

# An Electrostatics Framework Relating Ionization Potential (and Electron Affinity), Electronegativity, Polarizability, and Ionic Radius for Monatomic Species

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Received July 26, 1993. Revised Manuscript Received November 29, 1993\*

**Abstract:** Consideration of effective nuclear charge  $Z_{\text{eff}}e$  in an electrostatic model, together with the pairwise combination of ionization potentials  $I$  (or of  $I$  with electron affinity), yields both a value of  $Z_{\text{eff}}$  related to electronegativity and an averaged charge radius  $r$  related to polarizability. For anions the value of  $r$  is within a few percent of the experimental in-lattice radius from XRD. For cations, the positive charge external to the closed shells interacts with the latter as with a dielectric, again in accord with a model yielding realistic cation radii  $R$ : apart from Li salts,  $r + R$  values accord well with experimental lattice parameters, demonstrating further the applicability of electrostatic continuum models.

From a successful precedent<sup>1</sup> elaborated in the following section, electron affinities may be equated with the self-energies of the anions formed, but with particulate electrons represented by an extra interaction with partly-screened nuclear charge in an intraatomic interaction additional to electrostatic charging. This expedient allows the apparently *negative* self-energies of the stable anions to be rationalized, and in this paper now leads to relationships between the title quantities for monoatomic anions, cations, and neutrals.

Classical electrolyte theories of Debye and Hückel, Bjerrum, Brønsted, Born, and their schools employed electrostatic charging processes and models, but ion sizes and interionic distances as either input data or fitted parameters commonly remain uncertain. Recent applications of classical electrostatics to solvation in systems of biological and physicochemical interest<sup>2–7</sup> underline the importance of clarifying the physical validity of the approximate accord often achieved with experiment. In addition to solvation energies, lattice energies have been used in sphere-in-continua calculations,<sup>1,8–10</sup> again often involving an assignment of ionic radii.<sup>11</sup> Anion and cation radii are assumed to be additive in many analyses of interionic distances in crystals.<sup>12</sup> The major contrast in methods of assignment of individual values lies between criteria based on XRD-determined electron-density minima between ions<sup>1,12</sup> and other methods usually relying on theoretical criteria.<sup>13–15</sup>

Kindred questions arise in the assignment of individual ionic polarizabilities from observed total crystal values, but here the availability of excellent theoretical (wave-mechanical) values for

small cations in isolation,<sup>16</sup> and the almost unquestionable assumption of their invariance on incorporation within crystals, provides an assured basis.<sup>16</sup> From electrostatics, the polarizability  $\alpha$  of a classical conductive sphere is given by the cube of its radius,<sup>17</sup> a result to be exploited below.

The remaining quantity, the electronegativity (“the power of an atom in a molecule to attract electrons to itself”) was deduced by Pauling<sup>11</sup> from empirical relationships of observed bond energies, later drawing alternative definitions. Thus Mulliken<sup>18</sup> proposed electronegativity to be simply the sum  $I + E$  of ionization potential and electron affinity, respectively. Allred and Rochow<sup>19</sup> took the force, exerted by the Slater<sup>20</sup> effective nuclear charge  $Z_{\text{eff}}^s$  on an electron at the covalent radius  $r_{\text{cov}}$  as defined by Pauling,<sup>11</sup> as the basis for constructing a table of electronegativities  $Z_{\text{eff}}^s e^2 / r_{\text{cov}}^2$  for many elements. The choice of *force* was arbitrary: Mulliken’s definition involves *energy* terms.

In this paper, two approaches are employed. Firstly, in an electrostatics-based formulation, radii  $r$  imputed to complete electron shells viewed as being conductive in nature are related to ionization potentials or where appropriate ionization potentials with electron affinities. Since atoms acquire charge by the transfer of electrons (a process only partly approximated by electrostatic charging processes hitherto envisaged), the additional interaction arising between real electron and partly-screened nucleus is accounted for by introducing an extra term into the energy expression. The resultant  $r$  values are checked against experimental touchstones (polarizabilities viewed classically, and for anions the so-called experimental crystal radii from XRD).

