

# Highly Asymmetric Electrolytes: Beyond the Hypernetted Chain Integral Equation

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**Abstract:** Corrections to the hypernetted chain (HNC) integral equation, based on an approximation for the sum of bridge graphs, have been evaluated for a model electrolyte solution asymmetric in both charge and size. The system was previously studied by the HNC integral equation and by the Monte Carlo simulation technique. The approximations for the sum of the bridge graphs are used, together with the Ornstein–Zernike equation, to obtain new pair correlation functions. The effect brought about by the approximate bridge functions is significant. The corrected correlation functions are in much better agreement with the simulation results than the predictions of the usual, unmodified HNC equation. Accordingly, this improved theory may yield more reliable analysis of the experimental data.

## 1. Introduction

The addition of polyelectrolyte (ionic colloids, micelles, or proteins) to a solution of simple electrolyte may yield dramatic changes in the thermodynamic and kinetic properties of the system. For example, rates of reaction between charged species can be enhanced or retarded this way.<sup>1</sup> This interesting behavior of the polyelectrolyte–electrolyte system leads to important applications, including a very promising one in the field of solar energy conversion.<sup>2</sup> Polyelectrolyte effects upon reaction rates and equilibrium can be understood *quantitatively* only if the spatial correlations between the small ions around the polyion are known. Accurate structural information of this kind can be obtained from the hypernetted chain (HNC) integral equation<sup>3–9</sup> or from Monte Carlo computer simulations,<sup>10,11</sup> both used in several recent studies of ionic colloids.

Polyelectrolyte systems can be modeled as asymmetric electrolytes, containing large and highly charged polyions and small ions bearing one or two charges. This approach is more realistic than traditional one-component models of colloidal solutions,<sup>12</sup> placing equal emphasis on all ionic species in the solution. In this way, experimental data for various partial structure factors may be analyzed.<sup>9</sup>

In a previous paper,<sup>11</sup> Monte Carlo computer simulation results were presented for a model electrolyte asymmetric in both charge and size. We studied model solutions where the asymmetry in charge is 15:1 and the asymmetry in size is about 10:1. The computer data for various correlation functions are compared with the HNC results for the same model in order to assess the validity of the integral equation. The hypernetted chain integral equation is known to be very successful in describing the structural and thermodynamic properties of 1:1 electrolytes, but with increasing charge the theory becomes less reliable.<sup>13–15</sup> The principal conclusion is that HNC theory predicts that the counterions are too close to (a) each other and also (b) to the polyion. Both polyion–counterion and especially counterion–counterion correlation functions are overestimated by the integral equation, and the deviations from the simulation results increase with increasing the charge on the polyion. This in turn leads to an underestimate of the polyion–polyion pair correlation function. The electrolyte solution as viewed by the HNC approximation is less structured; the same effect may be produced by addition of a simple electrolyte to a system. This fact must be considered when intermolecular structure factors, obtained experimentally, are analyzed with the help of the HNC integral equation.

The HNC integral equation, though superior to other theories in describing Coulombic systems, shows systematic deviations from the Monte Carlo data for highly charged liquids,<sup>11,13–15</sup> which seriously limits its applicability. We are particularly interested

in studying the catalytic effect of polyelectrolytes, and for this application, accurate counterion–counterion correlation functions are needed. In addition, the HNC equation is also internally inconsistent (as are many approximate theories); that is, the predicted thermodynamic properties, such as the osmotic pressure, may depend strongly on the route of calculation. The reason lies in the fact that the HNC approximation neglects a class of terms, called bridge graphs,<sup>16</sup> in the cluster expansion for the pair correlation function. One scheme of improvement of the HNC approximation is based on the h-bond resummation of Stell,<sup>17</sup> and developed by Iyetomi and Ichimaru.<sup>18</sup> It provides an approximation for the bridge graph terms missing from the HNC equation. This improvement to the HNC theory is investigated here for asymmetric electrolytes.

