PHYSICAL REVIEW B VOLUME 27, NUMBER 10 15 MAY 1983

Ionic character of polar crystals: An extended Mulliken scheme for electronegativities

R. E. Watson
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

L. H. Bennett
National Bureau of Standards, Washington, D.C. 20234

J. W. Davenport
Physics Department, Brookhaven National Laboratory, Upton, New York 11973

(Received 6 December 1982)

The total energy of an atom can be expressed in terms of the charge q on the atom as $E(q)=E(0)+\alpha q+\beta q^2+\gamma q^3$. It is shown that the expected charge transfer q, which brings the intra-atomic energy of the atoms to a minimum, between otherwise isolated noninteracting atoms, is proportional to the difference in the α's of the constituent elements, i.e., $q=c\,\Delta\alpha$. Thus α provides a well-defined electronegativity scale, and if the third-order term γq^3 may be neglected, then $\alpha=\Phi_m$, which is the original Mulliken scale. The quadratic term βq^2 acts to oppose charge transfer, and therefore the coefficient c, relating q to $\Delta\alpha$, depends on what elements are involved and on their relative concentration in a well-defined manner. This implies an asymmetry in charge transfer with concentration. Spectroscopic data indicate that γ, though small, is not negligible and, in such a case Φ_m is not a proper electronegativity. The extended Mulliken scheme, involving α and β, is relevant to the energetics of charge transfer and hence to the ionic character of insulating and semiconducting compounds. It allows simple baseline estimates to be made of such character. Other factors contribute to charge transfer and some of the complications associated with transition-metal compound formation are explored.

I. INTRODUCTION

The competition between atomic constituents for valence-electron charge pervades the thinking of bonding in molecules and solids. Such effects are traditionally encompassed in electronegativity scales, the more electronegative element being the one which most successfully competes for the valence-electron charge. The use of electronegativity scales has had a checkered history because they involve but part of what is normally a complex bonding situation. Nevertheless, there is a natural and proper tendency to view the charge transfer deduced in a calculation or experiment in the light of one's expectations concerning electronegativity trends. In addition, electronegativity scales occur in a number of Hamiltonians such as that of Miedema's[1] and in a number of parametrizations of alloys involving quantities such as solubilities, crystal structures, and volume effects. The present investigation reflects the needs of the preceding paper.[2] There it was assumed that the energy associated with the ionic character of a polar crystal can be written as a sum of inter- and intra-atomic terms. An estimate of the intra-atomic energy involved in taking an anion and cation from charges $\pm q$ to $\pm(q+\Delta q)$ is required. We will employ spectroscopic data to estimate these here. In doing this, we will encounter the Mulliken electronegativity[3] parameter, which is an average of the tendency of the neutral atom to keep the valence electrons it has and to gain another, namely

$$\Phi_M=\frac{\epsilon(0)+\epsilon(-1)}{2}\ , \tag{1}$$

where $\epsilon(0)$ and $\epsilon(-1)$ are the ionization energies of the neutral and negative ion, respectively, the latter being the electron affinity. The Φ_m (or some other electronegativity scale, Φ) depends on what valence electron, or linear combination of valence electrons, is involved in the ionization process and on the appropriate atomic configuration, e.g., $2s^22p^2$ or $2s\,2p^3$ for atomic carbon. After a choice is made on these matters, the charge, $+q$ and $-q$, of a pair of ions which brings the sum of their intra-atomic energies to a minimum can be estimated, where

$$q=c\,\Delta\Phi\ . \tag{2}$$

Generally it is presumed that c is a constant, but it is not. It depends on what the atomic constituents are and, if concentrations other than 50-50 are allowed, upon concentration. One implication of this is that the charge transfer associated with element A embedded in B can be quite different from that for B in A, on purely atomic grounds. Such charge-transfer asymmetries are seen experimentally.[4] The fact that c is not a constant follows trivially from the properties of successive ionization energies of atoms but, trivial or not, this fact seems to have been only sometimes recognized in the literature.[5]

In the remainder of this section we will explore the energetics of ionization of free atoms. In doing this we will exploit the observation that successive ionization energies vary approximately linearly with q, the state of ionization. In the process contact will be made with the Mulliken scale and those related electronegativity scales which are based on spectroscopic or pseudopotential data. The fundamental aspect of Mulliken's approach will be seen. Section II will be devoted to fitting ionization energies in order to provide the parameters appropriate to the intra-atomic energy terms needed in the preceding paper. This can be done with experimental or computed ionization energies. We have chosen to use the former. This avoids questions of correlation energy effects but introduces situations where the spectroscopic data are inaccurate or lacking. Sufficient results were obtained with the spectroscopic data that the investigation was not extended to include calculations. While the principal concern of this paper is charge transfer, bonding often involves changing valence-electron configurations. For example, d-electron transfer in transition- and noble-metal alloys is accompanied by s-p transfer in the opposite direction.[6] The single site energetics of s-d screening involves the same considerations as that of charge transfer and this matter is considered in Sec. III. This is juxtaposed against other factors affecting d-electron transfer. Given the parameters obtained in Sec. II, the factors on the right-hand side of Eq. (2) may be evaluated and estimates made of the ionization states $+q$ and $-q$ which minimize the total energy appropriate to a pair of isolated noninteracting atoms. These, we believe, provide a useful reference point for considering the state of ionization attributed to a polar crystal constructed from the same elements. Such estimates are reported in Sec. IV. Finally, the assumption that the ionization energies vary linearly with q is not always strictly true as can be seen from Figs. 1 and 2. The consequence of such deviations are considered in Sec. V.

