values obtained are more reliable, than those calculated by the first method in which the functional relation is open to considerable doubt. Consequently, P^- values were obtained by a least squares fit to the corresponding valence states P^0 , P^+ , P^{++} and P^{+++} .

Results

The procedure described was used to calculate the orbital electronegativities for a wide variety of valence states of the elements of the first two rows of the periodic system. The promotion energies obtained for the states of the highest valence are given in Table II. (40) The resulting orbital electronegativities with the corresponding valence state ionization potentials and electron affinities are given in Table III.

In the last column of this table the orbital electronegativities are transformed to values comparable with Pauling's. Since the zero point of Pauling's scale is arbitrary, there is no compelling reason to anticipate the previously reported direct proportionality between the Mulliken and Pauling scales (28); however, a linear relation must hold, if both definitions represent the same property. The correlation between the two scales was consequently obtained by fitting, by least squares, the best straight line to the selected electronegativities shown in Figure 3. Values for those valence states were applied, which most probably correspond to the compounds used for the evaluation of Pauling's electronegativities; these values are designated by asterisks in Table III. As seen in Figure 3, the correlation is highly satisfactory and can be represented by

$$0.168(XM - 1.23) = X_p \quad (6)$$

Based on the considerations outlined, it is possible to define electronegativity as a property only of bonding orbitals or other singly occupied orbitals.

TABLE II
PROMOTION ENERGIES (IN eV.)

No. of val. elec- trons	Valence state		Li	Be +	B ++	C +++
(1)	s		0.0	0.0	0.0	0.0
	p		1.847	3.958	5.997	8.002
		Li ²⁺	Be	B +	C ++	N +++
(2)	sp	1.083	3.362	5.746	8.040	10.304
	pp	2.284	7.168	12.237	17.139	22.004
	didi	0.809	2.720	4.674	6.595	8.496
	di π	1.684	5.265	8.992	12.590	16.154
	trtr	1.362	4.345	7.433	10.431	13.400
	tr π	1.884	5.899	10.073	14.106	18.104
	tete	1.616	5.105	8.724	12.228	15.702
		Be ²⁺	B	C +	N ++	O +++
(3)	spp	2.889	5.621	8.492	11.228	13.956
	ppp	6.040	12.129	18.231	24.377	30.409
	didi π	2.365	4.738	7.124	9.505	11.870
	di π π	4.464	8.875	13.362	17.803	22.183
	trtrtr	2.190	4.443	6.668	8.930	11.175
	trtr π	3.706	7.398	11.130	14.845	18.513
	tetete	3.284	6.586	9.901	13.223	16.505
		B ²⁺	C	N +	O ++	F +++
(4)	sppp	5.059	8.479	12.130	15.533	18.970
	didi π π	4.048	7.193	10.393	13.523	16.682
	trtrtr	3.712	6.764	9.814	12.854	15.919
	tetetete	3.542	6.549	9.524	12.519	15.538
		C ^{-a}	N	O +	F ++	Ne +++
(3)	s ² ppp	0.682	1.082	1.536	1.941	2.335
	sp ² pp	9.254	14.292	19.224	24.291	29.301
	di ² di π π	4.968	7.687	10.380	13.116	15.818
	didi π ² π	8.208	12.867	17.476	22.151	26.795
	tr ² trtr π	5.931	9.255	12.551	15.890	19.199
	trtrtr π ²	7.858	12.392	16.893	21.437	25.960
	te ² tetete	6.326	9.920	14.391	17.098	20.680
		N ^{-a}	O	F +	Ne ++	Na +++
(2)	s ² p ² pp	0.290	0.537	0.708	0.885	1.081

TABLE II (cont'd.)

PROMOTION ENERGIES (IN eV.)

No. of val. elec- trons	Valence state		Li	Be +	B + +	C + + +
	sp ² p ² p	11.799	16.969	21.988	27.112	32.328
	di ² di ² π π	0.290	0.537	0.708	0.885	1.081
	di ² diπ ² π	6.074	8.753	11.348	13.998	16.705
	didi ² π ² π	10.772	15.558	20.210	24.967	29.782
	tr ² tr ² tr π	4.166	6.014	7.801	9.627	11.497
	tr ² trtr ² π ²	7.526	10.864	14.104	17.416	20.781
	te ² te ² tete	5.818	8.400	10.903	13.462	16.068
		0 -a	F	Ne +	Na + +	Mg + + +
(1)	p	-0.011	0.017	0.036	0.056	0.092
	s	15.036	20.892	26.903	32.778	38.614
			Na	Mg +	Al + +	Si + + +
(1)	s		0.0	0.0	0.0	0.0
	p		2.103	4.429	6.673	8.874
		Na -a	Mg	Al +	Si + +	P + + +
(2)	sp	0.984	3.121	5.342	7.485	9.616
	pp	1.822	6.422	11.146	15.596	20.347
	didi	0.820	2.757	4.691	6.598	8.566
	diπ	1.404	4.772	8.244	11.527	14.981
	trtr	1.191	4.060	6.988	9.786	12.726
	trπ	1.543	5.322	9.212	12.876	16.770
	tete	1.362	4.681	8.081	11.306	14.719
		Mg -a	Al	Si +	P + +	S + + +
(3)	spp	2.594	4.856	7.263	9.464	11.786
	ppp	5.947	10.628	15.380	19.977	24.742
	didiπ	2.278	4.320	6.443	8.399	10.527
	diπ π	4.271	7.742	11.322	14.721	18.264
	trtrtr	2.173	4.142	6.170	8/044	10.108
	trtr π	3.572	6.542	9.604	12.495	15.545
	tetete	3.195	5.897	8.677	11.293	14.081
		Al -a	Si	P +	S + +	Cl + + +

TABLE II (cont'd.)

PROMOTION ENERGIES (IN eV.)

No. of val. elec- trons	Valence state		Li	Be †	B † †	C † † †
(3)	s ² ppp	0.745	0.831	1.002	1.126	1.174
	sp ² pp	4.867	7.891	11.084	13.942	17.131
	di ² diπ π	2.806	4.361	6.043	7.534	9.152
	didiπ ² π	4.674	7.450	10.313	12.959	15.864
	tr ² trtrπ	3.408	5.342	7.381	9.233	11.249
	trtrtrtrπ ²	4.610	7.303	10.057	12.631	15.442
	te ² tetete	3.692	5.795	7.986	10.001	12.192
	P ^{-a}	S	Cl ⁺	Ar ⁺⁺	K ⁺⁺⁺	
(2)	s ² p ² pp	0.180	0.309	0.397	0.491	0.591
	sp ² p ² p	6.686	9.462	12.293	15.089	17.846
	di ² di ² π π	0.180	0.309	0.397	0.491	0.591
	di ² diπ ² π	3.449	4.886	6.345	7.790	9.219
	didiπ ² π ²	6.203	8.747	11.358	13.914	16.446
	tr ² tr ² trπ	2.370	3.360	4.363	5.357	6.343
	tr ² trtrπ ²	4.313	6.093	7.912	9.701	11.472
	te ² te ² tete	3.328	4.707	6.111	7.496	8.869
	S ^{-a}	Cl	Ar ⁺	K ⁺⁺	Ca ⁺⁺⁺	
(1)	p	-0.003	0.036	0.057	0.089	0.129
	s	8.027	10.761	13.426	16.189	18.894

^a Extrapolated values.

TABLE III

VALENCE STATE IONIZATION POTENTIALS I_v , VALENCE
STATE ELECTRON AFFINITIES E_v AND ORBITAL ELECTRO-
NEGATIVITIES^a

		I_v	E_v	X_M	X_p
H (1)		13.60	0.75	14.34	2.21*
Li (1)	s	5.39	.82	6.21	0.84*
	p	3.54	.56	4.10	0.47
Be (2)	sp	σ 9.92	3.18	13.10	2.15
		π 5.96	0.11	6.07	0.82
	pp	6.11	.76	6.87	0.95
	didi	8.58	.99	9.57	1.40*
	π	σ 8.02	.92	8.94	1.29
		π 6.04	.43	6.47	0.88
	trtr	7.61	.59	8.20	1.17
	tr π	σ 7.38	.63	8.01	1.13
		π 6.06	.54	6.60	0.90
	tete	7.18	.51	7.69	1.09
B (3)	spp	s 14.91	5.70	20.61	3.25
		p 8.42	0.32	8.74	1.26
	ppp	8.40	3.46	11.86	1.79
	didi π	σ 12.55	2.12	14.68	2.27
		π 8.23	0.44	8.68	1.26
	di π π	σ 11.66	2.56	14.21	2.19
		π 8.41	1.89	10.30	1.53
	trtrtr	11.29	1.38	12.67	1.93*
	trtr	σ 10.97	1.87	12.84	1.96
		π 8.33	1.42	9.75	1.44
	tetete	10.43	1.53	11.97	1.81
C (4)	sppp	s 21.01	8.91	29.92	4.84
		11.27	0.34	11.61	1.75
	didi	17.42	3.34	20.77	3.29
		π 11.19	0.10	11.29	1.69
	trtrtr	σ 15.62	1.95	17.58	2.75
		π 11.16	0.03	11.19	1.68
	tetetete	14.61	1.34	15.95	2.48*
N (3)	s ² ppp	13.94	0.84	14.78	2.28
	sp ² pp	s 26.92	14.05	40.98	6.70
		p 14.42	2.54	16.96	2.65
	di ² di π π	σ 23.91	7.45	31.35	5.07

TABLE III (cont'd.)

VALENCE STATE IONIZATION POTENTIALS I_V , VALENCE
STATE ELECTRON AFFINITIES E_V AND ORBITAL ELECTRO-
NEGATIVITIES^a

		I_V	E_V	X_M	X_P
O (2)		14.18	1.66	15.84	2.46
	did π^2	σ 22.10	6.84	28.94	4.67
		π 14.11	2.14	16.25	2.53
	tr ² trtr π	σ 20.60	5.14	25.74	4.13
		π 14.12	1.78	15.90	2.47
	trtrtrtr π^2	19.72	4.92	24.63	3.94
	te ² tetete	18.93	4.15	23.08	3.68
	s ² p ² pp	17.28	2.01	19.29	3.04
	sp ² p ² p	s 36.07	18.44	54.51	8.98
		p 18.53	3.40	21.93	3.49
	di ² di ² $\pi\pi$	17.28	2.01	19.29	3.04
	di ² di π^2	σ 30.17	10.23	40.40	6.60
		π 17.91	2.71	20.61	3.26
	did π^2 π^2	28.71	9.51	38.22	6.23
	tr ² tr ² tr π	σ 26.65	7.49	34.14	5.54
		π 17.70	2.47	20.17	3.19
	tr ² trtrtr π	26.14	7.32	33.47	5.43
	te ² te ² tete	24.39	6.11	30.50	5.93
F (1)	s ² p ² p ² p	20.86	3.50	24.36	3.90*
	sp ² p ² p ²	38.24	24.37	62.61	10.31
Na (1)	s	5.14	0.47	5.61	0.74*
	p	3.04	0.09	3.13	0.32
Mg (2)	sp	s 8.95	2.80	11.75	1.77
		p 4.52	0.06	4.58	0.56
	pp	5.65	0.01	5.66	0.75
	did	7.10	1.08	8.18	1.17*
	di π	σ 7.30	0.78	8.08	1.15
		π 5.09	.03	5.12	0.65
	trtr	6.54	.52	7.06	.98
	tr π	σ 6.75	.38	7.13	.99
		π 5.27	.02	5.30	.69
	tete	6.28	.32	6.60	.90
Al (3)	spp	s 12.27	4.92	17.19	2.69
		p 6.47	1.37	7.84	1.11

TABLE III (cont'd.)

VALENCE STATE IONIZATION POTENTIALS I_V , VALENCE
STATE ELECTRON AFFINITIES E_V AND ORBITAL ELECTRO-
NEGATIVITIES^a

		I_V	E_V	X_M	X_P
Si (4)	ppp	6.50	4.89	11.39	1.71
	did π	σ 9.91	2.61	12.51	1.90
		π 6.36	1.45	7.81	1.11
	di π π	σ 9.39	3.66	13.05	1.99
		π 6.49	3.13	9.61	1.41
	trtrtr	8.83	2.11	10.94	1.64*
	trtr π	σ 8.65	2.94	11.59	1.74
		π 6.43	2.58	9.01	1.31
	tetete	8.17	2.58	10.75	1.59
	sppp	17.31	6.94	24.24	3.88
		9.19	2.82	12.01	1.82
	did π π	σ 14.06	4.07	18.12	2.85
		π 9.18	2.20	11.38	1.71
	trtrtr π	12.61	3.20	15.80	2.33
		π 9.17	2.00	11.17	1.67
P (3)	tetetete	11.82	2.78	14.59	2.25*
	s ² ppp	10.73	1.42	12.15	1.84
	sp ² pp	s20.20	8.48	28.68	4.62
		p12.49	1.98	14.46	2.23
	di ² di π π	σ 17.53	4.95	22.49	3.58
		11.61	1.68	13.29	2.03
	did π ² π	σ 16.78	4.77	21.55	3.42
		π 11.89	2.02	13.91	2.14
	tr ² trtr π	σ 15.59	3.74	19.33	3.05
		π 11.64	1.80	13.44	2.06
S (2)	trtrtr π ²	15.18	3.76	18.94	2.98
	te ² tetete	14.57	3.24	17.80	2.79
	s ² p ² pp	12.39	2.38	14.77	2.28
	sp ² p ² p	s20.08	11.54	31.62	5.12
		p13.32	3.50	16.83	2.63
	di ² di ² π π	12.39	2.38	14.78	2.28
	di ² di π ² π	σ 17.78	6.96	24.74	3.96
		12.86	2.94	15.80	2.45
	did π ² π ²	17.42	6.80	24.22	3.87
	tr ² tr ² tr π	σ 16.33	5.43	21.76	3.46

TABLE III (cont'd.)

VALENCE STATE IONIZATION POTENTIALS I_V , VALENCE
S
STATE ELECTRON AFFINITIES E_V AND ORBITAL ELECTRO-
NEGATIVITIES^a

		I_V	E_V	X_M	X_P
		12.70	2.76	15.46	2.40
	tr^2trtr^2	16.27	5.49	21.76	3.46
	te^2te^2tete	15.50	4.77	20.27	3.21
Cl (1)	$s^2p^2p^2p$	15.03	3.73	18.76	2.95*
	$sp^2p^2p^2$	24.02	14.45	38.47	6.26

^a The orbital electronegativities in Mulliken's scale X_M in (eV.) and in Pauling's scale X_P . The values with * have been used to obtain the correlation parameter in equation 6. For nomenclature see footnote . The numbers in parentheses after the elements indicate how many bonding electrons the element has in the particular valence state. C (4) carbon four bonding.

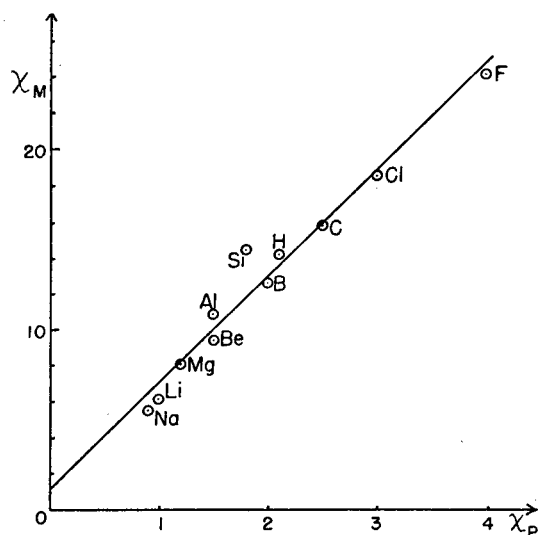


Fig. 3.—Correlation between Mulliken's and Pauling's electronegativity scale with the values used for the evaluation of the correlation coefficients. The equation found is $0.168(\chi_M - 1.23) = \chi_P$.

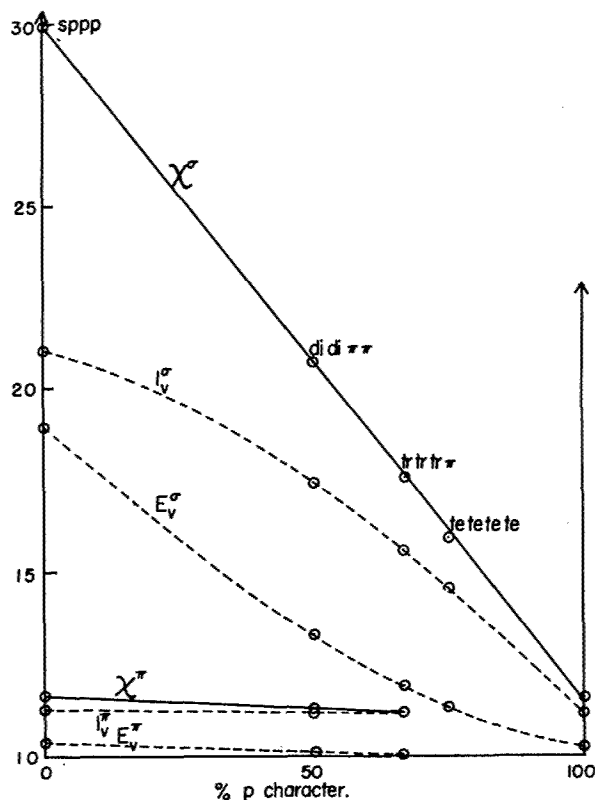


Fig. 4.—Electronegativity of carbon as a function of s character of the hybrid orbital. Dotted lines give electron affinity and ionization potential as function of s character of the hybrid orbital.

Lone pairs and electron holes (vacant orbitals) cannot be treated in the same manner, since here electron affinity and ionization potential respectively lose their meaning.

It is interesting to note the extent to which the electronegativities obtained in this work depend on the character of the orbital. As may have been expected, the electronegativities for σ orbitals are considerably larger than those for the π orbitals. Also, the electronegativity increase with increasing s character anticipated by Walsh (32) and Bent (2) is borne out of the data observed.

An important feature is the linear relation observed between s character of the π orbital and its electronegativity, which is shown in Figures 4 and 5, where the electronegativities of the orbitals of the form

$$\psi = \cos \alpha (s) + \sin \alpha (p)$$

are plotted against $\cos^2$ for C and N.

This aspect makes electronegativities of intermediately hybridized orbitals available by linear interpolation. Such intermediate hybrids are undoubtedly needed in compounds of N and O, probably of the halogens, where some hybridization is likely, and even in carbon. (13)

Calculations for d orbital hybrids of second row elements have not been possible because of lack of spectroscopic data. These results would be of considerable interest, especially for the elements Si to Cl, where use of d orbitals has frequently been postulated. Computations of electronegativities of positive ions are now in progress, and it is hoped that values for partially charged atoms may also be obtained. (41) It was found in this Laboratory that these values are urgently required in order to get explanations (13) for hybrid and ionic character of chemical bonds consistent with n.q.r. frequency changes and other molecular properties.

These subjects have been studied in a recent review article by Bent. (2) By considering compounds of the type X-A-Y, he has examined qualitatively the influence of the more electronegative group Y on the character of the bond X-A. He has attempted to explain the observed changes in the X-A bond, when going from X-A-X to X-A-Y by considering only rehybridization of atom A, combined with the postulate that the electronegativity of an orbital of A increases when its s character increases. The first conclusion, that A becomes more electronegative in its bond to X is reasonable. But, the second conclusion drawn, that this is only due to increased s character in the bonding orbital of A toward X, appears dubious. As Coulson (5) has shown, the bond strength is not only governed by the overlap, but also by the energy match of the bonding orbitals; e.g. the bond is stronger, the better the energies match. If this concept is applied in Bent's picture, it is easily seen that increasing the s character of the A orbital toward X upsets the energy match of A with X, and also a corresponding increase of p character in the orbital toward Y makes the energy mismatch larger. But, if we consider, in addition to rehybridization, partial charges on the atoms, all the examples presented can be explained, and the energy match will be found to improve.

Thus, it must be pointed out that the picture given by Bent is questionable, since for simplicity's sake he has chosen not to introduce partial charges which is a serious approximation in a valence bond treatment.

In order to make a more complete study possible, it is necessary to examine thoroughly the dependence of the orbital electronegativities on partial charges on the atoms.

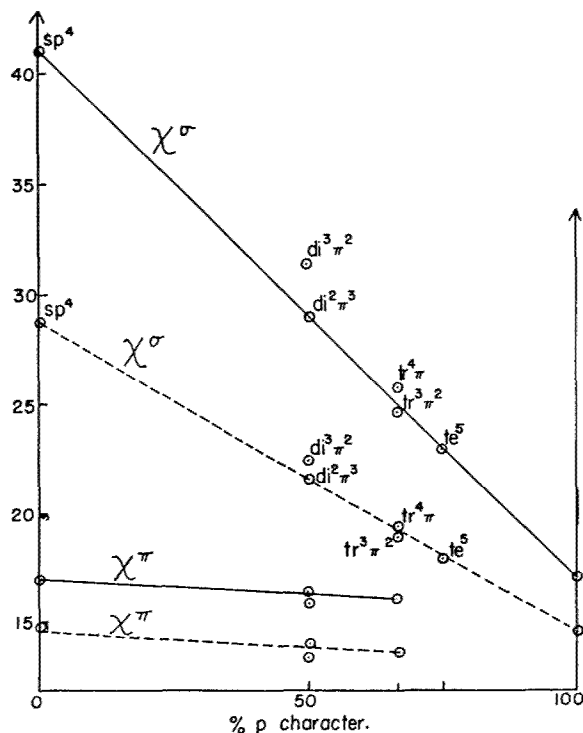


Fig. 5.—Electronegativities of nitrogen and phosphorus as a function of s character of the hybrid orbital. Solid line, nitrogen; broken line, phosphorus.

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- (36) To prevent confusion of hybrids with pure s and p orbitals, the notation introduced by Mulliken will be used throughout this paper; i.e., te tetrahedral = (sp^3), tr = trigonal = (sp^2), di = digonal = (sp).
- (37) The notation is that used in Condon and Shortly, ref. 30.
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- (41) Note Added in Proff - Such values have been obtained and are in the process of publication.

APPENDIX II

Electronegativity II

Bond and Orbital Electronegativities

By Jurgen Hinze, M. A. Whitehead and H. H. Jaffe

A new definition for electronegativity is proposed as $\chi = dE(n)/dn$, where $E(n)$ is the energy of an atom in its valence state as a function of the occupation, n , of the orbital for which the electronegativity is expressed. This definition is found for singly occupied orbitals to be identical with Mulliken's definition of electronegativity. The given representation, although equivalent to previous concepts, permits in addition the computation of orbital electronegativities of vacant and doubly occupied orbitals and of groups. A new term bond electronegativity is defined, as the electronegativity of orbitals forming a bond, after charge has been exchanged between them. It is shown that this process of charge exchange will equalize the electronegativity of the two orbitals forming a bond to lower the energy of the molecule. Such a treatment leads directly to a new definition and clear understanding of ionic character in terms of charge transferred between the bond-forming orbitals.

The concept of electronegativity has had extremely wide use and considerable success in systematizing experimental chemical data. Nonetheless, it has never been quite adequately defined. Thus, in recent numerical work on electronegativities, it was necessary to define the concept of orbital electronegativity to indicate that this is a property, not of the atom as such, but of an individual orbital of the atom. In addition it seemed again unreasonable that this quantity was measured in units of energy (e.g., eV.). Pauling's verbal definition of electronegativity: "The power of an atom in a molecule to attract electrons to itself" suggests, not the units of energy, but of potential, e.e., energy/charge. This was recognized recently by Iczkowski and Margrave, (2) who redefined electronegativity as a derivative of energy with respect to charge. Their definition is not completely satisfactory; first, it ignores completely the orbital dependence of electronegativity; second, it assumes that the energy of an atom is a continuous and single-valued function of its charge. That the function is not single-valued is apparent from the fact that a variety of different valence states with different energies are readily obtained for a given element.

For trigonally hybridized carbon, when the charge is + 1 or - 1, we have reported two energies, considerably different, depending on the distribution of the electrons.

We have developed a definition of electronegativity (or better orbital electronegativity) which is mathematically defensible-although based on some assumptions-and which promises to be extremely useful in all the areas in which electronegativity has generally been applied. Since this definition is capable of sensitively accounting for effects due to hybridization and other orbital changes, it should attain further usefulness in the determination of semi-empirical parameters for LCAO-MO calculations and possibly even for calculations by the Pariser-Parr method. In addition, the new definition leads immediately to a further concept, the bond electronegativity, which will be effective in the estimation of ionic character and related properties, and which appears to bear a close relation to Sanderson's stability ratio. (9)

The Definition - Following Pauling, we desire that the orbital electronegativity be a measure of the power of an atom, as it may exist in a molecule, to attract an electron in a given orbital to itself, thus the orbital electronegativity should be defined as the derivative of the energy of the atom with respect to the charge in the orbital, i.e., the number of electrons in the orbital

$$X_j = \partial E / \partial n_j$$

where n_j is the occupation number of the j 'th orbital, the orbital electronegativity of which is X_j .

This definition implies two assumptions: (a) that the occupation number n_j may have both integral and nonintegral values, and (b) that once assumption a is made, then the energy E is a continuous and differentiable function of n_j .

Strictly speaking, neither of these assumptions is valid. In formal quantum mechanics, the number of electrons is a cardinal number, and has meaning only for integral values. Nevertheless, in certain applications of quantum mechanics to valence problems, and particularly in dealing with the assignment of electrons to individual atoms, it has become quite customary and useful to speak of partial charges on atoms, thereby implying fractional values for occupation numbers. This implies possibly an over-emphasis of a population analysis in which the electron described by a molecular orbital $a\phi_A + b\phi_B$ of atoms A and B in the ratio of the squares of the coefficients a and b .

However, n_j may be understood to represent the average charge residing in an orbital and can thus be used as a continuous variable, which ranges from 0 to 2. These limits are imposed, since it does not seem possible to assign a meaning to a negative occupation number, and exceeding the value of 2 would be a violation of the Pauli principle.

Assumption b is possibly the more drastic one. The calculation of the energy of a valence state is achieved by expansion into a series of parameters, the so-called Slater-Condon parameters, F's and G's, each of which is in itself an integral over the radial part of the wave function of the atom. Alternatively, the energy of the valence state can be obtained as a weighted average of certain spectroscopic states. Whether one prefers a completely theoretical, a priori calculation, or a semi-empirical procedure based on observed spectroscopic data, the calculation of the energy is feasible only for integral values of n_j , 0, 1 and 2. However, given the three values of $E(n_j)$ - $E(0)$, $E(1)$ and $E(2)$ -one can postulate that E is a continuous function of n_j . At the defined points it is also singlevalued, so that the postulation that E be differentiable provided one has accepted its continuity, seems perfectly reasonable.

Once one accepts the assumption b, one can still imagine an infinite number of possible functional relations; any three parameter equation can be fitted to these three points. The simplest such relation is obviously a quadratic (parabola): Figure 1. This relation, equation 1, will be chosen here as the relation of choice for two

$$E(n_j) = a + bn_j + cn_j^2 \quad (1)$$

reasons: (1) because of its mathematical simplicity, and (2) particularly because, at $n_j = 1$, the slope of this curve, e.e., the orbital electronegativity by our definition, is equal to $(E(2)-E(0))/2$ according to a well-known property of parabolas. But this quality is equal to $(E(2)-E(1) + E(1)-E(0))/2$, where $E(2)-E(1)$ is the electron affinity, E_v , and $E(1)-E(0)$ is the ionization potential, I_v ; in other words the orbital electronegativity as defined is equal to $(I_v + E_v)/2$, identical to Mulliken's definition. (6)

Thus, the definition given above, with the assumed energy relation of equation 1, contains the Mulliken definition as a special case. Since the Mulliken and Pauling definitions have been shown to be substantially equivalent, it is apparent that our new definition represents a generalization of the original definitions, and will leave previous work substantially unaffected.

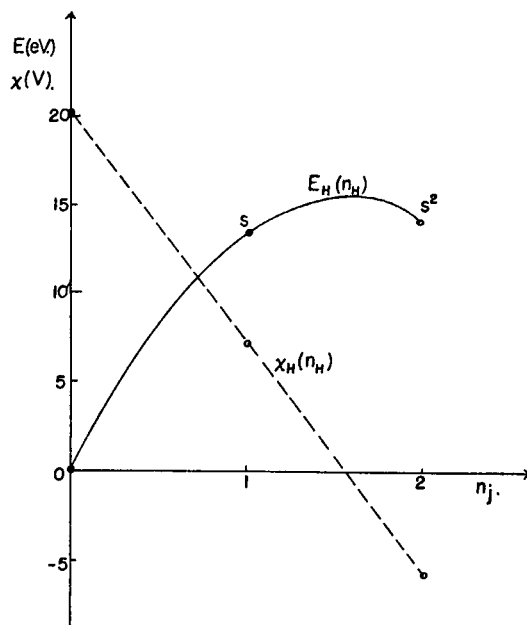


Fig. 1.—The energy and electronegativity of hydrogen as a function of the occupation number n_H of the 1s-orbital.

The fact that our new definition, with the assumptions a and b above, contains the Mulliken definition as a special case may well be regarded as a justification of the assumptions.

Differentiation of equation 1 with respect to n_j gives the orbital electronegativity of the orbital j : Figure 1.

$$X_j = E / n_j = b + 2cn_j \quad (2)$$

This equation 2, together with the assumptions a and b, give a meaning to n_j for fractional values, as long as $0 \leq n_j \leq 2$, and would suggest immediately that, for a given orbital j , one can define an electronegativity as a function of n_j . This possibility, however, requires closer scrutiny.

The entire value of the electronegativity concept, as it has been used up to now, hinges on the fact that it gives a measure of the power by which an atom, in its valence state, attracts an additional electron for bond formation. Consequently, electronegativity is a property of an atom before a bond is formed.

If one assumes a coordinate covalent bond as formed from a pair of electrons on one atom, and a vacant (virtual) orbital on the other, the concept is readily extended to electron pairs and vacant orbitals. Thus the orbital electronegativity concept in the accepted sense is valid for values of $n_j = 0, 1$ and 2 only. The meaning of values obtained for fractional values of n_j will be examined in the next section.

Ionic Character and Bond Electronegativity. - Before proceeding to an examination of the meaning of $\chi(n_j)$ for non-integral values of n_j , it will be necessary to examine the concept of ionic character. This concept originated logically in the valence bond method (resonance theory) as the fraction of ionic structure in the complete wave function; thus, if the wave function of a compound was given as, $a\psi(A-B) + b\psi(A-B^-)$, b^2 is the ionic character. Similarly, using the lowest approximation of molecular orbital theory, neglecting overlap, in which a chemical bond is described by two electrons occupying an orbital $a\psi_A + b\psi_B$, the absolute value of $|1-2b^2|$ becomes the approximate measure of the excess charge on B, and hence the ionic character. Neither definition is completely satisfactory, because of the problems arising out of overlap populations (the electrons not readily assignable to either atom, but apparently residing in the bond); however, any more elegant definition loses simplicity.

Unfortunately, the calculations to obtain the ionic character from the above quantum mechanical definitions cannot, in general, be made, and empirically established ionic character values have frequently been used to provide a measure of the wave function. For this purpose, empirical relations have been postulated, from which ionic character may be derived. Most notable among these is the relation to dipole moment (5) which, however, is open to serious criticism. (7) The most common way of estimating ionic character, however, depends on the fact that it is related to electronegativity differences, as first observed by Pauling. Unfortunately, several different relations have been postulated, e.g. (5), (1)

$$i = 1 - \exp \frac{1}{2}(X_A - X_B)^2$$

$$i = \frac{1}{2}|X_A - X_B|$$

If we now consider the process of bond formation as starting from two atoms, A and B, each possessing one unshared electron, we may arbitrarily divide it into two steps: the pairing of two electrons, forming a purely covalent bond, in which the occupation numbers n_A and

n_B remain unity, as in the free atoms followed by a transfer of charge, changing the numbers n_A and n_B to their final values in the compound. Such charge transfer, however, will occur only if the two orbitals considered overlap strongly. We will now consider this second process in case of strong overlap from two different points of view.

