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Semi-Empirical SCF Molecular Orbital Treatment for Valence Electron Systems. II. Small Ionic Intermediates

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Familiar small ionic intermediates are treated by the semi-empirical SCF method previously proposed for all valence electron systems by the present authors. The calculated orbital energies are compared with the results of other full SCF calculations and the experiments. The agreements between them are satisfactory. Utilizing the calculated orbital charge distributions and the atomic dipole values, the reactivities and the most reactive centers of these ions are discussed. The calculated results on the proton affinities and the excitation energies of various compounds are also presented.

It is well known that, in certain circumstances, vairous ionic intermediates, including ionic reagents, have been observed; the reactivities of these ions have been investigated experimentally and or theoretically by many researchers.[1] Non-empirical or semi-empirical calculations have been performed on the electronic structures of several ion, for example, N_3^-, NO_2^+, HF_2^-,[2] NH_4^+,[3] OH^-, H_3O^+,[4-6] CN^-,[7] NO_2^+, NO_2^-, NO_3^- and CO_3^-.[8] In these treatments, however, scarecely no discussions of the reactivities of these ions in relation to their electronic structures have been made, except those in Refs. 6 and 7.

The present paper will present the electronic structures of about twenty ions, ions which are familiar to chemists as nucleophilic and electrophilic reagents and which are comparatively small molecules with a closed-shell configuration. The method of calculation is the semi-empirical SCF treatment for all valence electrons and their parameters; preliminary results have already been given in a previous paper,[9] where the calculated results for various small molecules were in good accordance with the other non-empirical calculations and with the experimental values. The geometries of the compounds to be treated are shown in Table 1. The values listed in this table are cited from Ref. 10. For the unknown compounds, the values of related compounds are adopted.

TABLE 1. THE GEOMETRIES OF IONS

Ion	Symmetry	Bond distance (Å) and Bond angle (°)
CN^-	$C_{\infty v}$	CN=1.14
CN^+	$C_{\infty v}$	CN=1.17
$CH_3^-(CH_3^+)$	C_{3v}	CH=1.09, ∠CHC=tetrahedral
CH_3^+	D_{3h}	CH=1.09, ∠CHC=120
OH^+	$C_{\infty v}$	OH=1.0289
OH^-	$C_{\infty v}$	OH=0.944
HOO^-	C_s	OH=0.97, OO=1.49 ∠HOO=100
OH_3^+	C_{3v}	OH=0.96, ∠HOH=117
OH_3^+	D_{3h}	OH=0.96, ∠HOH=120
CH_3O^-	C_{3v}	CH=1.09, CO=1.43, ∠HCH=tetrahedral
NH_4^+	T_d	NH=1.031
NH_2^-	C_{2v}	NH=1.03, ∠HNH=107
NO_2^+	$D_{\infty h}$	NO=1.154
$NO_2^-(NO_2^+)$	C_{2v}	NO=1.24, ∠ONO=115
NO_3^-	C_{3v}	NO=1.243, ∠ONO=120
$NO^+(NO^-)$	$C_{\infty v}$	NO=1.0619
$NCO^-(NCO^+)$	$C_{\infty v}$	NC=1.207, CO=1.171
$N_3^-(N_3^+)$	$D_{\infty h}$	NN=1.12

Results and Discussion

In this section, the general trends of the electronic structures of these ions will be discussed, and then the characteristics of the individual ions will be described.

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[1] *E. g.*, C. K. Ingold, "The Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca (1953); J. O. Edwards, "Inorganic Reaction Mechanisms," Benjamin, N. Y. (1964).

[2] E. Clementi, *J. Chem. Phys.*, **34**, 1468 (1961); E. Clementi and A. D. McLean, *ibid.*, **39**, 323 (1963).

[3] M. Krauss, *ibid.*, **38**, 564 (1963).

[4] J. L. J. Rosenfeld, *ibid.*, **40**, 384 (1964).

[5] J. W. Moskowitz and M. C. Harrison, *ibid.*, **43**, 3550 (1965).

[6] G. Klopman, *J. Am. Chem. Soc.*, **87**, 3300 (1965).