To the extent that successive ionization energies do vary linearly with q, the total energy of an atom has linear and quadratic terms in q, i.e.,

$$E(q)=E(0)+\alpha q+\beta q^2 \,. \tag{3}$$

The deviations from linearity displayed in Figs. 1 and 2 are well described by adding a term γq^3, where γ is small, but nonzero. We neglect this term here because its determination requires having three

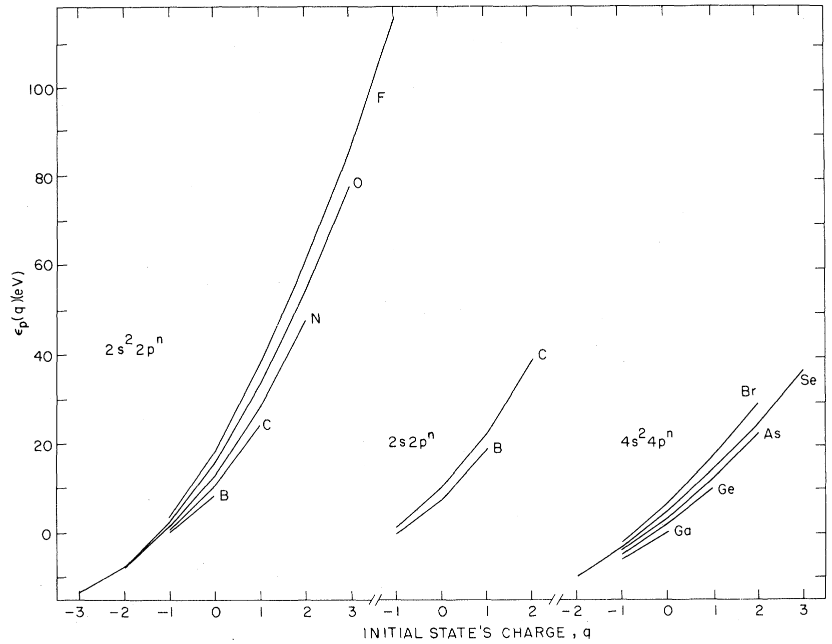

FIG. 1. Ionization energies, as a function of the state of ionization, for main group elements in the $2s2p^n$, $2s^2 2p^n$, and $4s^2 4p^n$ averages of configuration where p electrons are lost in the ionization process.

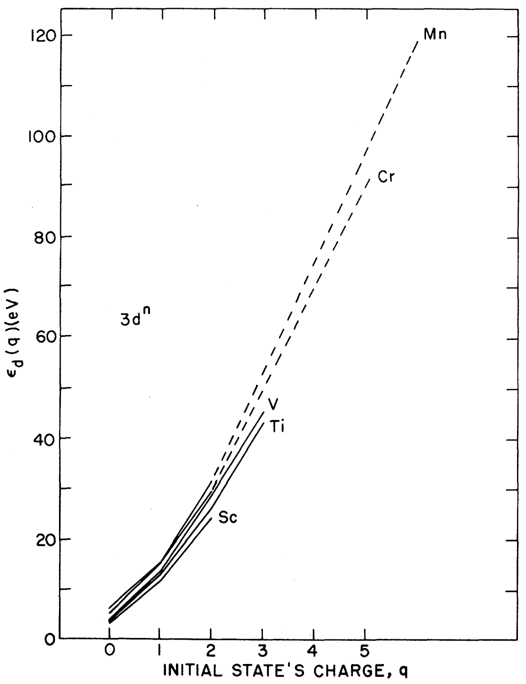

FIG. 2. Ionization energies, as a function of state of ionization, for the first transition-element row in the averages of the $3d^n$ (no $4s$ or $4p$) configurations.

or more ionization energies and there are a number of cases where we have but two: two for s shells since there are but two electrons per shell and two for a number of other cases due to lack of data. In terms of the same parameters, an ionization energy is

$$\begin{aligned}\epsilon(q) &= E(q+1)-E(q)\\ &= \alpha+\beta+2\beta q\ .\end{aligned} \tag{4}$$

The Mulliken electronegativity, from Eq. (1), is

$$\Phi_M = \alpha\ , \tag{5}$$

which is the first derivative, with respect to q, of the total energy of the neutral atom. This is a physically appealing result and has been recognized[5] for some time. The 2β, multiplying q in Eq. (4), is the interelectronic Coulomb (plus exchange and correlation) interaction between a pair of valence electrons. The curvature in Figs. 1 and 2, which is not accounted for in Eqs. (3)—(5), is due to the interaction increasing slightly with increasing ionization due to the contraction of the charge distribution of the valence electrons which are not yet ionized.

Clearly α and β depend on the configuration of the neutral atom and on the electrons, s, p, or d, or some combination thereof involved in ionization. Pauling recognized[7] the role of such factors and Moffitt, in his derivation[8] of the Mulliken scale, referred to σ and π bonding effects. St. John and Bloch obtained[9] separate s- and p-orbital electronegativities for the main-group elements and employed the average of these as an element's electronegativity. They used the inverse of an ionization energy. As a practical matter it is convenient to employ a single[10] one-electron energy or its inverse and allowing contact[11] to be made with pseudopotentials. The problem is that Φ is then some combination of α and β

$$\Phi = \alpha + (2q+1)\beta\ , \tag{6}$$

and while α encourages charging, β [which involves the quadratic term in q in Eq. (3)] *discourages* charging. Φ could still be taken as proportional to α if, by chance, the ratio of α/β were a constant. However, this ratio varies by better than an order of magnitude for the α and β obtained in the next section and thus the Φ, defined by Eq. (6), is not a proper measure of electronegativity in the sense of Eq. (2).