If we wish to describe the two electrons forming the bond A-B as in a state of equilibrium, we must require that the potential which each electron sees on both atoms A and B be equal. This means that we obtain a restrictive condition on the equilibrium values of the occupation numbers n_A and n_B , since

$$X_{eq}(n_A) = X_{eq}(n_B)$$

Furthermore the sum of n_A and n_B is 2. By plotting $X_A(n_A)$ against n_A and similarly for B (n_B varies from 2 to 0 as n_A varies from 0 to 2), we obtain Figure 2, where the intersection of the two straight lines (each of the form of equation 2) gives the equilibrium values of n_A and n_B .

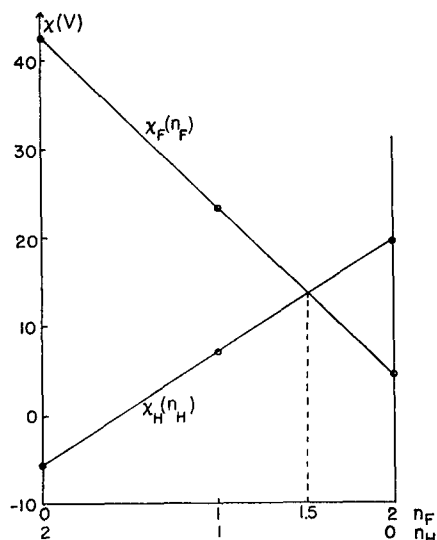


Fig. 2.—Electronegativities of A and B (using hydrogen and fluorine as examples) in an AB bond as a function of n_A and n_B .

Mathematically equivalent to this procedure, but physically equally interesting, is a consideration of the energetics of the transfer of electrons from A to B (or vice versa).

Transfer of an infinitesimal amount of charge (an infinitesimal change in n) from A to B (or vice versa) is accompanied by a reduction of charge on A, requiring an expenditure of energy equal to $(dE_A(n_A)/dn_A)dn_A$, while at the same time an amount of energy equal to $(dE_B(n_B)dn_B)$ is released. Equilibrium is reached when the transfer involves no further change in energy, e.e., since $dn_A = dn_B$, when

$$dE_B(n_B)/dn_B = dE_A(n_A)/dn_A$$

or in other words, when the electronegativities given by equation 2 are equal.

The electronegativities for these fractional values of n_j then have the special property that they are the same for the two atoms forming a chemical bond, or better for the orbitals of the two atoms which combine to form the bonding MO. For this reason we suggest for this electronegativity the term bond electronegativity, and would like to repeat that they must not be confused with the concept of electronegativities as defined by Pauling.

The concept of bond electronegativity lends itself particularly well to a definition of ionic character. According to the bond electronegativity concept, the ionic character is the amount of charge transfer necessary to make the bond electronegativities of the bonded atoms equal: In other words, the ionic character, $|n_j - 1|$ (where it is immaterial which of the n_j 's of the two atoms is taken, since their sum is equal to 2) is obtained by equating $\overset{\text{bond}}{X}A^{n_j}$ and $X\overset{\text{bond}}{B}^{n_j}$, i.e.

$$i = |n_{Aj} - 1| = \left| \frac{b_B - b_A + 2(c_B - c_A)}{2(c_A + c_B)} \right| = \left| \frac{\Delta X}{2(c_A + c_B)} \right| \quad (3)$$

The numerator of equation 3 is the electronegativity difference (i.e., the difference in orbital electronegativities). The denominator, however, is a function not directly expressible in terms of the electronegativity difference, and consequently no simple relation between ionic character and electronegativity is possible. However, Gordy's relation (1) which postulates the ionic character as linear in the electronegativity difference, seems to be most nearly obeyed.

Group Orbital Electronegativities. - The definition of orbital electronegativity introduced above permits further the determination of the orbital electronegativities of groups.

Thus it has long been considered desirable to obtain electronegativities, not only of a tetrahedral carbon atom, but of the group X_3C with respect to an atom Y with which it forms a bond in the compound X_3CY . Considerable purely empirical work has been done on such group electronegativities (3); however, no reasonable fundamental procedure seems to have been developed.

Using our definition of orbital electronegativity and our supplementary assumptions a and b, it is now possible to derive group orbital electronegativities in a manner exactly analogous to atomic orbital electronegativities. Take as an example the simple case of a molecule $XBeY$ in which we desire the group electronegativity of the group XBe , in order to discuss the bond with Y. In the terminology of the chemist, in general, the bond XBe has some ionic character, so that the charge on the Be atom, or better the occupation number of the Be orbital forming the BeX bond, is not exactly 1, but n . Assuming the two bonds of Be to be formed by diagonal hybrid orbitals the Be atom in the group is $di_1^n di_2^{1-n}$, and the orbital electronegativity of the XBe group is the derivative of the energy of the Be atom with this electronic structure with respect to the occupation number n_2 of the orbital di_2 . The assumption of the continuity of the energy of the atom with respect to the occupation numbers permits us to construct the diagram shown in Figure 3. in which we have three separate quadratic curves of the type described by equation 1, corresponding to variation of one of the occupation numbers, while the other is held constant at 0, 1 or 2, respectively.

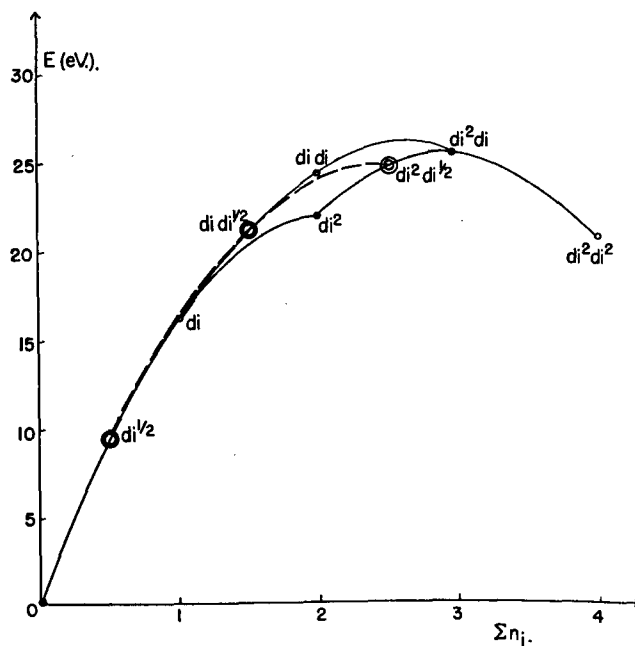


Fig. 3.—The various energy parabolas for diagonally hybridized beryllium.

Interpolation on each of these three quadratics permits us to find three points corresponding to di^ndi^0 , di^ndi^1 and di^ndi^2 , which are indicated in Figure 3 by open circles, and which, together define another quadratic curve of the type of equation 1, which is indicated on Figure 3 by a heavy dashed curve, assuming $n_1 = \frac{1}{2}$. The slope of this curve at the point di^ndi^1 is the group orbital electronegativity of the XBe group.

The same arguments and logic can be extended to any arbitrary system. Thus, in the case of a radical X_3C , or even $XYZC$, with electronic structures $te_1^{n_x} te_2^{n_x} te_3^{n_x}$, or $te_1^{n_x} te_2^{n_y} te_3^{n_z} te_4$, the process, as illustrated in Figure 4, involves successive construction of a set of quadratics from which will be interpolated the points for n_x ; from the quadratics formed by these will be interpolated points with n_y , and from the quadratics formed from these will finally be interpolated three points with n_z , giving rise to the single parabola which gives the electronegativity of the group.

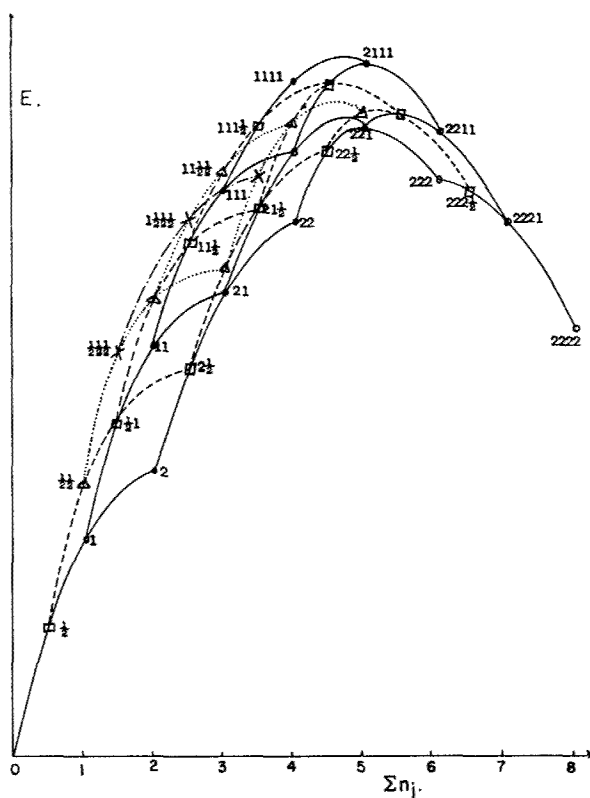


Fig. 4.—The various energy parabolas for tetrahedrally hybridized carbon.

Although the process is long, it is fundamentally straightforward. The special problems involved, which arise out the necessity of evaluating the energy of valence states which are not readily available, will be discussed below.

This procedure, then, provides a route toward the group orbital electronegativity of any group, provided only that the various n 's within this group are either available, or may be estimated. Such estimation might be made empirically, but a completely self-consistent procedure is possible, which will be outlined in the next section.

Self-consistent Group Orbital and Bond Electronegativities. - The procedure to obtain group orbital electronegativities outlined in the preceding paragraph requires the occupation numbers for the bonds within the group. On the other hand, the occupation numbers were derived above from bond electronegativities. A combination of the two approaches, in conjunction with either an iterative method or an analytical solution, will provide a means of calculating ionic characters, bond electronegativities, etc., throughout a molecule. Take as an example, the molecule X_3CY . Assume that we have some reason to believe that the CX bond is about 10% ionic. Using $n_X = 0.9$, we can now obtain the electronegativity curve for the X_3C group as a function of n_Y . We can use the bond electronegativity concept (together with the electronegativity curve for Y), to calculate n_Y . Using this value of n_Y we can get an electronegativity curve in terms of n_X , from which, in conjunction with the electronegativity of X , we obtain a corrected curve for electronegativity as a function of n_Y . Provided we have started with a reasonable assumption, this procedure should yield a self-consistent set of n -values quite rapidly, from which the charge distribution in the molecule become apparent.

In order to test whether electronegativities obtained by use of the new definition, the bond electronegativity concept and the ionic character obtained thereby have meaning, we have calculated the electronegativities of a series of groups for which previous literature values were available. The results of these calculations are shown in Table I. In the case of NH_2 , PH_2 , OH and SH , the calculations required of the hybridization of the central atoms. These were obtained from the bond angles. Although this procedure may be questionable, it is the best presently available. The group electronegativities obtained are in reasonable agreement with the rather widely divergent literature values. More important, trends obtained are exactly those anticipated from chemical information and intuition, and all expected regularities obtained.

TABLE I
GROUP ELECTRONEGATIVITIES

CH ₃		2.30	1.93	2.33	2.63, ^d	2.34 ^f		
CH ₂ Cl		2.47	2.13	2.55	2.74, ^d	2.48, ^f	3.22 ^g	
CHCl ₂		2.63	2.32	2.77	2.88, ^d	2.62, ^f	3.22 ^g	
CCl ₃		2.79	2.50	2.98	3.03, ^d	2.76, ^f	3.25, ^g	2.99 ^g
H ₂ N	22.5	2.82	2.61	2.96	3.40, ^d	2.99, ^e	3.63, ^g	3.36, ^g
					1.70 ^h			
H ₂ P	5	2.06	1.76	2.04	2.20, ^d	2.99 ^g		
HO	20	3.53	3.45	3.82	3.89, ^d	3.51, ^c	3.86, ^g	3.79, ^g
					2.30 ^h			
HS	5	2.35	2.11	2.38	2.61, ^d	2.45, ^e	2.92 ^g	2.54 ^g

^a Estimated from bond angles. ^b Group electronegativity in the fluoride. ^c Group electronegativity in the hydride. ^d J. K. Wilmhurst, J. Chem. Phys., 27, 1129 (1957). ^e B. P. Daley and J. N. Schoolery, J. Am. Chem. Soc., 77, 3977 (1955). ^f Ref. 10. ^g J. K. Wilmhurst, J. Chem. Phys., 28, 733 (1958). ^h J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, J. Am. Chem. Soc., 76, 5185 (1954).

In a previous section we have pointed out that the electronegativity of an element is a property of the element in its valence state, independent of the bond it will form. This is no longer true for a group electronegativity. A group electronegativity must depend on the bond that the group will form because, by definition, it is a property of the group obtained by an adiabatic breaking of this bond. Thus, the entire electron distribution in the group is assumed to be identical to that in the final compound. This is a limitation which applies to all group electronegativities and suggests that any empirical values must depend on the compound from which they are obtained. To demonstrate the importance of this effect, we have calculated the group electronegativities of the groups in Table I not only for the free group but also for the group as it exists in the hydride and in the fluoride. It is seen that the differences are significant, although the trends have remained the same.

As another example of the use of the new definition, we have calculated the group electronegativities of a series of groups for which Taft σ^* -values are available. It has long been postulated that these σ^* -values are a function of electronegativity. (10) The data obtained are shown in Table II. If these group electronegativities are plotted against the σ^* -values, a single smooth curve is obtained for the various fluorinated methyls and another smooth curve for the various chlorinated methyls. However, neither hydrogen nor the monobromo- or monoiodomethyls fall on either of these curves.

As was pointed out in the preceding paragraph, group electronegativities must depend to some extent on the molecule in which the group finds itself. Consequently, it seemed of interest to repeat the calculations of the group electronegativities of the same groups in an environment at least similar to that from which σ^* -values were obtained; that is, bonded through a carboxo group. These values are also listed in Table I and are graphed in Figure 5. It is immediately seen that the values for the fluorinated methyls, together with that for hydrogen, methyl and ethyl, fall on a straight line. The same line includes the point for 1,1,1-trifluoroethyl. The chloromethyls and 1-chloroethyl fall on a separate line and if methyl itself is to be included, this line shows a distinct curvature and does not comprise hydrogen. Bromo- and iodomethyl fall on neither of these lines.

The calculations have been made on the assumption that none of the halogens are hybridized. This is very likely an incorrect assumption, especially since recent calculations based on NQR data have indicated considerable s-character in chlorine, bromine and iodine organic compounds.

TABLE II
GROUP ELECTRONEGATIVITIES AND σ^+ -VALUES

Groups	σ^+ ^a	x_g^b	x_g^c
H	0.49	2.20	2.20
CH ₃	0.00	2.30	2.00
CH ₂ F	1.10	2.61	2.39
CHF ₂	2.05	2.94	2.81
CF ₃		3.29	3.27
CH ₂ Cl	1.05	2.47	2.21
CHCl ₂	1.94	2.63	2.41
CCl ₃	2.65	2.79	2.60
CH ₂ Br	1.00	2.40	2.12
CHBr ₂		2.49	2.22
CBr ₃		2.57	2.31
CH ₂ I	0.85	2.38	2.08
CHI ₂		2.44	2.16
CI ₂		2.50	2.22
CF ₃ CH ₂	0.92		2.36
CH ₂ ClCH ₂	.38		2.07
CH ₃ CH ₂	-.10		2.01

^a Tafts σ^+ -values from M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1956. ^b Group electronegativity, if orbital considered is singly occupied. ^c Group electronegativity, if group is bonded to carboxo group.

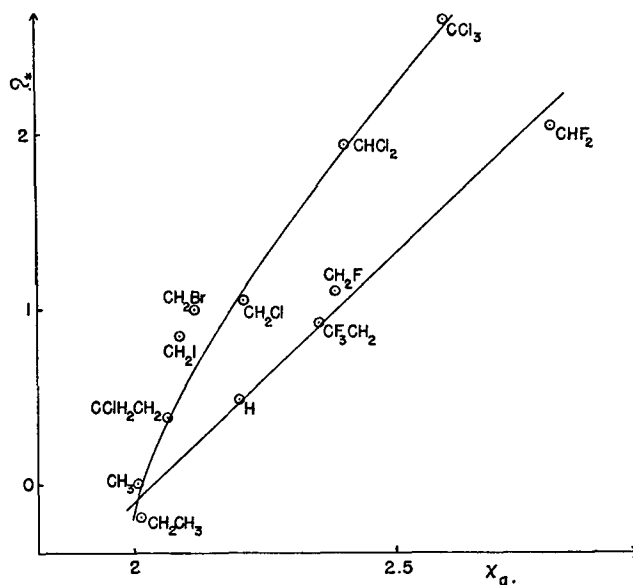


Fig. 5.—Group electronegativities for groups bonded to a carboxo group plotted *versus* Taft's σ^* -values.

It seems further very likely that the s-character in chlorine exceeds considerably that in fluorine because the promotion energy is much higher and because energy matching makes hybridization in fluorine particularly unlikely. If we assume fluorine to be unhybridized, repetition of all the calculations for the chloromethyls with somewhere between 15 and 20% s-character brings the points on to the line of the fluoromethyls. Similarly, the two points for bromo- and iodomethyl would fall onto the curve for the fluoro compounds if one assumes between 20 and 25% s-character. These amounts of s-character appear reasonable. It is also possible that the carbon atom rehybridizes somewhat and such rehybridization might well tend to equalize these curves. This effect, however, cannot be adequately treated at this time.

Calculations

The atomic orbital electronegativities are quite readily obtained. In order to obtain the quadratic curve of the form of equation 1 we require, for any given element X, the energies of three valence states $E(0)$, $E(1)$ and $E(2)$. If we arbitrarily define the energy scale such that

$$\begin{aligned} E(0) &= 0, \text{ then} \\ E(1) &= +I_V, \text{ and} \\ E(2) &= +I_V + E_V \end{aligned}$$

and therefore

$$E(n) = \frac{1}{2}(I_V - E_V)n^2 + \frac{1}{2}(3I_V - E_V)n \quad (4)$$

and the derivative

$$X(n) = dE(n)/dn = (I_V - E_V)n + \frac{1}{2}(3I_V - E_V) \quad (5)$$

where the constant a of equation 1 has become equal to zero due to the arbitrary choice of the zero of the energy scale. Consequently, the three orbital electronegativities of interest are

$$\begin{aligned} X(0) &= \frac{1}{2}(3I_V - E_V) \\ X(1) &= \frac{1}{2}(I_V + E_V) \\ X(2) &= \frac{1}{2}(3E_V - I_V) \end{aligned}$$

Since the three points above describe necessarily a straight line, the bond electronegativities are simultaneously completely defined. The quantities I_V and E_V for the elements of the first two rows of the periodic system have been reported previously, and for the transition series they are in process of publication. The magnitude of the previously reported orbital electronegativities remains unchanged by the new definition. (11) The orbital electronegativities of vacant orbitals and lone pairs, up to now unobtainable, are given in Tables III and IV for the elements of interest of the first two rows of the periodic system.

Computation of the energy of group electronegativities is considerably more difficult. Thus examination of Figure 3 shows that, in addition to the valence states of Be^+ , Be^0 and Be^- , valence states of Be^{2+} and Be^{2-} are required. Be^{2+} produces no problems, and the energies have actually been calculated and reported. But we already had a problem of obtaining values for Be^- , since we required extrapolations. The situation becomes much more serious in the case of multiply negative ions, since no observations are available, and consequently no reasonable extrapolation schemes appear available.

TABLE III

ELECTRONEGATIVITY OF VACANT ORBITALS

Occupied orbitals	X_{σ}^0	X_{π}^0	X_{σ}^0	X_{π}^0
	Be		Mg	
sp	..	0.10	..	0.24
pp	1.81	- .30	1.75	- .43
didid	..	.02	..	.20
di π	1.30	- .10	1.21	- .10
π π	0.97	..	0.79	..
trtr	.94	-0.07	.91	0.00
tr π	.79	..	.67	..
tete	.64	..	.58	..
	B		Al	
spp	..	1.06	..	0.82
ppp	3.67	..	3.52	..
didid π	..	1.18	..	0.98
trtrtr	..	1.22	..	1.03
trtr π	2.59	..	2.16	..
tetete	2.32	..	1.93	..

TABLE IV
ELECTRONEGATIVITIES OF LONE PAIRS

Occupied orbitals	X_{σ}^2	X_{π}^2	X_{σ}^2	X_{π}^2
	N		P	
s^2_{ppp}	5.66	..	3.68	..
sp^2_{pp}	..	1.21	..	1.88
$di^2_{di\pi\pi}$	2.26	..	2.08	..
$didi\pi^+\pi$	..	1.05	..	1.59
$tr^2_{trtr\pi}$	1.58	..	1.73	..
$trtrtr\pi^2$	..	0.99	..	1.49
te^2_{tetete}	1.32	..	1.59	..
	O		S	
$spp^2_{p^2}$	..	2.04	..	1.71
$s^2_{p^2pp}$	7.44	1.42	4.52	1.50
$didi\pi^2\pi^2$	..	1.92	..	1.76
$di^2_{di\pi^2\pi}$	3.56	1.73	2.60	1.60
$di^2_{di^2\pi\pi}$	3.75	..	2.59	..
$trtrtr^2\pi^2$	2.74	1.78	2.21	1.66
$tr^2_{tr^2tr\pi}$	2.81	..	2.16	..
$te^2_{te^2tete}$	2.45	..	2.01	..
	F		Cl	
$sp^2_{p^2p^2}$	..	2.28	..	2.54
$s^2_{p^2p^2p}$	9.10	2.26	6.52	2.10
$didi^2\pi^2\pi^2$	4.50	2.27	3.90	2.32
$di^2_{di^2\pi^2\pi^2}$	4.96	2.26	3.98	2.10
$trtr^2_{tr\pi^2}$	3.70	2.28	3.30	2.25
$tr^2_{tr^2tr^2\pi}$	3.90	..	3.28	..
$te^2_{te^2te^2te}$	3.32	..	3.00	..

For the case of $\text{Be}(\text{di}_1^n \text{di}_2^1)$ illustrated in Figure 3 a very reasonable approximation method is available, which depends on the following consideration: The energy of the state $\text{di}_1^n \text{di}_2^2$, which can, according to Figure 3, be obtained only by an interpolation of a curve, which requires $\text{di}_1^2 \text{di}_2^2$ e.e., Be^{2-} , is given by

$$E(\text{di}_1^n, \text{di}_2^2) = (2 + n)I + J_{11} + 2nJ_{12} - nK_{12}$$

where the I, J and K are the usual integrals involved in the calculations of atomic energies. Similarly, the energy of the state $\text{di}_1^n - 1 \text{di}_2^1$ is given by

$$E(\text{di}_1^{n-1} + 1 \text{di}_2^1) = (2 + n)I - nJ_{11} + (n + 1)J_{12} - \frac{1}{2}(1 + n)K_{12}$$

Hence the energy difference between these two states, ΔE , is given by

$$\begin{aligned} E &= (1 - n)J_{11} - (1 - n)J_{12} + \frac{1}{2}(1 - n)K_{12} \\ &= (1 - n)L \end{aligned}$$

where $L = J_{11} - J_{12}/2$. Since each of the integrals J_{ij} and K_{ij} is a function of configuration, total number of electrons and nuclear charge, the function L just defined is a function of these quantities. Since it has long been shown that the different Slater-Condon parameters and hence the electron interaction integrals J and K can be reasonably extrapolated within an isoelectronic sequence, (8) it follows that the same is true for L. But the L's for the isoelectronic sequence B^- , C, N^+ and O^{2+} can be obtained as the energy difference of the equivalent two states.

There is one flaw in the above derivation: if $n > 1$, the second state, $\text{Be}(\text{di}_1^{n-1} + 1 \text{di}_2^1)$, is a state violating the Pauli principle, and cannot be dealt with. For cases of this type, another procedure is possible. In order to establish the desired quadratic equations, any three points are sufficient. When, as is the case for $\text{Be}(\text{di}_1^2 \text{di}_2^2)$, the energy value cannot be obtained, one may well establish the curve by use of three points, $n = 0$, $n = 1$, and an intermediate value, which is obtained by the method described in the preceding paragraph. Although this procedure is liable to greater uncertainties, it appears satisfactory.

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- (11) The XM values of (1) should be divided by 2, since reported for XM is $I_v - E_v$ and not $(I_v - E_v)/2$.

APPENDIX III

Electronegativity

III. Orbital Electronegativities and Electron Affinities of Transition Metals

by Jurgen Hinze and H. H. Jaffe

The orbital electronegativities of the neutral transition metals of the first transition series have been calculated by the Mulliken formula for a wide variety of hybrid states. The electron affinities needed in the process have been calculated by isoelectronic and iso-configurational extrapolation.

Orbital Electronegativities

In the first article (1) of this series electronegativities have been evaluated and reported for a variety of valence states of the neutral elements of rows one and two of the periodic system. Mulliken's definition (3) of electronegativity, given as

$$\chi = \frac{I + E}{2} \quad (1)$$

has been used for the evaluation since this definition has the best theoretical foundation (4,5) and can account sensitively for any valence state variations, provided the appropriate valence state ionization potentials and valence state electron affinities are used. In the second article (2) of this series the entire much-confused concept of electronegativity has been reinvestigated, and the following conclusions have been reached:

(a) Electronegativity is the property, not of an atom, but of an orbital of an atom in its valence state.

(b) The values of such orbital electronegativities depend strongly on the valence state considered, and, in the case of hybrids between s and p electrons, increase linearly with increasing s character of the hybrid orbital considered.

(c) Orbital electronegativity has meaning only for an orbital before it has formed a bond.

For the analogous but distinctly different property of an orbital after bond formation and charge exchange the term bond electronegativity is suggested.

(d) Mulliken's definition does not yield orbital electronegativities of vacant (virtual) orbitals or doubly occupied orbitals. However, a new definition was arrived at which includes Mulliken's definition as a special case for singly occupied orbitals. This definition was given as

$$x_j = \partial E(n_j) / \partial n_j \quad (2)$$

where n_j is the occupation of the orbital considered, j , and E is the energy of the atom as a function of this occupation. The energy relation postulated for this function is

$$E = a + bn_j + cn_j^2, \quad (3)$$

in which the constants a , b , and c can be determined from the known valence state ionization potentials and electron affinities. With this definition it is possible to evaluate orbital electronegativities for vacant and doubly occupied orbitals, and for partially charged atoms and groups. Combination of (2) and (3) gives Equation (1) for singly occupied orbitals, i.e., $n = 1$.

It is the purpose of this work to examine the dependence of the orbital electronegativity in the transition series on the valence state, not oxidation state. Here the picture is considerably complicated by the much larger variety of possible hybrids due to the availability of d orbitals. Computations of orbital electronegativities for a few hybrids of the transition elements have already been done (6), but the need for a more extensive investigation becomes apparent if it is realized that a priori quantum mechanical computations do not readily yield answers for molecules containing transition elements, since such systems are too complex. It is possible, however, to obtain valuable information in such complex systems by different semiempirical methods, such as ligand field theory (5), Mulliken's "Magic Formula" (7), or various forms of molecular orbital theory. Such semiempirical methods can make good use of electronegativities as well as valence state ionization potentials, electron affinities, and promotion energies, all of which are obtained and reported in this work.

The essential part of the evaluation of orbital electronegativities, following Equation (1), is the determination of the valence ionization potentials, I_v , and valence state electron affinities, E_v . The valence state ionization potentials are obtained by subtracting of the atom P^0 , and of the positive ion, P^+ , respectively. Analogously the valence state electron affinities are obtained by adding and subtracting to the ground state electron affinities the promotion energies of the atom, P^0 , and negative ion, P^- , respectively. Methods for the computation of promotion energies of atoms and positive ions are known (5), and ground state ionization potentials obtainable from spectroscopy are tabulated (10), hence the evaluation of valence state ionization potentials is straightforward. However, difficulties arise in the evaluation of valence state electron affinities. The promotion energy of negative ions, although not directly obtainable, can be extrapolated, as generally done, from isoelectronic sequences (5). However, no ground state electron affinities of the transition elements are available, consequently such values had to be determined in this work, as described in Part I (5).

Procedure

The computations of the promotion energies and hence the valence state ionization potentials and electronegativities are in general the same as described in detail in the first paper of this series (5).

(1) The hybrids listed in Table I, to which the computations are confined, are constructed using group theory and the procedure outlined by Kimball (8).

(2) The valence state promotion energies for these hybrids are evaluated using the method of Mulliken (12) and Van Vleck (18), i.e., the valence state energies are expressed as linear combinations of Slater parameters, the valence state equations. (11)

(3) Substitution of the Slater parameters, Table II, into the valence state equations derived gives the promotion energies required of atoms, positive ions, and negative ions, P^0 , P^+ , and P^- , respectively.

(4) The valence state ionization potentials and electron affinities are obtained from the corresponding ground state potentials, Table III, as

$$I_v = I_g + P^- - P^0$$

and

$$E_v = E_g + P^0 - P^-.$$

TABLE II

THE HYBRIDS CONSIDERED

<u>Point group</u>	<u>Configuration</u>	<u>Orbitals</u>	<u>Geometry</u>
Two-orbital hybrids			
D _{∞h}	(sp)	$\frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}z$	Linear
D _{∞h}	(dp)	$\frac{1}{\sqrt{2}}\sigma + \frac{1}{\sqrt{2}}z$	Linear
C _{2v}	(p ²)	x, y	Rectangular
C _{2v}	(ds)	$\frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}$	Rectangular
C _{2v}	(d ²)	$\frac{1}{\sqrt{2}}\sigma + \frac{1}{\sqrt{2}}$	Rectangular
Three-orbital hybrids			
D _{3h}	(sp ²)	$\frac{1}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}x$ $\frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}x + \frac{1}{2}y$	Trigonal planar
D _{3h}	(dp ²)	$-\frac{1}{\sqrt{3}}\sigma + \frac{\sqrt{2}}{\sqrt{3}}x$ $-\frac{1}{\sqrt{3}}\sigma - \frac{1}{\sqrt{6}}x + \frac{1}{\sqrt{2}}y$	Trigonal planar
D _{3h}	(d ² s)	$\frac{1}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}\sigma$	Trigonal planar
D _{3h}	(d ³)	$\frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}\sigma + \frac{1}{\sqrt{2}}\sigma'$ $-\frac{1}{\sqrt{3}}\sigma + \frac{\sqrt{2}}{\sqrt{3}}\sigma$ $-\frac{1}{\sqrt{3}}\sigma - \frac{1}{\sqrt{6}}\sigma + \frac{1}{\sqrt{2}}\sigma'$	Trigonal planar
C _{3v}	(d ² p)*	$\frac{1}{\sqrt{3}}z + \frac{\sqrt{2}}{\sqrt{3}}$ $\frac{1}{\sqrt{3}}z - \frac{1}{\sqrt{6}} + \frac{1}{\sqrt{2}}\sigma'$	Trigonal planar

TABLE II (cont'd.)

<u>Point group</u>	<u>Configuration</u>	<u>Orbitals</u>	<u>Geometry</u>
Four-orbital hybrids			
T_d	(sp^3)	$\frac{1}{2} (s + x + y + z)^\dagger$	Tetrahedral
T_d	(d^3s)	$\frac{1}{2} (s + \pi + \pi - \delta)^\dagger$	Tetrahedral
D_{4h}	(dsp^2)	$\frac{1}{2} (s + x + y + \delta)^\dagger$	Square planar
D_{4h}	(d^2p^2)	$\frac{1}{2} (\sigma + x + y + \delta)^\dagger$	Square planar
C_{3v}	(d^2sp)	$\frac{1}{2} (s + z + \delta - \delta')$	Trigonal pyramid
C_{3v}	(dp^3)	$\frac{1}{2} (\sigma + x + y + z)^\dagger$	Trigonal pyramid
C_{3v}	(d^3p)	$\frac{1}{2} (\sigma + \pi + \pi' + z)^\dagger$	Trigonal pyramid
C_{4v}	(d^4)	$\frac{1}{2} (\sigma + \delta + \pi + \pi')^\dagger$	Tetragonal pyramid
Five-orbital hybrids			
D_{3h}	$(dsp^3)^\dagger$	$0.314s - 0.485\sigma + \frac{\sqrt{2}}{3}x$ $0.314s - 0.485\sigma - \frac{1}{\sqrt{6}}x + \frac{1}{\sqrt{2}}y$ $0.594s + 0.384\sigma + \frac{1}{\sqrt{2}}z$	Trigonal bipyramid
D_{3h}	$(d^3sp)^*$	$\frac{1}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}\delta$ $\frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}\delta + \frac{1}{\sqrt{2}}\delta'$ $-\frac{1}{\sqrt{2}}\sigma + \frac{1}{\sqrt{2}}z$	Trigonal bipyramid

TABLE II (cont'd.)