[7] D. F. Shriver and J. Posner, *ibid.*, **88**, 1672 (1966).

[8] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

[9] T. Yonezawa, K. Yamaguchi and H. Kato, This Bulletin, **40**, 536 (1967).

[10] "Table of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, The Chem. Soc., London (1956) and (1965).

TABLE 2. THE COMPARISON OF THE HO ENERGIES BETWEEN OURS AND NON-EMPIRICAL RESULTS

Ion	HO orbital energy (eV)	
	Ours	Non-empirical
NO_2^+	−24.53	−23.98[2]
OH_3^+ (C_{3v})	−23.49	−25.75[5]*
NH_4^+	−23.36	−27.02[3]
OH^-	−1.26	−1.71[5]*
N_3^-	−4.67	+1.90[2]

* The geometries of these compounds are adopted to be most closed to ours.

Orbital Energy. In order to compare our results and those of non-empirical calculations, the calculated values of the highest occupied (HO) orbital energies of several ions are given in Table 2. Considering the differences in the adopted configurations between the above two methods, the two sets of results show considerably good agreements. In Table 3, the energies of the HO and the lowest vacant (LV) orbital of various ions are listed, together with the observed values of the electron affinity and the ionization potential of the corresponding radicals. Here, the HO orbital energy of the anion is approximately equal to the negative value of the electron affinity of the corresponding radical, while the LV orbital energy of the cation is approximately equal to that of the ionization potential of its radical. Referring to the values in Table 3, it may be said that the correspondence between the calculated and the observed values is almost satisfacotry; hence, our results allow us to discuss the physico-chemical properties of these ions qualitatively.

The LV orbitals of the cations fall in a range of about −10 eV, and the HO orbitals of the anions, in one of −5— −1 eV, whereas in H_3O^+ and NH_4^+, the situations are different *i. e.,* these LV orbitals lie in higher energy regions.

Charge Distribution. The calculated net charges of the A atom (Q_A) and the bond populations between the A and B atoms (M(A—B)) in various ions are presented in Table 4. In Table 5, the values of the atomic orbital (AO) coefficients of the HO orbitals in the anions and those of the LV orbitals of the cations are listed, where the notations S_A and x_A denote the valence s AO and px AO of the A atom, and where h_j is the ls AO of the jth hydrogen atom. From Table 5, it may be seen that the AO coefficients of the HO orbitals of the anions are nearly equal to those of the LV orbitals of the related cations with similar configurations, for example, in CN and OH ions. These results suggest that the most reactive sites are the same in the cations and its anions, if the geometries of these two ions are almost identical with each other.

TABLE 3. THE HO AND LV ORBITAL ENERGIES OF IONS (in unit of eV)

(a) Anions

Ions	HO	LV	E_A*
NO_3^-	−7.25	+9.90	3.88[a]
NCO^-	−5.33	+12.61	—
N_3^-	−4.67	+13.05	2.3[b]
NO_2^-	−3.85	+9.68	4.0,[d] 3.82,[c] 1.62[a]
HOO^-	−3.48	+13.76	3.0[e]
CN^-	−3.10	+12.10	3.2,[f] 2.80[g]
CH_3O^-	−2.28	+20.39	—
OH^-	−1.26	+20.43	2.2,[h] 2.8[i]
CH_3^-	−1.25	+21.30	1.1[h]
NH_2^-	−1.15	+21.04	1.2[j]

* E_A is the electron affinity of the corresponding radical.

a) K. B. Yatsimirskii, *Izvest. Akad. Nauk. S. S. S. R. Otdel. Khim. Nauk.*, **1947**, 411, 453.

b) J. Weiss, *Trans. Faraday Soc.*, **43**, 119 (1947).

c) R. K. Curran, *Phys. Rev.*, **125**, 910 (1962).

d) A. L. Farragher, F. M. Page and R. C. Wheeler, *Discussions Faraday Soc.*, **37**, 203 (1964).

e) J. Weiss, *Trans. Faraday Soc.*, **31**, 966 (1935).

f) J. T. Herron and V. H. Dibler, *J. Am. Chem. Soc.*, **82**, 1555 (1960).

g) R. Napper and F. M. Page, *Trans. Faraday Soc.*, **59**, 1086 (1963).

h) H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

i) F. M. Page, *Discussions Faraday Soc.*, **19**, 87 (1955).

j) F. M. Page, *Trans. Faraday Soc.*, **57**, 1254 (1961).