The actual role of the β terms is seen by summing Eq. (3) for A and B sites to obtain the energy for an A^qB^{-q} compound, taking the derivative of this energy with respect to q and, setting this derivative equal to zero, solving for q. One obtains

$$q = -\frac{\alpha_A - \alpha_B}{2(\beta_A + \beta_B)} \tag{7}$$

with the associated energy

$$E(A^qB^{-q}) - E(A^0B^0) = -\frac{(\alpha_A-\alpha_B)^2}{4(\beta_A+\beta_B)}\ . \tag{8}$$

The constant of proportionality in Eq. (2) is seen to involve the inverse of the sum of the two β's and thus depends on what elements are involved in compound formation. If instead of a 50-50 compound one considers an $A^qB_n^{-q/n}$ compound where the n majority sites, B, are uniformly charged, then Eqs. (7) and (8) become

$$q = -\frac{\alpha_A - \alpha_B}{2[\beta_A + (\beta_B/n)]} \tag{9}$$

and

$$E(A^qB_n^{-q/n}) - E_n(A^0B_n^0) = -\frac{(\alpha_A-\alpha_B)^2}{4[\beta_A+(\beta_B/n)]}\ . \tag{10}$$

There is an asymmetry in the charging as a function of composition and this depends on the relative values of the β's.

In the preceding paper[2] we were concerned with the energy involved in bringing the A^qB^{-q} compound from the bulk ionic charge $\pm q$ to a different charge $\pm(q+\Delta q)$ at a crystal surface. Again, employing Eq. (3) for the individual ions, the intra-atomic energy per AB molecule is

$$E(A^{q+\Delta q}B^{-q-\Delta q})-E(A^{q}B^{-q})$$
$$=2q\,\Delta q\left[(\beta_A+\beta_B)+\left[\frac{\alpha_A-\alpha_B}{2q}\right]\right]$$
$$+(\Delta q)^2(\beta_A+\beta_B)\ . \tag{11}$$

Here the $\beta_A+\beta_B$ term contributes to *both* the linear and quadratic terms in Δq. It is the combination of inter- and intra-atomic terms, which are linear in Δq, which drive Δq to a nonzero value at the surface and, from Eq. (11), we see that this involves a competition of intra-atomic factors. If the more electronegative element, with the larger α, is in fact the anion in the crystal then $(\alpha_A-\alpha_B)/2q$ is negative while $\beta_A+\beta_B$ is positive. In general the latter, being a sum, prevails.

II. FITS FOR α AND β

The linear and quadratic factors, α and β, can be obtained from a pair of ionization energies known from experiment or calculation. We will employ experimental ionization energies[12] and electron affinities.[13] Correlation effects are thus incorporated into the data but at the cost[14] of having incomplete and occasionally incorrectly assigned data. Individual spectral terms were averaged over so as to obtain ionization energies for the center of gravity of the atomic configuration[15] where Hund's-rule multiplet effects are averaged out. This appears to be the best choice except for the $3d$ transition-metal ions with their strong Hund's-rule effects.

Fits for nontransition elements are listed in Table I. Considerable uncertainty should be attached to the second digit after the decimal point. The results are based on the electron affinities and the neutral-atom ionization potentials except for the divalent alkaline-earth elements and Zn, Cd, and Hg where $\epsilon(0)$ and $\epsilon(+1)$ were, of necessity, employed. (To the extent that the ionization energies vary linearly with q, of course it does not matter which energies are involved in the fit.) The first columns of the table assume that the monovalent and divalent atoms involve s-electron transfer while the polyvalent elements involve p transfer. As has already been noted, the polyvalent systems may be in s^2p^n configurations which are energetically more favorable or in the sp^n characteristic of tetrahedral bonding, and results are reported for p-electron excitations out of both. The differences in α and β are of significance. As was also noted, the energetics of charge transfer also depend on what valence electrons are involved, and some measure of this is provided by the third column of the table where the ionization has been taken to be half s and half p in character. Here divalent Mg has been assigned a $3s^13p^1$ neutral-atom configuration and $3s^{1/2}3p^{1/2}$ in the $+1$ ion. Similarly C^- is taken to be $2s^22p^3$; neutral C, $2s^{3/2}2p^{5/2}$; and C^+, $2s2p^2$. Thus the neutral-atom configurations of the polyvalent elements are the mean of the sp^n and s^2p^{n-1}. The α reflect the fact that valence p electrons are less tightly bound than the valence s and thus the $\alpha(s^{1/2}p^{1/2})$ are less than the $\alpha(s)$ of the monovalent and divalent ions and greater than the $\alpha(p)$ of the polyvalent systems (compare Figs. 3 and 4).

Considering the $\alpha(s^{1/2}p^{1/2})$, which are obtained in an equivalent way for the divalent and polyvalent elements, or considering a particular s- or p-electron electronegativity, we see, in Fig. 3, that the α for elements in one column of the Periodic Table as a rule do not overlap those in adjacent columns with the exception of the $2p$ elements, B, C, N, and O. This is characteristic of many electronegativity scales: Similar but more severe overlapping occurs in the Pauling scale.