The second approach involves ionizations of outer,  $s$ , electrons, assumed to interact with the closed inner shells as with dielectric material ascribed realistic values of permittivity. The particulate-electron/unscreened-nucleus interaction is again encompassed by a suitable energy term, in an elaboration of the classical model giving derived “dielectric” radii  $R$  amenable to test. Throughout, the *only* nonexperimental input is the set of free-cation polarizabilities from wave-mechanics which fix the scale for separation contributions; otherwise solely experimental data are employed as touchstones. Details of the processes employed are analyzed in Discussion.

\* Abstract published in *Advance ACS Abstracts*, January 15, 1994.

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### Self-Energies of Closed-Shell Species, Mean Electron-Loss Radii $r$ , Electronegativities, Polarizabilities, and Anionic Radii

**Halides.** Kavanau<sup>21</sup> sought to resolve an apparent paradox regarding anion self-energies, arising as follows. A classical sphere of charge  $-1$  has a self-energy which is positive (i.e., with respect to an otherwise identical uncharged sphere), whereas for say  $\text{Cl}^-$ , the charge-acquisition step  $\text{Cl}^0 + e \rightarrow \text{Cl}^-$  generates a negative energy change. Kavanau proposed that the (classical) self-energy of  $\text{Cl}^-$ , which is positive, is more than countered by the intraatomic interaction of the charge-conferring electron with the only partially screened nuclear charge  $+Z_{\text{eff}}$ . In solvation models, the intraatomic term is identical in both condensed-phase and isolated-ion charging processes and is thus eliminated. This model of anions was applied<sup>1</sup> to the lattice energies of alkali halide crystals  $\text{MX}$  ( $\text{M}^+ =$  alkali metal ion,  $\text{X}^- =$  halide ion), the environment about each lattice ion being treated as a dielectric continuum, assigned the observed bulk permittivity value. Derived  $\text{X}^-$  radii agreed well with XRD-based values, but in addition the calculation procedure<sup>1</sup> gave the correct *signs* of actual deviations from additivity of anion + cation radii, a second-order effect.

Here only the in vacuo charging processes are contemplated, yielding the two-term expressions afforded by Kavanau's approach. The electron affinity  $E$ , for the process  $\text{Cl} + e \rightarrow \text{Cl}^-$ , is accordingly given by

$$-E = (Ze)^2/2r' - Z_{\text{eff}}e^2/r' \quad (1)$$

where  $Z$  is the charge number (here  $-1$ ),  $e$  is the protonic charge, and  $r'$  the radius of the charged sphere. The first term represents the classical self-energy, the second the intraatomic interaction of electron as particle with unscreened nuclear charge. (To avoid algebraic clutter, charge squared is expressed in coulomb<sup>2</sup>/ $4\pi\epsilon_0$ ,  $\epsilon_0$  being the permittivity of empty space, i.e., in electrostatic units.) To proceed in identical fashion for the ionization  $\text{Cl} \rightarrow \text{Cl}^+ + e$ , the ionization potential  $I_1$  is correspondingly

$$I_1 = (Ze)^2/2r'' + Z_{\text{eff}}e^2/r'' \quad (2)$$

where the penultimate electron of the closed shell is deemed to see the same  $Z_{\text{eff}}$  as is experienced in (1) by its opposed-spin partner in  $\text{Cl}^-$ . Taking the difference between (2) and (1) and putting  $r$  equal to the harmonic mean of  $r'$  and  $r''$ , one obtains

$$I_1 + E = 2Z_{\text{eff}}e^2/r \quad (3)$$

This is already a satisfactory result, since in (3) the left-hand side is the Mulliken electronegativity and the right encompasses the electron/unscreened-nucleus interaction, akin to the Allred-Rochow formulation but now in terms of energy, as is appropriate to the Mulliken definition. Here  $r$  is an average electron-loss radius of the outermost electron pair of the  $\text{Cl}^-$  closed shell, but  $Z_{\text{eff}}$  and  $r$  are yet to be separated. Invoking  $r$  again in place of  $r'$  and  $r''$  allows solution of (1) and (2), since then

$$I_1 - E = e^2/r \quad (4)$$

Hence  $r$ , the harmonic mean for the two electrons as defined by (3) and (4), is determined from  $I_1$  and  $E$ . The halides  $\text{X}^-$  may thus be viewed as classical conductive spheres, with a  $Z_{\text{eff}}$  interaction superimposed to encompass the quantal nature of the electrons removed.

