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Estimation of Electronegativity Values of Elements in Different Valence States

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The electronegativities of 82 elements in different valence states and with the most common coordination numbers have been quantitatively calculated on the basis of an effective ionic potential defined by the ionization energy and ionic radius. It is found that for a given cation, the electronegativity increases with increasing oxidation state and decreases with increasing coordination number. For the transition-metal cations, the electronegativity of the low-spin state is higher than that of the high-spin state. The ligand field stabilization, the first filling of p orbitals, the transition-metal contraction, and especially the lanthanide contraction are well-reflected by the relative values of our proposed electronegativity. This new scale is useful for us to estimate some quantities (e.g., the Lewis acid strength for the main group elements and the hydration free energy for the first transition series) and predict the structure and property of materials.

1. Introduction

The definition of electronegativity (EN) as an attracting power between the atom and electron originated from Pauling's pioneer work in the 1930s. Pauling was the first chemist to establish an EN scale on the basis of thermochemical data, which has been extensively used for qualitative and quantitative discussions of many chemical facts.[1] Over the past 70 years, the concept of EN has been continuously modified, debated, and expanded. The dependence of many physical and chemical properties of atoms and molecules on EN has led to many correlations, and thus various different EN scales have been proposed.[2,3] Simultaneously, comprehensive theoretical studies about various EN scales have been carried out to check their reliabilities, explore their applications, or search for their intrinsic correlations.[4−6] EN is not only very useful in understanding chemical bonds and explaining many chemical phenomena, but is also of great significance for materials science, in which this parameter is applied to rationalize the geometries and properties of quite complex systems.[7−9] It has been found that the EN difference among constituent elements is an important factor influencing the stability of the supercooled liquid in glassy alloys.[10] Recently, efficient visible light active photocatalysts have been synthesized through chemical substitution according to the EN of metal ions.[11] Such findings indicate that EN has been playing an important role in predicting the properties of materials and designing new materials.

Although EN is often treated as an invariant property of an atom, as in Pauling's scale, it actually depends on the chemical environment of the atom [e.g., valence state and coordination number (CN)]. Mulliken determined the EN of elements in different valence states by using their ionization energies and electron affinities;[2] unfortunately, the obtained EN values are insufficient due to the lack of electron affinities. Sanderson proposed a method to compute the EN of elements in different valence states on the basis of partial charges and bond energies;[12] however, the obtained EN values are only limited to transition metals. To the best of our knowledge, a complete EN scale of elements in different oxidation states, CN, and spin states has not yet been suggested.

In the present work, we try to propose an EN scale for elements in different valence states and with the most common CN in terms of effective ionic potential. This new EN scale is more comprehensive and reasonable. Some important chemical phenomena, such as the ligand field stabilization, the first filling of p orbitals, the transition-metal contraction, and especially the lanthanide contraction, are well-reflected in the relative values of our proposed EN. It is found that there is a perfect linear correlation between our EN values and Luo's scale, which is based on the covalent potential.[13] This finding is not surprising, due to the fact that the theoretical supports for both scales come from the absolute EN theory of Parr and Pearson. The new EN scale can be used to quantitatively estimate the Lewis acid strength for the main group elements in their highest oxidation state (Supporting Information, Figure S1). For the transition metals, the hydration free energy of a divalent cation can be measured as a function of its EN (Figure S2). Our EN scale thus can be helpful in studying the coordination and bonding of coordination compounds. In addition, our present work can be used to qualitatively judge the nature and strength of chemical bonds; therefore, it may give researchers a useful guide to reasonably predict the structure and property of new materials.