The α's do not always vary smoothly across a set of elements. Some of this reflects problems with the experimental data but much of the detail is real. Generally it is expected[7] that the electronegativities decrease with increasing quantum number n of the valence shell for some column of the Periodic Table with the values for the $2p$ elements marked by larger than the others. On the whole the $2p$-element α's are markedly larger, however, for the sp^n configuration and with the $\alpha(s^{1/2}p^{1/2})$, the $4p$ elements generally have larger α than do the $3p$. This trend appears to be due to the screening associated with the fact that the $4p$ elements are the first row to have a closed d shell in the ion core. The same effect was found[10] for elements in the boron and carbon columns when Φ was taken to be a weighted average of s- and p-orbital electronegativities based on the first ionization potentials alone; i.e., α and β were included with equal weight in the definition of the Φ. The effect is also apparently seen[16] in experiments involving a sequence of AuX_2 compounds where X is Al, Ga, or In.

If α increases on going from one element to another, in general, so does β, as is seen by comparing Figs. 3 and 5; however, the ratio α/β varies from 1 to almost 4 for the results in the table, with most values lying between 1 and 2. Schemes where the electronegativity is some combination of α and β, rather than α alone, are thus in some numerical difficulty.

TABLE I. α (eV/e) and β (eV/e^2) for main-group elements; n designates electron state whose count is changing.

	s^n		$(s^{1/2}p^{1/2})^n$	
	α	β	α	β
H	7.18	6.42		
Li	3.00	2.40		
Na	2.84	2.30		
K	2.42	1.92		
Rb	2.33	1.85		
Cs	2.12	1.77		
Be	4.88	4.44	3.80	4.15
Mg	3.95	3.67	3.69	3.05
Ca	3.23	2.88	3.15	2.39
Sr	3.02	2.67	2.47	2.36
Ba	2.82	2.40	2.81	1.96
Zn	5.11	4.29	4.45	3.49
Cd	5.03	3.96	4.33	3.25
Hg	6.27	4.16	5.07	3.37

	sp^n		s^2p^n		$sp^x(s^{1/2}p^{1/2})^n$	
	α	β	α	β	α	β
B	4.39	3.94	4.11	4.19	6.99	4.20
Al	3.43	3.60	3.14	2.85	5.81	3.07
Ga	4.19	2.39	3.02	2.92	6.36	3.24
In	3.90	2.31	2.75	2.87	5.80	3.16
Tl	3.74	2.87	2.93	2.54	6.77	3.11
C	6.65	4.58	5.59	5.08	9.97	5.36
Si	5.07	3.18	4.28	3.49	7.84	3.76
Ge	5.30	3.68	4.21	3.35	8.28	4.06
Sn	5.06	3.30	3.99	2.83	7.60	3.59
Pb	5.02	3.40	4.26	2.57	8.77	3.42
N	7.6	6.2	7.34	5.84	12.93	6.06
P	6.98	4.91	5.97	4.21	10.27	5.06
As	6.15	5.65	5.99	3.67	10.01	4.13
Sb	5.6	3.9	4.98	3.47	9.35	4.26
Bi	5.0	3.8	4.53	3.62	9.04	3.95
O			9.13	6.73	17.39	6.65
S			7.14	4.48	11.22	4.27
Se			6.71	4.12	11.43	3.16
Te			6.25	3.56	10.66	4.21
F			11.04	7.61	21.79	7.93
Cl			8.66	5.02	14.44	5.46
Br			8.01	4.49	15.47	6.52
I			7.36	3.86	12.17	3.24

Consider now the transition- and noble-metal elements. Unfortunately, there are but limited spectroscopic data for the 4*d* and 5*d* elements and they are poorly represented in Table II. The results of first two columns of the table assume *s*-electron transfer with fixed monovalent and divalent d^n shells. These results may have some relevance to the ionic character of transition-metal salts. The third column assumes half *s* and half *d* transfer with the neutral atom in the "metallic" d^ns configuration while the last column represents *d*-electron transfer alone from the same d^ns neutral-atom configuration.

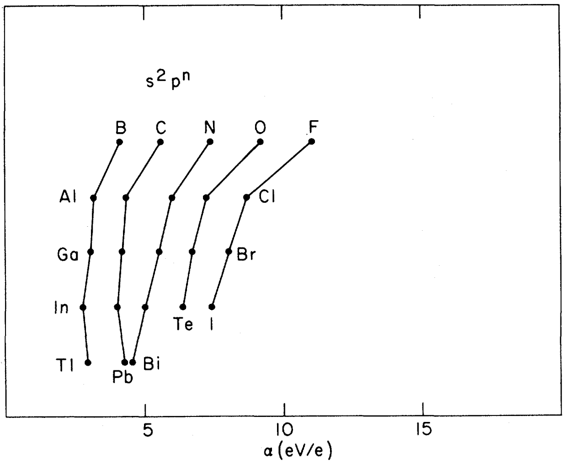

FIG. 3. Electronegativity parameter α as obtained in the averages of the s^2p^n configurations for the polyvalent main-group elements.

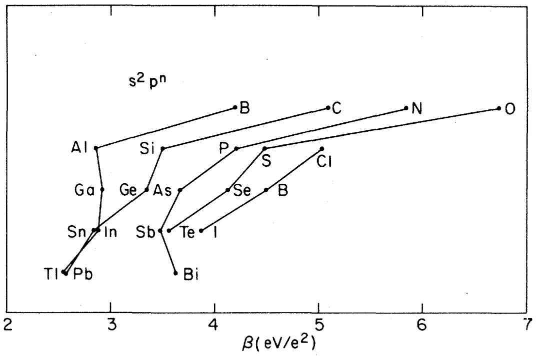

FIG. 5. Quadratic parameter β as obtained for the averages of the s^2p^n configurations of the polyvalent main-group elements.