<u>Point group</u>	<u>Configuration</u>	<u>Orbitals</u>	<u>Geometry</u>
C _{4v}	(d ² sp ²)†	$0.059s - 0.496\sigma^+ \frac{1}{\sqrt{2}}x + \frac{1}{2}\delta$ $0.059s - 0.496\sigma^+ \frac{1}{\sqrt{2}}y + \frac{1}{2}\delta$ $0.993s + 0.117\sigma^-$	Tetragonal pyramid
C _{4v}	(d ⁴ s)	$\frac{1}{\sqrt{5}}s - \frac{1}{\sqrt{20}}\sigma^+ \frac{1}{\sqrt{2}}x + \frac{1}{2}\delta$ $\frac{1}{\sqrt{5}}s - \frac{1}{\sqrt{20}}\sigma^+ \frac{1}{\sqrt{2}}y + \frac{1}{2}\delta$ $\frac{1}{\sqrt{5}}s + \frac{2}{\sqrt{5}}\sigma^-$	Tetragonal pyramid
C _{4v}	(d ⁴ p)	$\frac{1}{\sqrt{5}}z - \frac{1}{\sqrt{20}}\sigma^+ \frac{1}{\sqrt{2}}x + \frac{1}{2}\delta$ $\frac{1}{\sqrt{5}}z - \frac{1}{\sqrt{20}}\sigma^+ \frac{1}{\sqrt{2}}y - \frac{1}{2}\delta$ $\frac{1}{\sqrt{5}}z + \frac{2}{\sqrt{5}}\sigma^-$	Tetragonal pyramid
Six-orbital hybrids O _h	(d ² sp ³)	$\frac{1}{\sqrt{6}}s^+ - \frac{1}{\sqrt{2}}z + \frac{1}{\sqrt{3}}\sigma^-$ $\frac{1}{\sqrt{6}}s^+ - \frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{12}}\sigma^+ + \frac{1}{2}\delta$ $\frac{1}{\sqrt{6}}s^+ \pm \frac{1}{\sqrt{2}}y - \frac{1}{\sqrt{12}} - \frac{1}{2}\delta$	Octahedral

* No choice of coefficients yields equivalent orbitals; thus, standard coefficients are chosen.

† The coefficients are chosen so that all orbitals are equivalent, i.e., yield the same overlap integral in an iron (Ψ) - carbon (sp³) bond.

‡ The other three hybrids are given by the same combination, but with signs: ++-- , +-+- , +--+ .

TABLE I

SLATER-CONDON PARAMETER USED

Part 1

	(d^n)	$(d^{n-1}s)$	$(d^{n-1}p)$	$(d^{n-2}s^2)$	$(d^{n-2}sp)$	$(d^{n-2}p^2)$
Ca	46,662	21,103	37,840	0	19,458	40,097
Sc	41,958	18,588	38,349	101	21,821	(47,811)
Ti	51,825	25,988	46,945	7,689	32,161	(60,386)
V	59,273	35,556	69,532	18,052	58,439	(97,125)
Cr	70,925	64,771	84,588	46,520	80,396	(114,300)
Mn	67,566	64,119	104,024	71,228	105,667	(144,437)
Fe	43,472	34,343	65,528	44,665	88,375	(132,000)
Co	27,886	18,226	47,518	31,157	(68,610)	(106,000)
Ni	14,729	2,071	32,071	14,763	(58,653)	(102,000)
Cu	---	0	30,701	12,020	(66,683)	(121,000)
Sc ⁺	11,282	1,323	28,966	11,736	47,473	(77,574)
Ti ⁺	16,059	10,904	41,374	25,100	64,399	(104,000)
V ⁺	32,569	29,801	61,053	(35,000)	75,088	(115,000)
Cr ⁺	61,815	58,593	95,001	69,088	(110,000)	(151,000)
Mn ⁺	52,752	71,029	111,343	90,809	(134,000)	(180,000)
Fe ⁺	29,330	56,713	104,727	108,061	(155,000)	(210,000)
Co ⁺	(13,354)	(46,767)	(88,585)	(95,556)	(140,000)	(186,000)
Ni ⁺	603	26,584	75,184	(90,000)	(145,000)	(200,000)
Cu ⁺	0	24,457	72,907	86,979	139,358	(193,000)
Ca ⁻	67,857	26,272	35,324	-24,898	-20,757	-8,378
Sc ⁻	71,081	22,175	32,837	-19,622	-10,766	5,772
Ti ⁻	56,731	12,519	44,063	-32,984	6,878	43,250
V ⁻	89,098	58,513	57,833	2,231	26,792	48,600
Cr ⁻	105,802	71,525	103,321	34,395	56,334	78,874
Mn ⁻	73,590	21,919	42,471	-6,226	36,750	78,000
Fe ⁻	55,169	9,868	19,852	-27,686	-7,780	12,000
Co ⁻	29,458	-20,315	-8,765	-57,453	-22,052	11,000

TABLE I

Part 2

F2(pp)	F2(pd)	F2(dd)	F4(dd)	G1(pd)	G3(pd)	G1(sp)	G2(sd)
93	108	(400)	(10)	364	8	4,195	746
(200)	68	580	22	182	32	2,744	1,095
(220)	229	770	47	326	26	2,092	1,534
(240)	786	747	51	1,169	114	3,618	1,813
(260)	35	953	82	3	14	10,320	1,462
(280)	217	1,141	97	914	-14	2,841	1,192
(300)	211	1,190	76	24	36	4,078	1,285
(320)	201	1,408	119	159	0	(2,500)	1,143
(340)	130	1,629	121	200	16	(3,000)	1,339
(360)	315	---	---	391	35	(6,200)	(1,600)
(300)	242	737	51	380	3	8,243	1,218
(350)	434	797	32	450	32	7,275	1,182
(370)	382	961	70	310	36	5,690	1,942
(390)	459	1,051	81	483	58	(7,000)	1,747
(410)	(350)	480	134	1,660	12	(13,000)	1,302
(430)	319	1,346	113	261	30	(4,000)	1,591
(450)	353	(1,500)	(120)	(250)	(30)	(4,000)	(1,237)
(470)	342	1,637	122	238	32	(4,000)	1,541
(490)	159	1,720	132	266	21	7	2,894
50	-298	363	12	-86	32	-1,787	378
70	76	579	24	342	16	-1,506	1,126
90	1,113	443	21	1,855	170	236	1,879
110	-280	1,426	30	-1,654	16	7,640	1,622
130	115	936	81	1,567	-289	1,682	793
150	69	880	32	-202	12	4,156	1,333
170	60	1,179	116	80	-32	1,000	745
190	101	1,538	110	134	11	5,993	-216

TABLE III
GROUND STATE ELECTRON AFFINITIES AND
IONIZATION POTENTIALS

<u>Element</u>	<u>E_g (ev)</u>	<u>I_g (ev)</u>
Ca	0.11	6.11
Sc	0.46	6.56
Ti	1.25	6.83
V	1.19	6.74
Cr	3.54	6.76
Mn	1.17	7.34
Fe	3.13	7.90
Co	3.29	7.86

Finally, the orbital electronegativities are given in Mulliken's scale as

$$x_M = \frac{I_v + E_v}{2},$$

which are converted to Pauling units by (4):

$$x_p = 0.336(x_M - 0.615). \quad (4)$$

The Slater Parameters

The Slater parameters used for the evaluation of the valence state promotion energies of atoms and positive ions are those obtained previously (3) by an extensive fitting of Slater equations to the corresponding observed atomic energy levels (10). For the evaluation of promotion energies more Slater parameters are needed than can be obtained from one configuration alone. Consequently it is necessary to use those Slater parameters which are obtained when several configurations are fitted simultaneously. This implies that equivalent parameters have the same value in different configurations. That this is not true is known. However, it has been shown (3) that the uncertainties inherent in Slater's treatment of the many-electron atom are not increased significantly by assuming that the Slater parameters are equal for different configurations. In fact, the representation of spectroscopic data by Slater's equations is often better if different configurations are considered simultaneously rather than any one configuration individually. Thus, in the level of the approximations necessary to use empirical Slater parameters, it is valid to use values obtained from fitting several configurations simultaneously. The values used are listed in Table II, where the values in parentheses, not obtainable directly, had to be estimated as follows.

The values of $G_1(sp)$ of Co, Ni, and Cr^+ through Ni^+ are estimated so that they follow the same general trend indicated by the parameters determined. The parameters $G_1(sp)$ and $G_2(sd)$ of Cu cannot be evaluated independently from the atomic energy levels observed; however, the parameter $G_1(sp) + G_2(sd)$ is obtained, which gives the value of $G_1(sp)$ after $G_2(sd)$ has been estimated. The values of $W(d^{n-2}sp)$ of Co, Ni, and Fe^+ are obtained by adding to the corresponding apparent of $W(d^{n-2}sp)$'s determined, which include some $G_1(sp)$, the values of $G_1(sp)$ estimated. Similarly the value of $W(d^{n-2}sp)$ of Mn^+ is obtained by adding to the value determined the values of $G_1(sp)$ and $F_2(pd)$ estimated.

The $W(d^{n-2}sp)$'s of Cr^+ , Co^+ , and Ni^+ as well as the $W(d^{n-2}s^2)$'s of V^+ and Ni^+ are determined so that they follow the trend indicated by the other parameters. Only the value of $F_2(pp)$'s must be assumed freely. Fortunately the $F_2(pp)$'s are known to be small and of no great importance here, since they will influence only the energies of valence states with several p electrons, and such states are rather high in energy anyway. With the $F_2(pp)$ assumed, it is possible to calculate the values of $W(d^{n-2}p^2)$ of the elements Sc, Ti, V, Mn, and Sc^+ from the apparent values computed which contain $-5F_2(pp)$. All other $W(d^{n-2}p^2)$ which had to be extrapolated are obtained from the relation

$$W(d^{n-2}p^2) = 2W(d^{n-2}sp) - W(d^{n-2}s^2), \quad (5)$$

which implies that the promotion of two s electrons to p electrons requires twice as much energy as the promotion of one. Here the change of the electronic interaction of the different configurations is neglected. This is not too serious, since the d electron configuration is kept constant and the other changes, involving only one electron pair, are small.

The values of $F_2(dd)$ and $F_4(dd)$ of Ca cannot be obtained separately, thus they had to be assumed inside the range of the values determined. The same is true for Co^+ , where the parameter obtained is $F_2(dd) - 5F_4(dd)$. Here $F_2(dd)$ is calculated after $F_4(dd)$ has been assumed. The assumed $F_4(dd)$ of Co^+ permits also the evaluation of $G_2(sd)$ from the parameter $G_2(sd) + 21F_4(dd)$ computed. With the values of $G_1(pd)$ and $G_3(pd)$ which have been estimated for Co^+ it is finally possible to calculate the values of $W(d^n)$, $W(d^{n-1}s)$, $W(d^{n-1}p)$, and $W(d^{n-2}s^2)$ from the parameters obtained from spectral data, $W(d^n) - 49F_4(dd)$, $W(d^{n-1}s) - 147F_4(dd)$, $W(d^{n-1}p) - 18G_1(pd) - 189G_3(pd) - 147F_4(dd)$, and $W(d^{n-2}s^2) - 294F_4(dd)$, respectively.

The Slater parameters for negative ions cannot be determined from spectral data, since no spectra of negative ions are observed. Their magnitude is extrapolated linearly from the corresponding parameters of atom and positive ion in an isoelectronic sequence. Such a linear relation has been shown for lighter elements by Rohrllich (16) and is here assumed to hold also for the transition series, since there is no other method on hand to estimate the parameters or valence state promotion energies of negative ions. However, it must be pointed out that the Slater parameters of negative ions reported in Table II are relatively uncertain, since only two known numbers in an isoelectronic sequence could be used for the extrapolation.

Furthermore, it should be noted that the W's given for negative ions have no absolute significance, since they are not based on the ground state of the negative ions; the same is true for the valence state promotion energies reported for negative ions.

Results

The present paper considers only the elements Ca through Cu, and the ions Sc^+ through Cu^+ . This restriction is necessary because of the limitations of experimental information on spectroscopic states involving incompletely filled d shells; for other elements of the third period the evaluation of the Slater-Condon parameters needed is not possible. Consequently, P^- values, and hence electronegativities of d-hybrid orbitals are obtainable only for the elements Sc to Co.

In Table IV the resulting orbital electronegativities of these elements are given in Pauling's units together with the corresponding promotion energies P^0 , P^+ , and P^- and the valence state ionization potentials and electron affinities, I_v and E_v , respectively.

There are numerous possible ways of distributing the non-valence electrons of the valence shell. Only distributions of maximum multiplicity have been considered, in keeping with Hund's rule, except where the s orbital is not included in the hybrid; s^2 configurations were also considered. In no case was occupation of hybrid orbitals by valence electrons considered.

Computations have been made for all possible arrangements of the non-bonding electrons in the available orbitals. Reported, however, are only those arrangements of the non-valence electrons which give rise to the lowest promotion energy of the atom. (9) These distributions of the electrons in the orbitals not involved in hybridization are given in column 3 of Table IV.

Ground State Electron Affinities

The extensive efforts made to evaluate or determine electron affinities have been carefully reviewed by Pritchard (15), but in spite of all attempts no electron affinities of transition elements have been reported so far. Experimental and extrapolation methods seem to fail; the previous, as well as the more recently derived, extrapolation methods (7), (1) are reported to hold only for the first two rows of the periodic system. The method of Ginsberg and Miller (2), which they claim will hold for heavier elements as well, cannot be applied in the transition series.

TABLE IV

ELECTRONEGATIVITIES OF TRANSITION METALS

<u>Ele- ment</u>	<u>Hy- brid</u>	<u>Configu- ration</u>	<u>P⁰</u>	<u>P⁺</u>	<u>P⁻</u>	<u>I_v</u>	<u>E_v</u>	<u>X</u>
Sc	sp ²	000000	3.58	6.70	-6.35	9.68	7.36	2.66
	dp ²	000000	5.31	5.96	-1.29	7.21	4.03	1.68
	d ² s	000000	2.41	0.68	1.43	4.82	-1.60	0.33
	d ³	000000	4.48	1.04	7.98	3.12	-6.08	-0.69
	d ² p	000000	5.01	3.09	3.28	4.64	-0.85	0.43
Ti	sp	100010	2.68	2.20	-3.86	6.36	2.70	1.32
	dp	001010	4.55	2.53	1.89	4.81	-1.19	0.40
	p ²	100010	6.11	4.08	-2.21	4.80	4.48	1.35
	ds	011000	1.63	0.57	-2.36	5.77	0.15	0.79
	d ²	001010	4.23	1.00	5.59	3.59	-5.21	-0.47
	sp ²	000010	6.22	8.85	-3.76	9.46	6.14	2.41
	dp ²	000010	6.74	7.42	-1.65	7.51	4.55	1.82
	d ² s	100000	2.05	0.81	-1.18	5.59	-0.62	0.63
	d ³	001000	4.43	1.12	5.73	3.52	-5.15	-0.47
	dsp	100000	3.17	3.55	-2.59	7.21	1.91	1.33
	d ² p	100000	4.93	3.53	1.67	5.43	-0.59	0.61
	sp ³	000000	11.21	19.77	-3.68	15.39	11.04	4.23
	d ³ s	000000	1.91	0.95	-1.00	5.88	-0.93	0.62
	dsp ²	000000	6.64	11.63	-3.21	11.82	6.00	2.79
	d ² p ²	000000	6.88	9.06	-1.51	9.01	4.55	2.07
	d ² sp	000000	3.96	5.52	-2.69	8.39	2.81	1.67
	dp ³	000000	10.87	16.22	-3.40	12.19	10.43	3.59
	d ³ p	000000	5.49	4.52	3.02	5.86	-1.38	0.55
	d ⁴	000000	4.43	1.09	5.75	3.48	-5.17	-0.48
V	sp	100110	3.67	3.07	-1.41	6.13	2.18	1.19
	dp	001110	4.47	3.03	2.87	5.30	-1.32	0.46
	p ²	101010	7.34	5.06	4.39	4.46	0.04	0.55
	ds	011010	3.36	0.57	7.39	3.95	-6.95	-0.70
	sp ²	100010	8.15	9.12	2.78	7.71	2.46	1.50
	dp ²	001010	7.73	8.21	4.77	7.22	0.04	1.01
	d ² s	011000	1.92	1.41	1.52	6.23	-2.52	0.41
	d ³	011000	3.77	1.10	8.00	4.07	-7.15	-0.71
	d ² p	011000	5.33	4.22	4.56	5.63	-2.15	0.38

TABLE IV (cont'd.)

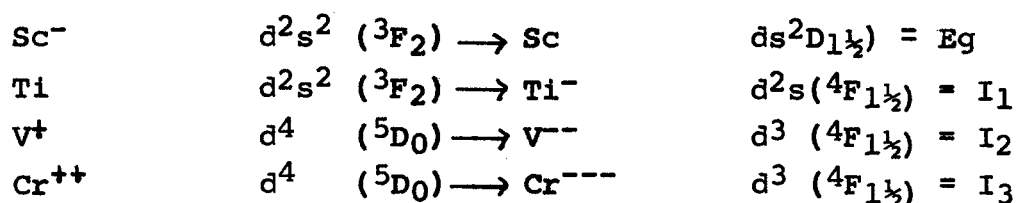
Element	Hybrid	Configuration	P^0	P^+	P^-	I_V	E_V	X
	sp^3	100000	14.14	18.29	10.99	10.89	0.23	1.66
	d^3s	000010	2.15	2.03	1.79	6.63	-2.56	0.48
	dsp^2	100000	8.26	11.42	3.11	9.89	2.24	1.83
	d^2p^2	001000	7.74	9.99	5.15	8.99	-0.33	1.25
	d^2sp	100000	4.76	6.10	0.79	8.08	1.05	1.33
	dp^3	000010	11.96	15.90	9.63	10.68	-0.59	1.49
	d^3p	000010	5.26	5.02	5.11	6.49	-2.77	0.42
	d^4	000010	3.97	1.37	8.30	4.14	-7.24	-0.72
	dsp^3	000000	14.20	20.34	11.05	12.88	0.23	1.99
	d^3sp	000000	4.37	7.53	1.44	9.91	0.01	1.46
	d^2sp^2	000000	8.46	12.75	4.14	11.02	1.40	1.88
	d^4s	000000	2.16	2.09	2.13	6.66	-2.89	0.43
	d^2p^3	000000	11.89	16.55	9.81	11.41	-0.84	1.57
	d^4p	000000	5.43	5.60	5.00	6.91	-2.48	0.54
Cr	sp	011110	3.84	4.32	-5.72	7.24	10.19	2.72
	dp	011110	4.72	3.74	4.19	5.79	1.15	0.96
	p^2	111010	8.58	6.48	-0.69	4.66	9.90	2.24
	ds	111010	1.59	1.61	1.23	6.78	0.98	1.10
	d^2	011020	5.69	3.68	11.52	4.74	-5.21	-0.27
	sp^2	011010	10.78	11.40	-9.84	7.38	21.25	4.60
	dp_2	011010	10.11	10.02	1.64	6.67	9.10	2.44
	d^2s	111000	2.55	2.86	3.13	7.07	.04	0.99
	d^3	012000	5.97	4.04	11.74	4.83	-5.15	-0.25
	d^2p	111000	5.81	5.99	5.96	6.94	0.47	1.04
	sp^3	100010	21.30	21.13	-13.98	6.59	35.91	6.93
	d^3s	100010	2.98	3.44	4.04	7.22	-0.44	0.93
	dsp^2	011000	12.29	14.16	-7.77	8.63	20.69	4.72
	d^2p^2	000002	10.61	13.16	5.76	9.31	5.47	2.28
	d^2sp	011000	6.35	8.34	-0.92	8.75	7.90	2.59
	dp^3	000002	16.51	18.79	0.98	9.04	16.16	4.03
	d^3p	000110	6.41	6.81	6.39	7.16	0.64	1.10
	d^4	000020	5.97	4.07	11.71	4.86	-5.12	-0.24
	dsp^3	000010	22.71	23.68	-11.72	7.74	35.06	6.98
	d^3sp	001000	7.03	10.38	-0.54	10.10	8.21	2.87
	d^2sp^2	001000	13.81	16.04	-5.01	8.99	19.44	4.57
	d^4s	000010	3.33	3.90	4.67	7.33	-0.72	0.90
	d^4p	000010	6.65	7.42	6.85	7.53	0.42	1.13
	d^2sp^3	000000	23.32	25.63	-11.58	9.08	35.53	7.29

<u>Ele- ment</u>	<u>Hy- brid</u>	<u>Configu- ration</u>	<u>P⁰</u>	<u>P⁺</u>	<u>P⁻</u>	<u>I_v</u>	<u>E_v</u>	<u>X</u>
Mn	sp	111110	3.44	3.22	-10.67	7.22	10.41	2.75
	dp	011120	6.96	5.57	-1.44	6.04	4.70	1.60
	p ²	111110	8.01	5.36	-20.89	4.78	25.20	4.83
	ds	211010	3.56	3.51	-1.67	7.38	1.52	1.29
	d ²	012002	4.86	7.20	17.30	9.77	-16.15	-1.27
	sp ²	110110	10.80	11.90	-18.61	8.53	25.71	5.55
	dp ²	011110	9.86	9.87	-15.32	7.44	21.48	4.65
	d ² s	211000	4.31	4.45	0.10	7.57	0.50	1.15
	d ³	022000	6.58	5.00	8.91	5.85	-6.04	-0.23
	d ² p	211000	8.06	7.52	0.65	6.89	3.71	1.57
	sp ³	011010	19.85	24.55	-32.08	12.12	48.23	9.93
	d ³ s	100020	4.68	5.05	1.37	7.80	-0.40	1.04
	dsp ²	011010	12.07	15.54	-15.35	10.91	23.72	5.61
	d ² p ²	011010	10.88	12.40	-12.30	8.95	19.48	4.57
	d ² sp	111000	6.47	8.52	-5.29	9.48	8.06	2.74
	dp ³	011010	18.00	20.45	-29.89	9.89	44.18	8.88
	d ³ p	000120	8.13	7.91	1.73	7.20	2.69	1.45
	d ⁴	000012	3.21	8.43	-2.83	12.66	2.34	2.31
	dsp ³	001010	21.29	28.02	-29.51	14.17	47.09	10.09
	d ³ sp ²	011000	6.71	10.75	-3.09	11.46	6.10	2.74
	d ² sp ²	001010	13.00	18.13	-14.07	12.56	23.37	5.83
	d ⁴ s	000020	4.71	5.21	1.74	7.93	-0.74	1.00
	d ² p ³	001010	18.78	21.72	-28.48	10.37	43.56	8.85
	d ⁴ p	000020	8.26	8.41	2.31	7.57	2.25	1.44
	d ² sp ³	000010	21.80	30.71	-26.71	16.34	44.81	10.06
	d ⁴ sp	100000	7.40	10.56	-3.21	10.59	6.91	2.73
	d ⁵ p	000001	7.09	10.94	-3.12	11.29	6.51	2.78
	d ³ p ³	001000	19.55	25.10	-24.90	12.98	40.75	8.82
Fe	sp	111120	1.57	2.87	-9.21	9.20	7.25	2.56
	dp	012120	5.59	4.94	-1.30	7.24	3.36	1.57
	p ²	211110	4.17	5.28	-13.55	9.02	14.18	3.69
	ds	211020	2.19	2.21	-2.85	7.92	1.50	1.38
	d ²	022020	4.56	2.76	6.84	6.10	-5.82	-0.15
	sp ²	111110	0.94	10.60	-16.05	17.56	13.46	5.00
	dp ²	011120	5.63	11.29	-10.07	13.55	12.17	4.11
	d ² s	122000	2.97	3.82	-1.44	8.75	0.87	1.41
	d ³	012002	2.31	8.59	-5.26	14.18	4.04	2.85
	d ² p	122000	6.23	7.43	0.01	9.10	2.68	1.77
	sp ³	011110	4.37	28.28	-20.45	31.82	21.29	8.71

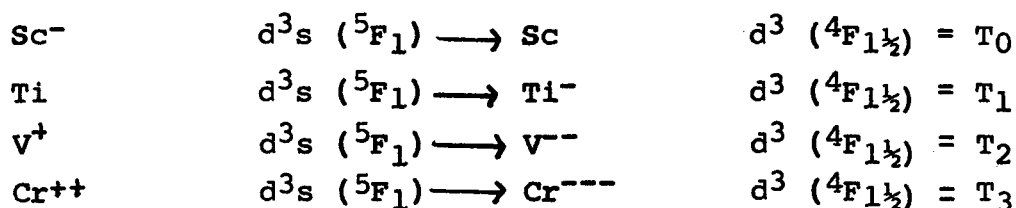
<u>Ele- ment</u>	<u>Hy- brid</u>	<u>Configu- ration</u>	<u>p⁰</u>	<u>p⁺</u>	<u>p⁻</u>	<u>I_v</u>	<u>E_v</u>	<u>X</u>
	d ³ s	200020	2.79	3.62	-0.81	8.73	0.07	1.27
	dsp ²	111010	2.80	16.09	-13.31	21.19	12.58	5.47
	d ² p ²	012010	6.39	14.29	-7.96	15.80	10.82	4.27
	d ² sp	211000	4.19	10.19	-5.29	13.90	5.96	3.13
	dp ³	011110	4.41	21.43	-20.46	24.92	21.34	7.57
	d ³ p	000220	6.69	8.82	0.89	9.94	2.26	1.84
	d ⁴	000022	2.31	8.63	-5.29	14.22	4.07	2.86
	dsp ³	011010	5.79	33.70	-18.40	35.81	20.66	9.28
	d ³ sp	012000	4.64	13.06	-3.94	16.32	5.05	3.38
	d ² sp ²	011010	3.84	19.99	-11.25	24.04	11.56	5.77
	d ⁴ s	000000	3.91	7.63	-2.81	11.61	3.19	2.28
	d ⁴ p	000012	4.23	19.50	-7.60	23.17	8.30	5.08
	d ² sp ³	001010	6.83	38.01	-16.48	39.08	19.78	9.68
	d ⁴ sp	200000	4.77	12.62	-4.11	15.75	5.35	3.34
	d ⁵ p	000002	4.25	20.19	-7.50	23.84	8.22	5.18
	d ³ p ³	011000	6.49	28.73	-16.38	30.14	19.35	8.11
Co	sp	211120	3.42	3.73	-6.73	8.18	4.73	1.96
	dp	022120	5.11	4.61	-2.41	7.36	2.10	1.38
	p ²	211120	7.11	6.02	-4.36	6.77	6.05	1.95
	ds	122020	1.56	2.34	-5.39	8.64	1.53	1.50
	d ²	012022	1.66	8.98	-7.66	15.18	3.90	3.00
	sp ²	111120	8.43	9.88	-3.42	9.31	6.42	2.43
	dp ²	012120	8.95	11.40	-3.17	10.31	6.70	2.65
	d ² s	222000	2.71	4.90	-3.86	10.04	1.15	1.67
	d ³	022002	1.66	9.17	-7.87	15.37	4.11	3.07
	dsp	211020	4.95	5.73	-4.82	8.64	4.35	1.97
	sp ³	111110	14.86	17.99	1.33	10.99	8.10	3.00
	dsp ²	211010	10.23	13.41	-2.79	11.05	7.60	2.92
	d ² p ²	022010	9.55	13.77	-2.44	12.08	6.57	2.92
	d ² sp	122000	6.04	9.06	-4.59	10.88	5.21	2.49
	dp ³	011120	14.13	20.47	-1.23	14.20	9.94	3.85
	dsp ³	011110	17.25	21.54	2.23	12.14	9.59	3.44
	d ³ sp	022000	6.16	10.94	-4.77	12.64	5.51	2.84
	d ² sp ²	012010	11.56	14.99	-1.47	11.30	7.61	2.97
	d ² p ³	011020	15.19	21.98	-0.05	14.65	9.82	3.90
	d ⁴ p	000022	8.26	13.91	-5.31	13.52	8.15	3.43
	d ² sp ³	011010	18.83	25.15	3.04	14.18	10.36	3.92
	d ³ p ³	012000	16.14	26.03	0.03	17.75	10.69	4.57

* The six numbers of this column refer, in order, to the number of electrons occupying the $d_{z^2} = \sigma$, $d_{xz} = \pi$, $d_{yz} = \pi'$, $d_{x^2-y^2} = \sigma'$, $d_{xy} = \delta'$, and s orbitals.

Most of the extrapolations of electron affinities described are based on a relation between the ionization potentials of atoms in successive states of ionization in an isoelectronic sequence. Such methods must fail when the ground states in the isoelectronic sequence considered are not identical, which is the case in the transition series. Generally such extrapolation formulas will require the use of equivalent ionizations in an isoelectronic sequence. This may be illustrated on the sequence of ionizations required to extrapolate the electron affinity of scandium. The corresponding ground state ionizations are:



A sequence of equivalent transitions, which could be used for the extrapolation is:



Generally, ionizations of type $d^ns \longrightarrow d^n$ have been chosen here for the equivalent transitions, since only in such cases are sufficient spectral data available.

Extrapolation Procedure

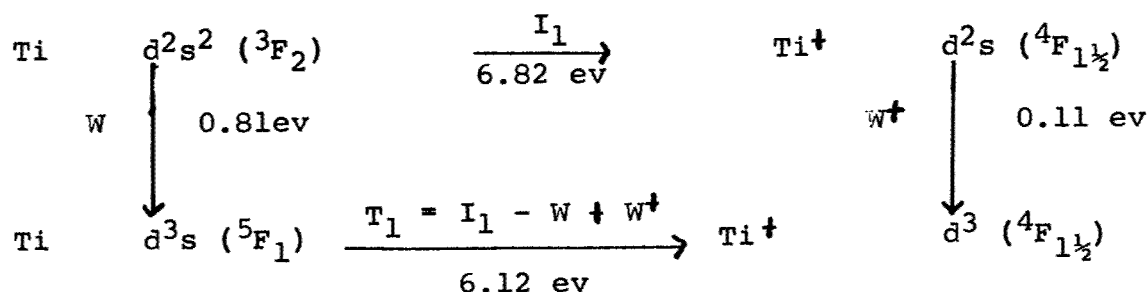
Edlen's extrapolation method (1) was chosen here since it appears to give the best representation with a minimum of initial information. The method suggested by Johnson and Rohrlich (7), apparently equally reliable, requires higher and more ionization potentials for the extrapolation, which is a decided disadvantage, especially in the transition series, where higher ionization potentials are quite uncertain. Edlen obtains the electron affinity T_0 from the successive equivalent ionizations T_1 , T_2 , and T_3 respectively by the following expression,

$$T_0 = 3T_1 - 3T_2 + T_3 + \frac{3\left(T_1 - 2T_2 - T_3 - \frac{2R}{n^2}\right)\left(-T_1 + 2T_2 - T_3 + \frac{6R}{n^2}\right)}{T_1 - 4T_2 + 3T_3 - \frac{12R}{n^2}} \quad (6)$$

where R is the Rydberg constant and n the principal quantum number.

Since equivalent ionization processes of an isoelectronic sequence should be used in this expression, it is necessary to reduce the ground state ionizations to such values. This is done by adding and subtracting the appropriate term values, W, to the ground state potentials.

In the above example we obtain,



The required ground state ionization potentials and term values are obtained from Moore's tables (10). The T values generally calculated for the transition $d^ns \rightarrow d^n$ are listed in Table V together with the T_0 values obtained by extrapolation.

