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New Scale of the Ionic Character of the Chemical Bond Using Multiconfiguration SCF Wave Functions

Kazuhiro Ishida,* Shuichi Kadowaki, and Teijiro Yonezawa†
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
†Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606 and Institute for Molecular Science, Okazaki 444

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Two-configuration SCF wave functions constructed with multiconfiguration SCF localized-orbitals are obtained for several molecules, cations, and anions. The weights of the valence-bond resonance-structures are obtained from the wave functions for these molecules and molecular ions. A new formula of the ionic character of a chemical bond is proposed using these weights. For these neutral molecules, the values calculated from this formula are consistent with Pauling's scale of the ionic character. The present formula is shown to be applicable even for molecular ions.

The ionic character is an important concept in understanding chemical bonds. Several scales of the ionic character in relation to the electronegativity difference were proposed by Pauling,[1] by Hannay and Smyth,[2] by Nethercot,[3] by Hinze, Whitehead, and Jaffe,[4] and by others. They are not so satisfactory. Coulson[5] defined a scale of the ionic character from the weight of the ionic structure in the valence-bond wave function. However, few calculations have been performed along this line, so that the validity of this scale has not been confirmed extensively.

In the present paper, we propose a new scale for the ionic character using the weights obtained from the two-configuration SCF wave function constructed with multiconfiguration SCF localized molecular orbitals (MCSCF-LMOs).[6,7] Properties of this wave function (referred to as Ψ[2c] from now on) and its relation to the ionic character are described in the second section. In the third section, we apply the new scale to simple molecules and molecular ions: LiF, LiH, HF, H_2O, NH_3, CH_4, H_2, OH^-, NH_2^-, CH_3^-, H_3O^+, and NH_4^+. The values calculated are compared with the observed partial charges[8] and other scales. The present scale is shown to be in an excellent agreement with Pauling's scale as improved by Nethercot[3] for these neutral molecules.

Theory

The Ψ[2c] is fully described in a previous paper.[7] It can be briefly sketched as follows:

A Ψ[2c] wave function to discuss the nature of a local bond, say A–B, in a polyatomic molecule can be expressed as

$$\Psi[2c] = a_1 \| (\text{other MCSCF-LMOs}) \sigma_{AB} \bar{\sigma}_{AB} \| + a_2 \| (\text{other MCSCF-LMOs}) \sigma^*_{AB} \bar{\sigma}^*_{AB} \|, \tag{1}$$

where σ_{AB} is the bonding orbital, σ^*_{AB} is the corresponding antibonding orbital, a_1 and a_2 are the configuration mixing coefficients. All orbitals are the MCSCF-LMOs and can be expanded in terms of atomic orbitals (AOs) χ_t. All LCAO coefficients and the configuration mixing coefficients are optimized variationally.

The bonding orbital σ_{AB} and the antiboding orbital σ^*_{AB} can be expressed as

$$\begin{aligned} \sigma_{AB} &= \sum_{p}^{\text{on A}} \chi_p c_p + \sum_{q}^{\text{on B}} \chi_q c_q + \sum_{r} \chi_r c_r, \\ \sigma^*_{AB} &= \sum_{p}^{\text{on A}} \chi_p d_p + \sum_{q}^{\text{on B}} \chi_q d_q + \sum_{r} \chi_r d_r, \end{aligned} \tag{2}$$

where the subscript p denotes the numbering of AO's on atom A, q denotes that of AO's on atom B, and r denotes that of AO's on other atoms. Since σ_{AB} and σ^*_{AB} (also the other orbitals) are MCSCF-LMOs, all of c_r and d_r (which are the LCAO coefficients of AO's on the other atoms) can usually be neglected. Neglecting the last term in Eq. 2 and then substituting Eq. 2 into Eq. 1, we have the following equation, which clarifies the physical significance of the Ψ[2c]:

$$\Psi[2c] \simeq \Psi(A^-B^+) + \Psi(A^+B^-) + \Psi(A{:}B), \tag{3}$$

where

$$\Psi(A^-B^+) = \sum_{p}^{\text{on A}} \sum_{p'}^{\text{on A}} b_{pp'} \| (\text{other MCSCF-LMOs}) \chi_p \bar{\chi}_{p'} \|, \tag{4}$$

$$\Psi(A^+B^-) = \sum_{q}^{\text{on B}} \sum_{q'}^{\text{on B}} b_{qq'} \| (\text{other MCSCF-LMOs}) \chi_q \bar{\chi}_{q'} \|, \tag{5}$$

$$\Psi(A{:}B) = \sum_{p}^{\text{on A}} \sum_{q}^{\text{on B}} b_{pq} \| (\text{other MCSCF-LMOs}) (\chi_p \bar{\chi}_q - \chi_p \bar{\chi}_q)/\sqrt{2} \|, \tag{6}$$

$$b_{pp'} = a_1 c_p c_{p'} + a_2 d_p d_{p'}, \quad b_{qq'} = a_1 c_q c_{q'} + a_2 d_q d_{q'},$$
$$b_{pq} = \sqrt{2}(a_1 c_p c_q + a_2 d_p d_q).$$