For the most part, the α increase across a transition-metal row, implying an increasing electronegativity as is expected. The α involving *s*-electron transfer alone are in pretty good register with those of the main-group elements, particularly in the case for the divalent results. According to the Pauling scale, Φ is about the same for Pd, Pt, Te, H, and P, roughly the same for Fe, Co, Ni, Si, and Ge, similarly for Ti, Zr, and Be, and also for Sc, Y, and Mg. Comparison of Tables I and II shows the divalent transition-metal results to agree with this pretty well. The ratio of α/β for the *s*-electron excitations is also "well behaved" with values ranging between 1 and 2. Once *d*-electron transfer is involved, the results are not in line with those for the main-group elements. The α are smaller and the β larger than when *s* transfer alone is involved—the larger β follow from the fact that the valence *d* electrons are increasingly stable with respect to valence *s* (and *p*) with increasing ionization. Even if out of line with Table I, the α of the last column of Table II display features which make sense. For example, large values of α occur for Rh and Pd, and this is associated with these elements (along with Ag and La) having *d* levels which lie low in energy with respect to the *s*-*p* levels, both as free atoms and as metals. This is important to the relative roles of *d* and non-*d* bonding but less so to the net charge transfer.

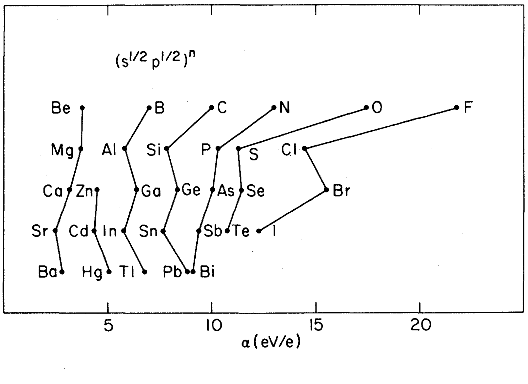

FIG. 4. Electronegativity parameter α as obtained in the averages of the $(s^{1/2}p^{1/2})^n$ configurations (see text) for the main-group elements.

Except perhaps for ionic salts, the parameters of Table II have little relevance to transition-metal charge transfer. This is because the transition metals are usually involved in metallic bonding where regardless of the change in *d*-electron count, that for the non-*d* is opposite, with the net charge transfer a small fraction of either. This follows from the fact that it is energetically favorable to screen charge transfer when there is the means to do so as in a metal. This is borne by band theory calculation and by experiment. For example, the alloying of Au involves[6] *s*-*p* transfer opposite to and some 10–20% greater than the *d*. The balance of *d* to non-*d* transfer is not generally known as a function of what transition element is involved but there is evidence that it varies.[4] α and β can be perfectly well defined for charge transfer in such cases. This would involve knowing the energies of atomic configurations where changes in *d* and non-*d* count are large compared with the change in ionization. Such energies are not accessible from spectral data but could be obtained from atomic calculations where the *d* and non-*d* electrons are of nonintegral count and the ionic charge is allowed to be a fraction.

TABLE II. α (eV/e) and β (eV/e^2) for transition- and noble-metal elements. The three stages of ionization are indicated for the four cases.

	Monovalent $(d^ns^2)^-,(d^ns)^0,(d^n)^+$		Divalent $(d^ns^2)^0,(d^ns)^+,(d^n)^{2+}$		$(d^ns)^0,(d^{n-1/2}s^{1/2})^+(d^{n-1})^{2+}$		$(d^ns)^0,(d^{n-1}s)^+,(d^{n-2}s)^{2+}$	
	α	β	α	β	α	β	α	β
Sc	3.38	2.31	3.57	3.08	1.62	3.56	-0.98	5.65
Ti	3.06	2.53	4.01	3.15	2.35	3.67	0.07	5.82
V	4.10	2.93	4.94	2.80	3.88	3.15	1.43	5.59
Cr	4.46	3.22	4.10	3.75	3.93	3.83	1.51	6.35
Mn	4.18	2.88	4.78	3.57	3.08	4.21	1.33	6.18
Fe	4.41	3.04	5.67	3.41	3.96	4.22	1.91	6.96
Co	4.17	2.71	5.52	3.48			1.80	7.20
Ni	4.50	3.01	5.14	3.75	4.32	4.22	2.97	6.97
Cu	4.48	3.25	4.77	4.27	4.31	4.88		
Y	3.67	2.30	3.89	2.79	2.40	3.07	0.70	4.14
Zr	3.97	2.42	4.03	3.28	2.86	3.59	1.42	4.79
Nb			5.0	2.7				
Mo	4.09	2.46	4.5	3.6				
Ru	4.47	2.68	4.31	4.04	3.8	4.6		
Rh	4.53	2.75	5.08	3.78	4.21	4.57	3.9	6.4
Pd	4.55	2.54	6.01	3.36	4.65	4.90	5.53	6.14
Ag	4.44	3.14	4.95	3.86	5.70	4.77		
La			3.12	2.71	2.01	3.18		
Lu			4.02	3.02			0.20	3.98
Pt	5.78	3.02	6.42	3.44	5.88	3.96		
Au	5.77	3.46	6.18	3.93	6.17	4.37		

Such calculations are outside the scope of the present paper. In addition, they would neglect one important factor associated with changing d count, namely that d bands hybridize upon alloying and the net gain or loss of d count depends[17] heavily on whether occupied or hole states are available for hybridization. Consider Au or Ni with their full or almost full d bands. Hybridization into these bands dilutes the Au or Ni character of the bands thus reducing the Au or Ni site d count. In contrast, Sc and Zr have largely empty d bands and the loss of local d character due to hybridization into their occupied levels is almost inevitably overpowered by the hybridization of their unoccupied levels into the occupied bands of the other alloy constituent. Thus such elements generally gain d character of their sites upon alloying. This effect occurs over and above any charge transfer due to the relative energies of the d levels or the Fermi energies of the constituents and the trend associated with it is consistent with experiment.[4,6]