2. Methodology

EN characterizes the ability of an atom to attract electrons from the atoms bonded to it. The EN of an element changes with its actual chemical environment. For a given element, the higher the oxidation state, the stronger its attraction for electrons. It has been found that the radius of a cation depends on its CN and oxidation state.[14] For the transition metals, the ionic radius is also affected by the multiplicity of the spin state. Therefore, we select ionic radius as one of the parameters to define the EN of elements in different valence states, from which the variation of ionic chemical environment can be well-reflected. Since each ion is surrounded by a certain number of opposite-charged ions to keep its stability in the compound, we define the EN of an element in view of valence states as "the

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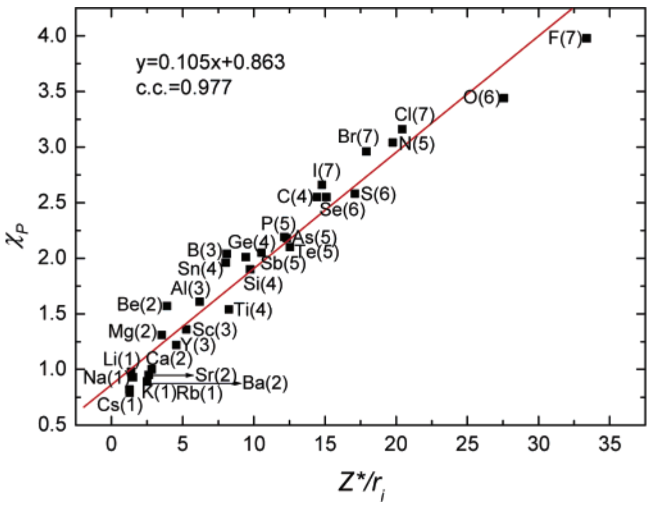

Figure 1. Correlation between Pauling electronegativity χ_P and effective ionic potential Z^*/r_i. The numbers in parentheses are oxidation states.

electrostatic potential at the boundary of an ion caused by its effective nuclear charge", i.e., the effective ionic potential

$$\varphi = Z^*/r_i \tag{1}$$

where Z^* is the effective nuclear charge and r_i is the ionic radius.

For a cation A^{m+} (where A represents an element, and m represents the charge number), there is a quantum formula describing the correlation between its effective nuclear charge Z^* and its ultimate ionization energy I_m[15]

$$I_m = R(Z^*/n^*)^2 \tag{2}$$

where n^* is the effective principal quantum number and R = 13.6 eV is the Rydberg constant. It should be noted that the data of the ultimate ionization energy I_m are numerically equal to those of the electron affinity of a named cation. For example, the second ionization energy of iron is used for Fe^{2+} (numerically equals the electron affinity of Fe^{2+}), while the third ionization energy is used for Fe^{3+} (numerically equals the electron affinity of Fe^{3+}).

Further, eq 2 may be transformed into the following equation

$$Z^* = n^*(I_m/R)^{1/2} \tag{3}$$

By substituting eq 3 into eq 1, we then obtain

$$\varphi = n^*(I_m/R)^{1/2}/r_i \tag{4}$$

In Figure 1, we plot the Pauling EN (χ_P)[1,16] against the effective ionic potential (Z^*/r_i), and the expression of our current EN scale for ions (χ_i) is determined through a linear regression

$$\chi_i = 0.105n^*(I_m/R)^{1/2}/r_i + 0.863 \tag{5}$$

where r_i is taken from Shannon's work.[17] Since the ionic substances crystallize most frequently in the structures with CN = 6, six-coordinated radii are thus selected herein. Furthermore, we in this work use the crystal radii rather than effective ionic radii, since the crystal radii correspond more closely to the physical size of ions in a solid, as suggested by Shannon.[17a] It should also be noted that the linear correlation cannot be obtained if we select Shannon's effective ionic radii. I_m is taken from the work of Lide and Emsley[18,19] (in the unit of eV). The effective principal quantum numbers that we currently adopt are as follows:[15] On the other hand, it should be noted that there

n	1	2	3	4	5	6	7
n^*	0.85	1.99	2.89	3.45	3.85	4.36	4.99

is a second familiar equation of quantum mechanics to describe the relationship between the ionic size and the effective nuclear charge of elements

$$r_i = a_0(n^*)^2/Z^* \tag{6}$$

where a_0 is the Bohr radius of the hydrogen atom, 0.529 Å.

Equation 6 can be written as

$$Z^* = a_0(n^*)^2/r_i \tag{7}$$

By substituting eq 7 into eq 1, we can obtain the following expression

$$\varphi = a_0(n^*/r_i)^2 \tag{8}$$

which is a simpler EN formula in terms of just two variables, n^* and r_i.