While atom polarizabilities  $\alpha$  in wave mechanics are proportional to the fourth power of the expectation value of the electron-nuclear distance,<sup>12</sup> a *cubic* relationship, of an *outer bound* for electronic charge comprising a classical conductive sphere, is not necessarily in contradiction; hence, in Table 1, values of  $\alpha_{\text{exp}}^{1/3}$  are matched against the  $r$  values from  $I_1 - E$  for<sup>22</sup>  $\text{X}^-$ , following the introductory rule that the  $\alpha_{\text{exp}}(\text{X}^-)$  are averages of experimental

**Table 1.** Anion Electron-Loss Radii  $r$ , Cube-Rooted Polarizabilities  $\alpha_{\text{exp}}^{1/3}$ , and Experimental In-Lattice Radii  $r_{\text{exp}}$

	$r, \text{\AA}$	$\alpha_{\text{exp}}^{1/3}, \text{\AA}$	$r_{\text{exp}}, \text{\AA}$
F <sup>-</sup>	1.03 <sup>a</sup>	1.05 <sup>b</sup>	1.13 <sup>c</sup>
Cl <sup>-</sup>	1.54	1.49	1.63
Br <sup>-</sup>	1.70	1.65	1.79
I <sup>-</sup>	1.95	1.86	2.05
O <sup>2-</sup>	<i>d</i>	1.33	
S <sup>2-</sup>	<i>d</i>	1.75	

<sup>a</sup>  $I$  and  $E$  values are from ref 22.  $\text{\AA} = 10^{-10}$  m. <sup>b</sup>  $\alpha_{\text{exp}}$  averages from ref 16. <sup>c</sup>  $r_{\text{exp}}$  from refs 1 and 12. <sup>d</sup> The second electron affinities, required for the calculation, are not measurable.

$\text{MX}$  values less the corresponding  $\alpha(\text{M}^+)$ . Experimental  $r_{\text{exp}}(\text{X}^-)$  values from XRD criteria<sup>1</sup> are also included in Table 1. Before evaluation, criteria of correspondence are needed: treating granular (i.e., electronic, nuclear, atomic) matter as featureless fluid/spheres/continua will at best involve the averaging of a small number of quantities, with concomitant rounding errors. Such rounding errors, if large, would be entirely damaging; if modest, the outcome could be instructive; if small, however, conclusions of some value should ensue. "Modest" will be taken as *within 15%* and "small" as *within 5%*: the latter is a quite acceptable rounding error in the averaging of particulate contributions from a small population to an overall gross quantity treated as being smoothly continuous. Differences between predicted and observed are henceforth ascribed to such rounding-off errors incurred in each calculation and judged as such. Tests on  $\text{X}^-$  are followed by examinations of data on rare gases, alkali metal ions, and alkaline earth ions.

Table 1 shows that  $r$  values from eq 4 are in good agreement with  $\alpha_{\text{exp}}^{1/3}$  for  $\text{X}^-$  and even in moderately good agreement with  $r_{\text{exp}}$  values, which alone are subject to thermal expansion. (Interestingly, the  $r_{\text{exp}}$  fall just between the cube roots of  $\alpha_{\text{exp}}(\text{X}^-)$  and of the  $\alpha(\text{X}^-)$  values "freed", by extrapolation, of cationic compression.<sup>16</sup>)  $r$  and  $r_{\text{exp}}$  differ most for F<sup>-</sup>, and divergences of similar magnitude can recur with first-row species. While chalcogenide ( $\text{Y}^{2-}$ )  $\alpha_{\text{exp}}^{1/3}$  values are included for comparison, the second electron affinities, required to calculate  $r$  by a closely similar procedure (involving  $0 \rightarrow 1^-$  and  $1^- \rightarrow 2^-$ ), are not accessible to experiment.