The $\Psi(A^-B^+)$ is an ionic structure in which two bonding-electrons belong to atom A (see Eq. 4). In the covalent structure $\Psi(A : B)$, those electrons are shared by the two atoms.

Let us define the following three weights, which include interference terms:

$$W(A^-B^+) = \|\Psi(A^-B^+)\|^2 + \langle \Psi(A^-B^+) | \Psi(A^+B^-) + \Psi(A{:}B) \rangle, \tag{7}$$

$$W(A^+B^-) = \|\Psi(A^+B^-)\|^2 + \langle \Psi(A^+B^-) | \Psi(A^-B^+) + \Psi(A{:}B) \rangle, \tag{8}$$

$$W(A{:}B) = \|\Psi(A{:}B)\|^2 + \langle \Psi(A{:}B) | \Psi(A^-B^+) + \Psi(A^+B^-) \rangle. \tag{9}$$

Using these weights of the structures, we can define a new scale of the ionic character for the local bond A–B as

$$\lambda_{AB} = [W(A^-B^+) - W(A^+B^-)] \times 100\%. \tag{10}$$

The more electronegative one of these two atoms should be referred to as A in Eq. 10. Thus λ_{AB} happens to be negative when atom A happens to be more positive than atom B, as seen in Table 5 for the CH_3^- anion.

Results and Discussion

Ab initio calculations of the ionic character λ_{AB} were performed in the observed geometries with the 6-31G basis set[9] and with the STO-3G basis set[10] for neutral molecules: LiF, LiH, HF, H_2O, NH_3, CH_4, and H_2, and for molecular ions: H_3O^+, NH_4^+, OH^-, NH_2^-, and CH_3^-. The dipole moment (μ) was also computed directly for each of these neutral molecules with the same basis set (*i.e.*, not obtained from λ_{AB}).

Geometry optimization is omitted. The optimization will not greatly affect the ionic character, since the change of the bond length will be less than 0.01 Å in the 6-31G basis set.[11] Table 1 shows the geometries used in the present calculations.

Table 1. The geometries of molecules and ions

Molecule	Bond length Å	Bond angle °	Ref.
LiF	1.5639		a
LiH	1.5953		a
HF	0.917		a
H_2O	0.956	105.2	b
NH_3	1.0173	107.8	b
CH_4	1.0940		b
OH^-	0.970		c
NH_2^-	1.0173	107.8	d
CH_3^-	1.0940	109.5	e
H_3O^+	0.96	117.0	f
NH_4^+	1.032		g

a) F.J. Lovas and E. Tiemann, *J. Phys. Chem. Ref. Data*, **3**, 609 (1974). b) G. Herzberg, "Molecular Spectra and Molecular Structure," D. Van Nostrand, Princeton, New Jersey (1967), Vol. 3. c) K.P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand Reinhold, New York, N.Y. (1979), Vol. 4. d) Estimated from ammonia. e) Estimated from methane. f) Y.K. Yoon and G.B. Carpenter, *Acta Crystallogr.*, **12**, 17 (1959). g) J. A. Ibers and D. P. Stevenson, *J. Chem. Phys.*, **28**, 929 (1958).

Table 2. The value of ionic character, λ_{AB}, the dipole moment calculated and that observed, and the observed partical charge. The calculations were performed with the 6-31G basis set

Molecule	λ_{AB} %	μ_{calc} Debye	μ_{obsd} Debye	$[\mu/er_e]_{obsd}$ %
LiF	94[a]	7.289[a]	6.28409[c]	83.675
LiH	49[b]	4.466[b]	5.8820[c]	76.762
HF	40	2.147	1.826526[c]	41.47
H_2O	32	2.504	1.94[d]	34.8
NH_3	24	2.228	1.468[d]	28.00
CH_4	11	0.0	0.0	...
H_2	0	0.0	0.0	...

a) P-type basis functions on lithium are excluded. b) P-type basis functions on lithium are excluded and a p_z-type basis function ($\alpha=0.25$) on hydrogen is added. c) See footnote (a) of Table 1. d) B. Starck, Landolt-Börnstein Table, New Series, II/4, Springer (1967).