A major difficulty is the determination of the ground state electron affinities from the calculated T_0 values. For this it is necessary to know the energy difference between the state considered of configuration d^ns and the ground state of the negative ion. These values must be calculated since no spectra of negative ions are observed. These energy differences have been evaluated by setting up the Slater equations of the required states and using the Slater-Condon parameters for the corresponding negative ions, Table II. The extrapolation of these parameters needed has been described above. In Table III the ground state electron affinities obtained are listed, together with the ground state ionization potentials of the same atoms.

Discussion

There are two major sources of error in the method described, and the electron affinities obtained cannot be expected to be highly accurate.

One uncertainty is introduced by the use of Edlen's extrapolation and the possible inaccuracy of the ionization potentials used. This uncertainty is believed to be small, an opinion supported by the small variation of the T_0 values extrapolated.

The second source of error is considerably more serious, as the method of obtaining the term values, W^- , for negative ions is much more doubtful. The linear extrapolation of Slater-Condon parameters from the corresponding isoelectronic sequence is quite questionable, especially since in many cases only two members of such a sequence are known. Unfortunately there exists no better simple method to obtain the values required.

In spite of such uncertainties inherent in the procedure, the values obtained are not only of the right order of magnitude, but they reflect also the changes and trends expected on chemical grounds. It is expected and observed that the values increase in going from Ca to V; the value calculated for Ti seems somewhat too large. The sudden rise observed for the electron affinity of Cr must be anticipated, since here the transition $d^5s^2 \longrightarrow d^5s$ gives rise to the ground state electron affinity, e.e., removal of an s electron, while in all other cases the transition is $d^ns^2 \longrightarrow d^{n-1}s^2$, removal of a d electron. The low value obtained for Mn appears reasonable because of the special stability of the half-filled shell. The removal of the extra d electron beyond the half-filled shell will not require much energy on account of the missing additional exchange energy of state d^6s^2 with respect to d^5s^2 .

The sudden rise to the values of Fe and Co seems to be too drastic and values about 1 ev lower would be anticipated in the light of the $Ca \longrightarrow V$ rise. This inconsistency is undoubtedly due to an overestimation of the term splitting of the negative ion. Unfortunately there is no method known at the moment by which more reliable values for the electron affinities of the transition metals can be obtained. But these roughly estimated values obtained here give at least a lead about magnitude and order, and are sufficient for the use in electronegativity calculations, for which purpose they have been determined. This is especially true here since the electronegativity computations are made especially to investigate the valence state dependence of the orbital electronegativities, and the differences between the electronegativities for different valence states of the same atom are not affected by the ground state electron affinities used. On the other hand, an uncertainty in the ground state electron affinity of 1 ev

results only in an error of 0.16 Pauling electronegativity units in the electronegativities computed. This weakens the comment frequently made about Mulliken's definition of electronegativity, saying, although Mulliken's definition is best justified and should give the most reliable values, it cannot be used since the electron affinities are not available. However, it will always be possible to estimate the electron affinities with an uncertainty limit of less than 1 ev.

It is remarkable to what degree the orbital electronegativities obtained depend on the hybrids considered. Unfortunately, due to the complexity of the hybrids, it is rather difficult to obtain a general and simple relation about the value of the orbital electronegativity as a function of s, p, or d character of the hybrids involved. Universally the electronegativities increase slightly with increasing s character of the orbitals and steeply with increasing p character. Similarly, the orbital electronegativity is generally higher for higher bonding valence states than for lower bonding ones. These increases, especially the steep increase with increasing p character, lead to some electronegativity values which are astonishingly high. Such are, for example, the values for the octahedral valence state d^2sp^3 of Cr, Mn, Fe, and Co. The explanation of such high values for just this valence state with an extremely high promotion energy cannot be given immediately. The meaning of these high values however will be investigated. Readily explainable are the unfamiliar high electronegativity values of other hybrids with high p character, and consequently high promotion energy. All these unstable hybrids can be substituted either completely or to any intermediate amount by other linear combinations of atomic orbitals, giving rise to more stable hybrids with the same geometry but electronegativities more in the familiar range. In this sense it is possible to substitute the unstable trigonal hybrids sp^2 and dp^2 by the hybrids d^2s or d^3 . The tetrahedral hybrid sp^3 can be substituted by the more stable d^3s ; actually any intermediate substitution of the three p orbitals by the corresponding d orbitals will lead to a tetrahedral hybrid. The low-energy hybrids d^3p and d^2sp can substitute for the unstable dp^3 . By substituting the s orbital by the d_{z^2} orbital, the high-energy dsp^2 hybrid can be reduced to the more stable d^2p^2 hybrid with the same symmetry; similarly the unstable dsp^3 hybrid is transformed into the low-energy d^3sp hybrid by substituting d for p orbitals.

A relation between the s, p, and d character of the hybrid orbitals and the electronegativity seems desirable. From the orbital electronegativity data given, the relation

$$x_h = a x_s + b x_p + c x_d \quad (7)$$

is suggested. Here x_h , x_s , x_p , and x_d are the orbital electronegativities of the hybrid, the s, p, and the d orbitals respectively, and a, b, and c give the amount of s, p, and d character respectively of the hybrid considered. From the data reported for different hybrids, the electronegativities of pure s, p, and d orbitals are easily evaluated using Equation 7, which in turn, with these electronegativities of the pure orbitals, can be used to evaluate the electronegativity of any intermediate and second-order hybrids. However, Equation 7 holds only if similar hybrids are considered, that means hybrids which will form the same number of bonds, and if the distribution of the non-valence electrons is equal.

TABLE V

ISOELECTRONIC ELECTRON AFFINITIES AND IONIZATION POTENTIALS

				T_1 (ev)	T_2 (ev)	T_3 (ev)	T_0 (ev)	
d^2s	($^4F_1$)	d^2	($^3F_2$)	5.71	13.57	23.86	0.74	Ca ⁻
d^3s	($^5F_1$)	d^3	($^4F_1$)	6.12	14.33	24.82	0.56	Sc ⁻
d^4s	($^6D_1$)	d^4	($^5D_0$)	6.48	15.01	25.94	0.75	Ti ⁻
d^5s	($^7S_3$)	d^5	($^6S_2$)	6.76	15.64	26.91	0.65	V ⁻
d^6s	($^6D_4$)	d^6	($^5D_4$)	7.09	16.18	27.73	0.85	Cr ⁻
d^7s	($^5F_5$)	d^7	($^4F_4$)	7.24	16.63	28.50	0.71	Mn ⁻
d^8s	($^4F_4$)	d^8	($^3F_4$)	7.43	17.11	29.29	0.62	Fe ⁻
d^9s	($^3D_3$)	d^9	($^2D_2$)	7.60	17.57	30.02	0.47	Co ⁻
$d^{10}s$	(^2s)	d^{10}	($^1s_0$)	7.72	17.96	30.70	0.33	Ni ⁻

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APPENDIX IV

Electronegativity IV

Orbital Electronegativities of the Neutral Atoms

of the Groups Three A and Four A

of Positive Ions of Groups One and Two

by Jurgen Hinze and H. H. Jaffe

The orbital electronegativities of the neutral atoms of the A elements of rows three and four, and of the monopositive ions of periods one and two are reported and briefly discussed.

In the preceding articles of this series, (1) electronegativity has been discussed, based on Mulliken's theoretically well justified (10), (11) definitions: (6)

$$X = \frac{I_v + E_v}{2} \quad (1)$$

This discussion leads to the conclusion that electronegativity is the property not of an atom, but of an orbital of an atom in a molecule. The electronegativities computed in the light of these considerations for the elements of the first and second rows of the periodic system and for the elements of the first transition series (5c) show that such orbital electronegativities are considerably dependent on the character of the orbitals considered, and differences of more than one Pauling unit in electronegativity of the same atom but different hybrid orbitals are no exception. Consequently, it seems of interest to have available orbital electronegativities for different valence states for the heavier elements also.

Furthermore, it has been indicated in the first article (5a) that, on the basis of Mulliken's definition, one has to expect considerably different electronegativity values for ions. To demonstrate this, and to make available orbital electronegativities of some positive ions we have computed such values for the elements of the first two rows of the periodic tables.

Procedure

The evaluation of the orbital electronegativities with Mulliken's definition has been described in detail in the first article of this series, (5a) and only a short outline will be given here. The essential part is the computation of the valence state ionization potentials, I_v , and electron affinities, E_v , or in the case of positive ions, the first and second valence state ionization potentials, I_v (1) and I_v (2), respectively.

a) Electronegativities of the neutral elements of rows three and four.

The valence state ionization potentials required are obtained from the ground state potentials, I_g , and the corresponding promotion of energies of the positive ion and atom, p^+ and p^0 , respectively, according to,

$$I_g = I_v - p^+ - p^0 \quad (2)$$

and analogously the valence state electron affinities are calculated from the ground state electron affinities, E_g , and the promotion energies of atom and negative ion, following,

$$E_v = E_g + p^0 - p^- \quad (3)$$

Here the valence state promotion energies represent the energies required to elevate an atom or ion to the valence state, which, as defined by van Vleck, (13) is the hypothetical "state" of an atom, chosen so that the interactions of the electrons of the atom are as nearly as possible the same as they would be if the atom is part of a molecule. The detailed description of the computation of such valence state promotion energies, following Mulliken's (10) and van Vleck's (13) method, has been given previously.

The Slater-Condon parameters, used here for the computation of the promotion energies, are those obtained and reported earlier. (7) It is again necessary to use the parameters determined from several configurations simultaneously, implying that equivalent parameters have the same value for the configurations. Although it is known that the assumption of the configuration independence of Slater-Condon parameters is questionable, it has been shown (7) that this assumption is acceptable on the level of the approximations inherent in the Slater-Condon treatment.

The promotion energies of the negative ions, which cannot be computed directly are obtained as described in the first article (5a) from a linear extrapolation of the corresponding promotion energies of successive states of ionization in an isoelectronic sequence. Such an extrapolation, however, is not possible for the promotion energies of Ca^- and Sr^- , since the necessary spectral information is not available for the isoelectronic positive ions. Consequently the promotion energies of Ca^- and Sr^- are estimated roughly, guided by the corresponding energies for Mg^- and Be^- , which are known. (5a) All the promotion energies computed and used for the evaluation of valence state ionization potentials and electron affinities are given in Table I.

Ground state ionization potentials, experimentally determined from spectral data, are accurately known. The values used here are chosen from Moore's tables. (9) Unfortunately, the ground state electron affinities are not so readily obtainable, and only the values for Br and I have been determined experimentally. (8) The values used for the other elements are those extrapolated by Ginsberg and Miller (4) The ground state ionization potentials and the electron affinities used are listed in Table II.

With the entries of Tables I and II, the valence state ionization potentials, valence state electron affinities, and the orbital electronegativities are really obtained using Equations 1, 2, and 3. The results are listed in Table III, where the last column gives the electronegativities in Pauling units, more familiar to the chemist. The transformation used is, (5a)

$$X_p = .336 (X_m - .615) \quad (4)$$

for orbital electronegativities of the positive ions of row one and two elements.

The evaluation of the orbital electronegativities for the positive ions of rows one and two of the periodic system is essentially the same as described above. However, it is much simplified, since the promotion energies required, of atoms, singly and doubly positive ions have already been computed, (5a) and the ground state first and second ionization potential can be taken from Moore's tables. (9) Thus, it is merely necessary to combine all these data analogously to Equations 2, 3, and 1 to obtain the valence ionization potentials and orbital electronegativities of the positive ions.

TABLE I

VALENCE STATE PROMOTION ENERGIES IN (eV)²Valence State

	K	Ca ⁺
s	0.0	0.0
p	1.614	1.697

	K ^{-b}	Cq	Se ⁺	Ga ⁺
sp	2.429	2.152	1.875	6.587
pp	1.517	4.863	8.209	14.424
didid	1.732	1.912	2.092	5.890
di π	1.974	3.508	5.042	10.505
trtr	1.815	2.949	4.083	8.889
tr π	1.820	3.959	6.093	11.811
tete	1.800	3.448	5.096	10.331

	Zn ^{-b}	Ga	Ge ⁺	As ⁺⁺	Se ⁺⁺⁺	Ca ^{-c}
spp	3.642	5.836	8.128	10.351	12.516	2.4
ppp	8.003	12.496	17.274	21.907	26.260	5.3
didid π	3.278	5.309	7.385	9.452	11.446	2.1
di $\pi\pi$	5.822	9.166	12.701	16.129	19.388	3.8
trtrtr	3.158	5.134	7.137	9.152	11.090	1.9
trtr π	4.934	7.822	10.846	13.803	16.622	3.2
tetete	4.460	7.106	9.857	12.566	15.150	2.8

	Ga ^{-b}	Ge	As ⁺	Se ⁺⁺
sppp	4.101	6.576	8.482	11.241
didid $\pi\pi$	4.236	6.367	8.179	10.470
trtr π	4.281	6.298	8.078	10.213
tetetete	4.303	6.263	8.028	10.085

	Ge ^{-b}	As ⁺	Se ⁺⁺
s ² ppp	0.923	0.889	0.855
sp ² pp	3.519	7.484	11.449
di ² di $\pi\pi$	2.222	4.187	6.152
didin ² π	3.426	7.137	10.848
tr ² trtr π	2.613	5.132	7.651

TABLE I (cont'd.)

	Ge ^{-b}	As	Se ⁻			
trtrtr π^2	3.394	7.021	10.648			
te ² tetete	2.800	5.575	8.350			
	As ^{-b}	Se	Br ⁺	Kr ⁺⁺		
s ² p ² pp	0.209	0.385	0.388	0.651		
sp ² p ² p	4.748	8.218	12.048	15.338		
di ² di ² $\pi\pi$	0.209	0.385	0.388	0.651		
di ² di ² π^2	2.479	4.302	6.218	7.994		
didi $\pi^2\pi^2$	4.538	7.749	11.280	14.331		
tr ² tr ² tr π	1.722	2.996	4.275	5.547		
tr ² trtr π^2	3.142	5.399	7.820	9.995		
te ² te ² tete	2.425	4.184	6.026	7.743		
	Se ^{-b}	Br	Kr ⁻	Rb ⁻⁻	Sr ⁻⁻⁻	
s ² p ² p ² p	0.064	0.153	0.224	0.302	0.403	
sp ² p ² p	8.379	10.951	13.511	16.118	18.655	
		Rb	Sr ⁻			
s		0.0	0.0			
p		1.579	1.827			
	Rb ^{-d}	Sr	Y ⁺	In ⁺		
sp	0.445	2.039	3.633	6.100		
pp	1.224	4.461	7.698	12.505		
didi	0.548	1.828	3.108	5.569		
di π	0.835	3.250	5.665	9.303		
trtr	0.749	2.752	4.755	7.999		
tr π	0.965	3.654	6.343	10.370		
tete	0.860	3.197	5.534	9.170		
	Cd ^{-b}	In	Sn ⁺	Sb ⁺⁺	Te ⁺⁺⁺	Sr ^{-c}
spp	4.054	5.695	7.405	9.214	10.687	2.4
ppp	8.079	11.697	15.237	18.711	22.437	5.3
didi π	3.791	5.254	6.795	8.504	9.721	2.1
di π	6.066	8.687	11.321	13.963	16.562	3.8
trtrtr	3.703	5.107	6.591	8.268	9.399	1.9
trtr π	5.279	7.494	9.745	12.064	14.175	3.2
tetete	4.862	6.860	8.905	11.065	12.900	2.8

TABLE I (cont'd.)

	In ^{-b}	Sn	Sb ⁺	Te ⁺⁺
s ² pp	0.072	0.399	0.402	1.107
sp ² p	5.383	7.467	9.660	11.689
p ² pp	8.874	11.707	16.779	18.493
did _i π ²	5.050	7.082	8.909	11.044
diπ ² π	7.129	9.587	13.220	15.091
di ² π	5.066	6.821	10.093	11.090
di ² diπ	2.656	3.933	5.031	6.398
tr ² trtr	3.147	4.940	6.240	7.875
tr ² trπ	5.024	6.866	9.165	11.003
trtrπ ²	6.398	8.709	11.699	13.671
te ² tete	4.975	6.856	9.313	10.906
sppp	4.562	6.419	7.906	9.948
did _i ππ	4.230	6.035	7.155	9.303
trtrtrπ	4.119	5.907	6.904	9.088
tetetete	4.064	5.843	6.779	8.980

	Sn ^{-b}	Sb	Te ⁺
s ² ppp	-0.304	0.291	0.886
sp ² pp	2.088	6.625	11.165
di ² diπ	0.892	3.458	6.024
did _i π ² π	2.036	6.295	10.554
tr ² trtrπ	1.267	4.367	7.467
trtrtrπ ²	2.018	6.185	10.352
te ² tetete	1.451	4.794	8.137

	Sb ^{-b}	Te	I ⁺	Xe ⁺⁺
s ² p ² pp	0.208	0.439	0.693	0.913
sp ² p ² p	4.102	6.954	10.697	13.107
di ² di ² ππ	0.208	0.439	0.693	0.912
di ² diπ ² π	2.154	3.696	5.695	7.008
did _i π ² π ²	3.877	6.551	10.054	12.313
tr ² tr ² trπ	1.505	2.610	4.028	4.976
tr ² trtrπ ²	2.704	4.603	7.077	8.689
te ² te ² tete	2.099	3.586	5.534	6.811

	Te ^{-b}	I	Xe ⁻	Cs ⁻⁻	Ba ⁻⁻⁻
s ² p ² p ² p	0.163	0.314	0.435	0.574	0.737
sp ² p ² p ²	6.318	10.167	11.263	15.839	18.960

TABLE I (cont'd.)

- a) Calculations have also been made for Valence States of the same elements with lower valence, such values are contained in J. Hinze, Ph.D. Dissertation, University of Cincinnati.
- b) Extrapolated values.
- c) Roughly estimated values.

TABLE II
GROUND STATE IONIZATION POTENTIALS
AND
ELECTRON AFFINITIES IN (eV)

	<u>Eq</u>	<u>Iq</u>
K	0	4.34
Ca	.11	6.11
Ga	.18	6.00
Ge	1.20	7.88
As	.65	9.81
Se	2.20	9.75
Br	3.55	11.84
Rb	0	4.18
Sr	.10	5.69
In	.20	5.78
Sn	1.00	7.34
Sb	1.10	8.64
Te	2.30	9.01
I	3.21	10.45

TABLE III

VALENCE STATE IONIZATION POTENTIALS, ELECTRON AFFINITIES AND
ORBITAL ELECTRONEGATIVITIES OF ELEMENTS OF ROW 3 AND 4.^a

<u>Atom</u>	<u>Configuration</u>	<u>Orbital</u>	<u>I_v</u>	<u>E_v</u>	<u>X_p</u>
K(V ₁)	s	s	4.34	1.46	.77
	p	p	2.73	.77	.38
Ca(V ₂)	sp	s	5.66	2.26	1.12
		p	3.96	-.24	.42
	pp	p	2.95	-.53	.20
	didi	g	5.47	1.02	.88
	di π	g	4.30	.42	.59
		π	3.87	-.38	.38
	trtr	g	4.30	.06	.52
	tr π	g	3.85	-.13	.42
		π	3.29	-.33	.29
	tete	g	3.51	-.04	.38
Ga(V ₃)	spp	s	14.58	5.57	3.18
		p	6.75	1.78	1.22
	ppp	p	7.92	8.40	2.54
	didi π	g	11.19	3.15	2.20
		π	6.58	1.10	1.09
	di π π	π	11.25	7.25	2.90
		g	7.33	5.09	1.88
	trtrtr	g	9.76	2.28	1.82
	trtr π	g	9.99	5.13	2.33
		π	7.07	3.69	1.60
Ge(V ₄)	tetete	g	9.22	4.02	2.02
	sppp	s	18.57	6.86	4.06
		p	9.43	4.26	2.09
	didi π π	g	14.21	5.35	3.08
		π	8.89	4.14	1.98
	trtrtr π	π	12.43	4.89	2.70
		g	8.72	4.11	1.95
As(V ₃)	tetetete	g	11.48	4.66	2.50
	s ² ppp	p	9.36	1.33	1.59
	sp ² pp	s	16.22	7.92	3.84
		p	12.16	3.38	2.40
	di ² di π π	g	13.39	4.63	2.82
		π	10.75	2.36	1.99
	didi π ² π	g	14.53	5.31	3.13

TABLE III (cont'd.)

Atom	Configuration	Orbital	I_v	E_v	X_p
Se(V ₂)		π	12.19	3.25	2.39
	tr ² trtr π	ρ	13.00	4.06	2.66
		π	11.24	2.64	2.12
	trtrtr π^2	ρ	13.84	4.53	2.88
	te ² tetete	ρ	12.80	3.81	2.58
	s ² p ² pp	p	11.68	2.52	2.18
	sp ² p ² p	s	20.49	10.36	4.97
		p	14.44	2.04	2.56
	di ² di ² π	π	11.68	2.52	2.18
	di ² di ²		17.29	6.44	3.78
			13.06	2.28	2.37
	did _{π} ² ² π	ρ	17.94	5.73	3.77
	tr ² tr ² tr π	π	15.68	5.14	3.29
		π	12.59	2.37	2.31
	tr ² trtr π^2	ρ	16.28	4.77	3.33
	te ² te ² tete	ρ	15.29	4.24	3.07
BR(V ₁)	s ² p ² p ² p	p	13.10	3.70	2.62
	sp ² p ² p ²	s	22.07	14.50	5.94
Rb(V ₁)	s	s	4.18	0	.50
	p	p	2.60	1.84	.54
Sr(V ₂)	sp	s	5.48	2.14	1.07
		p	3.65	-.36	.34
	pp	p	3.06	-.94	.15
	did _i	ρ	4.77	.93	.75
	di π	ρ	4.27	.15	.54
		π	3.35	-.65	.25
	trtr	ρ	4.16	-.15	.46
	tr π	ρ	3.87	-.46	.37
		π	3.26	-.65	.23
	tete	ρ	3.85	-.30	.39
In(V ₃)	spp	ρ	12.60	5.83	2.88
		π	6.19	.52	.92
	ppp	p	6.62	3.01	1.41
	did _i π	ρ	9.84	2.79	1.91
		π	6.11	.40	.88
	di π π	ρ	9.61	3.82	2.04
		π	6.40	1.76	1.16
	trtrtr	ρ	8.68	1.89	1.57

TABLE III(cont'd.)

Atom	Configuration	Orbital	I_v	E_v	x_p
Sn(V ₂)	trtr π	π	8.67	2.67	1.70
		π	6.30	1.29	1.07
	tetete	π	8.10	2.08	1.50
	s ² pp	p	6.94	.87	1.10
	sp ² p	s	16.34	7.94	3.87
		p	8.51	5.54	2.15
	p ² pp	p	12.10	10.11	3.52
	did π ²	π	12.81	6.35	3.01
	di π ² π	π	14.22	8.92	3.68
		π	10.30	7.82	2.84
	di ² π π	π	10.15	6.15	2.53
	di ² di π	π	13.04	4.40	2.72
		π	7.90	3.20	1.66
	tr ² trtr	π	11.43	4.61	2.49
	tr ² tr π	π	12.65	6.55	3.02
Sn(V ₄)		π	9.50	5.80	2.36
	trtr π ²	π	12.49	7.64	3.17
	te ² tete	π	11.57	6.16	2.77
	sppp	s	16.16	7.72	3.80
		p	8.32	5.33	2.08
	didi π π	π	12.64	6.15	2.94
		π	8.10	5.00	1.99
	trtrtr π	π	11.17	5.64	2.62
		π	8.02	4.89	1.96
	tetetete	π	10.40	5.39	2.44
Sb(V ₃)	s ² ppp	p	8.75	1.18	1.46
	sp ² pp	s	18.80	7.51	4.22
		p	11.68	3.62	2.36
	di ² di π π	π	15.27	4.35	3.09
		π	10.21	2.41	1.91
	didi π ² π	π	15.56	5.25	3.29
		π	11.25	3.52	2.27
	tr ² trtr π	π	13.89	3.97	2.79
		π	10.51	2.77	2.02
	trtrtr π ²	π	14.16	4.58	2.94
Te(V ₂)	te ² tetetete	π	13.16	3.79	2.64
	s ² p ² pp	p	11.04	2.58	2.08
	sp ² p ² p ²	s	20.78	9.09	4.81

TABLE II I(cont'd.)

<u>Atom</u>	<u>Configuration</u>	<u>Orbital</u>	<u>I_v</u>	<u>E_v</u>	<u>X_p</u>
		p	14.80	2.93	2.77
	di ² di ² ππ	π	11.04	2.58	2.08
	di ² diπ ² π	π	17.12	5.84	3.65
		π	12.91	2.76	2.43
	di ² di ² π ²	π	18.19	5.61	3.79
	tr ² tr ² trπ	π	15.36	4.75	3.17
		π	12.29	2.70	2.31
	tr ² trtrπ ²	π	16.26	4.69	3.31
	te ² te ² tete	π	15.11	4.20	3.04
I(V ₁)	s ² p ² p ² p	p	12.67	3.52	2.52
	sp ² p ² p ²	s	18.00	13.38	5.06

^a See footnote a, Table 1

The results obtained are listed in Table IV, where again the last column gives the electronegativities in Pauling units, converted using Equation 4.

Discussion

The Mulliken definition of electronegativity is the only non-empirical one available, and has received wide acclaim and acceptance; (10), (11) it is the only readily available scheme for distinguishing between different hybrids and different types of orbitals. However, in considering the problems of evaluation of electronegativity it has frequently been pointed out that the Mulliken electronegativity is difficult to compute because electron affinity data are required which are frequently not available. This apparent limitation of the Mulliken definition, however, is not at all serious. Generally the electron affinity can, by purely empirical guesswork, be estimated to within 1 e.v., and the resulting uncertainty in electronegativity is only of the order of 0.16 Pauling units. Thus, any uncertainties in the electron affinity obtained in the present work have very little effect on the resulting electronegativities.

The electronegativities obtained in the present work and listed in Table III for the neutral atoms of rows three and four, and in Table IV for the positive ions of rows one and two of the periodic system, show the considerable dependence on valence states that would be expected from the similar behavior of the electronegativities of the neutral atoms of rows one and two reported previously. (5a) Again, as already reported for the first two groups, the valence state electronegativities are linear functions of the hybridization parameter.

It seems of particular interest to compare the electronegativities obtained in this work with values for Group IV elements obtained empirically by other workers, (6) Our values for tetrahedral Ge and Sn are seen to be consistently somewhat higher than the empirical values (Ge 2.0, 1.8-1.9; Sn^{IV} 1.9, 1.8). This fact may, most likely, be ascribed to some hybridization with d orbitals in the heavy elements; the d orbitals have low orbital ionization potentials and electron affinities, and hence must have low orbital electronegativities. Even a relatively small contribution of such orbitals would consequently be expected to significantly depress the electronegativity. Unfortunately, a calculation of d orbital electronegativity by the Mulliken method is not feasible, because the necessary spectroscopic data are not available.

TABLE IV
ELECTRONEGATIVITY AND IONIZATION POTENTIALS
OF POSITIVE IONS

<u>Ion</u>	<u>Configuration</u>	<u>Orbital</u>	<u>I_v</u>	<u>E_v</u>	<u>X_p</u>
Be ⁺	s	s	18.21	9.32	6.10
	p	p	14.25	5.32	3.08
B ⁺	sp	s	25.40	14.05	6.42
		p	19.40	7.38	4.29
	pp	p	18.91	7.37	4.21
	didi	q	23.48	9.64	5.36
	diπ	q	22.16	8.94	5.02
		q	19.16	7.37	4.25
	trtr	q	21.72	8.33	4.84
	trπ	q	21.08	8.02	6.36
		q	19.08	7.37	4.23
	tete	q	20.93	7.88	4.63
C ⁺	spp	s	33.03	19.42	8.60
		p	23.93	9.91	5.48
	ppp	p	23.29	11.65	5.66
	didiπ	q	29.85	13.29	7.04
		q	23.86	9.83	5.45
	diππ	q	28.16	12.96	6.70
		q	23.61	10.78	5.57
	trtrtr	q	28.14	11.83	6.50
	trtrπ	q	27.36	11.91	6.39
		q	23.68	10.45	5.52
N ⁺	tetete	q	26.71	11.37	6.19
	sppp	s	41.84	25.59	11.12
		p	28.69	12.48	6.69
	didiππ	q	37.00	17.24	8.90
		q	28.70	12.06	6.64
	trtrtrπ	q	34.62	15.09	8.15
O ⁺		q	28.71	11.96	6.63
	tetetete	q	33.29	14.14	7.76
	s ² ppp	p	34.15	14.61	7.98
	sp ² pp	s	51.41	32.29	13.86
		p	34.22	15.86	8.21
	di ² diππ	q	46.80	23.45	11.59
		π	34.19	15.24	8.10

TABLE IV (cont'd.)

<u>Ion</u>	<u>Configuration</u>	<u>Orbital</u>	<u>I_v</u>	<u>E_v</u>	<u>X_p</u>
	didid ₂ ² π	g	44.56	22.34	11.03
		π	33.95	15.53	8.11
	tr ² trtr π	g	42.49	20.15	10.32
		π	34.08	15.30	8.09
	trtrtr ₂ ²	g	41.39	19.64	10.05
	te ² tetete	π	40.31	18.70	9.70
Mg ⁺	s	s	15.03	7.64	3.60
	p	p	10.60	4.67	2.36
Al ⁺	sp	s	20.15	11.32	5.08
		p	13.48	5.99	3.07
	pp	p	14.34	6.03	3.21
	didid	g	17.47	8.00	4.07
	di π	g	17.25	7.59	3.97
		g	13.92	6.00	3.14
	trtr	g	16.28	7.01	3.70
	tr π	g	16.28	6.74	3.68
		g	14.06	5.92	3.17
	tete	g	15.75	6.64	3.56
Si ⁺	spp	s	24.68	14.93	6.45
		p	16.56	8.61	4.02
	ppp	p	16.56	11.42	4.49
	didid π	g	21.43	10.95	5.23
		g	16.50	8.60	4.01
	di π π	g	20.62	11.56	5.20
		g	16.55	10.02	4.26
	trtrtr	g	19.96	9.99	4.83
	trtr π	g	19.62	10.57	4.87
		g	16.53	9.54	4.17
	tetete	g	18.97	10.08	4.67
P ⁺	sppp	s	31.24	18.61	8.17
		p	20.72	11.55	5.22
	didid π π	g	27.01	14.05	6.69
		g	20.69	10.96	5.11
	trtrtr π	g	25.14	12.72	6.15
		g	20.68	10.76	5.08
	tetetete	g	24.10	12.09	5.88
st	s ² ppp	p	22.91	11.05	5.50
	sp ² pp	s	35.18	21.13	9.25

TABLE IV (cont'd.)

<u>Ion</u>	<u>Configuration</u>	<u>Orbital</u>	<u>I_v</u>	<u>E_v</u>	<u>X_p</u>
		p	24.49	11.98	5.92
	di ² diπ π	ρ	31.57	16.09	7.80
		π	23.70	11.51	5.71
	didiπ ² π	ρ	30.61	15.78	7.59
		π	24.00	11.92	5.83
	te ² teteπ	ρ	28.99	14.38	7.08
		π	23.74	11.65	5.74
	trtrtrπ ²	ρ	28.51	14.33	6.99
	te ² tetete	ρ	27.65	13.64	6.73

Finally, the sensitivity of the electronegativity of the heavy elements to d orbital hybridization (5c) indicates that their electronegativities need to be considered as especially variable, since this hybridization itself is a sensitive function of many factors e.g. the formal charge.
(13)

The electronegativities calculated for the positive ions are, as might have been expected, considerably higher than for the neutral atoms. The magnitude of the difference may seem somewhat surprising, ranging from about a factor of 3 for the early members in a period to a factor of 2 in the late members. It must, however, be realized that these values refer to integral positive charges not compensated by inductive effects or ionic character, and are calculated from data applicable to the gaseous state, whereas the electronegativities are to be used for molecules in solution. Obviously, effects such as stabilization by solvation with polarization (charge shift) of solvent molecules may appreciably affect these values.