In the present work, the HNC predictions for a highly asymmetric, +1/–15, electrolyte (Run 5 from Table 1 of Reference 11) are used to evaluate the approximations for the bridge graph terms, as suggested by Bacquet and Rossky.<sup>13,14,17–19</sup> To describe the structure of this system, one needs three different pair correlation functions and, accordingly, three separate corrections to the HNC approximation. The results for the approximate bridge graphs terms are then used to obtain new correlation functions. This approximation has been termed the HNC+B theory.<sup>14</sup> Finally, both simplified theories, HNC and HNC+B approximations, are compared with the “exact” Monte Carlo results for this model electrolyte obtained by us previously.<sup>11</sup> Our principal

- (1) Morawetz, H. *Acc. Chem. Res.* **1970**, *3*, 354.
- (2) Sassoon, R. E.; Rabani, J. *J. Phys. Chem.* **1970**, *8*, 6389 and references therein.
- (3) Beresford-Smith, B.; Chan, D. Y. C. *Chem. Phys. Lett.* **1982**, *92*, 474.
- (4) Belloni, L. *Chem. Phys.* **1985**, *99*, 43.
- (5) Bratko, D.; Friedman, H. L.; Zhong, E. C. *J. Chem. Phys.* **1986**, *85*, 377.
- (6) Khan, S.; Morton, T. L.; Ronis, D. *Phys. Rev. A* **1987**, *35*, 4295.
- (7) Fushiki, P. *J. Chem. Phys.* **1988**, *89*, 7445.
- (8) Bratko, D.; Friedman, H. L.; Chen, S. H.; Blum, L. *Phys. Rev. A* **1986**, *34*, 2215.
- (9) Derian, D.; Belloni, L.; Drifford, M. *J. Chem. Phys.* **1987**, *86*, 5708.
- (10) Linse, P.; Jönsson, B. *J. Chem. Phys.* **1983**, *78*, 3167.
- (11) Vlachy, V.; Marshall, C. H.; Haymet, A. D. J. *J. Am. Chem. Soc.* **1989**, *111*, 4160.
- (12) Verwey, E. J.; Overbeek, J. Th. G. *Theory of Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.
- (13) Rossky, P. J.; Dudowicz, J. B.; Tempe, B. L.; Friedman, H. L. *J. Chem. Phys.* **1980**, *73*, 3372.
- (14) Bacquet, R.; Rossky, P. J. *J. Chem. Phys.* **1983**, *79*, 1419.
- (15) Ichiye, T.; Vlachy, V.; Haymet, A. D. J. *J. Am. Chem. Soc.* To be submitted.
- (16) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: London, 1986.
- (17) Stell, G. In *The Equilibrium Theory of Classical Fluids*; Frisch, H. L., Lebowitz, J. L., Eds.; Benjamin: New York, 1964; Chapter II-4.
- (18) Iyetomi, H.; Ichimaru, S. *Phys. Rev. A* **1982**, *25*, 2434; **1983**, *27*, 3241.
- (19) Wiechen, J. *J. Chem. Phys.* **1986**, *85*, 7364.

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conclusion is that HNC+B approximation yields much better agreement with the computer data than the original HNC integral equation.

## 2. Model Asymmetric Electrolyte

The calculations presented in this work apply to the system studied previously by Monte Carlo simulations and by the HNC approximation.<sup>11</sup> The solution contains polyions with charge  $-15e$ , where  $e$  is elementary charge, and a balancing number of positive monovalent counterions. The molecules interact via the potential energy

$$u_{ij}(r) = u_{ij}^*(r) + z_i z_j e^2 / (4\pi\epsilon_0\epsilon_r r) \quad (1)$$

where  $i$  and  $j$  label either counterions (c) or polyions (p). Also,  $z_i$  is the number of positive or negative charges carried by the particular ion, and  $r$  is the distance between the centers of molecules. The solvent is not treated explicitly; it is assumed to merely modify the potential energy (eq 1) via the value of the permittivity  $\epsilon_r$ . The short-range part of the potential energy is given by

$$\beta u_{ij}^* = [A_{ij}/(r_i^* + r_j^*)] \exp[(r_i^* + r_j^* - r)/R] \quad (2)$$