Furthermore, if we combine eqs 4 and 8, a third EN formula can be obtained

$$\varphi = I_m/(Ra_0) \tag{9}$$

which is clearly a simplified version of Mulliken's EN in terms of just the ionization energy I_m.

From both quantum formulas 2 and 6, we can find that if compared to the ionic radius, the ionization energy is more sensitive to the effective nuclear charge. Taking the lanthanide (Ln) series as an example, the effective nuclear charge of trivalent Ln deduced from eq 6 shows a monotonic increase across the whole series. When derived from the ionization energy by eq 2, it shows a gradual increase and then a sharp decrease at the last element along the atomic number 57−64 and 64−71 (i.e., from La to Gd and Gd to Lu), respectively, from which the Ln contraction and "gadolinium break" phenomena can be well-reflected. In addition, eq 9 has omitted an important parameter, i.e., the ionic radius; therefore, the variation of the chemical environments of an ion (such as the spin state and CN) cannot be well-reflected. Furthermore, eq 4, including three important parameters, is selected to calculate the EN of cations, which enables us to comprehensively consider their actual chemical environments. Herein, eq 4 forms the basis of our calculations of various ions with different valence states, CN, etc.

3. Results and Discussion

By using eq 5, EN values of a cation with different oxidation states, spin states, and CN are calculated. Taking Mg^{2+} as an example, the parameters I_2 = 15.035 eV, n^* = 2.89, r_i = 0.86 Å, and R = 13.6 eV finally lead to χ_i = 1.234 for Mg^{2+}. EN values of the six-coordinated cations are summarized in Table 1 (all the detailed data are tabulated in Table S3). EN of elements in valence states with the most common CN (according to ref 20) for main group elements are listed in Table 2. EN of cations with the most common CN for group IB−VB and VIB−VIIIB metals are gathered in Tables 3 and 4, respectively. By using the available ionic radius data of trivalent Ln,[17a,21] we can calculate the EN of trivalent Ln in different coordination

TABLE 1: EN of the Six-Coordinated Cations[a]

period		IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			1B	IIB	IIIA	IVA	VA	VIA	VIIA
II		Li	Be											B	C	N	O	F
	χ_i	(1)1.009	(2)1.273											(3)1.714	(4)2.380	(5)2.939 (3)2.164	(6)3.758	(7)4.368
	χ_P	0.98	1.57											2.04	2.55	3.04	3.44	3.98
III		Na	Mg											Al	Si	P	S	Cl
	χ_i	(1)1.024	(2)1.234											(3)1.513	(4)1.887	(5)2.139 (3)1.642	(6)2.659 (4)1.973	(7)3.008 (5)2.274
	χ_P	0.93	1.31											1.61	1.90	2.19	2.58	3.16
IV		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	χ_i	(1)0.998	(2)1.160	(3)1.415	(4)1.730 (3)1.499 (2)1.225	(5)2.030 (4)1.795 (3)1.545 (2)1.267	(6)2.475 (3)1.587 (2L)1.322 (2H)1.287	(7)2.651 (4)1.912 (2L)1.343 (2H)1.263	(3L)1.651 (3H)1.556 (2L)1.390 (2H)1.292	(3L)1.693 (3H)1.621 (2L)1.377 (2H)1.321	(4)2.037 (3L)1.695 (3H)1.650 (2)1.367	(2)1.372 (1)1.163	(2)1.336	(3)1.579	(4)1.854 (2)1.314	(5)2.159 (3)1.589	(6)2.448 (4)1.869	(7)2.744 (5)2.107
	χ_P	0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96
V		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
	χ_i	(1)0.998	(2)1.139	(3)1.340	(4)1.610	(5)1.862 (4)1.690 (3)1.501	(6)2.101 (5)2.006 (4)1.808	(7)2.384 (5)2.002 (4)1.773	(5)2.099 (4)1.848 (3)1.576	(5)2.167 (4)1.863 (3)1.622	(4)1.876 (3)1.562 (2)1.346	(2)1.333 (1)1.097	(2)1.276	(3)1.480	(4)1.706 (2)1.181	(5)1.971 (3)1.476	(6)2.180 (4)1.467	(7)2.417 (5)1.587
	χ_P	0.82	0.95	1.22	1.33	1.60	2.16	1.90	2.20	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.10	2.66
VI		Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
	χ_i	(1)0.998	(2)1.126	(3)1.327	(4)1.706	(5)1.925 (4)1.735 (3)1.536	(6)2.175 (5)1.991 (4)1.784	(7)2.507 (6)2.317 (4)1.853	(7)2.573 (6)2.362 (4)1.888	(5)2.183 (4)1.881 (3)1.649	(5)2.159 (4)1.895 (2)1.432	(5)2.195 (3)1.550 (1)1.113	(2)1.326 (1)1.165	(3)1.524 (1)1.050	(4)1.746 (2)1.225	(5)1.895 (3)1.399	(6)2.168 (4)1.575	(7)2.423
	χ_P	0.79	0.89	1.10	1.30	1.50	2.36	1.90	2.20	2.20	2.28	2.54	2.00	2.04	2.33	2.02	2.00	2.20
		Fr	Ra	Ac	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	χ_i	(1)1.012	(2)1.151	(3)1.363	(4)1.608 (3)1.348	(4)1.646 (3)1.374	(3)1.382	(3)1.391	(3)1.410	(3)1.433 (2)1.181	(3)1.386	(4)1.733 (3)1.410	(3)1.426 (2)1.213	(3)1.433	(3)1.438	(3)1.455 (2)1.231	(3)1.479 (2)1.237	(3)1.431
	χ_P	0.70	0.90		1.12	1.13	1.14		1.17		1.20		1.22	1.23	1.24	1.25		1.27