It may further be worth noting that the ion commonly encountered as an intermediate in organic chemistry, say C(tr, tr, tr). An electronegativity can also be obtained for an "ion" in which the charge is accumulated on the central atom by inductive charge transfer, (5b) say C(tr^{2/3}tr^{2/3}tr^{2/3}π). The electronegativity of an "ion" formed in this way tends to be slightly lower than for the more normal one; thus, as a comparison,

$$x \left[\text{C}^+ (\text{tetete}) \right] = 6.19; x \left[\text{C}^+ (\text{te}^{2/3} \text{te}^{2/3} \text{te}^{2/3} \text{te}) \right] = 6.11$$

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APPENDIX V

Slater-Condon Parameters From Spectral Data

by Jurgen Hinze and H. H. Jaffe

The quantum mechanical theory of the many electron atom by Slater, (13) described in more detail in many texts, (2) is based on the central field approximation and perturbation theory. According to this treatment it is possible to express the energy, $\bar{W}_g$, of any spectroscopic state, g , of an atom with a total of N electrons as,

$$\bar{W}_g = \sum_{i=1}^N I(n_i, l_i) + \sum_{i < j}^N J(n_i l_i m_{li} s_i l_j m_{lj} s_j) - K(n_i l_i m_{li} s_i l_j m_{lj} s_j) \quad (1)$$

Where $I(n_i, l_i)$ represents the coulomb attraction integral between an electron, with principal quantum number n_i and angular quantum number l_i , and the atomic core. J and K represent the coulomb repulsion and exchange integrals, respectively, of electrons i and j .

If the operator $1/r_{ij}$ in the integrals J and K is expanded into spherical harmonics, it is possible to separate these two integrals into their spin, angular and radial parts, and integrate in closed form over the known spin and angular parts of the wave functions. With this, Equation reduces to,

$$\begin{aligned} W_g = \sum_{i=1}^N I(n_i l_i) + \sum_{i < j}^N \sum_K a_K(l_i m_{li} l_j m_{lj}) \\ F_K(n_i l_i l_j) - \int (m_{si} m_{sj}) b_K(l_i m_{li} l_j m_{lj}) \\ G_K(l_i m_{li} l_j m_{lj}) \end{aligned} \quad (2)$$

In cases where s , p , and d electrons only are involved the summation parameter k never exceeds 4. In Equation 2 the a 's, b 's, and c , resulting from integration over angular and spin parts of the corresponding wave functions, are known. Thus they are unknown and not readily obtainable only the F 's and the radial dependent parts of the coulomb repulsion integrals,

$$F_k (n_i l_i n_j l_j) = \frac{e^2}{D(i l j)} \frac{r^k}{r^{k-1}} R(n_i l_i l r_i)^2 R(n_j l_j l r_j)^2 dr_i dr_j \quad (3)$$

and of the exchange integrals,

$$G_k (n_i l_i n_j l_j) = \frac{e^2}{D(i l j)} \iint \frac{r_i^k}{r_j^{k-1}} R(n_i l_i l r_i) R(n_j l_j l r_j) R(n_i l_i l r_j) R(n_j l_j l r_i) dr_i dr_j \quad (4)$$

These F's and G's above, generally referred to as Slater-Condon parameters, are of considerable importance in the semiempirical theories of bonding. Use has been made of these parameters particularly for the evaluation and interpretation of spectral data of complexes with ligand field (3) or crystal field theory. (7) Since valence state promotion energies are readily computed, if the Slater-Condon parameters are known, (2) it is evident that the parameters are of considerable importance for the Pariser-Parr method, (9) Mulliken's "Magic" formula (6) and various forms of MO theory. Furthermore, promotion energies, obtainable from Slater parameters, permit the evaluation of valence state ionization potentials and orbital electronegativities. (13)

Two methods are on hand for the evaluation of these parameters. One is the a priori integration of 3 and 4. This, however, is cumbersome, especially since good Hartree-Fock functions are frequently not available. The other method permits the empirical determination of most of the parameters of interest by fitting equations of type 2 to the corresponding atomic energy levels, determined by spectroscopy.

Both methods have been used in the past for the determination of some Slater-Condon parameters for a number of elements; however it appears worthwhile, due to their importance, to determine and report once a set of empirically determined parameters, as complete as possible, rather than having them determined individually whenever they are needed. An extensive empirical determination has become especially feasible due to the complete listing of atomic energy levels by Moore. (5)

Computational Procedure

In this work the Slater-Condon parameters are determined empirically by fitting Equation 2 to the corresponding spectroscopic energy

levels of Moore's tables. Before this could be done, however, it was necessary to transform Equation 2 since in Equation 2 some parameters appear with the same coefficient throughout any one configuration. Such parameters, fortunately less important, do not contribute to the energy differences between the multiplets, and consequently cannot be obtained explicitly from energy level data. These unobtainable parameters are all those which arise from interactions of closed shell electrons and the $\underline{I}$'s, $\underline{F}_0$'s, and $\underline{G}_0$'s. They are all collected into constant term, $\underline{W}_h$, characteristic for each configuration, $\underline{h}$. The makeup of these $\underline{W}_h$'s is listed in Table I, ignoring the contributions of lower closed shells and the $\underline{I}$'s. The magnitude of the configuration characteristic constants $\underline{W}_h$ will depend strongly on the choice of the origin of the energy scale. Chosen here as zero of the energy scale was always the energy of the spectroscopic ground state of the corresponding atom or ion.

With this, Equation 2 becomes, for a configuration $\underline{h}$ with $\underline{n}$ outer electrons,

$$W_g = W_h - \sum_{i,j}^n \sum_k \left[\underline{a}_k (ilj) F_k (ilj) b_k (ilj) G_k (ilj) \right] \quad (5)$$

where, for configurations containing $\underline{s}$, $\underline{p}$, and $\underline{d}$, outer electrons only, the following Slater-Condon parameters are left, $\underline{F}_2(\underline{pp})$, $\underline{F}_2(\underline{pd})$, $\underline{F}_2(\underline{dd})$, $\underline{F}_4(\underline{dd})$, $\underline{G}_2(\underline{pp})$, $\underline{G}_1(\underline{pd})$, $\underline{G}_3(\underline{pd})$, $\underline{G}_2(\underline{dd})$, $\underline{G}_4(\underline{dd})$, $\underline{G}_1(\underline{sp})$, and $\underline{G}_2(\underline{sd})$. However, it should be noted that, $\underline{F}_2(\underline{pp}) = \underline{G}_2(\underline{pp})$, $\underline{F}_2(\underline{dd}) = \underline{G}_2(\underline{dd})$, and $\underline{F}_4(\underline{dd}) = \underline{G}_4(\underline{dd})$, and $\underline{F}_4(\underline{dd}) = \underline{G}_4(\underline{dd})$, therefore only eight parameters are to be determined.

The coefficients of these eight parameters have been evaluated for all energy levels, which can arise from configurations containing $\underline{s}$, $\underline{p}$, and $\underline{d}$ electrons only. (8) No coefficients have been evaluated for configurations with two $\underline{s}$, six $\underline{p}$, and more than five $\underline{d}$ electrons. Two $\underline{s}$ and six $\underline{p}$ electrons both represent closed shells, thus give no rise to multiplet separations. It is not necessary to consider more than five $\underline{d}$ electrons since Shortley (11) has shown that, aside from an additive constant common to an entire configuration here included in $\underline{W}_h$, the multiplets belonging to configuration $\underline{1}_a^{\alpha-x} \underline{1}_b^{\beta-x}$ are given the same Equation's 5 as those for configuration $\underline{1}_a^x \underline{1}_b^y$, if α and β represent the maximum number of electrons allowed in a shell.

Thus the coefficients for $\underline{d}^S$ are the same as for $\underline{d}^2$ and for p^4d^3 .

In cases where there are more multiplets of a kind to one configuration, e.g. configuration $\underline{d}^3$ gives rise to two $^3\underline{D}$ states, only the sums of the corresponding coefficients for all the identical states have been obtained, consequently such states could be used for the determination of the parameters only if all the possible states of the same kind in the configuration considered had been observed.

Slater's treatment of the many electron atom is far from correct, many approximations are to be made, most serious of all, configurational interaction is neglected. Consequently it cannot be expected that Equation 5 represent the energy states of an atom exactly. However, in this work it is desired to find sets of parameters which will represent the observed atomic spectral data best in connection with Equation 5. Thus for the determination of the Slater parameters all atomic energy levels available from Moore's tables have been used without discrimination. All multiplets belonging to a configuration considered have been reduced to their center of gravity, since in Slater's treatment the small spin-orbit coupling is ignored. The atomic energy levels, after being reduced to their centers of gravity give, combined with Equation 5, sets of simultaneous linear equations from which the $\underline{W}_h$'s and the Slater parameters have been determined, using a least squares multiple regression procedure. (13)

It was pointed out by Hartee (3) that corresponding Slater parameters will be different for different configurations of the same atom or ion, but on the other hand, the parameters determined from one configuration alone are not always sufficient, especially for valence state promotion energy calculations. Consequently, in such cases, different configurations have to be pooled together for a regression analysis. There is, however, considerable doubt about the validity of such a procedure which must yield the same parameters for the different configurations.

To investigate the uncertainties introduced by multiple configuration fitting and to find the difference between the parameters obtained by fitting of different configurations individually we have made regression analyses of,

- a) different configurations of an atom or ion pooled together
- and,
- b) single configurations separately.

Results and Discussion

The results of the regressions, considering atoms and ions with closed d shells, are reported in Table II. Listed are the parameters obtained by a "total" regression, considering together all the energy levels available of the configurations s^2p^{n-2} , sp^{n-1} , and p^n , where

the s and p orbitals have the same principal quantum number. In Table III the parameters obtained for the atoms and singly positive ions of the elements of the first transition series, with open d shells, are given. Here the "total" regression involved simultaneous fitting of all the energy levels available of the configurations

$3d^n$, $3d^{n-1}4s$, $3d^{n-1}4p$, $3d^{n-2}4s^2$, $3d^{n-2}4s4p$, and $3d^{n-2}4p^2$.

the variance ratios, F , and the standard deviations, σ , corresponding to the parameters of the total regressions, are listed in both tables. Parameters and variance ratios obtained from single configuration fitting are reported also; furthermore, literature values, if available, are entered into the tables for comparison.

If the Slater-Condon parameters are significantly different in different configurations, the variance ratio (F) for the total regression would have to be considerably smaller than the corresponding F values for all the individual regressions in the same element. On the other hand, if the parameters have identically the same values in all configurations, F for total regression would be some form of a weighted mean (weighted by the number of degrees of freedom) of the F 's for individual regressions. Examination of the tables shows that in almost every case the total regression F lies somewhere between the individual regression F 's. Exceptions toward higher F occur where for some configurations insufficient data are available to perform a regression (implying an infinite F since the parameters are uniquely determined). Total regression F 's lower than individual regression values are observed only for Si, Be, Sn, S^+ , V, V^+ , Cr^+ , Mn^+ , and Cu^+ ; of these the values for Si, V^+ and Mn^+ are just barely outside the range. It actually appears as if the total regression values lay, as a whole, close to the weighted mean demanded by equal Slater-Condon parameters. Further, it may be noted that the F 's for none of the configurations examined are consistently higher in a series of elements than for any other type of configuration. From these observations it may be concluded that the approximations involved in the Slater-Condon scheme for a single configuration are considerably greater than the approximations contained in the assumption of configuration independent parameters.

This is, of course, a very fortunate circumstance, since this assumption is a necessary one in many applications of the semiempirical scheme.

The configuration independence of the Slater-Condon parameters is further supported by the finding, evident from the tables, that the parameters obtained individual configurations are rarely outside the uncertainty limits of the total regression values, as specified by the standard deviations. The uncertainties obtained from individual regressions are generally of the same order of magnitude as the values obtained from total regression, and the total regression parameter values generally lie within the probable range of the individual regression values. The data obtained permit further several interesting observations. The representation of the atomic energy levels by Slater's equations becomes better for higher positive ions and worse for heavier elements. This is probably due to the neglect of configuration interactions in Slater's treatment. Such interactions will be small if the energy levels are far apart, and the lighter the element and the more positive an ion, the farther apart are the energy levels. In case of heavier elements the neglect of spin-orbit interaction may become a deciding factor also.

The linear relation between corresponding Slater parameters of isoelectric ions, observed by Rohrlach, (10) is well reflected in the parameters obtained. Of interest also is the observed increase of the parameters in a sequence where the number of outer electrons increase. This shows that an outer electron will not screen as effectively as an inner one, as is expected. In the transition sequence this trend is pronounced only for the $F_2(\underline{dd})$'s. The other parameters, fortunately not that important, are quite unsteady due mainly to the uncertainties involved in their determination, which is considerable for some of them, especially for $G_2(\underline{sp})$ and $G_2(\underline{sd})$.

The parameters obtained for different configurations in cases of single configuration fitting are frequently in good agreement with one another, considering the limits of uncertainty specified by their standard deviations. Nevertheless, there are some considerable differences, e.g. the $F_2(\underline{pp})$ of Al, C and N^+ , etc. The general trends observed in these discrepancies open up some aspects which appear to be significant. The $F_2(\underline{pp})$'s determined for configuration s^2p^{n-2} are in general larger than those for configuration p^n . These differences decrease for positive ions and are, for some highly positive ions, even inverted. The differences between the values observed is apparently not due to different screening of s and p electrons since one would

expect an s electron to screen better than a p electron, and the order of the parameters should be inverted, as is observed only for a few highly positive ions. The sequence as it is observed, however, may well be attributed to a correlation effect, indicating that electrons in p orbitals can stay in the time average further apart, if they are not influenced also by an electron in an s orbital. This explanation is consistent with the observation that the effect is most pronounced in heavy atoms or low positive ions, where the p orbitals are large and the p electrons have thus a chance of staying far apart from each other.

The analogous observation is made also for the $F_2(\underline{dd})$'s determined for single configurations. Their values are generally larger for configurations $\underline{d}^{n-2}\underline{s}^2$ than for configurations $\underline{d}^{n-1}\underline{s}$ which again are larger than the values of configurations $\underline{d}^n$.

Comparison of the data obtained in this work with literature values shows universally good agreement, which is not too surprising, since frequently a similar procedure has been used for the determination of the parameters. Serious discrepancies exist between the values of $F_2(\underline{pp})$ for Mg, Al^+ , and Si^{++} obtained here and those determined by Skinner and Pritchard (12). Their values for Al^- and Si^{--} are obtained from the energy difference between the $1\underline{d}$ and $3\underline{p}$ states of configuration $\underline{p}^2$. This difference, corresponding to $6F_2(\underline{pp})$, gives rise to highly negative values for $F_2(\underline{pp})$. However, if the $1\underline{s}$ state of configuration, $\underline{p}^2$, observed only in Si^{++} , is included, $F_2(\underline{pp})$ takes a positive value as reported here. In this work the $1\underline{s}$ state not observed for Al^- and Mg, has been extrapolated linearly from the higher isoelectronic ions before the parameters have been determined.

Another discrepancy is found between the values for $F_2(\underline{sd})$ of Se through Mn determined here empirically and the values obtained by Brown (1) by integration of Equation 4 with approximate Slater type functions. The values obtained by integration are higher by about 1000 cm^{-1} , which may well be attributed to the use of nodeless $4s$ functions. The good agreement between the empirical values of $F_2(\underline{dd})$ and $F_4(\underline{dd})$ and the ones obtained by integration confirm this explanation, since $3\underline{d}$ functions do not have nodes as the Slater type functions used.

The high negative value obtained here for $G_2(\underline{sp})$ of V^- appears strange. This seems to be due to a possible wrong assignment of the $1\underline{H}$ state of configuration $\underline{d}^2\underline{sp}$ of V^- . There are only three states observed in configuration $\underline{d}^2\underline{sp}$ of V^- , the states $1\underline{H}$, $5\underline{G}$, and $5\underline{F}$.

Unfortunately, the $G_1(\underline{sp})$ dependence of these states are not clearcut, since their Slater equations have different coefficients also for $F_2(\underline{pd})$, $F_2(\underline{dd})$, $F_4(\underline{dd})$, $G_1(\underline{pd})$, $G_3(\underline{pd})$, and $G_2(\underline{sd})$, while the coefficient for $G_1(\underline{sp})$ is one for the state $1\underline{H}$ and -1 for the states $5\underline{G}$ and $5\underline{F}$. Nevertheless, it can be said with certainty that the high negative value for $G_1(\underline{sp})$ of V^+ is not due to the uncertainty in the parameters involved in its determination. This is seen from an inspection of the corresponding states of the isoelectronic Ti, where the $1\underline{H}$ state is about 16500 cm^{-1} higher than the $5\underline{F}$ and $5\underline{G}$ state, while in V^+ the $1\underline{H}$ state is only 3000 and 6000 cm^{-1} higher than the $5\underline{G}$ and $5\underline{F}$ states, respectively.

TABLE I

THE FORM OF THE CONSTANT TERMS OF CONFIGURATION

$W(d^2)$	$= F_0(dd)$
$W(d^3)$	$= 3F_0(dd)$
$W(d^4)$	$= 6F_0(dd)$
$W(d^5)$	$= 10F_0(dd)$
$W(d^6)$	$= 15 F_0(dd) - 14 F_2(dd) - 126 F_4(dd)$
$W(d^8)$	$= 28 F_0(dd) - 42 F_2(dd) - 378 F_4(dd)$
$W(d^9)$	$= 36 F_0(dd) - 56 F_2(dd) - 504 F_4(dd)$
$W(d^{10})$	$= 45 F_0(dd) - 70 F_2(dd) - 630 F_4(dd)$
$W(ds)$	$= F_0(sd)$
$W(d^2s)$	$= 2F_0(sd) + F_0(dd)$
$W(d^3s)$	$= 3F_0(sd) + 3 F_0(dd)$
$W(d^4s)$	$= 4F_0(sd) + 6 F_0(dd)$
$W(d^5s)$	$= 5F_0(sd) + 10F_0(dd)$
$W(d^6s)$	$= 6F_0(sd) - G_2(sd) + 15 F_0(dd) - 14 F_2(dd) - 126 F_4(dd)$
$W(d^7s)$	$= 7F_0(sd) - 2G_2(sd) + 21 F_0(dd) - 28F_2(dd) - 252 F_4(dd)$
$W(d^8s)$	$= 8F_0(sd) - 3G_2(sd) + 28 F_0(dd) - 42F_2(dd) - 378 F_4(dd)$
$W(d^9s)$	$= 9F_0(sd) - 4G_2(sd) + 36 F_0(dd) - 56 F_2(dd) - 504 F_4(dd)$
$W(d^{10}s)$	$= 10F_0(sd) - 5G_2(sd) + 45 F_0(dd) - 70 F_2(dd) - 630 F_4(dd)$
$W(dp)$	$= F_0(pd)$
$W(d^2p)$	$= 2F_0(pd) + F_0(dd)$
$W(d^3p)$	$= 3F_0(pd) + 3F_0(dd)$
$W(d^4p)$	$= 4F_0(pd) + 6F_0(dd)$
$W(d^5p)$	$= 5F_0(pd) + 10F_0(dd)$
$W(d^6p)$	$= 6F_0(pd) + 14G_1(pd) + 147G_3(pd) + 15F_0(dd) + 14F_2(dd) -$ $126F_4(dd)$
$W(d^7p)$	$= 7F_0(pd) + 8G_1(pd) + 84G_3(pd) + 21F_0(dd) - 28F_2(dd) -$ $252F_4(dd)$
$W(d^8p)$	$= 8F_0(pd) - 2G_1(pd) + 21G_3(pd) + 28F_0(dd) - 42F_2(dd) -$ $378F_4(dd)$
$W(d^9p)$	$= 9F_0(pd) - 4G_1(pd) - 42G_3(pd) + 36F_0(dd) - 56F_2(dd) -$ $504F_4(dd)$

$$\begin{aligned}
W(s^2) &= F_0(ss) \\
W(ds^2) &= F_0(ss) + 2F_0(sd) - G_2(sd) \\
W(d^2s^2) &= F_0(ss) + 4F_0(sd) - 2G_2(sd) + F_0(dd) \\
W(d^3s^2) &= F_0(ss) + 6F_0(sd) - 3G_2(sd) + 3F_0(dd) \\
W(d^4s^2) &= F_0(ss) + 8F_0(sd) - 4G_2(sd) + 6F_0(dd) \\
W(d^5s^2) &= F_0(ss) + 10F_0(sd) - 5G_2(sd) + 10F_0(dd) \\
W(d^6s^2) &= F_0(ss) + 12F_0(sd) - 6G_2(sd) + 15F_0(dd) - 14F_2(dd) - 126F_4(dd) \\
W(d^7s^2) &= F_0(ss) + 14F_0(sd) - 7G_2(sd) + 21F_0(dd) - 28F_2(dd) - 252F_4(dd) \\
W(d^8s^2) &= F_0(ss) - 16F_0(sd) - 8G_2(sd) + 28F_0(dd) - 42F_2(dd) - 378F_4(dd) \\
W(d^9s^2) &= F_0(ss) - 18F_0(sd) - 9G_2(sd) + 36F_0(dd) - 56F_2(dd) - 504F_4(dd) \\
\\
W(sp) &= F_0(sp) \\
W(dsp) &= F_0(sp) + F_0(sd) + F_0(pd) \\
W(d^2sp) &= F_0(sp) + 2F_0(sd) + 2F_0(pd) + F_0(dd) \\
W(d^3sp) &= F_0(sp) + 3F_0(sd) + 3F_0(pd) + 3F_0(dd) \\
W(d^4sp) &= F_0(sp) + 4F_0(sd) + 4F_0(pd) + 6F_0(dd) \\
W(d^5sp) &= F_0(sp) + 5F_0(sd) + 5F_0(pd) + 10F_0(dd) \\
W(d^6sp) &= F_0(sp) + 2G_1(sp) + 6F_0(sd) - G_2(sd) + 6F_0(pd) + 14G_1(pd) + 147G_3(pd) - 14F_2(dd) - 126F_4(dd) \\
W(d^7sp) &= F_0(sp) + 2G_1(sp) + 7F_0(sd) - 2G_2(sd) + 7F_0(pd) + 8G_1(pd) + 84G_3(pd) - 21F_0(dd) - 28F_2(dd) - 252F_4(dd) \\
W(d^8sp) &= F_0(sp) + 2G_1(sp) + 8F_0(sd) - 3G_2(sd) + 8F_0(pd) + 2G_1(pd) - 28F_0(dd) - 42F_2(dd) - 378F_4(dd) \\
W(d^9sp) &= F_0(sp) + 2G_1(sp) + 9F_0(sd) - 4G_2(sd) + 9F_0(pd) - 4G_1(pd) - 42G_3(pd) + 36F_0(dd) - 56F_2(dd) - 504F_4(dd) \\
\\
W(p^2) &= F_0(pp) \\
W(dp^2) &= F_0(pp) + 2F_0(pd) \\
W(d^2p^2) &= F_0(pp) + 4F_0(pd) + F_0(dd) \\
W(d^3p^2) &= F_0(pp) + 6F_0(pd) + 3F_0(dd) \\
W(d^4p^2) &= F_0(pp) + 8F_0(pd) + 6F_0(dd) \\
W(d^5p^2) &= F_0(pp) + 10F_0(pd) + 10F_0(dd) \\
\\
W(p^3) &= 3F_0(pp) \\
W(p^4) &= 6F_0(pp) \\
W(p^5) &= 10F_0(pp) \\
\\
W(sp^2) &= 2F_0(sp) + F_0(pp)
\end{aligned}$$

$$\begin{aligned}
 W(sp^3) &= 3F_O(sp) + 3F_O(pp) \\
 W(sp^4) &= 4F_O(sp) + 6F_O(pp) \\
 W(sp^5) &= 5F_O(sp) + 10F_O(pp)
 \end{aligned}$$

$$\begin{aligned}
 W(s^2p) &= F_O(ss) + 2F_O(sp) - G_1(sp) \\
 W(s^2p^2) &= F_O(ss) + 4F_O(sp) - 2G_1(sp) + F_O(pp) \\
 W(s^2p^3) &= F_O(ss) + 6F_O(sp) - 3G_1(sp) + 3F_O(pp) \\
 W(s^2p^4) &= F_O(ss) + 8F_O(sp) - 4G_1(sp) + 6F_O(pp)
 \end{aligned}$$

TABLE II

SLATER PARAMETERS OF ELEMENTS WITH CLOSED d SHELLS

Part 1

	Be	B ⁺	C ⁺⁺	N ⁺⁺⁺	Mg	Al ⁺	Si ⁺⁺
F ^a	67	203	287	387	10	40	65
W(s ²) ^a	0	0	0	0	0	0	0
Δ	6467	6532	7771	8606	15666	12947	14076
W(sp) ^a	32273	55372	77359	98984	28471	46883	67886
Δ	4597	4619	5495	6086	11078	9155	9952
	32273	55373	77359		28471	48683	67886
W(p ²) ^a	60829	105677	149093	191795	55509	94636	131642
Δ	3931	3965	4717	5224	9509	7859	8544
	61265	106115	149615				
F ₂ (pp) ^a	857	1986	3090	4078	1056	1346	1723
Δ	606	612	728	806	1467	1213	1318
b	639	1767	2829		(1589)	-1455	-1321
G ₁ (sp) ^a	10292	18024	24992	31711	6580	11166	14997
Δ	4597	4619	5495	6086	11078	9155	9953
	10292	18024	24992		6580	11167	14997
F ^a	395	1160	1466	1992	155	157	167
c	434	1449	1940	3003	166	84	144
d	370	940	1005	1328	-	-	167
W(s ² p) ^a	0	0	0	0	75	191	373
Δ	4694	4158	4970	5329	5502	7974	11303
b	0	0	0	0	0	0	0
e		43					
W(sp ²) ^a	63804	97695	130348	162336	50764	74775	98075
Δ	2854	2528	3022	3240	3345	4849	6874
c	63925	97780	130337	162337	50975	75012	98368
b	63662	97561	130123	162063	51984	74293	97648
e		97695					

TABLE II

Part 1 (cont'd.2)

	Be	B [†]	C ^{††}	N ^{†††}	Mg	Al [†]	Si ^{††}
W(p ³) ^a	109650	167067	226946	284793	91164	132856	167287
Δ	3393	3006	3593	3852	4664	6759	8172
d	107784	165747	226505	284776	87645	128886	162784
e		167067					
b,d		167198					
F ₂ (pp) ^a	1123	1903	2883	3758	517	836	1174
Δ	292	258	309	331	343	497	702
c	1333	2052	2933	3750	881	1246	1680
d	857	1715	2820	3755	48	306	531
b	1356	2071	2955	3783	897	1309	1738
e		1903					
b,d		1922					
G ₁ (sp) ^a	14522	22524	29671	36590	9031	13254	17310
Δ	2178	1929	2306	2472	2553	3700	5245
c	14753	22688	29726	36592	9434	13708	17870
b	14410	22401	29396	36249	9201	12770	16885
e		22524					
	C	N [†]	O ^{††}	F ^{†††}	Si	P [†]	S ^{††}
F							
a	246	1816	10079	8706	454	110	131
b	189	206	209	208	85925	122094	49786
c	610	2289	7969	11116	582	103	89
W(s ² p ²) ^a	7714	11591	15194	18660	5821	8738	9949
Δ	4987	2696	1498	1993	1892	5727	6641
f	7768	11723	15541	19379	5249	7425	9470
b,f	7686	11602	15382	19182	5244	7414	9460
e	7225						
W(sp ³) ^a	111502	161777	208035	25504	79418	99039	132235
Δ	5280	2855	1586	2110	2441	6115	7746
c	113956	163122	208979	255650	76995	96741	130325
b,c	109083	162135	207891	254589	70644	106671	139989
e	114929						

TABLE II

Part 1 (cont'd.3)

	C	N ⁺	O ⁺⁺	F ⁺⁺⁺	Si	P ⁺	S ⁺⁺
W(p ⁴) ^a	163515	245202	327238	410028			
Δ	8061	4359	2421	3221			
d	112262	221016	319922	423752			
e							
F ₂ (pp) ^a	1455	2220	3013	3870	730	760	1533
Δ	448	242	134	179	218	527	765
f	1428	2154	2840	3510	1015	1417	1772
c	1805	2412	3148	3960	399	432	1260
d	-2816	204	2404	5014			
b,f	1469	2214	2919	3608	1015	1419	1776
b,c	1665	2568	3266	4083	(660)	1209	1870
e	1700						
G ₁ (sp) ^a	18545	27118	34053	40897	12938	12837	19304
Δ	2453	1326	737	980	1369	2815	4644
c	18545	27118	34053	40897	12120	12873	18576
b,c	17281	27500	33993	40912	(9000)	15908	21405
e	19116						
	N	O ⁺	F ⁺⁺	Ne ⁺⁺⁺	P	S ⁺	Cl ⁺⁺
F a	6436	10050	9666	10335	427	10778	7049
f	-	-	-	-	23323	34804	34459
c	4195	7124	8379	9698	405	104774	2939
W(s ² p ³) ^a	30613	42495	54330	65450	16697	23790	29798
Δ	1430	1543	1987	2317	2410	683	1076
f	28840	40467	51558	62163	18790	24611	29941
b,f	29231	40985	52198		18765	24580	29912
W(sp ⁴) ^a	191615	255631	322022	386732	82143	128300	162392
Δ	2359	2545	3277	3823	3976	1127	1775
c	192946	256980	324022	389151	79396	127222	162204
b,c	190523	256680	323688	-	79877	-	-
W(p ⁵) ^a	276378	375399	475095	573734	-	-	-
Δ	3156	3405	4384	5114			

TABLE II

Part 1 (cont'd.4)

	N	O ⁺	F ⁺⁺	Ne ⁺⁺	P	S ⁺	Cl ⁺⁺
F ₂ (pp) ^a	2084	2867	3682	4439	951	1521	1973
	123	133	171	199	207	59	92
f	1602	2275	2910	3534	1250	1638	1993
c	2198	2982	3854	4646	716	1429	1957
b,f	1887	2651	3378	-	1247	1634	1989
b,c	(2125)	3000	3875	-	688	-	-
G ₁ (sp) ^a	24085	30918	38167	45202	2817	9800	11641
	918	990	1275	1487	1547	439	691
c	24212	31046	38357	45431	2557	9698	11624
b,c	(23505)	30777	38049	-	2991	-	-
	O	F ⁺	Ne ⁺⁺	Na ⁺⁺⁺	S	Cl ⁺	Ar ⁺⁺
F a	3658	4053	4213	4018	46802	63372	43888
W(s ² p ⁴) ^a	34399	45657	56629	67854	22247	27975	33366
Δ	1807	2192	2621	3195	256	285	423
b	34906	46273	57367	-	22297	28039	33453
W(sp ⁵) ^a	266151	336107	405240	481461	126282	163334	202446
Δ	4681	5681	6793	8280	662	739	1096
b,l	222917	276928	331921	-	93544	126640	158879
F ₂ (pp) ^a	2227	2959	3666	4380	1464	1835	2178
Δ	179	217	260	316	25	28	42
b	2291	3036	3758	-	1470	1843	2190
G ₁ (sp) ^a	31766	37326	42445	49891	8269	10986	14860
Δ	1350	1639	1960	2388	191	213	316
c	(32204)	37323	42442	-	(7112)	10984	14856

a Total regression, Configurations s²pⁿ⁻², spⁿ⁻¹ and pⁿ together.

b See reference 16.

c Regression of configuration spⁿ⁻¹.

d Regression of configuration pⁿ.

e I.J. Goldfarb and H. H. Jaffe, J. Chem. Phys. 30, 1622 (1959).

f Regression of configurations s²pⁿ⁻².

h W(pⁿ)-5F₂(pp). i W(spⁿ⁻¹)-2G₁(sp). k W(spⁿ⁻¹)-3G₁(sp).

l W(spⁿ⁻¹)-2F₂(pp).