where  $R$  has the units of length and is set equal to 0.1 nm. As usual,  $\beta = 1/kT$ , where  $T$  is the absolute temperature and  $k$  is Boltzmann's constant. The parameters in eq 1 and 2 apply to Run 5 of Table I in ref 11, namely, the length scale of the polyion  $r_p^* = 1.625$  nm and the length scale of the counterion  $r_c^* = 0.175$  nm, and the prefactors in the potential energy are given by  $A_{pp} = A_{cc} = 0.715$  nm and  $A_{pc} = 10.725$  nm. The concentration of polyions is 0.804 mmol/dm<sup>3</sup>, and the value of  $\beta e^2/(4\pi\epsilon_0\epsilon_r) = 0.715$  nm. This set of parameters is chosen frequently to mimic an aqueous electrolyte solution at 298 K.

## 3. Approximations for the Bridge Graph in HNC Theory

The structure of the model electrolyte is described by the pair correlation functions,  $g_{ij}(r) = h_{ij}(r) + 1$ , and the direct correlation functions  $c_{ij}(r)$ , defined via the Ornstein-Zernike equation<sup>16</sup>

$$h_{ij}(r_{ij}) = c_{ij}(r_{ij}) + \sum_k \rho_k \int dr_k c_{ik}(r_{ik}) h_{kj}(r_{kj}) \quad (3)$$

where  $\rho_k$  is the number density of component  $k$ . The diagrammatic expansion of  $h_{ij}(r_{ij})$  for a system with the pair potential  $u_{ij}$  leads to the formally exact equation<sup>16</sup>

$$h_{ij}(r_{ij}) = \exp[-\beta u_{ij}(r_{ij}) + B_{ij}(r_{ij}) + h_{ij}(r_{ij}) - c_{ij}(r_{ij})] - 1 \quad (4)$$

In this equation,  $B_{ij}$  is the sum of elementary or bridge graphs. If  $B_{ij}$  is known, equations 3 and 4 may be solved for the structure of the electrolyte. In the absence of a better approximation,  $B_{ij}$  is frequently set to 0, which is called the HNC approximation. In previous work,<sup>11</sup> we have used this approximation (with the long-range Coulomb terms renormalized appropriately) to obtain all the pair correlation functions  $g_{ij}$  for a model, highly asymmetric electrolyte. A density expansion of the HNC equation for the pair correlation functions is accurate to the level of three particle contributions; the first integral not included in the HNC integral equation involves four molecules and is proportional to  $\rho^2$ .

An approximation for the sum of the bridge graphs,  $B_{ij}$ , has been proposed by Iyetomi and Ichimaru<sup>18</sup>

$$B_{ij}(r_{12}) \approx \frac{1}{2} \sum_k \sum_l \rho_k \rho_l \int dr_3 dr_4 h_{ik}(r_{13}) h_{kj}(r_{32}) h_{il}(r_{14}) h_{lj}(r_{42}) h_{kl}(r_{34}) \quad (5)$$

where  $i, j, k, l$  are the species subscripts for molecules 1, 2, 3, and 4, respectively. The leading (normalized) bridge graph involves coordinates of four molecules and the functions  $h_{ij}$  that are obtained from the HNC approximation. The derivation of eq 5 is given for a single component in ref 18, in the context of the one-component plasma. A similar approach was used to evaluate corrections to the HNC equation for 2:2 electrolytes<sup>13,14</sup> and molten salts.<sup>19</sup> In all cases, a measurable improvement over the HNC approximation was obtained.

**Table I.** Corrections to the Polyion-Counterion Correlations,  $\exp[B_{pc}(r)]$ , Evaluated from Equation 5, Using Both the Monte Carlo Integration (MCI) Method and the Legendre Polynomial Expansion (LP)

	$r, \text{ nm}$							
	1.80	2.00	2.15	2.30	2.50	3.00	5.00	7.00
MCI		0.88	0.92	0.88	0.90	0.91		
LP	0.859	0.866	0.872	0.878	0.882	0.889	0.941	0.99

**Table II.** Corrections to the Counterion-Counterion Correlation Function,  $\exp[B_{cc}(r)]$

	$r, \text{ nm}$							
	0.50	0.75	1.00	1.50	2.00	3.00	4.00	5.00
MCI			0.94	0.97	0.99	1.00	1.0	1.0
LP	0.859	0.905	0.936	0.973	0.99	1.01	1.01	1.01

Equation 5 can be solved by various numerical techniques. For example, one can use Monte Carlo numerical integration (MCI).<sup>20</sup> Alternatively, the two-center integrals appearing in the expression for  $B_{ij}$  can be evaluated by a Legendre polynomial expansion method.<sup>14,18,19,21,22</sup> Both methods are used in this work, and the results are presented in Tables I and II. The numerical accuracy of the methods and some details concerning calculations are discussed in the next section.