Table 2 shows the comparison of the λ_{AB} with the observed partial charge and the comparison of the calculated dipole moment with that observed for neutral molecules. The relative error of the dipole moment calculated to that observed is 50% at most. For a better agreement, polarization functions should be added to the basis set. The difference of the λ_{AB} from the observed partial charge is 10% at most (except for LiH). The λ_{AB} would be less sensitive than the dipole moment with respect to the absence of the polarization functions. In the case of the STO-3G basis set, the values of the λ_{AB} are too small in all molecules (*i.e.*, only 2% for LiF, 31% for LiH, 12% for HF, 11% for H_2O, and 10% for NH_3). Good λ_{AB} seems to require the 6-31G level basis-set at least.

The basis-set dependence of the λ_{HLi} for LiH was investigated by using various basis-sets. These results are in Table 3. In the STO-3G basis-set, the values of both the calculated dipole moment and the λ_{HLi} are extremely small. In the original 6-31G basis-set in which p-type basis functions on lithium (abbreviated to p(Li) from now on) are included, the calculated value of the dipole moment is in excellent agreement with the observed value, but the value of λ_{HLi} is in rather poor agreement with the observed partial charge.

Table 3. The basis-set dependence of the value of the ionic character for LiH molecule

	Basis set	E Hartree	μ Debye	λ_{HLi} %
(I)	STO-3G[a]	−7.85446	1.798	8
(II)	STO-3G[b]	−7.86932	3.580	31
(III)	Dunning's [4s/2s] set[c]	−7.98381	4.089	36
(IV)	Dunning's [4s/3s] set[c]	−7.98488	4.227	38
(V)	(IV)+p_z-GTO($\alpha=0.25$) on H	−7.98994	4.270	47
(VI)	6-31G[d]	−7.99579	5.632	20
(VII)	(VI)+p_z-GTO($\alpha=0.36$) on H	−7.99808	5.564	26
(VIII)	6-31G[e]	−7.98415	4.479	42
(IX)	(VIII)+p_z-GTO ($\alpha=0.25$) on H	−7.98887	4.466	49
Experiment			5.8820[f]	76.762[g]

a) The scale factor of 1s-GTO on H is 1.2. b) The scale factor of 1s-GTO on H is 1.0. c) Ref. 12. d) Ref. 9. e) P-type basis functions on lithium are excluded. f) See footnote (a) of Table 1. g) Observed partial charge (there is no bond-moment due to a lone-pair in the LiH molecule).

	Li–F	Li–H	H–F	H–OH	H–NH$_2$	H–CH$_3$	H–H
(A)	Li$^+$:F$^-$ 94%	Li$^+$:H$^-$ 50%	H$^+$:F$^-$ 44%	H$^+$:OH$^-$ 37%	H$^+$:NH$_2^-$ 31%	H$^+$:CH$_3^-$ 22%	H$^+$:H$^-$ 22%
(B)	Li:$^-$F$^+$ 0%	Li:$^-$H$^+$ 0%	H:$^-$F$^+$ 3%	H:$^-$OH$^+$ 5%	H:$^-$NH$_2^+$ 7%	H:$^-$CH$_3^+$11%	H:$^-$H$^+$22%
(C)	Li· ·F 6%	Li· ·H 50%	H· ·F 53%	H· ·OH 59%	H· ·NH$_2$ 65%	H· ·CH$_3$ 73%	H· ·H 55%

Fig. 1. The weights of resonance structures for a local bond in neutral molecules.

The function p(Li) extends into the bonding region, so it can improve the description of the region. The resulting description near the center of the electronic charge becomes reasonable (leads to a good dipole moment). However, the bonding electrons are accumulated in the p(Li) too much, so that the sharing ratio of the bonding electrons between Li and H is biased. In the 6-31G basis-set, the value of λ_{HLi} is remarkably improved by excluding the p(Li), as seen in Table 3 at basis-set (VIII). Further, the λ_{HLi} is improved by adding a p$_z$-type GTO on hydrogen to either the 6-31G set (without p(Li)) or the CGTO better values of λ_{HLi}, a larger basis set may be used and/or other configuration(s) may be taken into account.

Generally speaking, the λ_{AB} would be the sharing ratio of the bonding electrons between atoms A and B, so that λ_{AB} is sensitive to the balance of basis functions in the basis set used. Therefore, the p(Li) should be excluded from the 6-31G set for the calculations of λ_{XLi} as was done in the calculations for LiF and LiH.