TABLE II

Part 2

Pt++	Ca	Se†	Ga†	Zn	Sr	Y†	In†
275	952	-	-	-	2384	-	68
0	0	11736	0	0	0	-	0
8866	1083	-	-	-	628	-	10947
86782	19458	47473	59492	39701	18200	34396	53820
6269	766	-	-	-	444	-	7440
171299	39705	76474	115673	80719	36347	68418	105257
5381	657	-	-	-	381	-	6644
2041	134	-	-	76	102	1804	1248
830	101	-	-	-	59	-	1025
18408	766	-	-	-	444	-	7740
328	55	149	231	379	-	83	220
176							
-							
634	551	1178	1960	2917	1475	2834	4384
8927	7296	7439	6284	5910		7564	5776
121066	59962	83618	105651	126906	57279	75497	93608
5428	4442	4529	3826	3599	-	4605	3517
121331							
215805	-	155977	-	-	-	-	-
211368							
1542	927	1316	1640	1910	976	1324	1755
556	606	618	522	491	-	628	480
2001							
950							
20579	9633	13440	16402	19242	7919	11121	13128
4142	3414	3481	2940	2766	-	3539	2703
21086							
3245	187	3678	7911	623	490	78	-
24035	887731	789010	-	-	4020	1072	-
1463	45852	-	-	-	-	52	-

TABLE II

Part 2 (cont'd.2)

P ⁺⁺⁺	Ca	Se ⁺	Ga ⁺	Zn	Sr	Y ⁺	In ⁺
11628	6777	8592	11670	14032	7161	11172	15485
1484	2556	706	799	4274	1228	6868	-
11526	6100	8706	11321	15854	7460	10999	15485
168661	58847	83099	123874	170661	69288	105685	111701
1915	3188	1171	1446	4735	2563	8012	
168231	55634	83099	124920	167929	73711	104998	
169815							
Cl ⁺⁺⁺	Ge	As ⁺	Se ⁺⁺	Br ⁺⁺⁺	Sn	Sb ⁺	Te ⁺⁺
2057	688	1446	1885	1350	1127	1224	1873
172	348	102	170	911	160	791	-
2108	1026	1388	1711	2261	977	1310	1873
1998	-383	1810	2059	440	1469	1125	-
2349							
25634	-954	-343	8930	-	3778	16051	7850
1074	2130	734	676	-	706	4803	--
25471	-954	-388	9192	-	4015	15790	-
25538							
As ⁺⁺⁺	As	Se ⁺	Br ⁺⁺	Sb	Te ⁺	Xe ⁺⁺⁺	
1647	207	17719	760	168	104	28	
41159	3630						
1288	192						
37194	15571	23361	27622	17243	22011	34683	
2741	3263	440	720	955	1544	4638	
35045	18371						
206276	77366	123821	-				
209098	73690						
208503							
-	-	-	-	-	1506	2427	
-	-	-	-	-	166	497	

TABLE II

Part 2 (cont'd.3)

As ⁺⁺⁺	As	Se ⁺	Br ⁺⁺	Sb	Te ⁺	Xe ⁺⁺⁺
2640	830	1568	1173			
236	280	47	77	102		
2333	1230					
2882	516					
-						
2919						
16212	2982	5141	-	-		
1759	2094	238	-	-		
16480	2635					
15933						
K ⁺⁺⁺	Se	Br ⁺	Kr ⁺⁺	Te	I ⁺	Xe ⁺⁺
41595	1.4.10 ⁶	-	87367	991099	4705	40080
38674	22454	26313	33118	23203	32321	37303
515	14	-	301	17	909	382
239472	-	130447 ^k	195232	-	142011	172270
1334	-	-	779	-	2355	990
2511	1433	1656	2064	1406	1980	2218
51	1	-	30	2	90	38
18107	-	-	12086	-	6445	8875
385	-	-	225	-	679	285

TABLE III

SLATER PARAMETERS OF TRANSITION METALS											
		Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
F	a	716	441	2229	244	1680	699	255	4369	1138	127061
	c	-	34364	2173	92086	1158	-	93	1684	-	-
	d	-	563	2845	-	4775	-	12223	10462	2693	-
	e	-	-	231	409	14526	658	18026	403	255	-
	f	-	164	802	-	-	-	-	-	-	-
W(d ⁿ) ^a		46662	41985	51825	59273	70925	67566	43472	27886	14729	-
	Δ	1050	3172	1481	4102	1929	1788	3588	687	821	-
W(d ⁿ⁻¹ s) ^a		21103	18588	25988	35556	64771	64119	34343	18226	2071	0
	Δ	1018	1048	583	2626	1670	2387	1545	390	581	118
	c	-	18878	23691	37052	62617	63756	32626	17716	2071	-
W(d ⁿ⁻¹ p) ^a		37840	38349	46945	69532	84588	14024	65528	47518	32071	30701
	Δ	766	1147	615	8727	1693	24138	5737	1364	677	118
	d	-	37693	47834	-	82160	-	63964	47620	32027	-
W(d ⁿ⁻² s ²) ^a		0	7689	18052	46520	71228	44665	31157	14763	71228	12020
	Δ	1440	1904	594	1432	1013	3661	3271	631	442	118
	e	-	-	7980	21577	51837	74342	51168	31777	14763	-
W(d ⁿ⁻² sp) ^e		19458	21821	32161	58439	80396	105667	88375	6110 ⁱ	49653	54283 ^k
	Δ	1018	1101	420	3379	2616	4731	30756	2446	2200	272
	f	-	21790	32095	-	-	-	-	-	-	-
W(d ⁿ⁻² p ²) ^a		40097	46811 ^l	59286 ^l	95925 ^l	-	143037 ^l	-	-	-	-
	Δ	838	2372	1224	15906	-	19088	-	-	-	-
F ₂ (pp) ^a		93	-	-	-	-	-	-	-	-	-
	Δ	80	-	-	-	-	-	-	-	-	-
F ₂ (pd) ^a		108	68	229	786	35	217	211	201	130	315
	Δ	146	108	47	417	179	177	171	34	66	12
	d	-	96	188	-	-	-	146	190	117	-
	f	-	115	39	-	-	-	-	-	-	-
F ₂ (dd) ^a		385 ^m	580	770	747	953	1141	1190	1408	1629	-
	Δ	155	116	39	99	58	103	139	37	88	-
	c	-	592	833	779	915	1134	799	1272	-	-
	d	-	580	815	-	837	-	1317	1435	-	-

TABLE III (cont'd.2)

		Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	e	-	-	917	1037	1268	1347	1387	1484	1629	-
	f	-	-	817	-	-	-	-	-	-	-
	g,c	-	660	(760)	900	1000	-	1250	1230	-	-
	g,e	-	-	900	1055	1300	1340	1430	1440	1500	-
	h,e	-	-	745	873	1007	1143	1270	1331 ^c	1538	-
F ₄ (dd)	a	-	22	47	51	82	97	76	119	121	-
Δ		-	20	6	12	4	10	15	5	12	-
	c	-	32	54	68	76	93	24	107		
	d	-	-11	62		89		100	118		
	e	-	-	67	80	90	86	114	121	121	
	f	-	-	59							
	g,c	-	45	(55)	-	65	-	105	100		
	g,e	-	-	65	80	90	105	120	110		
	h,e	-	-	54	63	73	83	92	96 ^c	112	
G ₁ (pd)	a	364	182	326	1169	3	914	24	159	200	391
Δ		152	171	65	633	146	928	294	91	53	24
	d	-	166	416		-78		53	165	195	
	f		89	-88							
G ₃ (pd)	a	8	32	26	114	14	-14	36	0	16	35
Δ		26	23	10	68	13	54	36	12	10	4
	d		59	4		11		8	0	15	
	f	-27	-47								
G ₁ (sp)	a	4195	2744	2092	3618	10320	2841	4078	-	-	7812 ⁿ
Δ		1018	1842	567	4875	2808	8533	11085	-	-	163
	f		5694 ⁿ	1846							
G ₂ (sd)	a	746	1095	1534	1813	1462	1192	1285	1143	1339	-
Δ		1018	631	287	748	287	630	1012	227	581	-
	c		1144	1292	1369	1358	1264	3077	1115	1339	-
	f			3662							
	h,c		3628	3122	2587	2164	1794	1526	1295	1112	
		Sc ⁻	Ti ⁻	V ⁻	Cr ⁻	Mn ⁻	Fe ⁻	Co ⁻	Ni ⁻	Cu ⁻	Zn ⁻
F	a	3681	1019	3303	1150	142	4787	14708	15485	2791	212468
	b	191	4295	3756	4379	1443					
	c	54	3817	33949	3106	9709		923			

TABLE III (cont'd.3)

		Sc ⁺	Ti ⁺	V ⁺	Cr ⁺	Mn ⁺	Fe ⁺	Co ⁺	Ni ⁺	Cu ⁺	Zn ⁺
	d		19707	9363	64777	193	3822		235120	8872	
	e									5966	
W(d ⁿ)	a	11282	16059	32569	61815	52752	29330	7474 ^o	603	0	-
Δ		306	812	548	1680	3297	419	290	586	2278	-
	b		17442	31966	61448	53365	28335				
W(d ⁿ⁻¹ s)	a	1323	10904	29801	58593	71029	56713	29127 ^p	26584	22457	0
Δ		402	715	573	1924	5463	621	496	332	110	197
	c		10804	30564	60784	88224	56570		26474	24457	
W(d ⁿ⁻¹ p)	a	28966	41374	61053	95001	11343	104727	60775 ^p	75184	72907	49063
Δ		234	857	573	3342	6011	7233	242	1210	1739	197
	d		41992	62235	92278	103929	101681		73955	73746	
W(d ⁿ⁻² s ²)	a	11736	25100	-	69088	90809	108061	60276	-	86979	63807
Δ		569	1599	-	1417	8849	1490	578	-	1200	197
	e				55915					87022	
W(d ⁿ⁻² sp)	a	47473	64399	75088	-	150954	-	-	139538	-	108244
Δ		402	1154	1011	-	13031	3432	-	-		115
W(d ⁿ⁻² p ²)	a	76471 ¹	-	-	-	-	-	-	-	-	-
Δ		569	-	-	-	-	-	-	-	-	-
F ₂ (pd)	a	242	434	382	459	-	319	353	342	159	522
Δ		40	93	74	212	-	94	26	30	116	20
	d		300	335	266	-	311	-	359	378	
F ₂ (dd)	a	737	797	961	1051	480	1346	908 ¹	1637	1720	
Δ		61	50	34	62	132	31	31	19	39	164
	b		854	822	1081	985	1261				
	c		784	1116	1117	1270	1299		1637		
			1072	1119	974	73	1327		1694		
										1894	
	g,b	740	(845)	880	1075	980	1270				
	g,c		1000	1100	1350	1390	1480		1600	1800 ^e	

TABLE III (cont'd.4)

		Sc [†]	Ti [†]	V [†]	Cr [†]	Mn [†]	Fe [†]	Co [†]	Ni [†]	Cu [†]	Zn [†]
F ₄ (dd)	a	51	32	70	81	134	113	-	122	132	
	Δ	8	7	5	7	21	4	-	7	27	
	b	53	76	75	91	97					
	c	20	81	100	94	116			118		
			82	86	113	141	136		139		
	e										136
	g,b	55	(55)		70	95	105				
	g,c		75	80	85	90	115		110	120 ^e	
G ₁ (pd)	a	380	450	310	483	1660	261	-	32	21	
	Δ	59	153	81	343	941	356	-	78	134	
	d		331	351	258	1177	540		229	324	
G ₃ (pd)	a	3	32	36	58	12	30	-	32	21	
	Δ	6	19	12	27	92	17	-	11	27	
	d		8	10	1	61	-23		17	32	
G ₁ (sp)	a	8243	7275	-5690	-	-	-		-	7	
	Δ	402	1836	849	-	-	-	-	-	1477	
G ₂ (sd)	a	1218	1812	1942	1747	1302	1591	3557	1541	2894	
	Δ	402	526	332	629	1279	227	203	194	1336	
	c		1694	1659	1536	1456	1613		1523	1808	

a Total regression, configurations, d^n , $d^{n-1}s$, $d^{n-1}p$, $d^{n-2}s^2$, $d^{n-2}sp$, $d^{n-2}p^2$ together.

b Regression of configuration of d^n .

c Regression of configuration $d^{n-1}s$.

d Regression of configuration $d^{n-1}p$.

e Regression of configuration $d^{n-2}s^2$.

f Regression of configuration $d^{n-2}sp$.

g L. E. Orgel, J. Chem. Phys. **23**, 1819 (1955).

h See reference 17.

i $\underline{W}(d^{n-2}sp) - 3\underline{G}_1(sp)$.

k $\underline{W}(d^{n-2}sp) - 2\underline{G}_1(sp)$.

l $\underline{W}(d^{n-2}p^2) - 5\underline{F}_2(00)$

m Contains $\underline{F}_4(dd)$.

n $\underline{G}(sp) - \underline{G}_2(sd)$.

o $\underline{W}(d^n) - 49\underline{F}_4(dd)$

p $\underline{W}(d^{n-1}s) - 147 \underline{F}_4(dd)$.

q $\underline{W}(d^{n-1}p) - 18 \underline{G}_1(pd) - 147 \underline{F}_4(dd)$.

r $\underline{W}(d^{n-2}s) - 294 \underline{F}_4(dd)$.

s $\underline{W}(d^{n-2}sp) - 7\underline{F}_2(pd) - \underline{G}_1(sp)$.

t $\underline{W}(d^{n-2}sp) - \underline{G}_1(sp)$.

u $\underline{F}_2(dd) - 5\underline{F}_4(dd)$.

v $\underline{G}_2(sd) - 21 \underline{F}_4(dd)$.

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APPENDIX VI

Nuclear Quadrupole Resonance of BrCl

by M. A. Whitehead and H. H. Jaffe

The ratio (F) of the NQR frequency (F_M) of an atom in a molecule to that (F_A) in the free atom,

$$F = F_M/F_A,$$

has frequently been expressed as

$$F = 1 + i - s^2 + d^2 - \pi \quad (1)$$

where i is the ionic character, s and d are the % s and d character, respectively, in the bonding hybrid orbital, and the plus or minus applies according to whether the atom concerned is the positive or negative end of the dipole, and π is the fractional π bond character. (2) The contributions of d orbitals have frequently been ignored, and in a molecule such as BrCl π must be zero. Equation (1) with neglect of d and π , actually is obtained by neglecting the presumable small term is^2 in Equation (2);

$$F = (1 + i)(1 - s^2). \quad (2)$$

In BrCl, two frequencies are observed, one for each atom, and each may be expected to be determined by an expression of the form of Equation (2). In these two expressions

$$F_{Cl} = (1 - i) (1 - s_{Cl}^2) \quad (3)$$

$$F_{Br} = (1 + i) (1 - s_{Br}^2), \quad (4)$$

i is the same, but s_{Cl} and s_{Br} may be different, since the two atoms may be differently hybridized. Multiplication of (3) and (4) yields

$$F_{Cl}F_{Br} = (1 - i^2) (1 - s_{Cl}^2) (1 - s_{Br}^2) \leq 1. \quad (5)$$

The limit of $F_{Cl}F_{Br} = 1$ implies $i = s_A = s_B = 0$, and hence $F_{Cl} = F_{Br} = 1$.

The experimental values obtained for this molecule are:
 $F_M^{Cl} = 51.8 \text{ Mc}$, $F_A^{Cl} = 54.87 \text{ Mc}$, $F_M^{Br} = 438.3 \text{ Mc}$, $F_A^{Br} = 384.9 \text{ Mc}$,²
hence, $F_{Cl} = 0.944$, $F_{Br} = 1.139$, $F_{Cl} \cdot F_{Br} = 1.075$, violating the
condition of Equation (5). The validity of neglecting π cannot be
questioned unless some $p\pi - d\pi$ resonance were postulated. The
discrepancy from $F_{Cl}F_{Br} = 1$ cannot be ascribed to experimental error,
not only because the magnitudes of the shifts are too large, but also
 $F_{Cl} \cdot F_{Br} = 1$ would imply $F_{Cl} = F_{Br} = 1$, which is obviously not the
case. Consequently, the only alternative appears to be to assume in-
volvement of d orbitals. Although use of $p\pi - d\pi$ hybridization can-
not be excluded, it seems more attractive to postulate use of d orbi-
tal in the bromine bonding orbital. This is partially justified
since Br is the positive end of the dipole, and consequently its d
orbitals are contracted. (1) Crude estimation shows that use of a
few percent of d character is sufficient to explain the observed Cl
frequency, without involvement of Cl s electrons, since the Br elec-
tronegativity is lowered and hence i increased. The Br frequency is
similarly explained, provided hybridization with d electrons exceeds
that with s electrons.

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APPENDIX VII

Orbital Energy Matching as a Factor in

the Interpretation of N.Q.R.

Frequencies in Halides

by M. A. Whitehead and H. H. Jaffe

The previous interpretations of the nuclear quadrupole resonance frequencies of the halogens in the halogen molecules and the inter-halogen compounds are considered, and the results are re-interpreted using Gordy's definition of ionic character and the assumption that the hybridization will occur to match the energies of the combining orbitals.

The interpretation of the frequency changes in nuclear quadrupole resonances of the halogens, in terms of changes in the ionic character of the bond and hybridization variations on the atom under examination, has given rise to two schools of thought. One, represented by Gordy, (8) maintains that the hybridization of the halogen is fixed and the frequency change is in consequence directly related to the ionic character of the bond. In this theory, hybridization is not generally considered but is called into play only in exceptional circumstances. The alternative approach is due to Townes and Dailey, (5), (26) who maintain that, provided the ionic character of the bond is above a certain minimum, the halogen is hybridized; the rule of thumb for assessing the hybridization is that, when the electronegativity difference exceeds 0.25 unit in the diatomic halides, the halogen at the negatively charged end of the molecule has 15% s character in the bonding orbital.

The complete Townes and Dailey relationship of the molecular eQq to the atomic eQq , where the atomic eQq is the frequency due to one unpaired electron in the z axis, e.e., $eQq_{\text{atomic}} = eQq_{zz}$, is ³⁻⁶

$$eQq_{\text{mol}} = [(1 - s^2 + i - \pi) + i(s^2 - d^2)] eQq_{\text{at}}, \quad (1)$$

where s^2 and d^2 are the s and d character present in the orbital, i is the ionic character and π , the double bond character. A quantity p may be defined by

$$p = eQq_{\text{mol}}/eQq_{\text{at}},$$

and if this is known it may be used to gain information about the amount of hybridization, ionic and π bond character. Unfortunately, s^2 , d^2 and i and π are all unknown, while p is the only measurable quantity; it is generally agreed (8)-(26) that both d and π are small in the diatomic halides, hence

$$p = (1 + i)(1 - s^2), \quad (2)$$

leaving one experimental datum and two unknowns. In order to solve this equation, one unknown must be found independently, and attempts have been made to derive a relationship between i and the electronegativity difference (3) between atoms A and B, and curves relating the ionic character to X have been proposed by Gordy (8), (7),

$$\Delta X = X_A - X_B, \quad (3)$$

and Townes and Dailey, (5) which allow determination of i and hence from (2) of s^2 .

On the basis of the results for Cl_2 and Br_2 , where $i = 0$, and of KCl and KBr , where $i = 100\%$, Gordy argues that there is no hybridization, unless $s^2 = d^2$ and consequently

$$\frac{1}{2} i = 1 - p, \quad (4)$$

while Townes and Dailey retain the s^2 term and have

$$\frac{1}{2} i + \frac{1}{2} i s^2 - s^2 = 1 - p, \quad (5)$$

from which they assess $s^2 = 0.15$ for diatomic halides whose ΔX exceeds 0.25 unit.

Figure 1 shows the plot of the ionic character, for several molecules, obtained using these theories, against ΔX . The curve due to Pauling, (18) who derived a relation between i and ΔX from a consideration of dipole moments, is also given; it is expressed by

$$i = 1 - \exp - \left[\frac{1}{4} (X_A - X_B)^2 \right].$$

It is interesting to note that this curve lies below those due to n.q.r. results. The curves are all theoretical. i -Values are shown as calculated from Equation (3) and (4); where the equations give different results two points are shown.

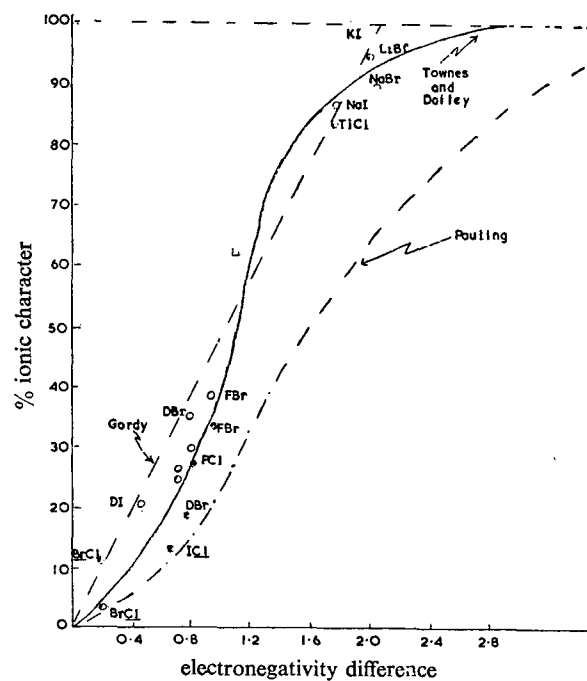


FIG. 1.—(I) theoretical curve from $i = \frac{1}{2}[X_A - X_B]$ with points from $i = 1 - \rho$; (II) theoretical curve from inclusion of s character in halogens and points from $\pm i \pm is^2 - s^2 = 1 - \rho$; (III) theoretical curve from $i = 1 - \exp[-\frac{1}{4}(X_A - X_B)^2]$ based on dipole moment data. The points give the ionic character of the bond, calculated from n.q.r. results of the atom underlined, using the appropriate equations of Gordy or Townes and Dailey.

● Townes and Dailey ; ○ Gordy ; ◐ Townes and Dailey and Gordy the same.

Gordy's initial curve $i = 1 - p$, actually levels off at the top for molecules such as the alkyl halides, which are considered to be completely ionic, and superimposes on the curves of Townes and Dailey. This curve led Gordy to propose that

$$i = \frac{1}{2}[X_A - X_B] \quad (6)$$

for $\Delta X \leq 2$, and

$$i = 1.00$$

for $\Delta X \leq 7$. It is this curve which is given in Figure 1. It is obvious that neither theory completely fits the facts for all cases.

The classic test of the two views lies in the interhalogen compounds in which it is possible to examine the bond from both ends. The results for BrCl and ICl are shown in Table 1. In BrCl, Townes and Dailey predict no hybridization as the electronegativity difference is only 0.2, so that their theory and Gordy's coincide.

The values for the ionic character of the bond as detected from the two atoms disagree markedly. In ICl, the assumption that no hybridization is present gives good agreement of the ionic character of the bond as calculated from the n.q.r. results of each atom, whereas the assumption of 15% character on the chlorine results in a wide discrepancy between the two assessments. Both the above approaches attempt to find the ionic character of the bond from the nuclear quadrupole results.

The earlier definitions (9), (10) of i involving the use of dipole moment data to relate i and ΔX were questioned (5) on the basis of m.o. theory. The wave function of a bonding electron is given by

$$\psi = a\psi_A - b\psi_B,$$

where ψ_A and ψ_B are the atomic orbitals on A and B. If ψ is normalized, then

$$a^2 - b^2 - 2abS = 1$$

where S is the overlap integral, and i for a heteropolar bond may be defined as $a^2 - b^2$, namely, the difference between the probabilities of finding the electron on A or B; any dipole moment assessment will always be too small.

The definition used in our work is that due to Gordy

$$i = \frac{1}{2}[X_A - X_B], \quad (7)$$

since this relationship is simple and i must be the same when measured from A or B, irrespective of whether Equation (7) is an exact relationship or not. The electronegativities to be used in later extensions of this work will not be the atomic X of Pauling or Gordy, but the orbital electronegativities (11), (12), (1) which reflect any changes in hybridization or bonding that the atoms may suffer, and hence provide a unique relation between S and i .

It appears more reasonable to use the discrepancy between the resonance frequencies and their expected linear relationship to the ionic character to find the change in hybridization. Neither the assumption of no hybridization, nor of a set percentage on the more negative halogen is reasonable or satisfactory.

In both the molecular orbital and valence bond theories of bonding, two requirements (18) must be met by the combining atoms before a strong bond can be formed between them. The first is that the two atomic orbitals forming the bond must overlap substantially: the second is that the atomic orbitals must have similar energies. The latter requirement is not often considered and the maximum difference of the energy of two orbitals which can still form a strong bond has never been estimated. It is, however, known that, other things being equal, the strongest bond is formed between orbitals of equal energy.

Coulson (2) has shown that the criterion of maximum overlap as developed by Pauling (18) and Slater (23) is valid only under certain conditions dependent on the energies of the combining atomic orbitals, E_a and E_b . From the normal variational treatment of a diatomic molecule,

$$E_i = H_{ii} = \int \psi_i^* H \psi_i dr,$$

and

$$E = \frac{H_{ab}}{S} = \frac{\int \psi_a^* H \psi_b dr}{\int \psi_a^* \psi_b dr},$$

where ψ_a, ψ_b are the atomic orbitals of atoms a and b, H is the Hamiltonian operator and S the overlap integral and i can stand for a or b. The principle of maximum overlap applies only when E_{ab} is less than

both E_a and E_b ; when E_{ab} lies between E_a and E_b the criterion is actually reversed, minimum overlap giving the most stable situation. Thus, other things being equal, the binding energy is greatest when the component a.o. have as nearly equal energies as is possible, (2) and if these energies (for diatomic or polyatomic molecules) are not of comparable value, no significant combination will occur.

The energy match thus governs which orbitals combine (for example, in HCl the energy match is responsible for the combination of the H(1s) with the Cl(2p)), and only then, when the energies are suitable, will the criterion of maximum overlap come into play (in HCl, causing the p orbital directed toward the hydrogen to be used in bonding).

Since a complete m.o. treatment does not involve concepts such as electronegativity and ionic character, the approach adopted in this paper is to use the basic requirements of m.o. theory and to investigate how they affect the interpretation of nuclear quadrupole resonance results in terms of the semi-empirical chemical concepts of electronegativity and ionic character.

The principle of energy is clearly illustrated in carbon monoxide, (12) where, in order to match the energies both the carbon and oxygen orbitals are hybridized, and the orbitals which bond are the predominantly p hybrid orbital of the oxygen and the predominantly s hybrid orbital of the carbon. The chemical and physical properties of CO are explained as are the differences between it and the isoelectronic N₂ molecule. More detailed quantitative m.o. calculations (21), (20) imply a similar qualitative picture.

The overlap requirement suggests that hybridization will occur in the halogens if the hybridized orbital is more suitable to overlap than the unhybridized one, and in the diatomic halogen molecules Cl₂, Br₂, I₂ it is reasonable to expect that some hybridization of s and p orbitals may occur to improve the overlap, since the sp hybrid presents a larger lobe of the atomic orbital to form the molecular orbital.

The difference in n.q.r. frequency between the molecules and the atoms should reflect this hybridization. There can be no ionic effect since the molecules are purely covalent, and the covalent bond as such does not affect the frequency, (7) only the changed distribution due to hybridization can do so. To avoid crystal state complications, gaseous state results are given wherever possible. (6) Then, (5) applying

$$p = eQq_{\text{molecular}}/eQq_{\text{atomic}} = 1 - s^2, \quad (8)$$

the hybridization present in the halogen molecules is found (Table II), where s is the coefficient of the s orbital in the hybrid wave function. If, then, in the pure covalent state, chlorine exhibits a certain, though small, amount of hybridization because this sufficiently improves the overlap of the atomic orbitals, and thereby more than offsets the promotion energy required, it appears that Gordy's assumption of no hybridization of chlorine in the diatomic halides is questionable.

The estimates of 0% hybridization for Br_2 and I_2 may well be too low since, as pointed out by Townes and Dailey, (5) the effect of d -orbital hybridization would operate in the opposite direction from s hybridization, and the two might actually cancel. The presence of d hybridization in halogen molecules is also predicted by Mulliken (16) with much double bond character in all three halogens Cl, Br and I. In what follows, d orbital hybridization will be neglected, but it will be shown that this neglect leads to contradictions. (24) The effect of inclusion of d orbitals will be treated in a later paper.

It is at this point necessary to consider the requirement of similar orbital energies for the formation of a stable chemical bond. This requirement is of no consequence in the halogen molecules (X_2) since symmetry provides perfect matching, so that hybridization in these compounds will be determined solely by a balance of increased bond energy due to improved overlap and promotion energy required in hybridization. An examination of the energies of the s and p orbitals of the halogens (Figure 2) (15) shows that hybridization should occur in the interhalogens on the halogen having higher p orbital energy, thus strengthening the bond; any hybridization on the atom of lower p orbital energy would weaken the bond. In the interhalogen compounds the positively charged halogen has the higher energy orbital and should accordingly be hybridized - a direct contradiction to the view of Townes and Dailey. When the halogen is joined to an atom which has the positive charge but cannot hybridize, such as hydrogen or deuterium, then the halogen, although negatively charged, may be hybridized.

Actually the sign of the charge of an atom is not the determining factor in hybridization, since it is always the atom with the higher energy atomic orbital which must hybridize. It seems possible, therefore, to stipulate that the atom having the higher energy atomic p orbital will hybridize with s character, and that the other atom will be less, if at all, hybridized then it is in the neutral diatomic molecule X_2 . Any inclusion of s hybridization at the energetically more stable atom must result in an increased amount of s character in the atomic orbital of the less stable atom.

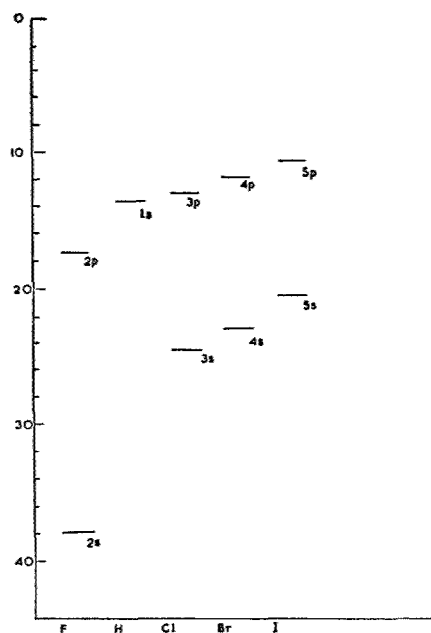


FIG. 2.—The energy levels of the *s* and *p* orbitals in the halogens and hydrogen atoms.

The electronegativity, and hence the ionic character, should not be considered as an independent variable since electronegativities depend on the valence state of the atom. (22) Perhaps the best method of finding the true state of affairs would be to use the ionic character $i = \frac{1}{2}(X_A - X_B)$ and the n.q.r. frequencies to find the *s* hybridization, and to use this to find the change in electronegativity of the atom and hence the change in the ionic character of the bond. The true hybridization and ionic character could then be found by applying a self-consistent treatment. Such a self-consistent treatment is now under examination in this laboratory.

The hybridization present in the molecules formed between the halogens, the halogens and hydrogen and the halogens and the pseudo-halogen cyanide group were recalculated using the foregoing ideas. The results are given in Table III. The calculations were made using Townes and Dailey's formulae:

$$eQq_{\text{molecular}} = (1 - s^2)(1 - i)eQq_{\text{atomic}}(\text{negatively charged atom}),$$

$$eQq_{\text{molecular}} = (1 - s^2)(1 - i)eQq_{\text{atomic}}(\text{positively charged atom}),$$

where s is the coefficient of the wave function of the s orbital's contribution to the molecular orbital (s^2 giving the fractional s character)

$$\psi = ss + \sqrt{1 - s^2}p_x,$$

and i is the fractional ionic character given by Equation (6). The change of sign for i occurs as the difference in electronegativity results in removing electron density from the positive atom thus increasing the spherical unbalance between the y and z axes and the x axis, raising the frequency. The reverse happens at the more electronegative atom. However, s hybridization always lowers the spherical unbalance and the frequency.