Once the approximation for  $B_{ij}$  is obtained on the basis of the previous HNC solution, it can be used to correct eq 4. Equations 3 and 4 are then solved iteratively, and a new set of pair correlation functions is obtained. In accordance with a previous study,<sup>14</sup> this "self-consistent" theory is called the HNC+B approximation. The predictions for the correlation functions are shown in figures below.

## 4. Results with Bridge Graphs Included

Predictions for the function  $\exp(B_{ij})$ , obtained by both Monte Carlo integration (MCI) and Legendre polynomial expansion method (LP) with eq 5, are collected in Tables I and II. In the preliminary stage of this work, we investigated the numerical accuracy of both methods. In particular, (i) both the influence of the number of integration steps and the integration domain in the MCI method and (ii) the effect of the truncation of the Legendre polynomial expansion were examined.<sup>23</sup> The MCI calculations are performed over at least  $2 \times 10^6$  steps and the polynomial expansion (LP method) includes all the polynomials up to  $L = 6$ . The integrals appearing in the LP method are solved over 151 points, using Simpson's rule.

As a test of our numerical algorithm we have repeated some of the earlier results for symmetric 2:2 electrolytes at concentration 0.005 mol/dm<sup>3</sup> (cf. Table II of ref 14). The agreement between two sets of LP results is within 4% for  $B_{++}$  ( $s_{++}$  in ref 14). This agreement is poorer for case of  $B_{+-}$  ( $s_{+-}$ ), where (probably due to the very rapid variation of the  $g_{+-}$  function) the largest difference is 8%. We judge the numerical uncertainty in our results for  $B_{ij}$ , used to evaluate corrections in Tables I and II, to be better than  $\pm 4\%$  for LP calculations and approximately  $\pm 8\%$  for the MCI method.

Inspection of the tables reveals that measurable corrections to the HNC results for  $g_{pc}$  and  $g_{cc}$  are to be expected. Our MCI and LP results are in very good agreement. The LP results, which are more accurate, are used in the subsequent calculations. The first (or "direct") corrections to the pair correlation functions may be evaluated with eq 6.<sup>14</sup> From these results, one can see that

$$g_{ij}(r) = g_{ij}^{\text{HNC}}(r) \exp(B_{ij}) \quad (6)$$

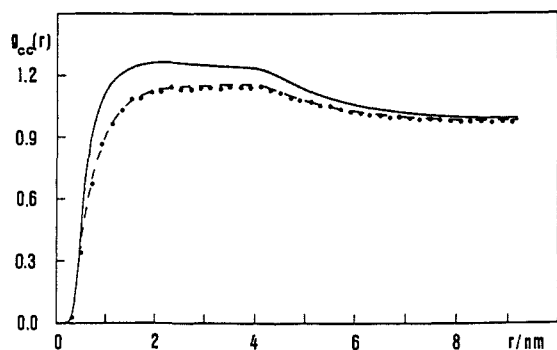
the inclusion of the approximate bridge graph produces the same effect as an additional repulsive potential. This can be understood

(20) Press, W. H.; Flannery, P. B.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, 1986.

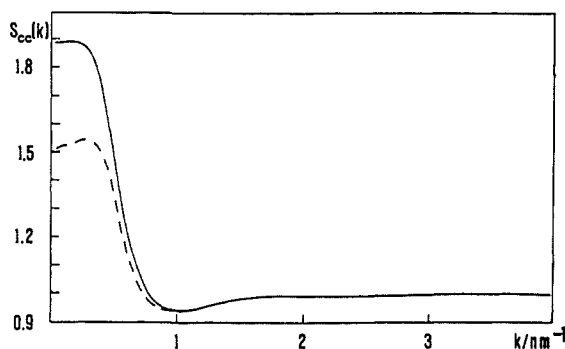
(21) Barker, J. A.; Monaghan, J. J. *J. Chem. Phys.* **1962**, *36*, 2564.

