

First-principles ionicity scales. II. Structural coordinates from atomic calculations

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Estimates of atomic size and electronegativity are obtained directly from first-principles calculations of the atomic valence electronic charge density. Significant information about the bonding in the solid state is extracted from the computed atomic parameters, and a first-principles mapping to the semiempirical Pauling ionicity scale is presented.

I. INTRODUCTION

In a previous paper¹ (hereafter referred to as I) we showed how a first-principles ionicity scale for octet binary compounds $A^N B^{8-N}$ can be constructed from the asymmetry in the valence charge distribution in a crystal. A significant part of the asymmetry was found to have its origin in the intrinsic differences between the charge densities of the constituent atoms. The recognition that atomic parameters can be used successfully in the study of bonding and structural trends in solids occurred early in the history of materials science. A variety of atomic parameters or atomic coordinates has been suggested. Two widely used parameters are the atomic size and the electronegativity or measure of the ability of an atom to attract electrons.

In this paper we present evidence that it is possible to arrive at a first-principles definition of atomic parameters such as size and electronegativity through the consideration of only the atomic valence electron charge density. The resulting first-principles parameters are remarkably accurate when used as coordinates for solid-state diagrams. They successfully delineate the regions of stability of the major crystalline structures and provide quantitative estimates of the bond length for octet binary compounds.

In addition, we show that it is possible to arrive at the Pauling ionicity scale through calculations involving only the atomic charge distributions, without the need for the explicit introduction of the concept of resonating bonds.

II. ATOMIC SIZE AND ELECTRONEGATIVITY

Although Pauling² arrived at his electronegativity concept through thermochemical ideas, there have been several attempts to explain the values of the electronegativity of the elements using more fundamental atomic properties. Mulliken³ showed its connection to the average of the ionization potential and the electron affinity. Gordy⁴ argued for a linear dependence of the electronegativity on the ratio $(Z_v + 1)/r_{cov}$, where Z_v is the total valence charge and r_{cov} is the covalent radius² of the atom.

We propose that a first-principles electronegativity scale can be established using only the valence charge

distribution of the neutral atom. First, we need a measure of atomic size. To this end, we introduce a mean valence radius r_m as

$$r_m = \frac{1}{Z_v} \int r \rho_v dV. \quad (1)$$

In this equation, r is the radial coordinate, ρ_v is the spherically symmetric valence charge distribution, and the integration extends to all space. The self-consistent atomic calculations are performed using a Herman-Skillman-like approach⁵ and the local-density approximation of density-functional theory.⁶

Other first-principles schemes have been developed to parametrize the atomic size. A popular choice is the Zunger-Cohen hard-core pseudopotential radii.^{7,8} These radii are angular-momentum dependent, however significant insight into bonding properties and electronegativity scales can be obtained by using just the s -orbital radii r_s .^{9,10} In particular, it was shown in Ref. 10 that the cation radii r_s^c provide a means of classifying the AB octets according to structure. Using r_m as a measure of cation size provides an equivalent separation of the AB group into zinc-blende (ZB), rocksalt (RS), and CsCl structure classes. Figure 1 shows that just four errors are made in the classification, with only CdO being appreciably displaced from the region where it belongs. We stress that the only information used in the preparation of the structure map is the valence charge density of the neutral atoms.

With r_m and the total valence charge Z_v as coordinates, Fig. 2 shows that high electronegativity is associated with high Z_v and small r_m (upper left corner), and low electronegativity elements tend to have large r_m and small Z_v (lower right corner). We find that a good fit to the Pauling scale of electronegativity is given by

$$X = 1.5 \sqrt{\frac{Z_v + 1}{r_m}} - 0.16. \quad (2)$$

Figure 3 and Table I compare the two scales. The Ib elements Cu and Ag (and to some extent the IIb elements Cd and Zn) are not well represented because of the ambiguity involved in the assignment of the d electrons to either the core or the valence shells. The fit is good considering the uncertainties inherent in the construction of