(b) Cations

Ions	HO	LV	I_p*
OH^+	−26.57	−12.85	13.18[a]
CN^+	−24.44	−12.27	15.13[b]
NO^+	−27.52	−11.51	9.4[c]
NO_2^+($D_{\infty h}$)	−24.53	−8.25	11.34,[d] 12.3[e]
NO_2^+(C_{2v})	−24.24	−10.91	
CH_3^+(D_{3h})	−22.63	−9.53	9.95[f]
H_3O^+(D_{3h})	−23.40	+1.60	—
NH_4^+	−23.36	+4.97	—

* The notation, I_p, refers to the ionization potential of the corresponding radical.

a) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **23**, 1364 (1955).

b) R. J. Kandel, *ibid.*, **22**, 1496 (1954).

c) H. D. Hagstrum, *Rev. Mod. Phys.*, **23**, 185 (1955).

d) R. J. Kandel, *J. Chem. Phys.*, **23**, 84 (1955).

e) D. M. Simpson and W. C. Price, *Proc. Roy. Soc.*, **A179**, 201 (1941).

f) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 2059 (1954).

Pople and Segal[11] calculated the atomic dipole moments of various small molecules and discussed

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[11] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, s 136 (1965).

TABLE 4. THE CALCULATED VALUES OF THE NET CHARGES OF THE ATOMS AND THE BOND POPULATIONS IN VARIOUS IONS

Ion $(A)_m$-$(B)_n$-$(C)_l$*	Net charge			Bond population	
	A	B	C	A-B	B-C
CN^-	−0.351	−0.649	—	1.509	—
CN^+	+0.864	+0.136	—	1.109	—
OH^-	−1.137	+0.137	—	0.242	—
OH^+	+0.371	+0.629	—	0.202	—
NO_2^-	−0.013	−0.494	—	0.664	—
NO_2^+	+0.528	+0.236	—	1.034	—
NO^-	−0.613	−0.383	—	0.619	—
NO^+	+0.500	+0.500	—	1.084	—
N_3^-	−0.724	+0.448	—	1.328	—
N_3^+	+0.283	+0.434	—	1.388	—
CH_3^-	−0.715	−0.095	—	0.716	—
CH_3^+	+0.319	+0.227	—	0.668	—
OH_3^+	−0.521	+0.507	—	0.446	—
NH_4^+	−0.592	+0.398	—	0.598	—
NH_2^-	−1.146	+0.073	—	0.543	—
NO_3^-	+0.707	−0.569	—	0.806	—
NCO^-	−0.781	+0.430	−0.649	1.452	0.962
NCO^+	+0.158	+0.646	+0.196	1.290	1.050
HOO^-	+0.276	−0.599	−0.678	0.473	0.220
H_3CO^-	+0.001	−0.021	−0.981	0.800	0.862

* *m*, *n* and *l* are integers (0, 1, 2, 3).

the relation between the charge distiributions and the magnitudes of the atomic dipoles. The values of the atomic dipole moments (μ_A) of various ions as obtained by the approximate formula,11) are recorded in Table 6. Generally speaking, the values of these ions are of the same order or are larger than those in H_2O and NH_3 whose magnitudes are mainly atributed to the lone-pair orbitals. Thus, the ions with the large atomic dipoles may be those with the σ lone-pair orbitals and exhibiting strong ability as σ donors.

Next, let us discuss the electronic structures of the individual ion.

NO_2^+, NO_2^- and NO_3^-. Among these, NO_2^+ is well known to be the most reactive reagent. The electronic structures of NO_2^+ and NO_2^- calculated by Hoffmann's method12) have already been given in our previous paper,13) but in the calculations the orbital energies of these ions were unreasonable and the charge inclinations seemed to be too large.