III. *d* TRANSFER WITH *s*-ELECTRON SCREENING

The preceding discussion argued that the relative availability of occupied and empty d states is important to the change in site d count. Nevertheless, it is of interest to estimate the d transfer, predicted by energy considerations alone, when screened by s-electron transfer. Consider the neutral-atom d^{n+1}, d^ns, and $d^{n-1}s^2$ configurations. If the d^{n+1} is termed the "negative" ion and the $d^{n-1}s^2$ "positive," the respective energies of the three configurations can be fit to obtain α and β, where α is the *effective* d-electron electronegativity. The results of doing this are shown in Table III. The α are larger, i.e., more positive at the upper ends of the transition-metal rows and larger for the $5d$ than for the $4d$ and, in turn the $3d$. Large α in this sense imply a preference for increased d count, thus the results in the table indicate a tendency based, in the Mulliken sense, on the energies of the levels which is opposite to the hybridization trend cited above. The large values of α for Rh, Pd, and Ag are another reflection of the fact that the d levels lie low, with respect to the non-d in these metals.

The β, the quadratic terms which resist charge transfer, are extraordinarily small. The evaluation of Eq. (7) for s-d transfer yields many cases where q is equal or greater than 1 in magnitude because of the small denominator. More often than not, Eq. (7) would predict that Sc, Ti, and Y are in the $d^{n-1}s^2$ and Rh, Pd, Ag, and Au in the d^{n+1} configuration

TABLE III. Effective *d*-electron electronegativity terms for transition and noble metals (see footnote below) where *s* transfer maintains charge neutrality and the "neutral" state is taken to be the metallic sd^n configuration.

	α (eV/e)	β (eV/e^2)
Sc	−2.16	0.19
Ti	−1.72	0.46
V	−1.54	0.82
Mn	−1.37	0.49
Fe	−0.79	0.62
Co	−0.87	1.04
Ni	−0.31	1.35
Cu[a]	−0.10	1.59
Y	−1.86	0.04
Zr	−1.12	−0.05
Mo	−0.57	0.42
Ru	0.29	0.76
Rh	0.99	0.45
Pd	1.69	0.61
Ag[a]	2.95	1.02
Ta	−0.94	−0.39
Ir	−0.77	0.74
Pt	0.45	0.59
Au[a]	1.49	0.26

[a] Lacking a d^{11} configuration for the noble metals, an extrapolation was employed to obtain these parameters.

TABLE IV. Ionic charges for various compounds deduced employing Eq. (7) for the 50-50 compound and Eq. (9) (with $n \to \infty$) for a dilute anion or cation. The cation is the first of the two elements listed and only the magnitude of the charge is tabulated.

	q 50-50 compound	q (per minority atom) dilute cation	dilute anion
NaCl	0.40	1.27	0.58
LiI	0.40	0.91	0.56
RbH	0.29	1.31	0.38
ZnO	0.18	0.47	0.30
MgO	0.25	0.71	0.38
AgCl	0.26	0.67	0.42
TiO	0.26	0.81	0.38
CsCl	0.48	1.85	0.65
MgHg	0.15	0.32	0.28
CsAu	0.35	1.03	0.53
MgAu	0.13	0.25	0.26
ZnAu	0.04	0.08	0.10
AgI	0.21	0.46	0.38
GaAs	0.12	0.41	0.17
GaP	0.19	0.58	0.28
InSb	0.14	0.37	0.22
BN	0.16	0.41	0.26

(d^{n+1} is, of course, d^{11} and inaccessible for Ag and Au). From experiment it would appear that this tendency does not prevail over the hybridization effect, but it may be important to the detailed balance of *d* and non-*d* electron transfer behavior.

IV. CHARGE TRANSFER BETWEEN ISOLATED ATOMS

Given the results of Tables I and II for α and β and Eq. (7), it is possible to ask what charge may be transferred between a pair of isolated noninteracting atoms so that the energy of the pair is at a minimum. Going to the crystalline compound involves Madelung potential terms, which further encourage ionic character, and hybridization effects, which discourage it, but Eq. (7) provides a relevant zeroth order estimate of the ionic character of a compound. Results for some of the compounds considered in the preceding paper are listed in Table IV. In general, the monovalent compounds with larger electronegativity differences have the largest q. But, note that the β's in the denominator of Eq. (7) are of significance; for example, the electronegativity difference of AuCs is roughly half that of MgO, yet q for AuCs is greater. The bulk of the compounds represented in Table IV are ionic or covalent in character and the q are, in general, somewhat smaller than what is normally attributed to these crystals, the discrepancy being the least for the alkali halides. It would appear that of the interatomic interaction terms which act to modify q in the crystal, Madelung effects predominate.

Equation (9) describes the charge transfer in the case where one atom A shares its transferred charge equally with n atoms B. This can be taken to the dilute limit where the β_B/n term in the denominator of the equation may be neglected. The results of doing this appear in the second and third columns of Table IV. They are quite asymmetric, showing that the dilute cation generally sustains larger charge transfer than the anion. By definition the cation has the smaller electronegativity, and to the extent that this implies a smaller β as well, one would expect the larger charging of the cation since β appears in the denominator. Of the cases considered, AuMg and AuZn provide exceptions to this rule. The asymmetries of Table IV are so substantial as to suggest that this factor is of significance to the asymmetries which occur in a sequence of compounds of varying chemical composition.