(22) Haymet, A. D. J.; Rice, S. A.; Madden, W. *J. Chem. Phys.* **1981**, *74*, 3033.

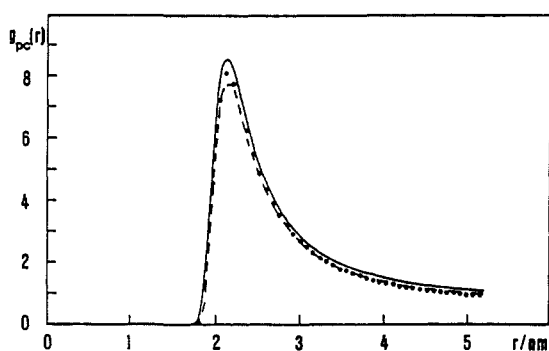
(23) Reščič, J. Diploma thesis, 1989, University E. Kardelj, Ljubljana, Yugoslavia.



**Figure 1.** The counterion-counterion correlation function,  $g_{cc}(r)$ , evaluation by several theoretical methods: Monte Carlo simulation results (symbols),<sup>11</sup> HNC approximation (full line), and the HNC+B theory (dashed line).



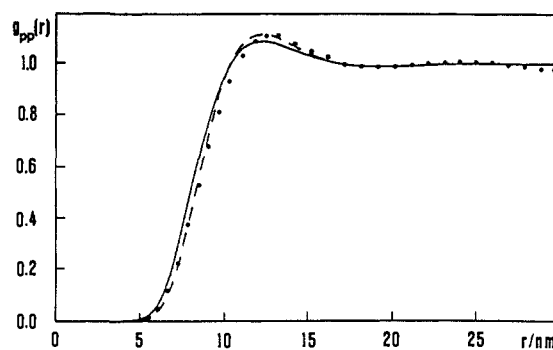
**Figure 2.** The partial structure factor,  $S_{cc}(k)$ , obtained from the HNC (full line) and HNC+B (broken line) approximations.



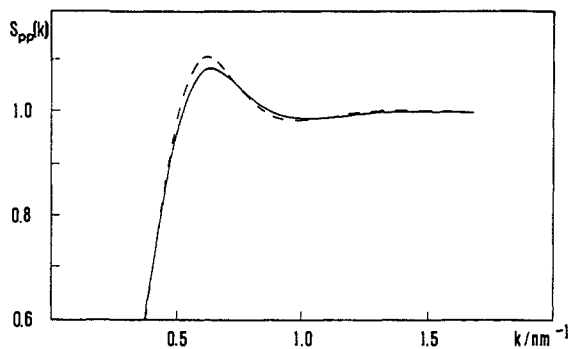
**Figure 3.** The counterion-polyion correlation functions,  $g_{pc}(r)$ ; the symbols are the same as in Figure 1.

with the help of the graphical representation of the first bridge graph missing in the HNC approximation (see Figure 11 of ref 13). The  $g_{cc}$  and  $g_{pc}$  correlation functions are greatly affected by the geometrical situation where four molecules are close to each other. In such a case, the first graph in the bridge function may be largely cancelled by the similar graph that is included in the HNC equation (but not in some other theories<sup>16</sup>). This situation is discussed in more detail in ref 11, 13, 14, and 24.