McEwen calculated the electronic structures of NO_2^- and NO_3^- by the semi-empirical method, including σ systems (the basic AO's are the hybridized orbitals).14) Table 7 presents some of the orbital energies obtained by McEwen and by the present calculations. The agreement between them is fairly good, but there are some discrepancies: the sequences of some orbitals in NO_3^- are

TABLE 5. THE COEFFICIENTS OF THE HO OF ANIONS AND THE LV ORBITALS OF THE CATIONS

Ion		MO
OH^-	HO(degenerate)	π_O, π'_O
OH^+	half occupied	π_O, π'_O
CH_3O^-	HO(degenerate)	$-0.03\pi_C-0.01\pi'_C+0.17h_1-0.14h_2-0.03h_3+0.93\pi_O+0.36\pi'_O$
		$0.01\pi_C-0.03\pi'_C-0.06h_1-0.11h_2+0.18h_3-0.36\pi_O+0.93\pi'_O$
$HO_1O_2^-$	HO	$0.43\pi_{O1}-0.93\pi_{O2}$
CN^-	HO	$-0.28s_C+0.61\sigma_C-0.11s_N-0.70\sigma_N$
CN^+	LV	$-0.24s_C+0.60\sigma_C-0.15s_N-0.70\sigma_N$
$CH_3^-(C_{3v})$	HO	$0.22s_C+0.94\pi_C-0.10(h_1+h_2+h_3)$
$CH_3^+(C_{3v})$	LV	$0.27s_C+0.93\pi_C-0.12(h_1+h_2+h_3)$
NO_2^-*	HO	$-0.22s_N-0.59y_N+0.01(s_{O1}+s_{O2})+0.64(y_{O1}+y_{O2})$
NO_2^+*(C_{2v})	LV	$-0.22s_N-0.56y_N+0.01(s_{O1}+s_{O2})+0.64(y_{O1}+y_{O2})$
$NO_2^+(D_{\infty h})$	LV(degenerate)	$0.78\pi_N-0.63(\pi_{O1}+\pi_{O2}),\ 0.78\pi'_N-0.63(\pi'_{O1}+\pi'_{O2})$
N_3^-	HO(degenerate)	$0.71(\pi_{N1}-\pi_{N3}),\ 0.71(\pi'_{N1}-\pi'_{N3})$
N_3^+	half occupied	$0.71(\pi_{N1}-\pi_{N3}),\ 0.71(\pi'_{N1}-\pi'_{N3})$
NCO^-	HO(degenerate)	$-0.71\pi_N-0.19\pi_C+0.68\pi_O,\ -0.71\pi'_N-0.19\pi'_C+0.68\pi'_O$
NCO^+	half occupied	$-0.71\pi_N-0.17\pi_C+0.69\pi_O,\ -0.71\pi'_N-0.17\pi'_C+0.69\pi'_O$
NO^-	half occupied	$0.85\pi_N-0.74\pi_O,\ 0.85\pi'_N-0.74\pi'_O$
NO^+	LV(degenerate)	$0.84\pi_N-0.75\pi_O,\ 0.84\pi'_N-0.75\pi'_O$
$OH_3^+(D_{3h})$	LV	$0.96s_O-0.62(h_1+h_2+h_3)$
NH_4^+	LV(three fold degenerate)	$0.31x_N-0.72y_N+0.60z_N-0.71h_1+1.11h_2-0.11h_3-0.29h_4$
		$0.58x_N+0.64y_N+0.48z_N-0.88h_1-0.29h_2+0.23h_3+0.94h_4$
		$0.74x_N-0.20y_N-0.62z_N-0.29h_1-0.23h_2+1.14h_3-0.62h_4$

* The directions of *y* AO's are parallel to the bisector of the valence angle of the nitrogen atom.

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12) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

13) H. Kato, K. Morokuma, T. Yonezawa and K. Fukui, This Bulletin, **37**, 1710 (1964).

14) K. L. McEwen, *J. Chem. Phys.*, **34**, 547 (1961).