Figure 1 shows the resonance-structures for a local-bond and their weights calculated for neutral molecules. The structures denoted by (A) and (B) are the ionic structures (A:$^-$ B$^+$) and (A$^+$:B$^-$), respectively. The covalent structure (A· ·B) is denoted by (C).**

The Ψ[2c] reduces to the Hartree-Fock wave function in the limit where a$_2$ goes to zero (see Eq. 1). The MCSCF-LMO reduce to the LMO in the limiting case. Therefore, the weights of resonance structures for the Hartree-Fock wave function can be calculated with the use of Eqs. 4—9 by seting a$_2$ to zero and using LMOs instead of MCSCF-LMOs. The results are as follows: The weights of the structures (A), (B), and (C) are 96, 0, and 4%, respectively, for LiF. For LiH, they are 66, 3, and 30%. For HF, they are 56, 6, and 38%. For H_2O, they are 47, 12, and 47%. For NH_3, they are 44, 15, and 52%. For CH_4, they are 36, 22, and 56%. They are 25, 25, and 50%, for H_2. In all molecules, the weight of the ionic structure calculated from the Hartree-Fock wave function is always larger than that calculated from the Ψ[2c] (see Fig. 1 for the values). The present weights calculated from the Ψ[2c] are reasonable, since the MO method usually overestimates the weights of the ionic structures.

Comparison with Other Scales. Several empirical relations between the ionic character and the electronegativity difference $|X_{\mathrm{A}}-X_{\mathrm{B}}|$, were proposed in the early days, for example, by Pauling[1] and by Hannay and Smyth;[2]

$$q_{\mathrm{P}} = [1-\exp(-|X_{\mathrm{A}}-X_{\mathrm{B}}|^2/4)] \times 100\%, \tag{11}$$

$$q_{\mathrm{HS}} = 16|X_{\mathrm{A}}-X_{\mathrm{B}}| + 3.5|X_{\mathrm{A}}-X_{\mathrm{B}}|^2\ (\%), \tag{12}$$

where q_{P} is the ionic character determined by Pauling and q_{HS} is that determined by Hannay and Smyth. Nethercot[3] recently proposed an improved relation:

$$q_{\mathrm{N}} = [1-\exp(-|X_{\mathrm{A}}-X_{\mathrm{B}}|^{3/2}/X_{\mathrm{GM}}^{3/2})] \times 100\%, \tag{13}$$

where X_{GM} is the geometric mean of X_{A} and X_{B}. Table 4 shows the values of these scales in comparison with the present λ_{AB} for several molecules.

The present scale λ_{AB} is in an excellent agreement with the Nethercot scale (the improved Pauling scale), as seen in Table 4.

TABLE 4. THE COMPARISON OF THE PRESENT SCALE OF THE IONIC CHARACTER λ_{AB} WITH OTHER SCALES: q_{P} BY PAULING, q_{HS} BY HANNAY AND SMYTH, q_{N} BY NETHERCOT. THE OBSERVED PARTIAL CHARGE IS AGAIN LISTED FOR CONVENIENCE

Molecule	q_{P}/%	q_{HS}/%	q_{N}/%	λ_{AB}/%	$[\mu/er_{\mathrm{e}}]_{\mathrm{obsd}}$/%
LiF	89	78	84	94	83.675
LiH	26	22	48	49	76.762
HF	59	43	42	40	41.47
H_2O	39	29	31	32	34.8
NH_3	18	17	19	24	28.00
CH_4	4	7	7	11	...
H_2	0	0	0	0	...

For Ionic Species. We further calculate λ_{AB} for several cation and anion molecules. It is difficult to obtain the "observed ionic character" of any bond in any ionic species. In addition, it will be difficult to extend any scale which makes use of the electronegativity difference to make it applicable to the ionic species. On the other hand, the λ_{AB} can be evaluated in the ionic species without any difficulty.

TABLE 5. THE VALUE OF THE IONIC CHARACTER λ_{AB} FOR ANION AND CATION CALCULATED WITH THE 6-31G BASIS-SET. THE VALUES FOR NEUTRAL MOLECULES ARE AGAIN LISTED FOR CONVENIENCE

Ion	λ_{OH}/%	Ion	λ_{NH}/%	Ion	λ_{CH}/%
OH$^-$	9	NH_2^-	0	CH_3^-	−12
H_2O	32	NH_3	24	CH_4	11
H_3O^+	50	NH_4^+	42		

Table 5 shows the values of λ_{AB} calculated with the 6-31G basis set for OH$^-$, NH_2^-, CH_3^-, H_3O^+, and NH_4^+ (geometries are shown in Table 1). In all cases, the λ_{XH} (X=C, N, O) shows an increase of about 20% from the neutral molecule to its cation (proton adduct), and also a decrease of about 20% to its anion (product from the elimination of a proton). Figure 2 shows the resonance structures and their weights for molecular

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** The sum of values of these weights is not always unity, because all of the c$_r$ and d$_r$ values in Eq. 2 are not always zero. In other words, the MCSCF-LMO are not completely localized.