A rough estimate of the ionization potential of the hybridized orbital, ignoring electron correlation, can be made from

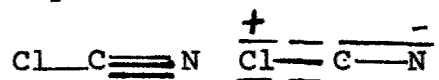
$$E = x_1E_1 - x_2E_2$$

where x_n is the fraction of the n th atomic orbital present, and E_n is the energy of that orbital. By this approximation the ionization potentials required in column 5 of Table IV are obtained, and it is seen that, in all cases, the hybridized orbitals of the two atoms are more closely matched in energy and hence are expected to give a stronger bond.

The results indicate that the electronegativity difference estimated for FCl by Gordy and Haissinsky (8), (9) is more suitable than the normal value of Huggins since it predicts a much better energy match of the orbitals, closing the gap from 4.41eV, whereas the Huggins value reduces it to 4.03. A greater assessment of ionic character in FBr would also produce a better energy match. The general trends in the amount of s hybridization obtained and shown in Table IV are not as expected. In order to match the energy of the orbital of a given atom, bromine should hybridize with more s character than chlorine; the results show that bromine displays nearly the same or less s character than chlorine. This suggests that d hybridization is occurring and masking a certain amount of s hybridization, for, while s hybridization always lowers the frequency, d hybridization invariably raises it. This conclusion is strengthened by the failure of the simple calculations for BrCl, ICl, DBr, DI and ICN. This fact may be ascribed to involvement of d orbitals as shown previously for BrCl. (24) Preliminary iterative calculations show that negative s values are obtained for BrCl, ICl and DI; for the halogen cyanides, HCl and HBr, decreasing values of s are obtained in going down the halogen series, contrary

to expectation. This result is presumably only an apparent one, and is due to neglect of d-orbital hybridization. Hence it may be concluded that involvement of d orbitals also must be considered in all compounds of Br and I. This conclusion is not inconsistent with the known results for Br₂ and I₂, provided s and d character have about the same magnitude. (5), (13)

The molecules HCN, ClCN, BrCN and ICN provide an interesting series in which the atomic and molecular frequencies of both the nitrogen and halogens are known but in which bonding occurs between the carbon and nitrogen, and possibly over the whole molecule:



(the second form being a more reasonable representation than a double bonded structure possessing formal charges ($\overset{+}{\text{X}}=\text{C}=\overset{-}{\text{N}}$), since it shows that the triple bond extends over the whole molecule).

The energy-level diagrams are given for HCN and XCN in Figure 3, the halogen hybridized orbitals being those predicted from the halogen resonance frequencies assuming only s hybridization and the lack of d or character; the presence of character in the halogen bonding would result (see Equation (1)) in a lower assessment of s character and a less stable energy level on the halogen. If the fraction of an electron present in an orbital is given by N then

$$p = [(N_x + N_y)/2 - N_z],$$

where the z axis is the CN axis and x and y represent the p orbitals. The values of N_x and N_y range from one in the free atom to two when each is doubly occupied, the cyanides lying between these limits. The value of N_z is given by

$$N_z^{\text{nitrogen}} = (1 + i)(1 + s^2)$$

since initially the p_z orbital holds one electron, and, with N negatively charged, both the ionic character and the s hybridization will raise this above unity, decreasing the field gradient.

In HCN there can be no π bonding between the hydrogen and the cyanide group, so the value of $(N_x + N_y)/2$ depends solely on the transfer of electron density from carbon to nitrogen, which is aided by the adjacent hydrogen, raising the frequency; at the same time, in order to match the H(1s) orbital the CH bonding carbon orbital will require

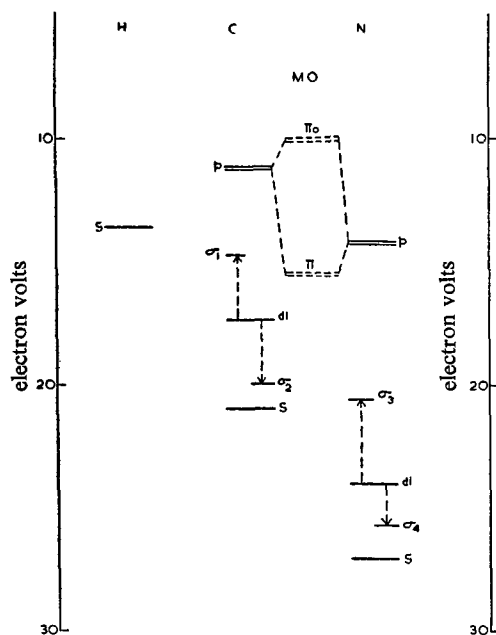


FIG. 3(a)

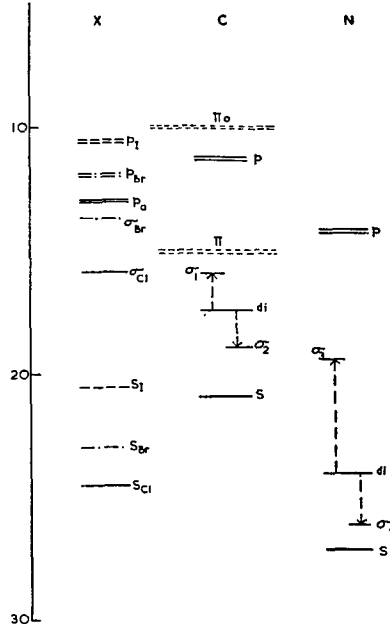


FIG. 3(b)

FIG. 3.—(a) The energies of the pure s and p atomic orbitals of H, C and N and the σ bond sp hybrids are shown. The *energy match* results in a decrease in the s character of one digonal orbital and an increase in the other, giving on C the orbitals σ_1 and σ_2 and on N, σ_3 and σ_4 . The molecular orbitals form between H($1s$) and σ_1 , and σ_2 and σ_3 ; σ_4 is the lone pair, predominantly s in character, and poor at co-ordinating. σ_1 = carbon CH orbital energy, σ_2 = carbon CN orbital energy, σ_3 = nitrogen NC orbital energy, σ_4 = nitrogen lone pair energy. The decrease in stability of σ_3 is twice the gain in stability of σ_4 since it contains only one electron while σ_4 contains two electrons. The effects on the n.q.r. frequency are: (I) π_0 , no effect as unoccupied; (II) π , increase; (III) s^2 , decrease; (IV) i , decrease. (b) The energies of the pure s and p atomic orbitals of C, N and the three halogens Cl, Br and I, and the sp hybridized σ bonds of the halogens are shown, as calculated from the n.q.r. halogen frequencies in these compounds. The *energy match* results in similar orbital rehybridization to that in HCN. The π molecular orbital energy levels are also shown as spreading over all three atoms; π is the bonding and π_0 the non-bonding orbital. The effects on the n.q.r. frequencies are: (I) π_0 , increased frequency; (II) π , increased frequency—less than in HCN; (III) s^2 , decreased frequency—more than in HCN; Cl > Br > I; (IV) i , decreased frequency—less than in HCN; I > Br > Cl.

less s than in the pure diagonal condition, so that the bond toward nitrogen possessing more than 50% has greater stability and the nitrogen will need less s than pure diagonal to match it, lowering the frequency. The ionic character can be assessed (14) as 35% for the CN bond, increasing the frequency.

In the halogenocyanides, the p orbitals available for π bonding show a decreasing tendency to hold the two electrons on progressing from Cl to I, hence releasing more to the nitrogen and increasing the frequency, but less than in the hydrogen cyanide. The ionic character of the CN bond progresses 12.5%, 17.5% and 25% tending to make the iodocyanide frequency the lowest, while the s hybridization required in a π bond energy match favours a higher frequency on descending the group.

These considerations are in accordance with the observed order of frequencies and the large gap between the frequencies of the hydrogen and halogen cyanides. Such explanations are, however, tentative, since d hybridization may be present in both the bromine and iodine compounds, while π bonding to the halogen requires a reassessment of the amount of s character. While less s character decreases the energy match, the partial positive charge placed on the halogen by the π bond, increases the stability of the levels; a corresponding decrease in stability occurs on the nitrogen levels. The overall energy level picture is most likely one of improved matching. A self-consistent treatment might unravel these interrelated effects of s^2 , d^2 , π and i as well as the dependence of the energy levels of an atom on the partial charge that the atom possesses.

TABLE I

		<u>Ionic character of bond</u>	
Compound		from eQqCl	from eQqX
Townes and Dailey Gordy	BrCl	.056	.110
Townes and Dailey Gordy	ICl	.115	.229
	ICl	.248	.229

TABLE II
s HYBRIDIZATION IN HALOGEN MOLECULES

Halogen	Cl ^o	Cl ₂	Br ^o	I ^o	I ₂
Frequency (Mc/sec)	54.87	54.2475	384.9	1146.42	1146.36
s-character		2%	0%		0%

TABLE III

HYBRIDIZATION OF THE DIATOMIC HALIDES
AND THEIR IONIC CHARACTER
FROM NUCLEAR QUADRUPOLE RESULTS

<u>Molecule X-Y⁻</u>	<u>eQq obs. in gaseous phase: Mc/sec</u>	<u>% ionic character a,b,25 $i = \frac{1}{2}(XA-XB)$</u>	<u>% s character in orbital from $\frac{eQq_M}{eQq_A} = (1-s^2)(1-i)$</u>
Cl ⁰ atomic	54.87		
F-Cl	73.0	{ 37.5 65 ^c	{ 3.27 19.4
Cl-Cl	54.47		
Cl-CN	32.9	20	4.9
Cl-D	27.309	47	9
Cl-H	26.696		8
Br ⁰ atomic	384.9		
F-Br	544.5	47	3.74
Br-Br	384.88	0	0
Br-CN	286.2	10	17.3
I ⁰ atomic	1146.42		
I-I	1146.36	0	0
Cl-CN	3.63	20	
Br-CN	3.83	10	
I-CN	3.80	5	
H-CN	4.58	25	
N ⁰ atomic	18.00		

(a) The CN electronegativity is taken as 2.6

(b) M. Huggins, J. Amer. Chem. Soc., 1953, 73, 4123. Kauzmann, Quantum Chemistry (Academic Press, 1958).

(c) Gordy, Microwave Spectroscopy (Johy Wiley and Sons, New York, 1953), p. 282 Haissinsky, J. Chim. Physique, 1949, 46, 298.

TABLE IV

THE ENERGIES OF THE HYBRIDIZED ORBITALS IN THE DIHALIDES

Molecule in gaseous state	Atomic p level energy in eV	Atomic s level energy in eV	% s character	Mismatch pure p levels in eV	Energy of hybridized orbital in eV	Mismatch of hybridized orbitals in eV
F	17.42	37.8	0	4.41	17.42	4.03 or 2.16
Cl	13.01	24.6	3.28 ^a or 19.4 ^b		13.39 or 15.26	
F	17.42	37.8	0	5.58	17.42	5.16
Br	11.84	23.0	38		12.26	
H	13.60		(100)	0.59	13.60	.477
Cl	13.01	24.6	9.2		14.077	
Cl	13.01	24.6	25	2.89	15.9	0
CN		sp ³ C = 15.9	-		15.9	
Br	11.84	23.0	17	4.06	13.74	2.16
CN		sp C = 15.9	-		15.9	

(a) from Huggins' electronegativities;

(b) from Gordy's and Haissinsky's estimation of ionic character; see footnotes to Table III

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- (24) This conclusion is most obvious in BrCl; cf. Whitehead and Jaffe, J. Chem. Physics, in press.
- (25) A new definition of the ionic character has been proposed (Wilmhurst, J. Chem. Physics, 30, 561 (1959)). But as this does not seem to us to be a reasonable one it has not been considered in this paper. The ionicities predicted in general give a bad energy level match between the combining orbitals, except in BrCl where it leaves the levels 0.28 eV apart. The scale of electronegativities by Brown, J. Amer. Chem. Soc., 1960, 83, 36, gives results similar to those calculated above on Huggins' scale.
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APPENDIX VIII

d-Orbital Involvement in BrCl and ICl

by M. A. Whitehead

An attempt is made to solve for the s-hybridization s and ionic character i of the halogens in BrCl and ICl from NQR data. It is shown that ignoring d hybridization gives untenable estimates of s and i . A tentative estimation of the d character is made.

In a previous note, (13) the existence of d hybridization in the bromine orbital in BrCl was suggested as necessary to explain the observed nuclear quadrupole frequency. The use of such a hybridization had been tentatively suggested earlier by Gordy, (4) who nevertheless preferred a solution in which the presence of 10% ionic character on the Br and 6% ionic character on the Cl explained the measured frequencies. Townes and Dailey, (3) on the other hand, preferred "15% s hybridization on the negatively charged halogen" as well as the presence of ionic character. Gordy (4) argued that the positively charged atom would be preferentially hybridized in order to match more closely the electronegativities of the bonded atoms. This view was extended in the paper of Whitehead and Jaffe, (12) who stated that the charge exhibited by the atom was, in fact, irrelevant; it was always the atom with the least energetically stable orbital which hybridized. Thus, in ICl the iodine hybridized, in HCl the chlorine. In subsequent papers (5)-(14) these authors also arrived at the view that hybridization and charge transfer (ionic character) will occur till the atomic orbitals bonding to form the molecular orbital have identical electronegativities, thus fulfilling the MO theory requirements for a strong bond. Except with regard to questions of charge, this view corroborates Gordy's original view. (4)

In the Townes and Dailey approach to the interpretation of nuclear quadrupole coupling constants, (1) the ratio of the molecular quadrupole moment to the atomic quadrupole moment p is given by

$$p = (1 - s + d) (1 + i) - \pi, \quad (1)$$

where s and d are the amounts of s and d hybridization in the bonding orbital, i is the ionic character, and π the amount of double-bond character.

It was shown (13) that the experimental results (10) for BrCl gave

$$p_{ClpBr} > 1, \quad (2)$$

which is also true for the product of the p 's for ICl, (10) whereas when π bonding is assumed zero, and d hybridization assumed absent, then Equation (1) becomes

$$p = (1 - s) (1 + i),$$

in which case Equation (2) would always be less than one for the p_{Clpx} product. If, as in Gordy's treatment, the s character is zero, then the product $p_{Clpx} = (1 - i^2)$ is still contrary to experiment.

These considerations lead to the prediction, in the earlier note, (13) that not only was d hybridization necessary, but that it would exceed the s hybridization. A new approach arose naturally from these observations and has been applied to both BrCl and ICl. While it is still impossible to determine, absolutely, the amount of d hybridization, its existence now seems irrefutable.

As before (13) we initially assume that there is no π bonding nor d character in either orbital, when in XCl ($X = Br$ or I)

$$p_{Cl} = (1 - s_{Cl}) (1 - i), \quad (3)$$

$$p_X = (1 - s_X) (1 + i), \quad (4)$$

or, eliminating the ionic character,

$$\left[p_{Cl} / (1 - s_{Cl}) \right] + \left[p_X / (1 - s_X) \right] = 2. \quad (5)$$

Thus, s_{Cl} can be expressed in terms of s_X , or vice versa.

One of the difficult concepts to fix is that of ionic character. The latest work on electronegativities (6), (7) however, is allowing a better approach to the definition to be made. In recent papers Iczkowski, (7) and subsequently Jaffe, (5) defined electronegativity from

$$E(n) = k + an + bn^2 + cn^3 \dots,$$

where $E(n)$ is the energy of the valence state of n electrons, and a , b , c , etc., are coefficients. It can be shown (7) that only the n and n^2 terms are large. The electronegativity X is defined as

$$X = dE(n)/dn = a + 2bn, \quad (6)$$

while the ionic character is defined as the charge transfer which results in the electronegativities of the orbitals forming the bond being equal (15)

$$\begin{aligned} X_A &= X_B, \\ a_A + 2b_A n_A &= a_B + 2b_B n_B, \end{aligned} \quad (7)$$

but, as there are only two electrons involved

$$\begin{aligned} n_B &= 2 - n_A, \\ a_A + 2b_A n_A &= a_B + 2b_B (2 - n_A), \end{aligned}$$

so that the ionic character i is given by

$$i = n_A - 1 = \left[\Delta X / 2(b_A - b_B) \right] (\Delta X = X_A - X_B) \quad (8)$$

Now the assessment of b_A and b_B is not directly expressible in terms of electronegativity difference, but it appears (6) that Gordy's (4) original definition (arrived at from nuclear quadrupole and dipole results) that

$$i = \frac{1}{2} [X_A - X_B] \quad (9)$$

is the most reasonable presently available assessment of ionic character. (16) It is therefore used in this paper as a definition of ionic character divorced from any relationship to its origins in nuclear quadrupole work, (12) but the electronegativities used are the Orbital Electronegativities (6) is defined as

$$X_{\text{orbital}}^{\text{Cl}} = s_{\text{Cl}} X_{0\text{Cl}}^{\text{s}} + (1 - s_{\text{Cl}}) X_{0\text{Cl}}^{\text{p}}, \quad (10)$$

where $X_{0\text{Cl}}^{\text{s}}$ is the orbital electronegativity of the chlorine s orbital. The orbital electronegativity is thus a linear combination of the s and p orbital electronegativities, where s is the amount of s character present in the orbitals.

Identical equations apply to the orbital of atom X. Thus, Equation (3) becomes

$$pCl = (1 - s_{Cl}) \left[1 - \frac{1}{2} \left\{ s_{Cl} X_{0Cl}^S + (1 - s_{Cl}) X_{0Cl}^P - s_X X_{0X}^S - (1 - s_X) X_{0X}^P \right\} \right] . \quad (11)$$

This may be performed similarly with p_X if desired. With the substitution of s_X from (4) this equation becomes a cubic in s_{Cl} alone and all other terms X_{0Cl}^S , X_{0Cl}^P , S_{0X}^P , p_X , and pCl being known, the s_{Cl} hybridization can be uniquely derived, and subsequently from (4) s_X ; these, together, define i . This approach, therefore, permits the reduction to one the variables to be related to the measured frequency ratio (on ignoring d character); there are no longer five variables and one empirical result to help unravel them, as was the case when both the atom S and Cl could display s , d , and i character. The view of Townes and Dailey (2) that it is impossible to separate ionicity and hybridization is, of course, true, but since they are mutually dependent, the unique determination of two hybridizations results in a direct assessment of i , using quadrupole data alone. The cubic is

$$\begin{aligned} & 2(X_{0Cl}^S - X_{0Cl}^P)s_{Cl}^3 + (-2X_{0Cl}^S + 4X_{0Cl}^P - 4 + cX_{0Cl}^S \\ & - a_{0X}^S - 2X_{0X}^P + aX_{0X}^P - cX_{0Cl}^P)s_{Cl}^2 + (4 - cX_{0Cl}^S \\ & - 2X_{0Cl}^P + cX_{0Cl}^P + aX_{0X}^S + 2X_{0X}^P - aX_{0X}^P - 2c \\ & + cX_{0Cl}^P - cX_{0X}^P - bX_{0X}^S + bX_{0X}^P - 4p_{Cl})s_{Cl} \\ & + (-2c_{pCl} - bX_{0X}^P + cX_{0X}^P + 2c - cX_{0Cl}^P + bX_{0X}^S) = 0, \end{aligned} \quad (12)$$

where a , b , and c are the coefficients in the rearranged form of Equation (5)

$$s_X = (as_{Cl} + b)/(2s_{Cl} + c). \quad (13)$$

The coefficients a , b , and c , together with the X_0 and p for $BrCl$ and ICl , are given in Table I, and the solutions to the cubics in Table II.

The bond lengths of $BrCl$ (2.138 Å) (15), (11) and ICl (2.30 Å)

TABLE I

TERMS REQUIRED IN THE QUADRATIC

<u>Compound</u>	<u>Atom</u>	<u>Orbital</u> electronegativities		<u>p^a</u>	<u>Hybridization</u> found			
		<u>X0s</u>	<u>X0p</u>			<u>A</u>	<u>B</u>	<u>C</u>
BrCl	Br	5.937	2.615	1.1387	s _{Br}	1.056	0.0827	-0.8613
	Cl	5.673	2.945	0.944	s _{Cl}	0.8613	0.0827	-1.056
ICl	I	5.065	2.513	0.7518	s _{Cl}	0.675	0.0768	-1.2482
	I	5.065	2.513	1.325	s _I	1.2482	0.0768	-0.675

^a See references (9) and (10)

TABLE II

SOLUTIONS FOR THE s HYBRIDIZATION
IN THE HALOGENS FROM THE QUADRATICS.^a

s_{Cl}	s_{Br}	s_{Cl}	s_I
+2.03	+0.61	+1.79	+0.59
-0.049	-0.035	-0.016	-0.052
+0.069	+1.89	+0.74	+2.82

^a Identical results whether s_{Cl} is solved and the corresponding s_x found, or vice versa.

show that double bonding is extremely unlikely, so that any explanation of the results depends upon the possibility of d hybridization occurring.

The positive results for s hybridization both in BrCl and ICl can obviously be discounted as no explanation could account for 2.0 s hybridization or the like.

The negative results are, however, very interesting, for while it is physically impossible to realize it, it can be explained.

If the bromine or iodine uses d orbitals, then Equation (4) should read

$$p_x = (1 - s_x + d_x)(1 + i), \quad (14)$$

so that the s_x carried through in the quadratic is actually $(s_x - d_x)$. If the chlorine d orbitals were used, a similar term would occur in Equation (3), but it is an unlikely situation considering the energy of the chlorine d orbitals (12), (8) and the hybridization in the bromine or iodine is more likely.

Thus, the results in Table II are those for $(s_x - d_x)$ and show that the $d_x > s_x$ in size as was proposed in our earlier note. (13) If this is so, then the occurrence of the negative result for chlorine can be accounted for, since the ionic character (9) depends upon (10), and while this is correct for the chlorine, for bromine or iodine it becomes

$$X_{\text{orbital}}^x = sX_{0x}^s + (1 - s - d)X_{0x}^p + dX_{0x}^d. \quad (15)$$

In the calculation, however, Equation (10) was used, so that no allowance for X_{0x}^d was made. Thus, the X^x orbital assessed is too small, the ionic character in consequence is too large. Therefore, the chlorine s hybridization in order to satisfy Equation (3) will have to be negative. At the same time, this negative s results in a smaller assessment for X_{0Cl} and a smaller ionic character; the result is thus a balance in accommodating the $(s_x - d_x)$ result by means of Equations (3) and (9).

The results show that the conclusion previously arrived at, (13) that the d hybridization must exceed the s hybridization in the bromine σ orbital of BrCl is also true of iodine, and that it does so by greater amount in iodine than in bromine.

Unraveling these effects is difficult. Making the following assumptions:

(1) There is no hybridization at all on the chlorine so that Equation (3) yields an estimate of the ionic character.

(2) The d orbital electronegativity of bromine and iodine is approximately 0.5 (present estimates in this laboratory of X_0^d for transition metals show them to be negative or very small), whence, Equations (14) and (15) can be used, then the following assessments of s_x and d_x are obtained. In BrCl the bromine exhibits 0.39 d and 0.32 s character; in ICl the iodine exhibits 0.17 d and 0.11 s character. These are obviously not correct, but at least give a "feel" for the amount of s and d character involved.

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- (15) "Interatomic Distances," edited by L. E. Sutton, Spec. Publ. 11, The Chemical Society (London) (1960).
- (16) The actual value of i would be altered by the denominator $b_A - b_B$, but no matter how, the theoretical value of p_{HPCl} would always be less than unity. The assumption that Gordy's equation can be used will alter the absolute values of any hybridization present, but not the relative amounts used.

APPENDIX IX

Orbital Electronegativities and the Determination of s and d Hybridization in Various Halides from Nuclear Quadrupole Resonance Frequencies

by M. A. Whitehead and H. H. Jaffe

The use of Orbital Electronegativities in the interpretation of NQR results for various halides is discussed, and an attempt to determine the amount of d hybridization in and bonding is made. The ionic characters are assessed.

Earlier reports have covered the relationships (1) between nuclear quadrupole resonance frequencies and the hybridization of halogen atoms, with energy match considerations included, and (2) between the orbital electronegativity and the valence state of atoms. (21), (22) The present paper deals with the relationship between the quadrupole measurements and the orbital electronegativity.

In the case of mono- and di-halide molecules it was established (21) that hybridization on the halogen with the less stable atomic orbital accounted well for the observed quadrupole frequency for either nucleus in the molecule, and resulted in a better match in the energies of the combining orbitals, corroborating Gordy's original views. (6) It was further shown (21), (22) that the possibility that the d orbitals of the halogens were involved in bonding was rendered quite probable, particularly in the case of BrCl. (2), (3)

In the previous work the valence state ionization potentials were used for the energy of the orbitals on the atoms, but it subsequently appeared that orbital electronegativity was a better approximation to orbital energy and this will be used in this paper.

On the basis of Molecular Orbital Theory, Coulson (1), (2) has shown that the energy of the atomic orbitals combining should be approximately equal. The energy he considered was given by

$$E_i = \int \psi_i^0 \psi_i dr \quad (1)$$

where ψ_i is the wave function of the atom i and $\hat{H}^0$ is the adjusted Hartree-Fock Operator. Thus for a strong bond between two atoms A and B,

$$E_A \simeq E_B$$

that is
$$\int \psi_a^* \hat{H}^0 \psi_a d\tau \simeq \int \psi_b^* \hat{H}^0 \psi_b d\tau$$

It was for this energy that the ionization potential was considered a sufficiently accurate measure.

Mulliken (16) has defined the Electronegativity of an atom as

$$\chi = 1/2 [EA - IP] \quad (2)$$

where EA and IP are the electron affinity and ionization potential of the atom respectively, and he holds (17) that this electronegativity is a good measure of the energy of molecular orbital theory, (16) hence

$$\chi_i \simeq E_i \quad (3)$$

Thus in this new form the theory states - in order to form a strong bond, the orbital electronegativities of the combining atomic orbitals should be approximately equal - the strongest molecular bond is formed when two atomic orbitals have equal orbital electronegativities. It is this approach which is used, and applied to the dihalides originally considered, and also to the symmetric polyhalides of group 3(B), 4 (C, Si, Ge, SN) and 5 (P, AS) and the mixed halides of carbon.

In the interpretation of nuclear quadrupole results (21), (22), (7) the ratio of the frequency of the atom in the molecule, eQq_M , to that of the free atom, eQq_A , is defined as ρ and in the theory of

$$\rho = eQq_M/eQq_A \quad (4)$$

Townes and Dailey (3), (7) this ratio is related to the ionic character of a bond, i , and the amount of s hybridization in the atomic orbital, s by the equation

$$\rho = (1 - s) (1 + i) - \pi \quad (5)$$

where π allows for any π bonding between the p orbitals of the atom and the available orbitals in the molecule; the s and i apply to the bond only.

The use of d orbitals is not considered and in a compound such as CCl_4 this is justifiable as the d orbitals are quite high in energy (12) and consequently unsuitable for bonding. To a first approximation, again perfectly true in CCl_4 , σ bonding may be ignored since the carbon has no orbitals to accept p electrons from the halogens.

In the diatomics, the ionic character i was defined, following Gordy, (5) as

$$i = 1/2 (\chi_A - \chi_B) \quad (6)$$

where χ_A and χ_B were the orbital electronegativities (19), (8) of the bonding atomic orbitals of the two atoms A and B of the diatomic molecule AB.

The latest work on electronegativities (10), (9) has allowed a more rigorous approach to the definition of ionic character which supports the definition due to Gordy but removes from it any dependence on NQR results. Iczkowski (10) and subsequently Hinze (9) defined electronegativity from

$$E(n) = K + an + bn^2 + cn^3 \dots$$

where $E(n)$ is the energy of the valence state of n electrons and a , b , c , etc. are energy coefficients. It can be shown (10) that only the n and n^2 terms are large. The electronegativity is defined as

$$= \frac{dE(n)}{dn} = a + 2bn$$

while the ionic character is defined as the charge transfer which makes the electronegativities, of the bonding orbitals identical

$$\chi_A = \chi_B$$

In the system there are only two electrons, so

$$n_B = 2 - n_A$$

but

$$a_A + 2b_A n_A = a_B + 2b_B n_B$$

hence

$$a_A + 2b_A n_A = a_B + 2b_B (2 - n_A)$$

so that if the ionic character is defined as

$$i = n_A - 1$$

then

$$i = \frac{\frac{1}{2} (\chi_A - \chi_B)}{(b_A + b_B)}$$

This makes i a dimensionless quantity, since $\frac{\partial (n)}{\partial n}$ $n = 1$ and b are energies, and with $b_A + b_B = 1$ this reduces to Equation (6). The assessment of b_A and b_B is not expressible in terms of electronegativity difference, but nevertheless it appears that Gordy's original definition (6) is the most reasonable at present available. The actual value of i will be altered by the denominator $(b_A + b_B)$ and absolute values may shift for the s character, but the change should not be significant.

In a polyatomic molecule, a new complication arises since the orbital electronegativity of the central atom will depend on the atoms or groups to which it is bonded. In order to account for this environmental factor, the method of Kagarise (18) and of Lagowski (13) is followed, in which the electronegativity of a central atom - say carbon - toward one of its neighbors is adjusted for the presence of all other neighbors by a correction calculated from their electronegativity, giving what will be called an effective electronegativity, χ_{eff} . This procedure has been quite successful in the correlation of infrared and NQR results, (15) and has been theoretically justified. (9)

The Method

It is desired to use Equation (5), omitting the last term (π), to solve for i and s . The ionic character i is assumed to be given by Gordy's relation, (6). The relation between orbital electronegativity of a hybrid χ_{hyb} and the individual orbital electronegativities of the pure s , and p orbitals, χ_s and χ_p , was found to be a simple linear relation: (8)

$$\chi_{\text{hyb}} = s\chi_s + (1-s)\chi_p \quad (7)$$

In recalculating the halides in the F, H and D cases and in the XCN cases, the χ_{eff} of the F, H and D was assumed to be pure unhybridized χ_p , while in the CN group the χ_{eff} of the C orbital towards the halogen was taken as 2.6 to bring it into line with the previous paper. (21)

Hence in the A-X halides

$$\left[\chi_{\frac{o}{2}}^s - \chi_{\frac{o}{2}}^p \right] \underline{s}^a - \left[\chi_{\frac{o}{2}}^s - \chi_{\frac{o}{2}}^p + 1 + \frac{\chi_{\frac{o}{2}}^A}{2} \right] \underline{s} + 1 + \frac{\chi_{\frac{o}{2}}^A}{2} - \frac{\chi_{\frac{o}{2}}^p}{2} - p = 0$$

where A has no quadrupole moment. But in BrCl and ICl where both halogens show a resonance we have

$$P_{Cl} = (1 - \underline{s}_{Cl}) (1 - i) \quad (5a)$$

$$P_X = (1 - \underline{s}_X) (1 + i) \quad (5b)$$

where i is given by (6) and χ_o^{hyb} for Cl and X are given by (7). This can be solved either by initially assuming a value for $\underline{s}_{Cl}$ or $\underline{s}_X$ and calculating the corresponding $\underline{s}_X$ or $\underline{s}_{Cl}$ and recalculating until $\underline{s}_{Cl}$ and $\underline{s}_X$ remain constant, or by the following procedure:

Rearranging and adding (5a) and (5b) to eliminate i ,

$$P_{Cl} (1 - \underline{s}_X) + P_X (1 - \underline{s}_{Cl}) = 2(1 - \underline{s}_X) (1 - \underline{s}_{Cl}) \quad (5c)$$

$\underline{s}_X$ can be expressed in terms of $\underline{s}_{Cl}$, P_{Cl} and P_X . Thus (5a) becomes a cubic in $\underline{s}_{Cl}$, giving three real roots, only one of which is chemically acceptable and yields a reasonable value of $\underline{s}_X$ when substituted in (5c).

In the tetrahalides the χ_o^{hyb} for the central atom is taken as the effective orbital electronegativity, which is, in a compound CABDE, for the CE bond, (the C orbital forming the bond with E) the appropriate hybrid orbital electronegativity of C, corrected by 1/6 of the difference of this quantity and the appropriate orbital electronegativities of A, B and D:

$$\begin{aligned} \chi_o^{eff}(C) &= \chi_o^{hyb}(C) + 1/6(\chi_o^{hyb}(A) - \chi_o^{hyb}(C)) + 1/6(\chi_o^{hyb}(B) - \chi_o^{hyb}(C)) \\ &+ 1/6(\chi_o^{hyb}(D) - \chi_o^{hyb}(C)) = 1/2 \chi_o^{hyb}(C) + 1/6 \chi_o^{hyb}(A) \\ &+ \chi_o^{hyb}(B) + \chi_o^{hyb}(D) \end{aligned} \quad (8)$$

where i is given by (6) and χ_o^{hyb} for Cl and X are given by (7).