TABLE 6. THE CALCULATED ATOMIC DIPOLE MOMENTS (in debye units)

Ion	Atomic dipole		
	Carbon	Nitrogen	Oxygen
CN^-	−3.57	+2.26	—
CN^+	−2.08	+1.46	—
CH_3^-	−2.48	—	—
$CH_3^+(C_{3v})$	−0.02	—	—
NO_2^+	—	0	+2.07
NO_2^-	—	−2.33	+1.77
NO_3^-	—	0	+1.93
OH^-	—	—	−1.52
OH^+	—	—	−0.75
OH_3^+	—	—	−0.51
$HO_1O_2^-$	—	−1.79[*2]	+0.77[*3]
N_3^-	0[*1]	−2.82[*4]	—
N_3^+	0[*1]	−2.76[*4]	—
NO^-	—	−2.54	+1.66
NO^+	—	−2.38	+1.55
NCO^-	0	−2.64	+1.80
NCO^+	0	−2.55	+1.69
NH_2^-	—	−2.41	—
OH_2	—	—	−1.95
NH_3	—	−1.65	—
CO	−3.50	—	1.42

[*1] The values for the central nitrogen atoms.
[*2] The value for the O_1 atom.
[*3] The value for the O_2 atom.
[*4] The value for the terminal nitrogen atom.

TABLE 7. THE ORBITAL ENERGIES OF NO_2^- AND NO_3^-

(a) NO_2^-*			(b) NO_3^-*		
	Ours	McEwen		Ours	McEwen
b_1	9.68	6.70	a_2''	9.90	5.33
a_1**	−3.84	−4.75	e''**	−7.26	−8.52
a_2	−5.41	−6.31	a_2''	−7.40	−8.44
b_2	−6.20	−6.31	e'	−7.54	−8.35
b_2	−8.69	—	e'	−12.41	—
b_1	−9.36	−10.56	a_2''	−14.14	−14.76
a_1	−9.63	−11.08	a_1'	−15.84	—
a_1	−15.11	—	e'	−28.19	—
b_2	−25.91	—	a_1'	−33.29	—
a_1	−28.48	—			

* The π orbitals are the a_2 and b_1 orbitals in NO_2^- and the a_2'' and e'' in NO_3^-.
** The HO orbitals.

different between the two sets of results, and our calculated LV orbital energies of the two ions are a little higher than those obtained by McEwen. As to the electron densities of the oxygen atoms in these ions, Pople and Segal[8)] obtained them as 5.883 in NO_2^+, 6.543 in NO_2^-, and 6.533 in NO_3^-, while the atom populations obtained by the present method are 5.764, 6.494, and 6.569 respectively.

The atomic orbital (AO) populations are as follows:

NO_2^+: $(s_N)^{1.34}(\sigma_N)^{0.76}(\pi_N)^{2.38}(s_O)^{1.75}(\sigma_O)^{1.20}(\pi_O)^{2.82}$[*1]

NO_2^-: $(s_N)^{1.50}(x_N)^{0.76}(y_N)^{1.67}(\pi_N)^{1.08}(s_O)^{1.81}(x_O)^{1.32}(y_O)^{1.90}(\pi_O)^{1.46}$[*2]

NO_3^-: $(s_N)^{1.26}(x_N)^{0.91}(y_N)^{0.91}(\pi_N)^{1.22}(s_O)^{1.74}(x_O)^{1.45}(y_O)^{1.79}(\pi_O)^{1.59}$[*2]

The reactivities of NO_2^+ and NO_2^- were discussed in our previous paper;[13)] similar conclusions can be drawn from the results of the present treatment. For the NO_3^- ion, the HO orbitals are the π′-type lone-pair orbitals localized on the oxygen atoms (the π′ AO's lie on the molecular plane), and the μ_A values are larger on the oxygen atoms. Thus, in this ion the most reactive sites for the nucleophilic reactions are the oxygen atoms.