**Rare Gases, Alkali Metals, and Alkaline Earths.** The  $r$ ,  $\alpha_{\text{exp}}^{1/3}$  correspondence for  $\text{X}^-$  is further tested on other species isoelectronic with the halides, the rare gases, and the closed-shell cations  $\text{M}^{z+}$ . From the set procedure, the equations modified appropriately for, e.g., Ar to give successively  $\text{Ar}^+$  and  $\text{Ar}^{2+}$  become

$$I_1 = (Z_1e)^2/2r' + Z_{\text{eff}}e^2/r' \quad (Z_1 = 1) \quad (1')$$

$$I_2 = (Z_2^2 - Z_1^2)e^2/2r'' + Z_{\text{eff}}e^2/r'' \quad (Z_2 = 2) \quad (2')$$

where the first term in (2') gives the electrostatic self-energy change for  $1^+ \rightarrow 2^+$ , and the second represents the intraatomic interaction again. Hence by difference, with  $r$  replacing  $r'$  and  $r''$

$$I_2 - I_1 = e^2/r \quad (4')$$

For the general case of  $I_k, I_l$  where  $k, l$  are successive integers, (1') and (2') lead to

$$Z_{\text{eff}} = \frac{1}{2} \frac{I_l + I_k}{I_l - I_k} - k \quad (3')$$

while (4') leads to

$$I_l - I_k = e^2/r \quad (4'')$$

Thus (4'') may be used for ionizations of the two outermost closed-shell electrons of  $\text{K}^+$  and  $\text{Ca}^{2+}$  isoelectronic with those of Ar.

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**Table 2.** Electron-Loss Radii  $r$  and (Polarizability) $^{1/3}$  Values of Rare Gases, Alkali-Metal Ions, and Alkaline-Earth Dications

	$r, \text{Å}$	$\alpha^{1/3}, \text{Å}$		$r, \text{Å}$	$\alpha^{1/3}, \text{Å}$
He	0.48	0.59 <sup>a</sup>	K <sup>+</sup>	1.02	1.05
Ne	0.74	0.73	Rb <sup>+</sup>	1.13	1.10
Ar	1.21	1.18	Cs <sup>+</sup>	<i>c</i>	1.31
Kr	1.39	1.35	Mg <sup>2+</sup>	0.49	0.42 <sup>b</sup>
Xe	1.59	1.59	Ca <sup>2+</sup>	0.88	0.78
Li <sup>+</sup>	0.31	0.29 <sup>b</sup>	Sr <sup>2+</sup>	1.02	0.92
Na <sup>+</sup>	0.59	0.53	Ba <sup>2+</sup>	<i>c</i>	1.14

<sup>a</sup> Rare-gas values are experimental.<sup>22</sup> <sup>b</sup> M<sup>2+</sup> values from ref 16. <sup>c</sup> Data unavailable.<sup>22</sup>

**Table 3.** Poorly Agreeing  $\alpha^{1/3}$  and  $r$  Values, from Averaging over Only Two Electrons

M <sup>0</sup> <sup>a</sup>	$r, \text{Å}$	$\alpha^{1/3}_{\text{exp}}, \text{Å}$
Ca <sup>0</sup>	2.50	2.92
Sr <sup>0</sup>	2.70	3.02
Ba <sup>0</sup>	3.00	3.41

<sup>a</sup> Data lacking for Be<sup>0</sup> and Mg<sup>0</sup>.