Combining Equations (5), (6), (7) and (8) one then obtains (the subscripts _o and superscripts ^{hyb} will be dropped, all electronegativities being understood to be orbital electronegativities, and to apply to hybrid orbitals unless otherwise superscripted by s or p to indicate pure s or p orbital electronegativities):

$$\begin{aligned}
 &= (1-\underline{s}_E) \left[1 + 1/2 \chi^{\text{eff}}(C) - \chi(E) \right] \\
 &= (1-\underline{s}_E) \left[1 + 1/4 (C) + 1/3 \underline{s}_A \chi^s(A) + (1-\underline{s}_A) \chi^p(A) - \underline{s}_B \chi^s(B) \right. \\
 &\quad \left. + (1-\underline{s}_B) \chi^p(B) + \underline{s}_D \chi^s(D) + (1-\underline{s}_D) \chi^p(D) - 2\underline{s}_E \chi^s(E) \right. \\
 &\quad \left. - 2(1-\underline{s}_E) \chi^p(E) \right] \tag{9}
 \end{aligned}$$

where the various $\underline{s}_A$ etc. are the amounts of s character of the different atoms A, B, C, D and E. Since the present paper deals with tetrahalide compounds for which only a single NQR frequency is known, only one of these $\underline{s}$ values, $\underline{s}_E$, can be obtained. Thus, some decision must be made about the others.

In the case of the totally symmetric compounds MX_4 , there is no problem; all the $\underline{s}_X$ are necessarily equal, because of symmetry, and the compounds, which are all known to be tetrahedral, must consequently be sp^3 hybridized (as long as d orbital effects are ignored), so that $\underline{s}_M = 0.25$. In the less symmetric types of compounds CXY_3 and CX_3Y_3 , there is not a priori reason why all C orbitals should be exactly sp^3 ; however, the experimental bond angles are generally rather close to tetrahedral, (22) and as such no other type of hybridization could uniquely be derived, even if it were assumed that the orbital necessarily points in the bond direction (orbital following). Consequently pure tetrahedral hybridization was assumed for all these compounds. When either X or Y was hydrogen, no allowance for its hybridization was needed, since hydrogen utilizes only 1s orbitals. Also when X or Y was fluorine, no s hybridization was used; F was assumed to use a pure 2p orbital, in agreement with the conclusion reached earlier that hybridization of F is energetically unlikely. (21) In the trihalides of the group 3 and group 5 elements, the valence angles deviate considerably from tetrahedral, and the hybridization was determined, assuming orbital following as the only readily available approach. With a bond angle of 120° in BCl_3 , $\underline{s}_B = 0.333$; in PCl_3 with an angle of 100° , $sp = 0.148$, and in $AsCl_3$ (103°), $\underline{s}_{As} = 0.184$.

In the treatment of the trihalides, of course, Equation (9) is slightly modified, since one of the ligand atoms is omitted.

For the various types of compounds, then, Equation (9) simplifies considerably, to give in each case a quadratic equation in the single quantity $\underline{s}$ which is to be evaluated. The resulting quadrations are readily obtained. (Appendix)

APPENDIX

$$\begin{aligned} \text{MX}_4: & \left[\frac{1}{4} (\chi^s - \chi^p) \right] \underline{s}^2 - \left[1 + \frac{1}{4} \chi^s - \frac{1}{2} \chi^p + \frac{1}{4} \chi_{(M)} \right] \underline{s} + 1 \\ & - \frac{1}{4} \chi^p + \frac{1}{4} \chi_{(M)} - \rho = 0 \end{aligned} \quad (10)$$

where χ^s and χ^p refer to atom X, and $\chi_{(M)}$ refers to the tetrahedral hybrid.

MX_3Y , where X is the element for which the NQR frequency is measured:

$$\begin{aligned} & \left[\frac{1}{3} (\chi^s - \chi^p) \right] \underline{s}^2 - \left[1 + \frac{1}{3} \chi^s - \frac{2}{3} \chi^p + \frac{1}{4} \chi_{(M)} + \frac{1}{12} \chi_{(Y)} \right] \underline{s} \\ & + 1 - \frac{1}{4} \chi_{(M)} + \frac{1}{12} \chi_{(Y)} - \frac{1}{3} \chi^p - \rho = 0 \end{aligned} \quad (11)$$

with the same definitions, except that (Y) is the appropriate hybrid orbital electronegativity of atom Y.

MX_2Y_2 , NQR frequency measured for X:

$$\begin{aligned} & \frac{5}{2} \chi^s - \chi^p \underline{s}^2 - \left[1 + \frac{5}{12} \chi^s - \frac{5}{6} \chi^p + \frac{1}{4} \chi_{(M)} + \frac{1}{6} \chi_{(Y)} \right] \underline{s} + 1 \\ & + \frac{1}{4} \chi_{(M)} + \frac{1}{6} \chi_{(Y)} - \frac{5}{12} \chi^p - \rho = 0 \end{aligned} \quad (12)$$

MX_2Y_3 where the NQR frequency of X is known:

$$\begin{aligned} & \frac{1}{2} (\chi^s - \chi^p) \underline{s}^2 - \left[1 - \frac{1}{2} \chi^s - \frac{1}{4} \chi^p + \frac{1}{4} \chi_{(M)} + \frac{1}{4} \chi_{(Y)} \right] \\ & \underline{s} + 1 - \frac{1}{2} \chi^p + \frac{1}{4} \chi_{(M)} + \frac{1}{4} \chi_{(Y)} - \rho = 0 \end{aligned} \quad (13)$$

MX_3 where now $\chi_{(M)}$ is the orbital electronegativity for the hybrid of B, P or As specified in the text.

$$\begin{aligned} 1/4(\chi^s - \chi^p) \underline{s}^2 - [1 + 1/4\chi^s - 1/2\chi^p + 1/4\chi_{(M)}] \underline{s} + 1 \\ + 1/4\chi_{(M)} - 1/4\chi^p - p = 0 \end{aligned} \quad (14)$$

In these equations, $\underline{s}$ is the only unknown; the χ are experimentally measured quantities taken from the literature. All orbital electronegativities are taken from work in this Laboratory, (8) and are reduced to the Pauling scale. All the equations are simple quadratics in $\underline{s}$, giving two real solutions. Of the two, only solutions in the range $0 \leq \underline{s} \leq 1$ have physical significance; always at least one, and in general only one, of the solutions was found to lie in this range, so that no problems of arbitrary or intuitive choice of the desired root arose. Once $\underline{s}$ is obtained in this way, it is readily substituted into Equation (7) to give χ_o^{hyb} and this in turn into Equation (6) to give $\underline{i}$.

Results and Discussion

The recalculated results (Table 1) for the monohalides and inter-halogen compounds show no appreciable change from those given previously. (21) However, the molecules DBr and DI now yield results for the halogen hybridization, whereas previously they failed. The molecules ICN, BrCl and ICl still fail to give reasonable results. Thus in BrCl the possible results for chlorine are -0.69s or 70.049s character, corresponding to -1.89s or -0.036s character for the bromine. This is not unexpected. If the Equation (5b) allows for d character in the bond then

$$x = (1 - \underline{s}_x + \underline{d}_x) (1 + i)$$

while (7) becomes, to a first approximation

$$\chi_o^{\text{hyb}} = \underline{s}\chi^s + (1 - \underline{s} - \underline{d})\chi^p + \underline{d}^d$$

The only reasonable result therefore is that involving -0.049s character for bromine, since 1.89s character is impossible. The minus result for chlorine is to be expected when the occurrence of d character is ignored, since for X(Br or I) the s_x is actually ($s_x - d_x$) and the whole s character of the bromine or iodine is consequently masked. Thus the hybrid electronegativity will be far too small, and the apparent ionic character too large. The chlorine will then give an apparently negative s hybridization in order to satisfy the cubic equation and Equation (5a).

These results support the qualitative assessments of Gordy, although he preferred to conclude that neither s nor d character was in fact involved. This is however untenable, since as previously shown, (22), (23) hybridization is necessary to explain that

$$p_{Br} p_{Cl} > 1.$$

a. The Tetrahalides of C, Si, Ge and Sn

The results for the symmetric tetrahalides of C, Si, Ge and Sn are given in Table II and for the unsymmetric carbon tetrahalides in Table III.

As most detailed data are available for carbon compounds, these will be discussed more fully, and the conclusions will then be applied to the tetrahalides of the other elements. As chlorine in CCl_4 is successively substituted by fluorine the orbital electronegativity towards chlorine is increased, and in order to match this the chlorine has to increase its hybridization; at the same time the increasing electronegativity of the carbon orbital means its contraction, so the amount of s needed for the best overlap is decreased; thus while the absolute amount of hybridization increases with substitution, the rate of increase tails off; in order to match electronegativities there is a simultaneous charge transfer from the chlorine to the central carbon, decreasing the ionic character of the bond.

With the hydrogen substitution, however, increased hydrogen substitution for chlorine in CCl_4 decreases the $\chi_o^{eff}(C)$, increasing the mismatch with the pure p of the chlorine, but the bonding sp^3 carbon orbital is expanded by substitution of H for Cl, so that chlorine s hybridization is needed to improve overlap; this increases the χ mismatch; the compromise arrived at is a decreasing amount of hybridization, sufficient to give directional character to the p orbital, and increasing charge transfer to match the χ and the space distribution. Both hybridization and charge transfer are energetically unfavorable and only the increased binding energy due to good overlap and good electronegativity match make them worthwhile. Work at present going on in this Laboratory permits us to assess the change in χ with charge, and preliminary results substantiate the above interpretations.

Lucken (14) has suggested that if the C-Cl bond is the same in the $CH_x Cl_{4-x}$ series then in a plot of ionic character against hybridization, Figure 1, the points should fall on a smooth curve or a straight line.

As is apparent, there is a distinct break at CCl_4 for the hydrogen and fluorine lines. If the hydrogen line is assumed "normal", then the fluorine curve is "abnormal".

Lucken postulated for these compounds that the fluorine p_z and antibonding $\text{C-Cl } \pi^*$ orbital overlap. This feed-in of electrons from the fluorine increases the ionic character of the bond and consequently decreases the frequency. The hyperconjugative double bonding forces the carbon to appear more electronegative than the mere inductive effect via the σ bonds.

It is impossible to distinguish between these views. However, if we assume that the second effect is true, then it is possible to estimate its size. If the line for the $\text{CH}_x \text{Cl}_{4-x}$ is extended through CCl_4 , the fluorine compounds would be expected to fall on this line. The ρ from these "assessed" i and s , ρ_{ass} , on subtracting from the experimental results yields the hyperconjugative π^h bonding.

If the relationship between the amount of s hybridization on the chlorine in the F compounds is plotted against the ionic character then three straight lines are obtained. These are plotted on Figure 1 and are seen to cut the extension of the hydrogen "normal curve". The cuts are

CF Cl_3	0.13i	0.77 <u>s</u>
CF ₃ Cl ₃	0.09i	0.12 <u>s</u>
CF Cl_3	0.05i	0.13 <u>s</u>

whence from $\rho_{\text{Cl}} = (1-i)(1-s) - \pi^h$

where π^h is the hyperconjugative π bonding to the antibonding π^* by the fluorine p , the π^h occurring are

CFCl ₃	.05
CF ₃ Cl ₂	.10
CFCl ₃	.13

Thus only 5, 10 or 13% of the hyperconjugative effect is needed to bring the fluorine measurements from the "normal" to "abnormal" curve. This is well within the estimates of Lucken, and the recent qualitative discussion of this effect by Williams. (24)

When the carbon tetrahalides are considered, the substitution of Cl by Br and I would be expected to follow a smooth sequence similar

to those in the polyhalides above, and reflecting the same arguments. The prediction would be that as the series is descended, the $\chi_{\text{eff}}^{\text{C}}$ is decreased, the χ_{P} (halogen) is smaller, more nearly matching $\chi_{\text{O}}^{\text{eff}}(\text{C})$ and hence the hybridization will smoothly decrease. This would be paralleled by a smooth decrease in the ionic character of the bond. Table II shows that these decreases do occur, but not very smoothly. Thus the s hybridization suddenly decreases to zero for iodine (0.004) from 7% for bromine and 10% for the chlorine compound. The χ show a smooth increase in value, and these together with the χ_{S} and χ_{P} would suggest that iodine would display a decrease in s% less than that displayed in going from Cl to Br. The break is no doubt due to the possibility of d character in the σ bond of the halogen in Br and I which masks the actual s hybridization; (23) thus it would normally be expected that the sequence Cl, Br and I would show increased s character, (23) since the chlorine P being the least well matched would be expected to use the least s character, as any s invariable increases the mismatch of the $\chi_{\text{O}}^{\text{Cl}}$ and $\chi_{\text{O}}^{\text{eff}}$. The d character is presumably used to improve overlap, since it offsets the mismatch of χ which would result in increasing s character in the sequence Cl, Br, I, and at the same time is less significant in determining the orbital size, and hence overlap, than the s character. The carbon tetrahedral and chlorine p orbitals display similar space distribution, chlorine using sufficient s to make the overlap a maximum without mismatching the χ severely; in bromine and iodine however the orbitals need to be made considerably more directional to make the overlap a maximum, and invoke d character to minimize the χ discrepancy.

The arguments also apply to the deuterium halides in Table I, where the s character actually increases from DCl to DBr and then decreases in going to DI. FCl to FBr shows an increase in s percentage. Thus all the systems show similar trends to the carbon tetrahalides.

The silicon, germanium, and tin tetrahalides would be expected to behave like the carbon cases, if the situation were the same in each compound as in the carbon predecessor. As can be seen from Table IV, the trend is the same in each group, but the absolute values, Table II, differ greatly. From both the values of χ and the spacial overlap requirements such absolute differences are difficult to explain, but the use of metal d orbitals as acceptors of halogen P electrons would result in just such an overassessment of s and i character. Thus using Equation (5)

$$P = (1 - \underline{s}) (1 + i) - \chi$$

and assuming that $\underline{s}$ and $\underline{i}$ for any MCl_4 , MBr_4 or MI_4 are the same as those in the carbon analogues, (an approach suggested by the similarity of the change in hybridization and ionic character in Table IV, which suggests some common constant absolute shift in the ionic and s characters determined), the $\overline{\Pi}$ bond orders in Table VI are obtained.

Thus d orbital participation in these compounds is of two kinds. The halogen d orbitals hybridize in the σ bond of the halogen: the metal d orbitals act as unhybridized acceptors for the halogen p electrons. There is at the moment no evidence of halogen $d \pi$ or metal $d \pi$ involvement.

Very interestingly, these values are all close together, supporting the idea of a common cause. In the elements Si, Ge, Sn there are available d orbitals, $3d$, $4d$ and $5d$ respectively (whereas in carbon $n=2$, there are no d orbitals) which can accept electrons from the halogens to form $p \pi - d \pi$ bonds. At this time we have no satisfactory way of assessing the χ of any vacant orbital; (24) let us assume for the sake of argument that $\chi \approx 1/2(EA)$ then this assumption suggests an order of magnitude for χ_d vacant - 0.1 whence it is difficult to see how the $d \pi$ could overlap at all well with the $p \overline{\Pi}$ halogen with $\chi_p = 3.5$ (Cl); 2.82 (Br) or 2.72 (I). A more detailed discussion and resolution of this contradiction must await a better understanding of orbital electronegativities of vacant orbitals, which is now under investigation in this Laboratory. (9) However, it is comforting to note that the present results are of the same order of magnitude and trend as those obtained (4) on the basis of Pauling electronegativity and his interpretation (18) of bond lengths. They differ very greatly from the predictions of Gordy, (6) but this is not surprising in view of his calculated values of effective electronegativity which for the silicon, germanium and tin halides are extremely low. It is also preferable to have no π bonding in the carbon cases where no suitable d orbitals occur to allow it, than the $\overline{\Pi}$ characters stipulated by Gordy.

b. The Trichlorides of B, P and As

The results obtained by use of Equation (14) for boron, phosphorus and arsenic trichlorides are shown in Table VII. Once again the ionic characters and hybridization of the halides are large, and unexpectedly so, in view of the closeness of the χ_M and χ halogen p and the lack of $\underline{s}$ character in the metal orbital. It appears that here, too, π bonding is important, in boron using the empty boron $p \pi$ orbital and in phosphorus and arsenic the empty d orbitals of the central atom. In these cases, however, no assessment of the amount of

bonding was readily possible, as it was in group four by comparison with the carbon compounds; in these cases again the difference in χ between an empty orbital ($\chi = 0.2$) and the chlorine $p(\chi = 3.152)$, seems too large.

It is interesting to note that the assumption of orbital following made above to evaluate hybridization in As and P is not critical. If an alternative extreme assumption were made, that p is purely sp^3 (tetrahedrally) hybridized, $\chi_o^{hyb}(p)$ would be 2.99, s would be 0.343, instead of 0.314, and i would be 0.275 instead of 0.306. The conclusions are unaltered. If working in the other direction, π character is estimated from known bond lengths (26) by the Pauling method, (24) giving 0.10 for PCl_3 and 0.077 for $AsCl_3$ then this would reduce s and i to 0.2312 and 0.25 respectively in PCl_3 and to 0.299 and 0.237 respectively in $AsCl_3$, while in BCl_3 it gives 0.35 as the π character corresponding to an s and i of 0.002 and 0.51 respectively. In the phosphorus and arsenic compounds the results seem more reasonable according to intuitive judgment.

TABLE I^f

RECALCULATED IONIC CHARACTERS AND HYBRIDIZATION OF THE DIHALIDES

Com-pound	<u>Orbital</u> χ_s	<u>Electrone-</u> <u>gativities</u>	<u>Orbital</u> <u>Hybridization</u> s	<u>Orbital</u> χ_{hyb}	<u>Electrone-</u> <u>gativity</u> χ_o^{eff}	<u>Bond</u> <u>Ionic</u> <u>Character</u> i
A B		χ_o^p				
F	1.33 ^a	3.90	0.048	3.08		0.40
F		2.95				
		3.90				
BR	1.41 ^a	2.61	0.067	2.82		0.54
H						
		2.61				
Cl	0.49	2.95	0.074	3.15		0.47
D						
		2.95	0.069	3.14		0.47
Cl	0.50 ^b					
		2.61				
D		2.61	0.107	2.97		0.38
		2.51	0.050	2.64		0.22
I	0.80 ^c				2.6 ^e	
CN						
Cl	0.60 ^a	2.95	0.147	3.35	2.6 ^e	0.38
CN						
Br	0.74 ^d	2.61	0.140	3.08		0.24

a. B. P. Dailey, J. Phys. Chem. 57, 490 (1953)b. R. Livingstone, J. Phys. Chem. 57, 496 (1953)c. H. Allen, J. Phys. Chem. 57, 501 (1953)d. A. L. Schwalow, J. Chem. Phys. 22, 1211 (1954).

e. Taken as 2.6 to keep results in line with previous paper. See Ref. 1.

f. Compare with W. Gordy, Discussions of Faraday Society 19, 18 (1955)

TABLE II

IONIC CHARACTER AND HYBRIDIZATION IN THE SYMMETRIC TETRAHALIDES

Com- pound		χ_o^s	Orbital	Electrone- gativities	Orbital Hybridi- zation	Orbital	Electrone- gativities	MX Bond Ionic Character
	MS ₄				$\underline{s}$	χ_o^{hyb}	χ_o^{eff}	
C					0.25C	2.51		
	Cl	0.746 ^d	5.69	2.95	0.097	3.21	2.86	0.174
	Br	0.83 ^e	5.93	2.61	0.069	2.84	2.68	0.08
	I	0.929 ⁱ	5.06	2.51	0.004	2.52	2.52	0.002
Si					0.25C	2.32		
	Cl	0.372 ^{df}	5.69	2.95	0.371	3.92	3.14	0.408
	Br	0.46 ^e	5.93	2.61	0.315	3.66	2.99	0.335
	I	0.580 ⁱ	5.06	2.51	0.262	3.18	2.75	0.215
Ge					0.25C	2.59		
	Cl	0.467 ^d	5.69	2.95	0.323	3.82	3.21	0.31
	Br	0.54 ^e	5.93	2.61	0.286	3.56	2.97	0.295
	I	0.587 ⁱ	5.06	2.51	0.293	3.26	2.92	0.169
Sn					0.25C	2.52		
	Cl	0.439 ^{df}	5.69	2.95	0.338	3.87	3.19	0.338
	Br	0.50 ^{eg}	5.93	2.61	0.307	3.63	3.08	0.275
	I	0.594 ^{ehi}	5.06	2.51	0.278	3.22	2.87	0.177

- a. The χ are calculated from averaging the eQqM01 which when the frequencies differ by less than 2% are not considered as due to chemical inequivalence of the atoms.
- b. The electronegativities are given in Pauling units from the Mulliken electron volt scale using (8) $\chi_{Pauling} = (\chi_{Mulliken} - 1.23)0.168$
- c. Assumed because of symmetry
- d. R. Livingstone, J. Phys. Chem. 57, 496 (1953)
- e. A.L. Schwalow, J. Chem. Phys. 22, 1211 (1954)
- f. H.G. Dehmelt, J. Chem. Phys. 21, 380 (1954)
- g. Schimamura, J. Sci. Hiroshima Univ. 17A, 17B, 383 (1954)
- h. Kojima, Tsukads, Ogawa and Schimauchi, J. Chem. Phys. 21, 2237 (1953)
- i. Compare the results in Discussions of the Faraday Society 19, 18 (1955)
- j. Robinson, H.G. Dehmelt and W. Gordy, J. Chem. Phys. 22, 511 (1954)

IONIC CHARACTER AND HYBRIDIZATION IN UNSYMMETRICAL CARBON TETRAHALIDES

Compound		b	Orbital		Electrone-	Orbital	Hybrid-	Orbital	Electrone-	Bond	CCl
			χ_o^s	χ_o^p	gativities	Hybrid-	zation	Orbital	gativities	Ionic	Character
							$\underline{s}$	$\underline{p}$	$\chi_o^{eff}(c)$	$\underline{i}$	
M											
C											
X3	Y	0.719 ^a	5.69	2.95			0.25 ^f	2.51			
Cl	F			3.90			0.14 ^f	3.33	3.01	0.16	
Cl	H	0.698 ^b	5.69	2.95			0.08 ^f	3.16	2.68	0.24	
			2.21				1.0	2.21			
X2	Y2	0.701 ^c	5.69	2.95			0.17 ^f	3.42	3.12	0.15	
Cl											
	F			3.90			0.0	3.9			
Cl		0.656 ^d	5.69	2.95			0.61 ^f	3.11	2.50	0.30	
	H		2.21				1.0	2.21			
X	Y3	0.694 ^{d,e}	5.69	2.95			0.19 ^f	3.47	3.19	0.14	
Cl				3.90			0.0	3.9			
Cl		0.620 ^{d,e,f}	5.69	2.95			0.04 ^f	3.06	2.36	0.35	
	H		2.21				1.0	2.21			

- a. R. Livingston, J. Chem. Phys. 19, 803 (1951)
- b. R. Livingston, J. Chem. Phys. 19, 1434 (1951)
- c. C.D. Akon and T. Iredale, J. Chem. Phys. 34, 340 (1961)
- d. H.O. Hooper and P.J. Bray, J. Chem. Phys. 33, 334 (1960)
- e. H.O. Hooper and P.J. Bray, Brown University, Rhode Island. Pamphlet (1960)
- f. Assumed values, see text

TABLE IV

CHANGE IN s HYBRIDIZATION (%)

	D	C	Si	Ge	Sn
Cl to Br	+3.86	-3.0	-5.6	- 3.7	- 3.1
Br to I	-5.69	-6.5	-5.3	+ 0.7	- 2.9

CHANGE IN IONIC CHARACTER (%)

	D	C	Si	Ge	Sn
Cl to Br	-6.36	-9.4	- 7.5	- 1.5	- 6.3
Br to I	-16.49	-7.8	-12.0	-12.6	- 9.8

TABLE V

IONIC CHARACTER AND HYBRIDIZATION IN THE CARBON TETRAHALIDES

	CCl_4	CFCl_3	CF_2Cl_2	CF_3Cl	CHCl_3	CH_2Cl_2	CH_3Cl
%s	9.7	14.3	17.4	19.3	7.9	6.12	4.3
%i	17.4	16.1	15.2	14.0	24.2	30.1	35.2

TABLE VI

- BOND CHARACTERS OF THE GROUP 4 TETRAHALIDES

	From Eqn. (5) and CX ₄ Results	From Pauling and Das and Hahn ^{a,b}	From Gordy ^c
SiCl ₄			
SiCl ₄	0.37	0.45 ± 0.12	0.30
SiBr ₄	0.37	0.60 ± 0.15	0.26
GeCl ₄	0.28	0.41 ± 0.16	0.14
GeBr ₄	0.29	0.16 ± 0.06	0.12
GeI ₄	0.34	0.11 ± 0.07	0.09
SnCl ₄	0.31	0.22 ± 0.11	0.09
SnBr ₄	0.33	0.25 ± 0.08	0.08
SnI ₄	0.34	0.21 ± 0.01	0.06

a. L. Pauling, "Nature of Chemical Bond, Cornell Univ. Press. 1960.

b. T.P. Das and E.L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy", Academic Press, 1958, p. 148.

c. W. Gordy, Discussions of the Faraday Soc. 19, 27, 1955.

TABLE VII

HYBRIDIZATION AND IONIC CHARACTER IN BCl_3 , PCl_3 and AsCl_3

Com- pound		<u>Orbital</u>	<u>Electrone- gativities</u>	<u>Orbital Hybridi- zation</u>	<u>hyb</u>	<u>eff</u>	<u>(M)</u>	<u>MCL Bond Ionic Character</u>
M	X_3	<u>s</u> O	<u>P</u> O	<u>s</u>	<u>o</u>	<u>o</u>	<u>i</u>	
B				0.33 ^a	1.92			
Cl	0.394 ^b	5.69	2.95	0.28	3.72	2.82		0.45
P				0.15 ^a	2.58			
Cl	0.477 ^c	5.69	2.95	0.31	3.80	3.19		0.31
As				0.18 ^a	2.82			
Cl	0.459	5.69	2.95	0.36	3.93	3.37		0.28

a. From bond angles; see text

b. T. Chiba, J. Phys. Soc. (Japan) 13, 860 (1958)c. E. A. C. Lucken and M. A. Whitehead, J. Chem. Soc. 2459 (1961).d. S. Ogawa, J. Phys. Soc. (Japan) 13, 618 (1958).

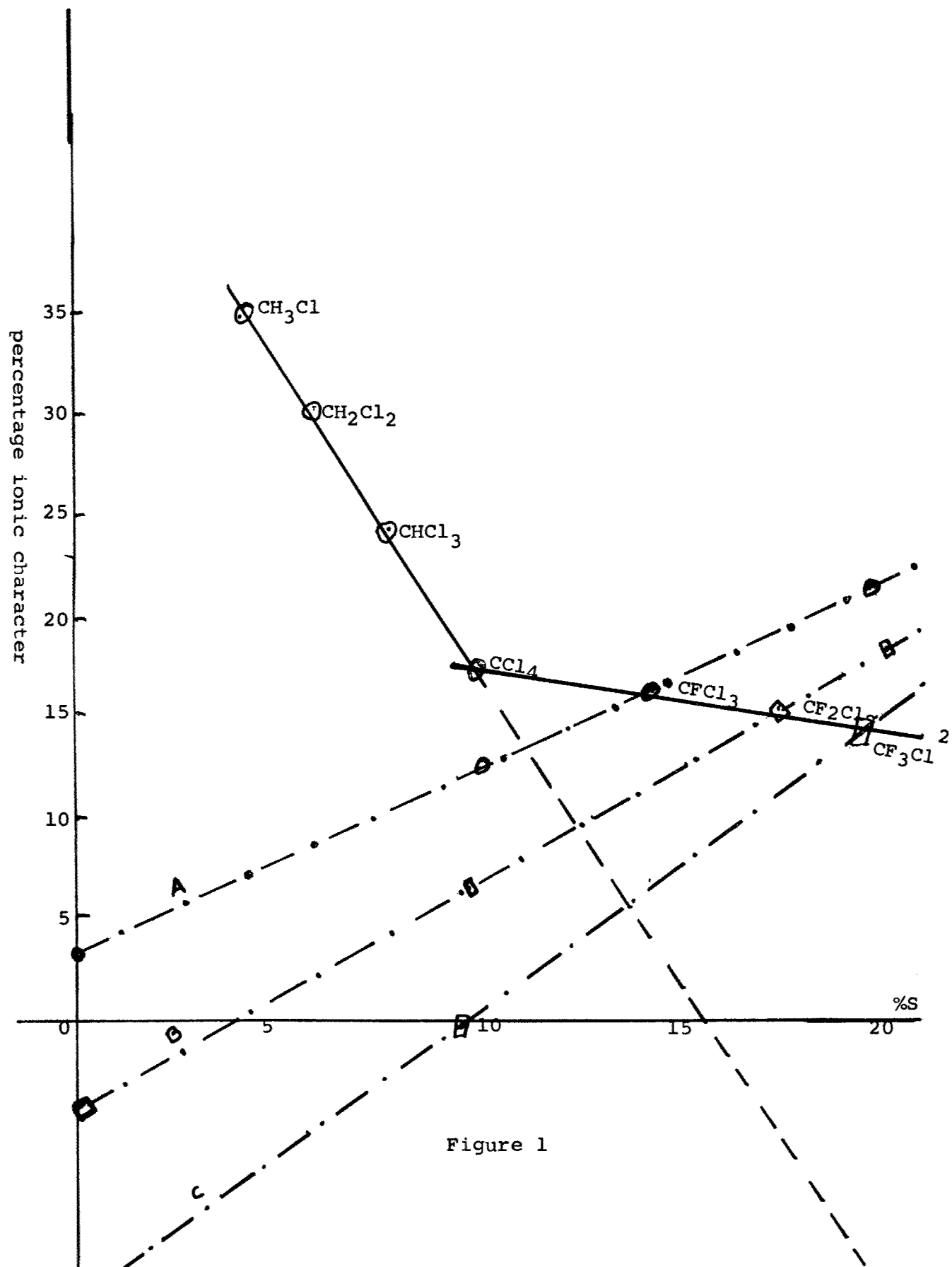


Figure 1

LEGEND

Figure 1

The percentage ionic character against percentage s hybridization in the chlorine χ orbital.

Curve 1 represents the "normal" curve for the change in ionic character with electronegativity determined from $\chi = \underline{s} \chi_s + (1 - \underline{s}) \chi_p$, and curve 2 the "abnormal" curve for the fluorine compounds, A, B and C are the change of i with $\underline{s}$ for the compounds CFCl_3 , CF_2Cl_2 and CF_3Cl and where they cut the extrapolation of curve A is the "expected" values for i and $\underline{s}$. The deviation from the extrapolated curve A to curve B is due to χ hyperconjugation.

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December 12, 2016

MEMORANDUM FOR AFRL/RXOP
ATTN: Robin Hayes

FROM: AFRL/RXAS

SUBJECT: Technical reports WADD-TR-61-84-PT-1 and WADD-TR-61-84-PT-2

I have read through both technical reports you sent me - reference WADD-TR-61-84-PT-1 (U) Empirical Methods for Calculation of Bond Energies. Part 1 dated May 1961 and WADD-TR-61-84-PT-2 (U) Empirical Methods for Calculation of Bond Energies. Part 2 dated Sep 1963. In both cases the computations that were done, while significant in the early 1960s, could be reproduced now with better accuracy by modern computational methods and equipment in a matter of a few hours. Thus the data presented in the reports is of historical value only. Since I saw no discussions of specific strategic materials or weapon systems, I conclude that both reports should be assigned a distribution statement A. If you have any further questions, please feel free to contact me by e-mail at alan.yeates@us.af.mil or by phone at 312-785-9138 or (937)255-9138 (comm).

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