V. NONLINEARITIES IN THE IONIZATION ENERGIES

The equations so far employed have assumed that successive ionization energies vary linearly with q, and this is not strictly true as can be seen in Figs. 1 and 2. The nonlinearities are well described by adding a q^3 term to Eq. (3), i.e.,

$$E(q)=E(0)+\alpha q+\beta q^2+\gamma q^3 \ , \tag{12}$$

from which it follows

$$\epsilon(q)=\alpha+\beta+\gamma+q(2\beta+3\gamma)+3\gamma q^2 \ , \tag{13}$$

and then the Mulliken electronegativity becomes

$$\Phi_m=\alpha+\gamma \ , \tag{14}$$

i.e., it is no longer equal to α which is $(dE/dq)_{q=0}$. Under these circumstances it would appear that α rather than Φ_m is properly termed the electronegativity. The determination of α, β, and γ requires three or more ionization energies and therefore cannot be done as a rule. Fits have been made for a sampling of p-electron excitations where the first ionization potential $\epsilon(0)$ was fit exactly and the remaining $\epsilon(q)$ were fit by least squares. The results appear in Table V. The β are usually identical in the two and the three parameter fits and when they are not, as in the case for N, this is a comment on the accuracy of the levels being fit. Again, granted that the levels can be fit by Eq. (12), and noting the Φ_m is unaffected by idiosyncrasies of the fit,

$$\alpha(3)+\gamma(3)=\alpha(2) \ ,$$

where the 2 and 3 refer to the two fits. This would be important if the γ were not so small in magnitude because, keeping terms linear in γ/β, Eq. (7) for the charge transfer becomes

$$q=-\frac{1}{2}\frac{\alpha_A-\alpha_B}{\beta_A+\beta_B}-\frac{3}{8}\frac{(\alpha_A-\alpha_B)^2(\gamma_A-\gamma_B)}{(\beta_A+\beta_B)^3}+\cdots \ . \tag{15}$$

Since $\gamma_A-\gamma_B$ need not be of the same sign as $\alpha_A-\alpha_B$, the second term may add or subtract from the first. This term is near zero valued with the significant change in the predicted q coming from the change in the first term due to the change in the α's. Use of Eq. (15) and the three parameter fits yields q for GaAs and GaP that are 30% larger than the values of Table IV. The more accurate determination of α, coming from a multipoint fit, such as these, is of modest numerical significance to the resulting prediction of charge transfer.

VI. CONCLUSION

In this paper we have investigated the Mulliken electronegativity scheme which translates the charge transfer question to one between isolated nonin-

TABLE V. Two- and three-parameter fits of p-electron ionization sequences for selected atoms and configurations.

	α (eV/e)	β (eV/e^2)	α (eV/e)	β (eV/e^2)	γ (eV/e^3)	Number of ionization potentials in fits
Bsp^n	4.39	3.94	3.85	3.94	0.54	3
Alsp^n	3.43	3.00	3.25	3.00	0.18	3
Gasp^n	4.19	2.39	3.78	2.39	0.41	3
Insp^n	3.90	2.31	3.90	2.31	0.0	3
Csp^n	6.65	4.58	6.10	4.57	0.57	4
Gesp^n	5.30	3.68	5.16	3.80	0.09	4
Pbsp^n	5.02	3.40	4.98	3.51	−0.07	4
Ns^2p^n	7.34	5.84	6.60	6.03	0.56	6
Nsp^n	7.6	6.2	6.9	6.1	0.9	5
Psp^n	6.98	4.91	7.27	4.91	−0.29	3
Ass^2p^n	5.49	3.67	5.01	3.80	0.36	4
Assp^n	6.15	5.65	6.35	5.68	−0.24	5
Sbsp^n	5.6	3.9	5.8	3.7	0.05	5
Os^2p^n	9.13	6.73	8.45	6.82	0.58	6
Ses^2p^n	6.71	4.12	6.53	4.10	0.19	6
Fs^2p^n	11.04	7.61	9.95	7.67	1.15	6
Cls^2p^n	8.66	5.02	8.38	5.07	0.23	6

teracting atoms. As Coulson emphasized,[18] this scheme has considerable physical and mathematical appeal. The approach yields an electronegativity α that is the linear term in q in the total energy of the atom, i.e.,

$$\alpha=\left[\frac{dE}{dq}\right]_{q=0} . \tag{16}$$

What seems to have been overlooked in the recent literature is that there is a quadratic term β which acts to oppose charge transfer. Given α and β for the constituent elements, it is then possible, using Eq. (7) or (9), to estimate the ionic charge natural to the compound prior to inserting the atoms into the crystal, and this was done in Sec. IV. Such an estimate has the greatest meaning for ionic or covalent compounds and can be straightforwardly extended to multicomponent systems although we have not done this here. The resulting q for such compounds appear to be somewhat smaller than the values normally attributed to these materials. It therefore appears that the net effect of interatomic interaction terms is to drive the ionicity further. The Madelung potential-energy terms, which do this, are quadratic in the charge, and thus make negative contributions added to the β's in the denominators of Eqs. (7), (9), and (15). Since these, like the intra-atomic terms, arise from Coulomb interactions and since they involve charge not on the affected atomic site(s), they are expected to be smaller than the intra-atomic terms, reducing the magnitude but not reversing the sign of the denominators. The overlap and hybridization terms, which resist ionic charging, are more complicated in origin.