We have evaluated also the approximation for the function  $B_{pp}$ , but it is very small and can be safely ignored here. There is negligible "direct" correction to the polyion-polyion correlation function due to the  $B_{pp}$  term, but since the three distinct  $g_{ij}$  are connected via the Ornstein-Zernike equation, a change of  $g_{pp}$  is expected upon iteration. This is confirmed in Figures 1-5, where the pair correlation functions and partial structure factors, obtained from the different methods, are compared. In Figure 1 we present the counterion-counterion correlation function,  $g_{cc}$ , obtained by Monte Carlo simulation<sup>11</sup> (symbols), the predictions of the HNC approximation (full line), and the HNC+B approximation (broken



**Figure 4.** The polyion-polyion correlation function,  $g_{pp}(r)$ ; the symbols are the same as in Figure 1.



**Figure 5.** The polyion-polyion partial structure factor,  $S_{pp}(k)$ ; the symbols are the same as in Figure 2.

line). The shape of this correlation function reflects the fact that counterions distribute themselves, most probably, on the surface of the polyion. The HNC equation grossly overestimates this function, while on the other hand the HNC+B approximation yields almost exact agreement with the computer results for the same model electrolyte. This is most encouraging, because  $g_{cc}$  is the function that seems to be relevant in studies of the catalytic effect in electrolyte-polyelectrolyte systems. The corresponding structure factor, which is the experimentally accessible quantity, is given in Figure 2.

In Figure 3 the polyion-counterion correlation function,  $g_{pc}$ , is presented. Again, the agreement between the HNC+B approximation and the simulation results is good, with the possible exception of the first peak, where this approximation (in contrast to the HNC equation) yields values of  $g_{pc}$  that seem to be slightly too low.

As mentioned above, there is negligible "direct" correction to  $g_{pp}$  from the bridge function  $B_{pp}$ . However, the other two bridge functions,  $B_{pc}$  and  $B_{cc}$ , do correct  $g_{pp}$  via the Ornstein-Zernike equation as shown in Figure 4. The HNC+B calculation agrees with the simulation data to high accuracy. The two major corrections over the ordinary HNC equation are (i) the position of the peak is pushed toward larger distances and (ii) its height is increased. The most relevant, experimentally measurable quantity is the polyion-polyion partial structure factor,  $S_{pp}(k)$ .<sup>25</sup> For this quantity, the comparison between the two approximate integral equations is presented in Figure 5. The HNC equation underestimates the structure of the solution, but the effect is not too dramatic for the values of these parameters. There is, however, an important difference between two theories in the small  $k$  domain not shown in Figure 5; the HNC equation overestimates the compressibility of the model solution. The ratio,  $S(0) = \kappa_T/\kappa_{T,ideal}$ , where  $\kappa_{T,ideal}$  is the isothermal compressibility of the ideal gas, takes the values 2.02 and 1.65 in the HNC and HNC+B approximations, respectively. In summary, if the HNC theory is used to analyze experimental results for  $S_{pp}(k)$ , the charge on the polyion predicted by the calculations may be too high.<sup>25</sup> The direction and magnitude of the corrections suggested by the HNC+B ap-

(24) Ichiye, T.; Haymet, A. D. J. *J. Chem. Phys.* **1988**, *89*, 4315.

(25) Bratko, E.; Sheu, E. Y.; Chen, W. H. *Phys. Rev. A* **1987**, *35*, 4359.

proximation are similar to those obtained recently<sup>26</sup> from the “ZH” integral equation.

## 5. Conclusions

The effects brought about by the inclusion of the approximate bridge functions in the HNC theory of asymmetric electrolytes are significant. The accuracy of all three correlation functions, as judged by comparison with our recent simulation results, is improved. The counterion-counterion correlation function, which may play an important role in studies of the polyelectrolyte effect on the reaction rate in electrolyte solutions, is in excellent agreement with the simulation results. This is also true for the polyion-polyion correlation function. There is some correction

to the partial structure factor  $S_{pp}(k)$ , which is the experimental observable.

For highly charged colloids the corrections are expected to be larger. A useful first test for situations where (i) solutions to the HNC equation exist and (ii) computer simulations are difficult, expensive, or unavailable is to calculate a “first-order” estimate to the corrections to the HNC equation from eq 5. Although it is impossible to give a definite conclusion on the basis of this example alone, it is expected that the HNC+B theory will yield a more realistic analysis of the experimental neutron and light-scattering experiments.

**Acknowledgment.** This work was supported in part by the U.S.–Yugoslav Joint Fund for Scientific and Technological Cooperation (Project No. 8717984).

(26) Belloni, L. *J. Chem. Phys.* **1988**, *88*, 5143.