[a] χ_i is calculated from eq 5 and χ_P is taken from Pauling's scale.[1,16] The numbers in parentheses are oxidation states, "L" means low-spin and "H" means high-spin.

TABLE 2: EN of Cations with the Most Common CN for Main Group Elements

IA			IIA			IIIA			IVA			VA			VIA			VIIA		
cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i
$\mathrm{Li^{+}}$	4	1.043	$\mathrm{Be^{2+}}$	3	1.669	$\mathrm{B^{3+}}$	3	3.189	$\mathrm{C^{4+}}$	4	2.432	$\mathrm{P^{5+}}$	4	3.003	$\mathrm{S^{6+}}$	4	3.833	$\mathrm{Cl^{5+}}$	3	3.469
	8	0.987		4	1.453		4	2.259	$\mathrm{Si^{4+}}$	4	2.245	$\mathrm{As^{5+}}$	4	2.499	$\mathrm{Se^{6+}}$	4	2.977	$\mathrm{Cl^{7+}}$	4	4.860
$\mathrm{Na^{+}}$	4	1.028	$\mathrm{Mg^{2+}}$	4	1.312	$\mathrm{Al^{3+}}$	4	1.691	$\mathrm{Ge^{4+}}$	4	2.116	$\mathrm{Sb^{3+}}$	4	1.476	$\mathrm{Te^{4+}}$	4	1.701	$\mathrm{Br^{5+}}$	3	2.550
	8	1.004		8	1.173		5	1.571	$\mathrm{Sn^{4+}}$	4	1.877	$\mathrm{Bi^{3+}}$	5	1.434	$\mathrm{Te^{6+}}$	4	2.480	$\mathrm{Br^{7+}}$	4	3.419
	9	0.998	$\mathrm{Ca^{2+}}$	7	1.145	$\mathrm{Ga^{3+}}$	4	1.755		8	1.599							$\mathrm{I^{5+}}$	3	2.224
	12	0.985		8	1.132	$\mathrm{In^{3+}}$	4	1.627	$\mathrm{Pb^{2+}}$	4	1.293							$\mathrm{I^{7+}}$	4	2.722
$\mathrm{K^{+}}$	4	0.999		12	1.092	$\mathrm{Tl^{+}}$	8	1.040	$\mathrm{Pb^{4+}}$	4	1.885									
	8	0.987	$\mathrm{Sr^{2+}}$	8	1.123		12	1.030												
	12	0.978		10	1.106	$\mathrm{Tl^{3+}}$	4	1.625												
$\mathrm{Rb^{+}}$	8	0.991		12	1.093		8	1.468												
	10	0.987	$\mathrm{Ba^{2+}}$	7	1.121															
	12	0.983		8	1.115															
$\mathrm{Cs^{+}}$	8	0.993		12	1.087															
	10	0.989	$\mathrm{Ra^{2+}}$	8	1.142															
	12	0.984		12	1.109															