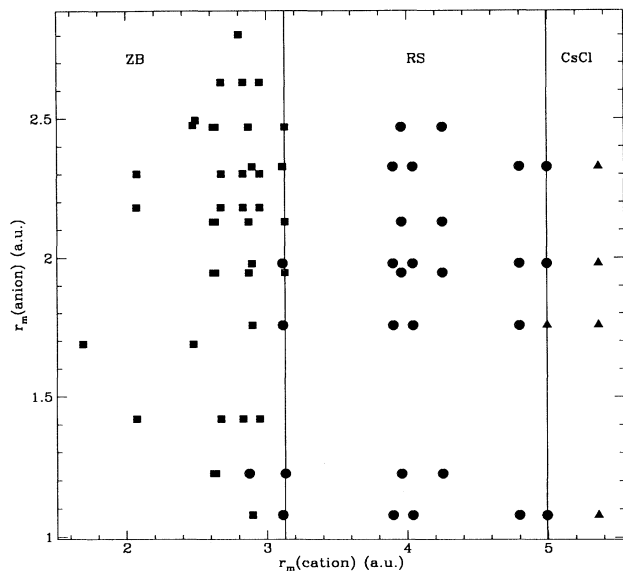


FIG. 1. Structure map for 72 AB octets. The vertical lines (at cation radii of 3.13 a.u. and 4.99 a.u.) separate the compounds into structural classes. Compounds with fourfold, sixfold, and eightfold coordination are represented by squares, circles, and triangles, respectively (see text).

the Pauling scale from thermochemical data. By using r_m as a first-principles estimate of the atomic size, the electronegativity defined by Eq. (2) is also free of the ambiguities associated with the assignment of a covalent radius to an element.

Since r_m is a measure of the size of an atom, it is of interest to investigate to what extent the observed values

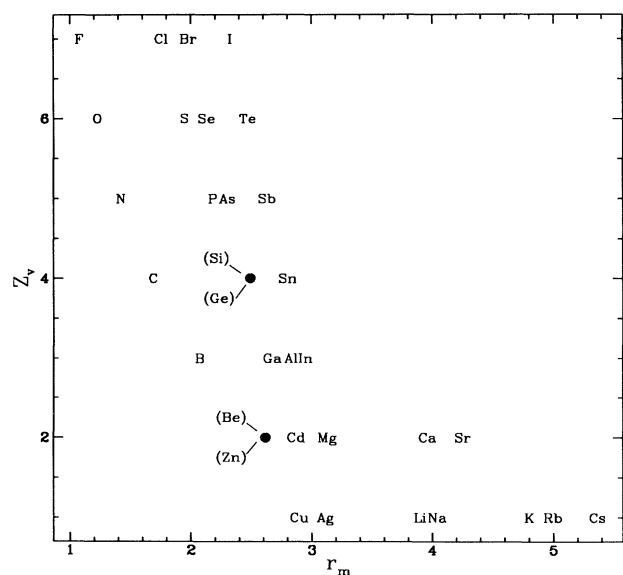


FIG. 2. Z_v vs r_m for some elements. (Si and Ge, and Zn and Be, share approximately the same coordinates.)

of the bond length in binary compounds are related to the sum of the radii of the constituent atoms. Zhang, Cohen, and Phillips⁹ established the linear relation

$$d(A, B) = a[r_s(A) + r_s(B)] + b - c|X_P(A) - X_P(B)| \quad (3)$$

between the Zunger-Cohen s -orbital radii, the Pauling electronegativity difference, and the bond length of tetrahedrally coordinated compounds. Here a , b , and c are constants. If we use the valence radii r_m instead of r_s and X instead of X_P , we find a relation of the same form:

$$d(A, B) = 1.08[r_m(A) + r_m(B)] - 0.74 - 0.155|X(A) - X(B)|, \quad (4)$$

which, unlike Eq. (3), also applies to sixfold-coordinated compounds (Fig. 4). Both the pseudopotential radii and our r_m are able to predict the coordination number of

TABLE I. Atomic parameters for a selection of elements. Z_v is the total valence charge, r_m the mean valence radius [Eq. (1)], X the calculated electronegativity [Eq. (2)], and X_P the Pauling electronegativity.

Element	Z_v	r_m (a.u.)	X	X_P
Ag	1	3.112	1.04	1.9
Al	3	2.830	1.62	1.5
As	5	2.301	2.26	2.0
B	3	2.073	1.92	2.0
Be	2	2.618	1.45	1.5
Br	7	1.980	2.86	2.8
C	4	1.689	2.42	2.5
Ca	2	3.959	1.15	1.0
Cd	2	2.871	1.37	1.7
Cl	7	1.757	3.04	3.0
Cs	1	5.361	0.76	0.7
Cu	1	2.896	1.09	1.9
F	7	1.078	3.93	4.0
Ga	3	2.674	1.67	1.6
Ge	4	2.493	1.96	1.8
I	7	2.326	2.62	2.5
In	3	2.949	1.59	1.7
K	1	4.798	0.81	0.8
Li	1	3.898	0.91	1.0
Mg	2	3.129	1.31	1.2
N	5	1.421	2.92	3.0
Na	1	4.040	0.90	0.9
O	6	1.226	3.42	3.5
P	5	2.181	2.33	2.1
Rb	1	4.994	0.79	0.8
S	6	1.947	2.68	2.5
Sb	5	2.630	2.11	1.9
Se	6	2.129	2.56	2.4
Si	4	2.475	1.97	1.8
Sn	4	2.802	1.84	1.8
Sr	2	4.251	1.10	1.0
Te	6	2.469	2.37	2.1
Zn	2	2.633	1.44	1.5