Hence also  $r$  values for Ne, Na<sup>+</sup>, and Mg<sup>2+</sup>; Kr, Rb<sup>+</sup>, and Sr<sup>2+</sup>; and for Xe, which are compared with  $\alpha^{1/3}(M^{z+})$  and  $\alpha^{1/3}_{\text{exp}}$  (rare gas) in Table 2.  $\alpha(M^{3+})$  values are lacking,<sup>16</sup> as are  $I_3$  of Ba and Cs;<sup>22</sup> we include  $\alpha^{1/3}_{\text{exp}}$  for the latter, as background to later calculations (Table 4, below).

The worst divergence arises in the two-electron case of He; the approximate agreement otherwise matches that for X<sup>-</sup> in Table 1, and in no case is there severe noncorrespondence. Two-electron shells might be expected to exemplify the poorest averaging of properties, in contrast with eight-electron shells where effects are distributed over a larger "population". Accordingly, for alkaline earth M<sup>0</sup> *s*<sup>2</sup>-electron systems, the  $r$  calculated from  $e^2/(I_2 - I_1)$  values<sup>22</sup> give unsatisfactory  $r, \alpha^{1/3}_{\text{exp}}$  matchings, as in Table 3. These modest to poor agreements, in the cases of photon interaction with but two *s* electrons in the  $\alpha$  measurements on M<sup>0</sup>, emphasize again that two is a very small population for averaging. In contrast, when positive charge is generated in, e.g., Ca<sup>2+</sup> by the loss of just such a pair of electrons, the nongranularity of the residual 2+ charge need not similarly evoke such substantial rounding errors just seen. This matters in considerations of cationic radii as follows.

### Positive-Charge Radii $R$ of Cations Comprising a Dielectric Body and a Conductive-Spherule Core

Table 1 shows that  $r_{\text{exp}}(X^-) > \alpha^{1/3}_{\text{exp}}(X^-)$  by some few percent, but for cations M<sup>z+</sup>,  $\alpha^{1/3}$  values are much smaller than in-crystal radii.<sup>12</sup> Stokes<sup>8</sup> has pointed out that by the exclusion principle closed shells are insulated from electrons external to them. This suggests that the positive charge (at a radius now labeled  $R$ ) resulting from removal of the external electron(s) might interact with the remaining closed shell as with a dielectric; just such a formulation will be pursued below. The fact that external *s* electrons have electron density at the nucleus indicates again that they will see a partly unscreened nuclear charge  $Z_{\text{eff}}$ , which also needs to be incorporated in the model.

Kirkwood's model<sup>23</sup> of an arbitrary charge distribution within a molecule or ion comprising matter of permittivity  $\epsilon_i$  provides a starting point. His summary omission of the self-energies of the charges (immaterial to his aim<sup>23</sup> of treating the solvation energies of zwitterions) causes problems with ions, for which such quantities are predominant. A remedy<sup>10</sup> was to envisage, as an artificial anchor for such charges, a small conductive spherule of radius  $R_b$  sited at the center of the ion, comprising otherwise

a dielectric sphere of radius  $R$  and (internal) permittivity  $\epsilon_i$ . In the general case<sup>23,10</sup> the sphere is immersed in an external medium of permittivity  $\epsilon$ . For such a sphere, the potential experienced by incremental incoming charge through the medium when the charge on the spherule is  $Q$ , is

$$Q/\epsilon_i R_b + \frac{Q}{R} \left( \frac{1}{\epsilon} - \frac{1}{\epsilon_i} \right) \quad (5)$$

While the argument is given in detail in ref 10, the terms may be envisaged to arise as follows. Incremental charges are transferred from infinity to the core; at the distance  $R$  the ( $\epsilon, \epsilon_i$ ) boundary is encountered, which gives rise to the bracketed term, while traverse from  $R$  to  $R_b$  through  $\epsilon_i$  can be associated with the first term. If the external medium is empty space, as for an isolated ion,  $\epsilon = 1$ , and the potential is then

$$Q/\epsilon_i R_b + \frac{Q}{R} \left( 1 - \frac{1}{\epsilon_i} \right) \quad (5')$$