TABLE 3: EN of Cations with the Most Common CN for Group IB−VB Metals

IB			IIB			IIIB			IVB			VB		
cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i
$\mathrm{Cu^{+}}$	2	1.318	$\mathrm{Zn^{2+}}$	4	1.426	$\mathrm{Sc^{3+}}$	8	1.347	$\mathrm{Ti^{4+}}$	4	2.017	$\mathrm{V^{4+}}$	5	1.865
	4	1.232		8	1.263	$\mathrm{Y^{3+}}$	7	1.314		5	1.857	$\mathrm{V^{5+}}$	4	2.466
$\mathrm{Cu^{2+}}$	4	1.486	$\mathrm{Cd^{2+}}$	4	1.353		8	1.291		8	1.597		5	2.185
	5	1.423		8	1.226		9	1.272	$\mathrm{Zr^{4+}}$	4	1.743	$\mathrm{Nb^{3+}}$	8	1.453
$\mathrm{Ag^{+}}$	2	1.235	$\mathrm{Hg^{2+}}$	2	1.511					8	1.518	$\mathrm{Nb^{5+}}$	4	2.120
	4	1.128		4	1.352					9	1.487		7	1.802
$\mathrm{Ag^{2+}}$	4	1.409		8	1.283				$\mathrm{Hf^{4+}}$	4	1.858		8	1.749
$\mathrm{Au^{3+}}$	4	1.693								8	1.602			

TABLE 4: EN of Cations with the Most Common CN for Group VIB−VIIIB Metals

VIB			VIIB			VIIIB								
cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i	cations	CN	χ_i
$\mathrm{Cr^{6+}}$	4	3.200	$\mathrm{Mn^{2+}}$	4	1.349	$\mathrm{Fe^{2+}}$	4	1.376	$\mathrm{Co^{2+}}$	4	1.426	$\mathrm{Ni^{2+}}$	4	1.470
$\mathrm{Mo^{5+}}$	4	2.292		8	1.216		8	1.236		8	1.253	$\mathrm{Pd^{2+}}$	4	1.483
$\mathrm{Mo^{6+}}$	4	2.506	$\mathrm{Mn^{4+}}$	4	2.189	$\mathrm{Fe^{3+}}$	4	1.726				$\mathrm{Pt^{2+}}$	4	1.586
	7	1.902	$\mathrm{Mn^{7+}}$	4	3.614		8	1.454						
$\mathrm{W^{6+}}$	4	2.596	$\mathrm{Tc^{7+}}$	4	2.950	$\mathrm{Os^{6+}}$	5	2.493						
	5	2.356	$\mathrm{Re^{7+}}$	4	2.982									

TABLE 5: EN of Trivalent Ln with CN Ranging from 6 to 12

CN	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6	1.327	1.348	1.374	1.382	1.391	1.410	1.433	1.386	1.410	1.426	1.433	1.438	1.455	1.479	1.431
7	1.301	1.324	1.348	1.357	1.364	1.381	1.402	1.358	1.382	1.397	1.402	1.409	1.422	1.446	1.399
8	1.281	1.298	1.319	1.330	1.338	1.356	1.377	1.336	1.355	1.371	1.377	1.380	1.396	1.415	1.372
9	1.264	1.281	1.301	1.311	1.319	1.335	1.355	1.315	1.334	1.348	1.353	1.355	1.370	1.388	1.348
10	1.249	1.264	1.287	1.295	1.300	1.315	1.336	1.293	1.313	1.326	1.334	1.333	1.346	1.364	1.325
11	1.238	1.253	1.272	1.280	1.285	1.298	1.315	1.278	1.297	1.309	1.312	1.315	1.328	1.344	1.307
12	1.225	1.240	1.258	1.265	1.270	1.283	1.299	1.263	1.281	1.293	1.296	1.298	1.310	1.326	1.290

environments (CN ranging from 6 to 12). The calculated results are listed in Table 5.