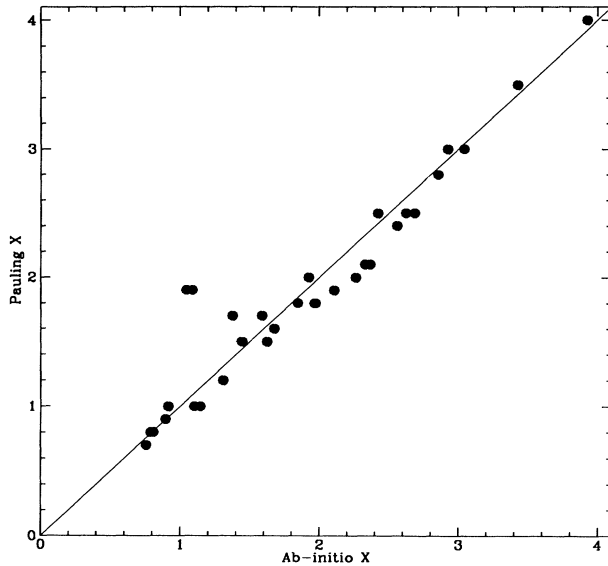


FIG. 3. Pauling electronegativity vs the proposed scale based on the atomic valence charge density.

a compound in the solid state (see Ref. 10 and Fig. 1), but only our first-principles coordinates r_m and X give correct bond lengths regardless of the crystalline environment. Due to the difficulties in defining r_m for the elements in the Ib and IIb groups of the Periodic Table, materials containing Cu, Ag, Cd, or Zn are not considered.

We are thus able to define useful first-principles estimates of atomic sizes [Eq. (1)] and electronegativities [Eq. (2)] using only information about atoms. These

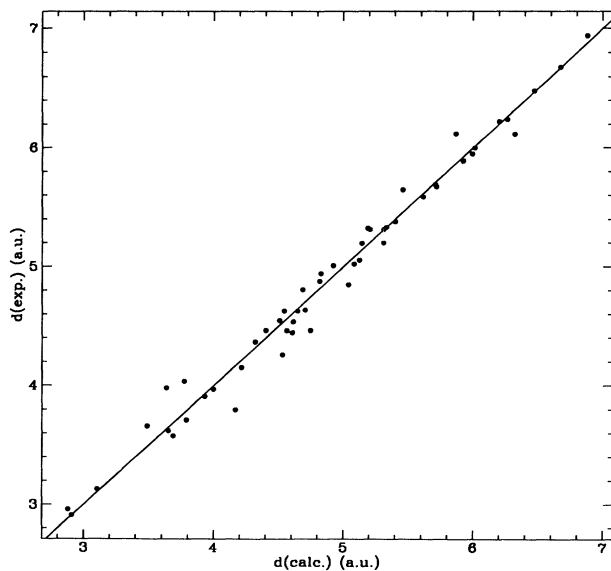


FIG. 4. Experimental bond length for $A^N B^{8-N}$ materials (with the exception of those containing Cu, Ag, Cd, or Zn) vs the values calculated with Eq. (4).

parameters are significant structural coordinates for the study of bonding in the solid state.

III. CONSTRUCTION OF PAULING'S IONICITY SCALE FROM ATOMIC CHARGE DENSITIES

In I we introduced the magnitudes S_S and S_A as indicative of the relative importance of the symmetric and antisymmetric components of the valence charge distribution in an $A^N B^{8-N}$ solid, and showed that the charge asymmetry coefficient g calculated from them [Eq. (14) in I] has many of the attributes of an ionicity parameter. This section deals with a different approach to the construction of a first-principles ionicity scale for $A^N B^{8-N}$ crystals. Unlike the method given in I, here we use only the valence charge distributions of the isolated, neutral, A and B atoms.