In an application of this model to real ions, the outermost *sp*<sup>3</sup> electron shell of a cation like K<sup>+</sup> is now supposed to comprise a dielectric of polarizability  $\alpha$  and permittivity  $\epsilon_i$ , within the hitherto undetermined radius  $R$  of positive charge. As before with X<sup>0</sup>, the electron, undergoing ionization to give the + charge, sees a conductive core bearing a constant unshielded nuclear charge  $Z_{\text{eff}}e$ . Just as for X, the interaction at the external boundary  $R$  is taken as classical, while within that boundary the  $Z_{\text{eff}}e$  field is presumed dominant, and  $Q/\epsilon_i R_b$  is replaced by  $Z_{\text{eff}}e/\epsilon_i R_b$  in (5'). Ionization yielding K<sup>+</sup> subject to this potential accordingly gives

$$I_1 = Z_{\text{eff}}e^2/\epsilon_i R_b + \frac{(Ze)^2}{2R} \left( 1 - \frac{1}{\epsilon_i} \right) \quad (Z = 1) \quad (6)$$

where the two terms again correspond to the intraatomic and classical interactions. From the same procedure but applied now to K<sup>-</sup>, from appropriately modified (6) the electron affinity  $E$  is obtained as

$$-E = -Z_{\text{eff}}e^2/\epsilon_i R_b + \frac{(Ze)^2}{2R} \left( 1 - \frac{1}{\epsilon_i} \right) \quad (Z = -1) \quad (7)$$

where the individual charge radii of the pair of electrons to which  $I$  and  $E$  refer have again been summarily averaged in  $R$ . Hence from the difference between (6) and (7),

$$I_1 - E = (e^2/R)(1 - \epsilon_i^{-1}) \quad (8)$$

from which one could calculate  $R$ , given  $\epsilon_i$ . Since in this model the polarizability  $\alpha$  is confined within a volume  $4/3\pi R^3$ , and  $\alpha$  values for cations are small, the Drude value<sup>24</sup>  $\epsilon_i = 1 + 3\alpha/R^3$  may be taken. Hence

$$I_1 - E = (e^2/R)\{1 - (1 + 3\alpha/R^3)^{-1}\} \quad (8')$$

which simplifies to

$$R^4 + 3\alpha R = 3\alpha e^2/(I_1 - E) \quad (9)$$

Further elaboration ensues from recognizing that  $\alpha^{1/3}$  has already been identified with  $r$ . Thus, consistently with the conclusions drawn from Tables 1 and 2,  $r$  or  $e^2/(I_3 - I_2)$  may now replace  $\alpha^{1/3}$  in (9), which gives

$$R^4 + 3Re^6(I_3 - I_2)^{-3} = 3e^8/(I_3 - I_2)^3(I_1 - E) \quad (10)$$

The root  $R$  of this quartic, in the range 0.5–2.5 Å, is hence accessible, from solely experimental values of  $I$  and  $E$ .

For the isoelectronic Mg<sup>2+</sup> group,  $(I_4 - I_3)^{-3}$  and  $/(I_4 - I_3)^3(I_2 - I_1)$  appear on the left-hand and right-hand sides of (10) (and

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**Table 4.** Values of Positive-Charge Radii  $R$  for Cations  $M^{z+}$  Used in Figure 1

ion	$R, \text{\AA}$	ion	$R, \text{\AA}$
Li <sup>+</sup>	0.67	Mg <sup>2+</sup>	0.80
Na <sup>+</sup>	1.07	Ca <sup>2+</sup>	1.26
K <sup>+</sup>	1.61	Sr <sup>2+</sup>	1.42
Rb <sup>+</sup>	1.75	Ba <sup>2+</sup>	1.59 <sup>a</sup>
Cs <sup>+</sup>	1.97 <sup>a</sup>	Cd <sup>2+</sup>	1.19 <sup>a</sup>
Ag <sup>+</sup>	1.37	Pb <sup>2+</sup>	1.40
Tl <sup>+</sup>	1.69		