3.1. EN of Main Group Elements. For main group elements in their highest oxidation state, EN increases from left to right across a period and decreases from top to bottom down a group, but some “anomalous” cases exist. The element hydrogen is not treated here due to its vanishingly small ionic radius, which was explained by the proton penetrating the electron cloud of another bonding atom.[17a] This is a quite complicated case. The EN value of hydrogen still becomes anomalous in other EN scales;[22a] therefore, much work is necessary to be carried out in this regard. Table 1 indicates that the EN of $\mathrm{Na^{+}}$ (1.024) is slightly higher than that of $\mathrm{Li^{+}}$ (1.009), which may be ascribed to the incomplete shielding of the first filling of the p electron.[15] The EN values of some p block elements in the fourth and sixth periods are larger than those of their lighter congeners, and both cases originate from the effect of the poorly shielded nuclear charge. The elements such as Ga and As, which follow after the first filling of d electron, and the elements such as Tl and Pb, which follow after the lanthanide series, are all affected by the increased effective nuclear charge and exhibit unusual properties. For instance, Tl and Pb exhibit a lower tendency to form stable compounds in their highest oxidation state, i.e., the inert pair effect. In addition, the stronger relativistic effects are the possible reason for the EN of $\mathrm{Fr^{+}}$ (1.012) and $\mathrm{Ra^{2+}}$ (1.151) being higher than those of $\mathrm{Cs^{+}}$ (0.998) and $\mathrm{Ba^{2+}}$ (1.126), respectively. From Table 2, we can find that the EN of cations decreases with increasing CN. This can indicate that the cation radius increases with increasing its CN; thus, the electrostatic potential at the ionic boundary decreases, i.e., the ability to attract electrons decreases.

The Lewis acid strength of a cation depends in a similar way on its oxidation state and CN.[23] There is a good linear correlation between Lewis acid strength (data are taken from Brown’s

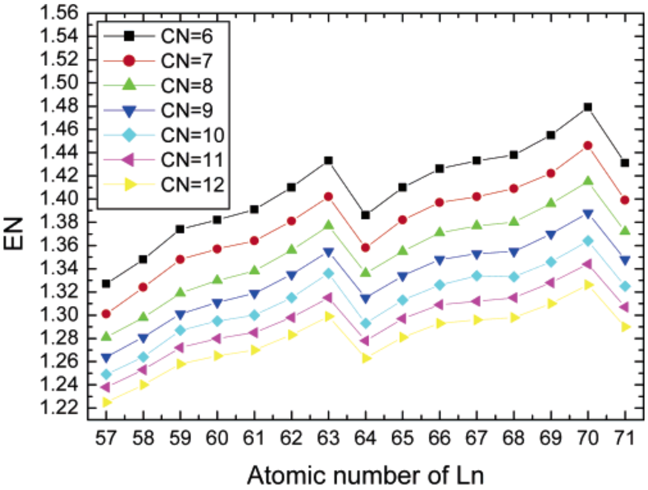

Figure 2. EN of trivalent Ln with different CN as a function of the atomic number of Ln.

work[23]) and the corresponding EN for the main group elements in their highest oxidation state; therefore, the Lewis acid strength can be quantitatively measured as a function of our EN scale (Figure S1).

3.2. EN of Transition Metals. The first transition series is most interesting and important in many ways in coordination chemistry. As shown in Table 1, EN varies with the spin state of transition metals. It is higher for the low-spin state than that for the high-spin one, which is mainly caused by the larger cation radius of the high-spin state.

The stability of transition-metal complexes is closely related to the electron-attracting power of divalent metal ions (M^{2+}). For 3d transition metals (i.e., from Mn to Zn), the stability of corresponding complexes increases in the order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$; this is the well-known Irving−Williams order,[15] an effect ascribed to the ligand field stabilization energy of M^{2+}.

EN values of six-coordinated M^{2+} from eq 5 are Mn^{2+} (1.303) $<$ Fe^{2+} (1.341) $<$ Co^{2+} (1.349) $<$ Ni^{2+} (1.367) $<$ Cu^{2+} (1.372) $>$ Zn^{2+} (1.336), which follows the current order (EN values of Mn^{2+}, Fe^{2+}, and Co^{2+} are the average value of low-spin and high-spin states).