We define the symmetric and antisymmetric combinations:

$$A_S = \int r^2 (\rho_A + \rho_B)^2 dV,$$

$$A_A = \int r^2 (\rho_A - \rho_B)^2 dV, \quad (5)$$

which differ from S_S^∞ and S_A^∞ in Eqs. (16) in I by the inclusion of the weighting factor r^2 (this translates into A_S and A_A having dimensions of energy). Figure 5 reveals the wealth of structural information contained in the coordinates A_S and A_A . First, it is pos-

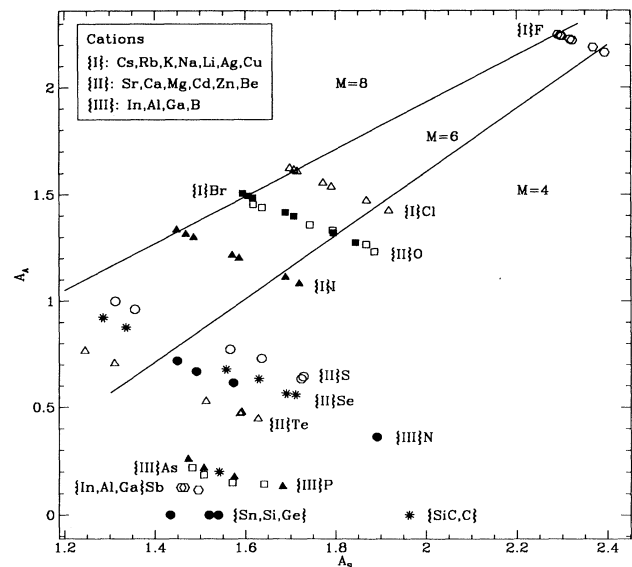


FIG. 5. A_A vs A_S for 72 AB octets. For each anion, the compounds are approximately aligned, represented by a common symbol, and their ordering (left to right) is given by the cation lists in the inset. Note that BSb does not exist, and that the IV-IV compounds are independently labeled. The lines separate compounds with different coordinations: zinc-blende, wurtzite ($M = 4$), rocksalt ($M = 6$), and CsCl ($M = 8$) structures.

sible to separate the fourfold-coordinated zinc blendes and wurtzites, the sixfold-coordinated rocksalts, and the eightfold-coordinated (CsCl structure) compounds by straight lines.^{11,12} Second, compounds with a given anion lie approximately on straight lines, and the different lines are very nearly parallel. The degree of alignment and parallelism worsens as the electronegativity difference decreases (III-V and IV-IV compounds). Third, the ordering of the AB compounds along a given “ B ” line is given by the mean atomic radius r_m defined by Eq. (1). Since there is an approximately linear correlation between the sum of the atomic radii and the bond length in the solid (Fig. 4), one can estimate the relative sizes of the latter for a series of materials directly from the figure.

To gain insight into the physical meaning of A_S and A_A , we plot in Fig. 6 the integrands in Eq. (5) for GaAs and NaCl, together with the valence charge densities of the individual atoms. We observe that the relative magnitude of A_S and A_A depends on the degree of (same center) overlap of the charge distributions of A and B . A_A is small compared to A_S when the two atoms have similar mean radii in the sense of Eq. (1), as is the case in GaAs. When the valence charge densities peak at significantly different distances from the origin, however, A_A rivals A_S in magnitude. Remembering the connection between atomic size and electronegativity discussed in Sec. II, we recognize that the magnitude controlling the relative size of A_S and A_A is the electronegativity difference. If, by analogy with Eq. (17) in I, we now define an atomic asymmetry coefficient

$$g_{\text{at}} = \sqrt{\frac{A_A}{A_S}}, \quad (6)$$

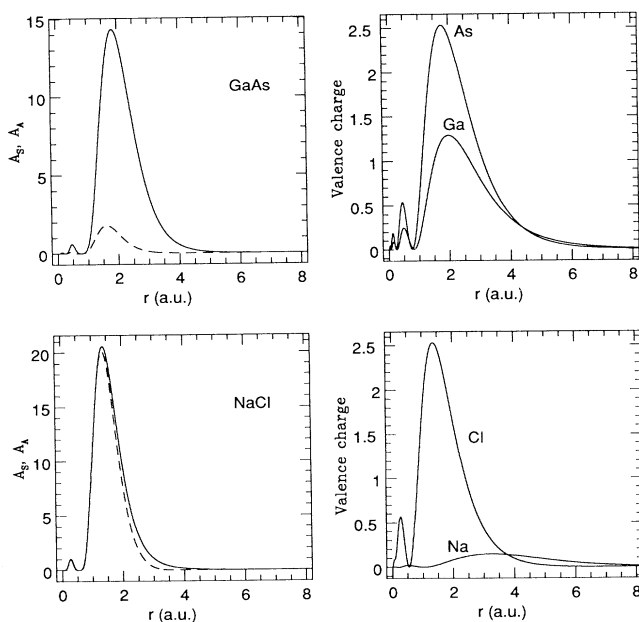


FIG. 6. Atomic overlap integrals and atomic valence charge densities for GaAs (upper panels) and NaCl (lower panels). On the left, the solid lines correspond to A_S , and the dashed lines to A_A .