# Electronegativity and Lewis Acid Strength

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**Abstract:** For main group elements in their highest oxidation state we show that a scale of Lewis acid strength derived from observed structures correlates with a scale of electronegativity derived from electron energies in the free atom. If the bonding geometry is also explicitly taken into account the same correlation holds for the same atoms in their next lower oxidation state. Although the two scales are conceptually quite distinct they correlate because both have a similar dependence on the screened nuclear charge and the ionic radius.

## 1. Introduction

Approaches to the definition of electronegativity range from empirical to fundamental and from theoretical to experimental, yet all the scales agree in the essential ordering of the elements in the Periodic Table. The reason for this agreement is that, in spite of their different origins, each of the scales samples the properties of the atom's outermost electrons, the ones most directly involved in chemical bonding. This paper explores two recently proposed scales based on quite different physical models: Allen's<sup>1</sup> free atom spectroscopic electronegativity and Brown's<sup>2</sup> scale of Lewis acid strength derived from the coordination numbers observed in solids. In spite of the different physical models underlying them, the two scales correlate well because both depend in a similar way on the screened nuclear charge and the ionic radius.

## 2. The Correlation between Spectroscopic Electronegativity and Lewis Acid Strength

In Allen's<sup>1</sup> scale, the free-atom spectroscopic electronegativity ( $\chi$ ) of main group elements is defined as the average energy of the valence shell s and p electrons (eq 1), where  $n_s$  and  $n_p$  are the

$$\chi = (n_s e_s + n_p e_p) / (n_s + n_p) \quad (1)$$

numbers and  $e_s$  and  $e_p$  are the spectroscopic energies of the valence s and p electrons, respectively. Allen points out that the spectroscopic electronegativity is a property of the free atom and that different values are expected once the atom is placed in a solid. When suitably scaled, his electronegativity scale is similar to other traditional scales such as those given by Pauling<sup>3</sup> and Allred and Rochow.<sup>4</sup>

**Table I.** Free-Atom Spectroscopic Electronegativities ( $\chi$ , Taken from Allen,<sup>1</sup> Table III) and Intrinsic Lewis Acid Strengths ( $S_a$ , Taken from Brown,<sup>2</sup> Table II) for Main Group Elements in Their Highest Oxidation State

element	$\chi$ , Ry	$S_a$ , vu	element	$\chi$ , Ry	$S_a$ , vu
Li	0.40	0.20	Ge	0.87	0.89
Na	0.38	0.16	Sn	0.79	0.68
K	0.32	0.13	N	1.33	1.67
Rb	0.31	0.12	P	0.98	1.25
Be	0.69	0.50	As	0.96	1.13
Mg	0.56	0.33	Sb	0.86	0.83
Ca	0.45	0.27	O	1.57	
Sr	0.42	0.23	S	1.13	1.5
B	0.89	0.87	Se	1.05	1.5
Al	0.70	0.57	Te	0.94	1.0
Ga	0.76	0.65	F	1.82	
In	0.72	0.50	Cl	1.25	1.75
C	1.11	1.35	Br	1.17	
Si	0.83	1.00	I	1.03	1.2

Brown's scale of Lewis acid strength ( $S_a$ ),<sup>5</sup> here called “average Lewis acid strength”, is defined for a given cation by eq 2, where

$$S_a = V/N_i \quad (2)$$

$V$  is the oxidation state of the cation and  $N_i$  is the average of the coordination numbers to oxygen observed in a large sample of

(4) Allred, A. L.; Rochow, E. G. *J. Nucl. Inorg. Chem.* **1958**, *5*, 264–268.

(5) The term “Lewis acid strength” was used in ref 2 to describe the quantity  $S_a$  defined by eq 2 because  $S_a$  allows one to predict which Lewis acids will bond to which Lewis bases (their numerical strengths must be equal). The scale, however, is derived entirely from the oxidation state and the coordination numbers observed in crystals and does not depend in any direct way on electron energies or free atom properties. If the term “Lewis acid strength” is read with this definition in mind the remarkable nature of the correlation will become more apparent.

(1) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003–9014.

(2) Brown, I. D. *Acta Crystallogr.* **1988**, *B44*, 545–553.

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