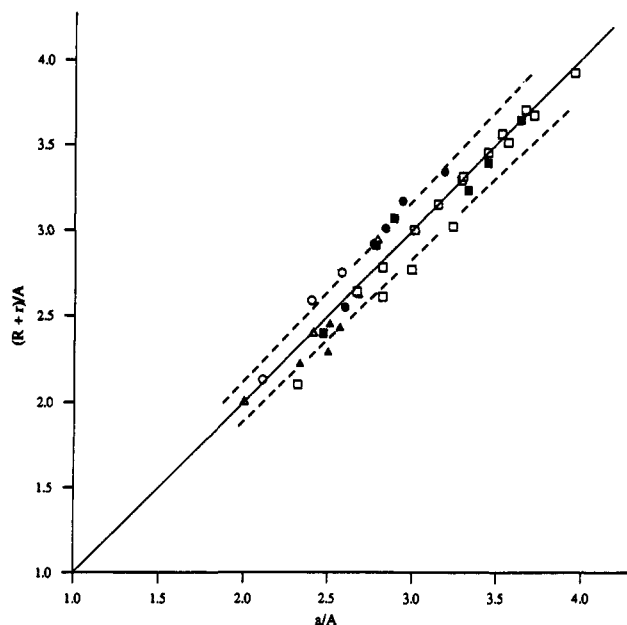
<sup>a</sup> Calculated from  $\alpha(M^{z+})$  values<sup>16</sup> since inner ionization potentials are lacking.<sup>22</sup>

for  $M^{3+}$ , which are not examined here, the factors  $(I_5 - I_4)^3$  and  $/(I_5 - I_4)^3(I_3 - I_2)$  are, respectively, involved).

The values of  $R$  (Table 4) so obtained for alkali-metal ions  $M^+$  and alkaline-earth ions  $M^{2+}$  also include entries for  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ .<sup>16</sup> Only for  $\text{Li}^+$  is the  $R$  value wrong, depending as it does on a clearly dubious  $\epsilon_i$  for matter comprising but two core electrons;  $R$  is about a third too small.<sup>1,12</sup> The remainder are tested by plotting  $r + R$  values for  $X^-$  and  $M^{z+}$ , as obtained solely from  $E$  and  $I$  data, against observed lattice parameters<sup>16</sup>  $a$  in Figure 1. In order to include chalcogenides  $Y^{2-}$ , in place of  $r$  the average values have been taken of  $\{\alpha_{\text{exp}}(Y^{2-})\}^{1/3}$  from experimental lattice values<sup>16</sup> less the cation contributions, since the requisite second electron affinities for O and S required to calculate  $r$  from appropriately modified (4) are not experimentally accessible.<sup>22</sup> Comparably, closed-shell ionization potentials missing<sup>22</sup> for Cs, Ba, and Cd necessitated the use of  $\alpha_{\text{exp}}(M^{z+})$  values,<sup>16</sup> rather than the  $I$ -derived quantities, in the calculations of  $R$  via eq 9 (still, note, from soundly derived experimental data). All Figure 1 points show conformity within 10%; most are within 5%. Apart from omitting  $\text{LiX}$ , no *ad hoc* rules were contemplated which might improve collinearity.