Complications arise when considering transition metals involved in metallic bonding where *d* and non-*d* charge transfer tends to be in opposite directions. It is possible to define α and β for such a case if one has an opinion of the ratio of the two transfers, but this neglects the changes in *d* count associated with hybridization of the *d* bands, where the change depends on the extent to which the bands are full or empty. For metallic systems, there is of course screening of these transfer effects. These hybridization effects appear to be important if only because the resulting transfer is consistent with a large number of experiments. In Sec. III we estimated α and β for *d* transfer assuming that *d* and non-*d* electron count changes exactly cancel. The result, which is a measure of the energetics of such transfer, was seen to oppose the hybridization effect. There are indications[4] that the competition between and magnitudes of the individual *d* and non-*d* transfer terms vary across a transition-metal row. Competition between the two above-mentioned factors is part of the reason why.

It was shown, Eqs. (7) and (9), that charge transfer is proportional to the difference in the α of the constituent elements. α is thus a proper "electronegativity" scale, albeit one defined for isolated noninteracting atoms. Φ_m, the scale originally defined by Mulliken, is the average of the electron affinity and the first ionization potential, and it was also shown here that this is equal to α, *provided* that the total energy of the atom involves terms linear and quadratic in q but none of higher order. In such a case Φ_m, like α, is a proper electronegativity scale.

The nonlinearities displayed in Figs. 1 and 2 indicate the presence of at least one higher-order term. This term is small but its presence does cause Φ_m to be unequal to α. In the case of GaP and GaAs, discussed in the preceding section, estimates of q are changed by 30% when this term is accounted for. As a practical matter, this term cannot always be extracted from spectroscopic data. Even when the term is accessible, it can be argued that a 30% correction in the value of q lies within the noise when it comes to associating the results of the model to a specific molecular or crystalline system.

Also, it was noted that some estimates of electronegativity scales have been based on single ionization energies. This procedure is unsatisfactory since the resulting Φ are some combination of α and β instead of α alone. Scales have also been derived in terms of pseudopotentials and whether or not there are problems with these depends on how this is done. In local-density theory the one-electron energy $\epsilon=dE/dn$ (n is the electron count) is[19] a "differential electronegativity." Suitably defined, such a differential term is exactly the electronegativity required in $q=c\,\Delta\Phi$ and the associated energy expression. The only problem is that it is not generally recognized that the "constant" of proportionality c, as well as the difference in Φ, depends on the elements involved.

In conclusion, given the atomic configurations and the valence electrons involved in charge transfer, and employing spectroscopic data or atomic calculations, it is possible to estimate the ionic character of a compound within the Mulliken scheme. This does not involve the interatomic bonding effects which contribute to charge transfer (though done for configurations approximating such bonding). However, it does provide a useful reference estimate with which to compare experiment or more detailed theory and it has the virtues of being simple to calculate and well defined. While the charge transfer depends primarily upon the difference in electronegativities, α, it also is quantitatively affected by the quadratic terms β which deter charging, and it is the latter which control the variation in ionicity with compound composition. Asymmetries in charge transfer are known to occur experimentally with varying chemical composition and it remains to be seen how well these are described within the Mulliken scheme.

ACKNOWLEDGMENT

This work was supported at Brookhaven by the Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

---

[1] For example, A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica 100B, 1 (1980).

[2] R. E. Watson and J. W. Davenport, preceding paper, Phys. Rev. B 27, 6418 (1983).

[3] R. S. Mulliken, J. Chem. Phys. 2, 782 (1934); 3, 573 (1935).

[4] For example, R. E. Watson, L. J. Swartzendruber, and L. H. Bennett, Phys. Rev. B 24, 6211 (1981). This involves transition-metal alloys where other factors, such as varying conduction electron screening, are at play.

[5] R. Ferreira, Adv. Chem. Phys. 13, 55 (1967), and references therein. Authors employing the quadratic term or its equivalent include C. K. Jorgensen, *Orbitals in Atoms and Molecules* (Academic, New York, 1962) and J. Hinze, M. A. Whitehead, and H. H. Jaffe, J. Am. Chem. Soc. 85, 148 (1963).

[6] See, e.g., R. E. Watson, J. Hudis, and M. L. Perlman, Phys. Rev. B 4, 4139 (1971).

[7] L. Pauling, *The Nature of the Chemical Bond,* 3rd ed. (Cornell University Press, Ithaca, New York, 1960).

[8] W. E. Moffitt, Proc. R. Soc. London Ser. A 196, 510 (1949).

[9] J. St. John and A. N. Bloch, Phys. Rev. Lett. 33, 1095 (1974).

[10] R. E. Watson and L. H. Bennett, J. Phys. Chem. Solids 39, 1235 (1978).

[11] For example, A. Zunger, Phys. Rev. B 22, 5839 (1980), and references therein.

[12] C. E. Moore, in *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Spec. Publ. No. 35 (U.S.G.P.O., Washington, D.C., 1971), Vol. 35.

[13] H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data 6, Suppl. 1 (1977); note that much of the data is based on interpolation and extrapolation.

[14] The regular behavior of the positions of the centers of gravity of configurations as a function of atomic Z and of ionization allow estimates to be made when the data are inadequate or wrong.

[15] G. H. Shortley, Phys. Rev. 50, 1072 (1936).

[16] For example, G. C. Carter, I. Weissman, L. H. Bennett, and R. E. Watson, Phys. Rev. B 5, 362 (1972).

[17] R. E. Watson and L. H. Bennett, Phys. Rev. B 18, 6439 (1978).

[18] C. A. Coulson, *Valence* (Oxford University Press, London, 1961).

[19] J. C. Slater, Adv. Quantum Chem. 6, 1 (1972); K. H. Johnson, Int. J. Quant. Chem. 115, 39 (1977).