For the first transition series, a good linear relationship is obtained between the hydration free energy (data are taken from ref 24) and the EN of divalent cation (Figure S2). It can be concluded that our EN scale is much better to study the structure and property of coordination compounds, since researchers can choose a proper EN value of any cation by including its actual chemical environments (i.e., its oxidation state, CN, and even spin state in the compound).

EN values of the third transition series are slightly larger than those of the second transition series. This behavior is expected due to the larger relativistic effects in the third row transition metals.

3.3. EN of Lanthanide Elements. In Figure 2, we plot the relationship between EN and the atomic number of Ln. It is found that the EN of trivalent Ln shows a gradual increase and then an abrupt decrease at the last element from La to Gd and from Gd to Lu, respectively, originated from the similar trend of the third ionization energy of Ln. Such a phenomenon can be well understood in view of the Ln contraction and “gadolinium break” in Ln chemistry. The pattern of EN for the trivalent Ln (from La to Lu) has minima at La, Gd, and Lu and maxima at Eu and Yb. This indicates that La^{3+}, Gd^{3+}, and Lu^{3+} are more stable than any other trivalent Ln, and indeed, the metals La, Gd, and Lu have no well-defined valence state other than the trivalent one. The stable oxidation states are related to the especially stable electron configuration of cations: La^{3+}, f^0 empty shell; Gd^{3+}, f^7 half-filled shell; Lu^{3+}, f^{14} filled shell. The trivalent Ln elements around these three ions are inclined to change their oxidation state to get more stability. Eu^{3+} and Yb^{3+} with higher EN values indicate that they are unstable and easily reduced to divalent cations; therefore, both $EuSO_4$ and $YbCl_2$ are well-known. On the contrary, Ce^{3+} and Tb^{3+} have a tendency to form tetravalent ions. These “anomalous” oxidation states are likewise related to the special electron configurations of these ions. Therefore, the changing trend of EN values of trivalent Ln is the real reflection of their 4f electron properties. Our EN scale reasonably explains the valence stability and valence change of some typical trivalent Ln. In addition, we can find that the EN of trivalent Ln decreases with increasing CN (Figure S3).

4. Conclusions

Our proposed EN scale is characterized by specific physical meaning and reliable theoretical basis, since eq 2 is derived from quantum mechanics and the larger relativistic effects on heavy elements have been taken into account. The very good linear relationship (Figure S4, correlation coefficient, cc, is 0.991) between our EN values and Luo’s scale[22b] gives a further powerful support to the reasonableness of our new EN scale. This new EN scale allows us to calculate the EN of cations with different oxidation states, spin states, and CN. In particular, the electron-attracting power of trivalent Ln is well-reflected in their EN values. EN values in Table 1 (the six-coordinated EN) can be regarded as the representative EN values of the elements in different valence states.

Our present work cannot only be used to quantitatively estimate the Lewis acid strength for the main group elements in their highest oxidation state and the hydration free energy of divalent cations for the first transition series, it can also be used to qualitatively evaluate the nature of chemical bonds. A cation with a larger EN value attracts electrons more strongly, and as a result, the electron cloud of the anion penetrates that of the cation, and thus a more covalent bond can be formed (e.g., $SnCl_2$ is an ionic crystal while $SnCl_4$ is a covalent one). The nature of chemical bonds in turn determines the bond strength and structure type of materials and, in conjunction with other factors, plays a crucial role in determining the property of materials. For instance, to be an effective transparent conducting oxide, a disperse conduction band can be obtained when the EN of cation is such that it enables a covalent interaction with oxygen.[25] In addition, EN is also an important factor affecting the d−d transition and charge-transfer transition in coordination chemistry, thus affecting the color of complexes.

We are quite confident that our new EN scale can be helpful to achieve a better understanding of chemistry facts and much more valuable in many areas of chemistry, for example, efficiently predicting the structure and property of materials and further designing new materials with novel properties through chemical substitutions are always a challenge for researchers, and the current work gives us a promising clue in this aspect.

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Supporting Information Available: Some typical applications of the currently proposed EN scale and some detailed data for our present calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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