OH^- and OH^+. The HO orbitals of the OH^- ion are degenerate, π-type lone-pair orbitals on the oxygen atom. The charge distribution and the magnitude of the atomic dipole also indicate that the oxygen atom in this ion is the reactive site for the nucleophilic reactions. For the OH^+ ion, the highest half-occupied orbitals are degenerate and are localized on the π or π′ AO of the oxygen atom; hence, this ion may sometimes behave like the biradical. This result agrees with the experimental fact that the OH^+ ion adds to the C-C double bond and that cyclization takes place.[15)]

The AO populations of these two ions are as follows:

OH^-: $(s_O)^{1.96}(\sigma_O)^{1.17}(\pi_O)^{4.00}(h)^{0.86}$

OH^+: $(s_O)^{2.04}((\sigma_O)^{1.59}(\pi_O)^{2.00}(h)^{0.37}$

From the above data, it may be seen that the 2s AO's of the oxygen atoms in these ions remain as the lone-pair orbitals, and that only the interactions between the $2p\sigma_O$ AO and 1s AO of the hydrogen atom contribute to the O-H bonding.

CH_3O^-. The HO orbitals of CH_3O^- are degenerate, π-type orbitals, in which the electrons are largely localized on the oxygen atom. The negative charge is located only on the oxygen atom. This situation is similar to that of OH^-. The AO populations are as follows:

CH_3O^-: $(s_O)^{1.90}(\sigma_O)^{1.12}(\pi_O)^{3.96}(s_C)^{1.19}(\sigma_C)^{0.91}(\pi_C)^{1.92}(h)^{1.00}$

HOO^-. This ion is produced from the ionic cleavage of a hydroperoxide; its configuration is assumed to be the same as that of the hydroperoxide

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[*1] The s_X, σ_X and π_X notations refer to the 2s, pσ and pπ AO's of the X atom.

[*2] The molecular planes of these compounds are on the xy-plane.

15) E. g., J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Pub., N. Y. (1956).

without one hydrogen atom.*3 The negative charge of the terminal oxygen atom is larger than that of the central one. The HO orbital is a π-type orbital, where the distribution of the electrons is the largest on the terminal oxygen atom. On the other hand, the atomic dipole is the largest on the central oxygen atom. Accordingly, it may be possible that both oxygen atoms become the active centers of the nucleophilic reactions.

The AO populations are as follows:

$$HO_1O_2^-:\ (h)^{0.72}(s_{O1})^{1.87}(x_{O1})^{1.31}(y_{O1})^{1.42}(\pi_{O1})^{2.00}$$
$$(s_{O2})^{1.98}(x_{O2})^{0.70}(y_{O2})^{2.00}(\pi_{O2})^{2.00}$$

where the O–O bond is parallel to the x direction. The findings on the AO populations indicate that π-type and σ-type lone-pair orbitals exist on oxygen atoms in the anion.

CN^- and CN^+. The CN^- ion is one of the most reactive reagents. The HO orbital is a σ lone-pair orbital, as in the CO molecule.⁹⁾ The μ_A value of the carbon atom is larger than that of the nitrogen atom, as may be seen in Table 6; its value is nearly equal to that of the carbon atom in CO. Thus, this anion is a strong σ donor and the carbon atom is more active than the nitrogen atom in the nucleophilic reactions. These results agree with the other theoretical and experimental findings.[7,16)] As to the CN^+ ion, the LV orbital is a σ lone-pair one, and so this cation may be a strong σ-type electron acceptor. The position which is susceptible to electrophilic attack is the carbon atom rather than the nitrogen atom.

The AO populations are as follows:

$$CN^-:\ (s_C)^{1.55}(\sigma_C)^{1.19}(\pi_C)^{1.61}(s_N)^{1.73}(\sigma_N)^{1.53}$$
$$(\pi_N)^{2.39}$$
$$CN^+:\ (s_C)^{1.59}(\sigma_C)^{0.26}(\pi_C)^{1.28}(s_N)^{1.79}(\sigma_N)^{0.36}$$
$$(\pi_N)^{2.72}$$

The AO populations of the 2s AO's of the carbon atoms in these ions are much larger than unity; this may suggest that the hybridizations of the carbon atoms in these two ions are extraordinary, since these values in the normal hydrocarbons are nearly equal to unity.