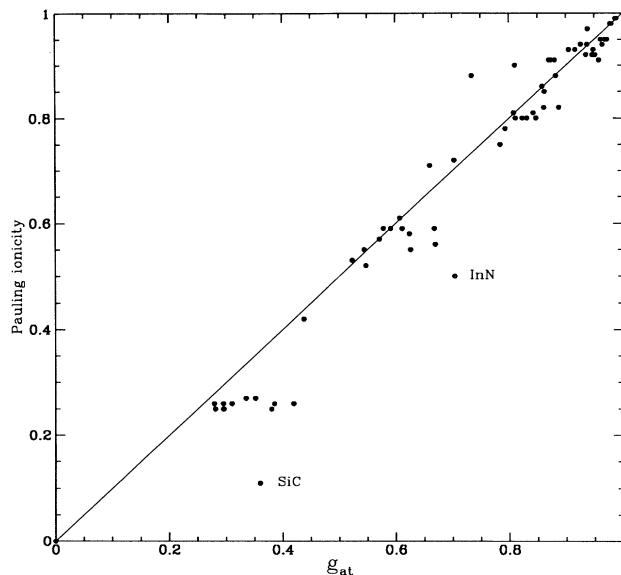


FIG. 7. Pauling ionicity vs the atomic asymmetry parameter g_{at} .

we would expect it, by analogy with Pauling’s construction [see Eqs. (2) and (3) in I], to serve as an ionicity parameter. Figure 7 shows that g_{at} corresponds¹³ to the Pauling ionicity as appropriate for *crystals* [Eq. (3) in I]. This may seem surprising, since, as we use only atomic information, we have in principle no way to account for the N/M factor that depends on the particular crystalline environment. However, we have already seen that M , the coordination number in the solid, can be predicted very accurately with the use of atomic radii (Fig. 1). The N/M factor is therefore built into our formalism, and it is not necessary to invoke the notion of resonant bonds to obtain a physically sound ionicity scale.¹⁴

IV. CONCLUSIONS

Using the valence charge density of isolated atoms as the only input, we have presented first-principles measures of the atomic size and electronegativity, and shown how significant insights into the structural and bonding characteristics of crystals follow from the consideration of these parameters. In particular, we have provided a first-principles mapping to Pauling’s ionicity scale for $A^N B^{8-N}$ solids.

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¹A. García and M. L. Cohen, previous paper, Phys. Rev. B **47**, 4215 (1993).

²L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell University Press, Ithaca, NY, 1960).

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

⁴W. Gordy, Phys. Rev. **69**, 604 (1946).

⁵F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

⁶P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

⁷A. Zunger and M. L. Cohen, Phys. Rev. B **18**, 5449 (1978); **20**, 4082 (1979); A. Zunger, *ibid.* **22**, 5839 (1980).

⁸S. B. Zhang, M. L. Cohen, and J. C. Phillips, Phys. Rev. B **36**, 5861 (1987).

⁹S. B. Zhang, M. L. Cohen, and J. C. Phillips, Phys. Rev. B

38, 12085 (1988).

¹⁰S. B. Zhang and M. L. Cohen, Phys. Rev. B **39**, 1077 (1989).

¹¹MgS and MgSe are borderline compounds which can exist in both the rocksalt and the wurtzite modifications. Our scheme places them in the region of fourfold coordination.

¹²It is not clear whether CuF (on the upper right corner in Fig. 5) is stable in the zinc-blende structure, if at all. See J. R. Chelikowsky and J. C. Phillips, Phys. Rev. B **17**, 2453 (1978); A. G. Sharpe, Adv. Fluor. Chem. **1**, 29 (1960).

¹³Our values for SiC (0.36) and InN (0.70) are significantly larger than Pauling's (0.11 and 0.50, respectively).

¹⁴Phillips has argued that Pauling's introduction of the N/M factor [Eq. (3) in I] artificially increases the separation of the ionicity values of fourfold- and sixfold-coordinated compounds. See J. C. Phillips, Rev. Mod. Phys. **42**, 317 (1970); *Bonds and Bands in Semiconductors* (Academic, New York, 1973).