## Discussion

The simple equations for  $r$  and  $R$  were based on electrostatic precepts with a superimposed intraatomic interaction term and were employed with solely experimental data, apart from the assigned  $\alpha(M^{z+})$  and  $\alpha(Y^{2-})$  values used in calculating some  $R$  and  $r$ , respectively. These radii provide a set of interionic distances in satisfactory accord with experimental lattice parameters for halides  $\text{MX}$  and  $\text{MX}_2$  (including salts of  $\text{Ag}^+$ ,  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  but excluding two-electron  $\text{Li}^+$ ) and for chalcogenides  $\text{M}_2\text{Y}$  and  $\text{MY}$ . Such a demonstration endorses the use of electrostatic continuum models for inferring real interionic distances to within a few percent, provided that electron/partly-screened-nucleus interactions are taken into account. The introduction of one simple term for the latter, together with other procrustean impositions, does impart an empirical character to the relationships, despite the clear basis in electrostatics; the great compression of complex interactions, encompassed in the  $Z_{\text{eff}}e/\epsilon_i$  term, is especially severe. Nevertheless, the  $2Z_{\text{eff}}e^2/r$  term which for halogens  $X$  is the Mulliken electronegativity, has *ipso facto* real significance in covalent bonding (and hence finds no further employment here for the ionic systems comprising  $M^{z+}$ ,  $X^-$ , and  $Y^{2-}$ ). The positing of precise  $r$  values may appear to infringe uncertainty, but the continuous, smeared-out, spherical-surface distributions imputed to the charges imply virtually infinite velocities of particulate entities bearing charge, which are thus necessarily devoid of mass.



**Figure 1.** Plot versus lattice parameter<sup>16</sup>  $a$  of values of  $r + R$  calculated from  $I$  or  $I + E$  data,<sup>22</sup> or ( $\text{Ba}^{2+}$  and  $\text{Cs}^+$ ) from such ionization data together with  $\alpha(M^{z+})$  values,<sup>16</sup> or ( $\text{O}^{2-}$  and  $\text{S}^{2-}$ ) from assigned crystal polarizabilities<sup>16</sup> alone. All examples from ref 16 (but  $\text{LiX}$  omitted on grounds of two-electron nonconformity in  $\text{Li}^+$ ). ( $\square$ )  $\text{MX}$  excepting  $\text{LiX}$  (see text); ( $\circ$ )  $\text{MO}$ ; ( $\bullet$ )  $\text{MS}$ ; ( $\Delta$ )  $\text{M}_2\text{O}$ ; ( $\blacktriangle$ )  $\text{MX}_2$ ; ( $\blacksquare$ )  $\text{AgX}$  and  $\text{TlX}$  excepting<sup>16</sup>  $\text{AgI}$ ,  $\text{TlF}$ . The full line is of unit slope, through the origin; the dashed lines show  $\pm 5\%$  deviation.

The cost of avoiding the catastrophe, by invoking insubstantial proxies in the place of electrons, is scarcely damaging. The incremental charging processes involved throughout are readily envisaged as adiabatic electron transfers from or to a waxing or waning electron donor ultimately placed at infinity.

The meaning of  $r$  is reasonably clear: apart from the  $Z_{\text{eff}}$  term, the outermost electrons of closed-shell  $X^-$ ,  $M^{z+}$ , or rare gases, as sampled by  $I$  and  $E$  (or  $I_k, I_l$ ), interact within the shell as on a conductive spherical surface of radius  $r$ . The significance of  $R$  calls for some scrutiny. In the present model,  $R$  denotes the distance of the spherical surface of positive charge from the origin, as allowed by  $Z_{\text{eff}}$  together with the bodily permittivity  $\epsilon_i$ , and signaled by the outer- $I$  (or  $I - E$ ) values. This positive charge is the charge left by the departed electrons, thus  $R$  indirectly also represents the averaged distance of the (predeparture) negative charge, within the validity of Koopmans' theorem. It is consistent therefore that in the lattice,  $R$  also represents the closet-approach distance for the negative peripheries of the surrounding  $X^-$  or  $Y^{2-}$  neighbors, and is thus properly a cation radius, applicable both *in vacuo* and within lattices.

In continuum theories of electrolytes, the practice of employing ion sizes or separations as receptacles of the accumulated approximations of the theories has resulted in a move to molecular dynamics, HNC, and kindred statistical methods. The present demonstration, of directly abstracting realistic interionic distances or radii from electrostatic-continuum models, contrasts with the practice still current of introducing arbitrary correction factors.<sup>25</sup>

(25) Basilevsky, M. V.; Chudinov, G. E.; Napolov, D. V.; Timofeeva, L. *M. Chem. Phys.* **1993**, *173*, 345–355.