NCO^- and N_3^-. These two anions are isoelectronic. The HO orbitals of both ions are π orbitals; the electrons are largely localized on the terminal nitrogen atom in N_3^- and on the nitrogen atom in NCO^-. The atomic dipoles of these nitrogen atoms are the largest in both the ions. Thus, these anions may act as strong π donors and also as σ donors. The terminal nitrogen atoms are shown to be the most reactive.

According to the present results, NCO^+ and N_3^+ ions with linear configurations have degenerate half-occupied orbitals. Thus, these cations may behave as biradicals, such as in OH^+.

The AO populations of these ions are summarized in Table 8. Except for the π-AO populations, the values of the other AO populations are nearly identical to each other in the cation and its anion.

TABLE 8. THE AO POPULATIONS OF N_3 AND NCO IONS

Compound	Atom	s	σ	π
N_3^+	N_t*	1.59	1.31	1.82
	N_c	1.34	0.89	2.36
N_3^-	N_t	1.57	1.30	2.86
	N_c	1.35	0.90	2.30
	N	1.63**	1.44**	1.76**
NCO^+	C	1.03	0.56	1.76
	O	1.82	1.52	2.46
	N	1.60	1.43	2.74
NCO^-	C	1.07	0.61	1.88
	O	1.78	1.50	3.36

* The notations N_t and N_c refer to the terminal and central nitrogen atoms.

** These are average values in two odd electron orbitals.

NO^+ and NO^-. In NO^+, the positive charges of the nitrogen and oxygen atoms are equal to each other, while the negative charge of the nitrogen atom is larger than that of the oxygen atom in NO^-. The LV orbitals in NO^+ are degenerate π orbitals, and the HO orbitals in NO^- are degenerate, half-occupied ones. The values of the atomic dipoles of the nitrogen atoms in both ions are larger than those of the oxygen atoms. Thus, the active centers in both ions are on the nitrogen atoms.

The AO populations are as follows:

$$NO^+:\ (s_N)^{1.73}(\sigma_N)^{1.05}(\pi_N)^{1.72}(s_O)^{1.88}(\sigma_O)^{1.34}$$
$$(\pi_O)^{2.28}$$
$$NO^-:\ (s_N)^{1.69}(\sigma_N)^{1.08}(\pi_N)^{2.84}(s_O)^{1.85}(\sigma_O)^{1.38}$$
$$(\pi_O)^{3.16}$$

In NO^-, the π AO populations of the nitrogen and oxygen atoms are nearly equal; they may behave as the O_2 molecule.

NH_2^-. This anion is isoelectronic to H_2O, and the electronic structure of this ion is similar to that of H_2O. For example, this HO orbital is a π-type lone-pair orbital, as in H_2O. The corresponding orbital energies of this ion, however, are much higher than those in H_2O. Thus, the nucleophilic reactivity of this ion may be considerably stronger than that of H_2O.

The AO populations are as follows:

$$NH_2^-:\ (s_N)^{1.79}(x_N)^{1.51}(y_N)^{0.84}(\pi_N)^{2.00}(h)^{0.93}$$

H_3O^+ and NH_4^+. The electronic structures of these two ions are very close to each other. That

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*3 In its radical, a triangular form has been proposed, but this configuration is not taken into account in this calculation.

16) *E. g.*, W. P. Griffith, *Quart. Revs.*, **16**, 188 (1962).

is, the hydrogen atoms in these cations keep bear large positive charges, the central atoms hold the negative charges, and the LV orbitals are situated in higher regions than those in the other cations investigated. Accordingly, these two cations act differently from the other cations; *i. e.*, these two cations may act as proton-donors, not as electron-acceptors like the other cations. This conclusion agrees with the results of experiments.1) For the H_3O^+ ion, the two geometries shown in Table 1 are adopted; the one is planar, and the other is pyramidal. According to our calculations, the planar form is slightly more stabilized than the pyramidal one (about 0.1 eV).