	$[O–H]^-$	$[H–NH]^-$	$[H–CH_2]^-$	$[H–OH_2]^+$	$[H–N_3]^+$
(A)	H^+: O^{2-} 19%	H^+: NH^{2-} 14%	H^+: CH_2^{2-} 9%	H^+: OH_2 52%	H^+: NH_3 45%
(B)	H:⁻ O 10%	H:⁻ NH 14%	H:⁻ CH_2 20%	H:⁻ OH_2^{2+} 2%	H:⁻ NH_3^{2+} 3%
(C)	H· ·O^- 70%	H· ·NH^- 73%	H· ·CH_2^- 76%	H· ·OH_2^+43%	H· ·NH_3^+ 53%

Fig. 2. The weights of resonance structures for a local bond in molecular ions.

ions. In Fig. 2, the structure denoted by (A) is the resonance structure in which two bonding-electrons belong to the more electronegative atom. The (B) is the resonance structure in which those electrons belong to the less electronegative atom. In structure (C), the bonding-electrons are shared between both atoms.

The weights of the resonance structures can also be evaluated from the Hartree-Fock wave function in the same manner as described in this section. The results are as follows: The weights of the structures (A), (B), and (C) are 32, 19, and 49%, respectively, for OH^-. For NH_2^-, they are 27, 28, and 54%. For CH_3^-, they are 9, 29, and 33%. For H_3O^+, they are 63, 5, and 35%. They are 57, 8, and 42% for NH_4^+. In all ions, the values of the weights of the ionic structures calculated from the Hartree-Fock wave function are always larger than those from the $\Psi[2c]$ (see Fig. 2 for the values). In the case of molecular ions, the present weights calculated from the $\Psi[2c]$ are reasonable (as well as for the case of neutral molecules).

Conclusion

The scale of the ionic character λ_{AB} presented here is reasonable not only for neutral molecules but also for molecular ions. One may apply this scale to systems with hydrogen bonding, organometalic compounds, complex ions, metal complexes, and so on. One may use an effective core-potential[13] in order to reduce the computational time. Even for this case, no modifications of the theory are needed.

To obtain good values of λ_{AB} requires that the 6-31G level basis-set ("double-zeta" level) be used and that some care be taken in the choice of the basis functions used in this basis set.

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References

1) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ., Ithaca, N.Y. (1960).

2) N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 171 (1964).

3) A. H. Nethercot, Jr., *Chem. Phys. Lett.*, **59**, 346 (1978).

4) J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, **84**, 540 (1962); J. Hinze, M. A. Whitehead, and H. H. Jaffe, *ibid.*, **85**, 148 (1963).

5) C. A. Coulson, "Valence," Oxford Univ., London (1952).

6) B. Levy, *Chem. Phys. Lett.*, **18**, 59 (1973).

7) K. Ishida, K. Kondo, and T. Yonezawa, *J. Chem. Phys.*, **66**, 2883 (1977).

8) The observed partial charge is obtained by dividing the observed dipole moment (μ) by the observed bond length (r_e) for diatomic molecules (the bond moment is used instead of the dipole moment for water and ammonia). The observed partial charge is not always the "observed ionic character," because the bond moments of lone-pairs make a large contribution to the dipole moment. Recently, Matcha and King [*J. Am. Chem. Soc.*, **98**, 3415 and 3420 (1976)] have discussed the relation between the dipole moment and the scale of the ionic character.

9) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972); J. D. Dill and J. A. Pople, *ibid.*, **62**, 2921 (1975).

10) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

11) J. A. Pople, "A Priori Geometry Predictions," in "Applications of Electronic Structure Theory," ed by H. F. Schaefer, III., Modern Theoretical Chemistry, Plenum Press, New York (1977), Vol. 4.

12) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970); **55**, 716 (1971).

13) For example, V. Bonifacic and S. Huzinaga, *J. Chem. Phys.*, **60**, 2779 (1974); P. Coffey, C. S. Ewig, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **97**, 1656 (1975); L. R. Kahn, P. Baybutt, and D. G. Truhlar, *J. Chem. Phys.*, **65**, 3826 (1976).