The AO populations are as follows:

$$H_3O^+:\ (s_O)^{1.97}(x_O)^{1.29}(y_O)^{1.42}(\pi_O)^{1.97}(h)^{0.49}$$

$$NH_4^+:\ (s_N)^{1.78}(x_N)^{1.27}(y_N)^{1.27}(\pi_N)^{1.27}(h)^{0.60}$$

The positive charge of the hydrogen atoms in the pyramidal H_3O^+ was calculated to be $+0.370$ by Pople *et al.*8) Our result, $+0.51$, seems to be too positive.

Proton-Affinity of Some Anions. The calculated values of the proton affinities of several anions and neutral molecules*4 are given in Table 9, together with the observed values. A detailed discussion will be reserved, since, unfortunately, few experimental values are available for comparison with the present results. From the values in the same table, it may be pointed out that the proton affinities of the anions are much larger than those of the neutral molecules with the lone-pair orbitals. In the present calculations, the following approximation is used17,18) (that is, the core-core repulsion energies are replaced by the Coulomb integrals between the valence s AO's of the atoms considered):*5

$$(1/r_{AB}=(s_A s_A \mid s_B s_B))$$

TABLE 9 THE CALCULATED VALUES OF THE PROTON AFFINITY OF SOME ANIONS

Compound	Calc.	Obs.
NCO^-	18.11	—
CH_3^-	17.52	—
CH_3O^-	16.68	—
NH_2^-	16.66	—
NO^-	15.90	—
HO^-	15.69	16.01—17.00a)
HOO^-	14.37	—
N_3^-	14.32	—
CN^-	13.27	—
H_2O	5.91	7.24—7.42b)
NH_3	7.65	7.55b)

a) R. Gaspar, I. Tamassy-Lenti and V. Kruglyak, *J. Chem. Phys.*, **36**, 740 (1962).

b) F. W. Lampe, J. L. Franklin and F. H. Field, "Progress in Reaction Kinetics," 1, Pergamon Press, (1961), p. 67.

The Shortest Transition Energy. The calculated singlet HO-LV transition energies (eV) for some ions are given in Table 10. Our calculated values are somewhat larger than the observed values, though the experimental values available for comparison are very few. A general trend observed in Table 10 is that the calculated values for the anions are larger than their ionization energies (cf. Table 3). These results suggest that the observations of the spectra in these anions are difficult due to the ionization. As to the cations, the transition energies are generally small, for example, HOO^+ and CN^+; moreover, OH^+, NCO^+ and N_3^+ especially may have triplet ground states, as is shown in Table 5. In the present treatment, the calculated excitation energies seem to be slightly larger, so that the improvement of this point will be necessary, as has been stated in a previous paper.9) This improvement will be published in the near future.19)

TABLE 10. THE TRANSITION ENERGIES OF SOME IONS (eV)

Ion	Calc.	Obs.
NO_2^-	4.05	3.50a)
NO_2^+	8.35	—
NO_3^-	8.52	6.26b)
CH_3O^-	12.35	—
NH_2^-	10.74	—
HO^-	9.19	—
N_3^-	8.47	—
HOO^-	5.80	—
CN^-	4.69	—
HOO^+	1.83	—
CN^+	1.67	—

a) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953).

b) R. P. Buck, S. Singhadeja and L. B. Rogers, *Annal. Chem.*, **26**, 1240 (1954).

The calculations have been carried out on the HITAC 5020 digital computer of the Computer Center of The University of Tokyo, to the staff of which the authors wish to give thanks.

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*4 The proton affinities, ΔW, in the $A+H^+ — AH^+$ process are calculated by the following equation:

$$\Delta W=W(A)-W(AH^+)$$

where $W(X)$ is the total energy of the X compound.

17) A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, **50**, 901 (1954).

18) G. Del Re and R. G. Rarr, *Rev. Mod. Phys.*, **35**, 604 (1963).

*5 If one calculates the $W(X)$ energy on the basis of the point charge interaction model for the core-core repulsion energy, the proton affinities of these compounds become too small.

19) H. Kato, H. Konishi and T. Yonezawa, This Bulletin, **40**, 1017 (1967).