Electronic Structures of the Oxocarbon Anions. III. Application of the Extended Hückel and Variable Electronegativity Extended Hückel Methods[1]

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The extended Hückel (EH) method with different basis functions and the variable electronegativity extended Hückel (VEEH) method are applied first to the calculation of the electronic structure of CO and then to that of three oxocarbon anions, $(C_4O_4)^{2-}$, $(C_5O_5)^{2-}$, and $(C_6O_6)^{2-}$. MO energies of CO calculated by both methods are closer to those computed by a non-empirical SCF method and also to observed values, compared with those obtained by the CNDO/1 method. It is also found for CO and the three anions that in the EH method the charge distributions are not dependent on the basis functions chosen and are much more localized on the oxygen atoms than in the VEEH method. The latter method yields a π-electron distribution which is close to that predicted by the variable electronegativity π-electron SCF method. The EH and VEEH methods predict reasonable values for the lower excitation energies of these oxocarbon anions; specifically the calculated $\sigma\rightarrow\pi^*$ excitation energy of $(C_4O_4)^{2-}$ agrees well with an observed value.

In previous papers,[3,4] the lower π-electronic states of three oxocarbon anions, $(C_4O_4)^{2-}$, $(C_5O_5)^{2-}$, and $(C_6O_6)^{2-}$, have been investigated by a Pariser-Parr-Pople type self-consistent field (PPP-SCF) method with configuration interaction including up to doubly excited configurations. The calculated lowest $\pi\rightarrow\pi^*$ transition energies for these anions were shown to be in good agreement with observed values. However, we have so far not referred to their σ-electronic structures, in other words we have assumed the sp^2 hybridized σ-skeletons for all anions. Recently, we observed a new absorption band of $(C_4O_4)^{2-}$ at 325 mμ with $\varepsilon=174$[5] and confirmed that this band is most probably due to an $n\rightarrow\pi^*$ transition.[6] Partly for explaining this theoretically and partly for elucidating the σ-structures of the anions, we feel the need of an all valence electron treatment not only for $(C_4O_4)^{2-}$ but for the series of oxocarbon anions.

For this purpose, we first take up the extended Hückel (EH) method.[7,8] As is well known, the method has many advantages but has some drawbacks also. Some disadvantages are: (1) in heteroatom-containing molecules, the resultant charge distribution becomes unrealistic, *i.e.* excess amounts of charge tend to concentrate on more electronegative centers; (2) the results for molecule ions are not good. To improve this, we first try to choose an appropriate basis set which is different from Slater orbitals ordinarily used. In so far as we know, such sort of attempts has not been made elsewhere.

Alternatively, several authors[9-12] have tried iterative methods in which matrix elements H_{pp} are assumed to be linear functions of a net atomic charge q_N or of both q_N and a total gross population in each AO (AO population).

Such iterative methods, however, do not always lead to satisfactory conclusions. For example, Carroll *et al.*[10] compared the usual EH calculation with the iterative one for small inorganic molecules and gave no definite answer to a question of which procedure was preferred. Duke[12] indicated, in the calculation of relatively small molecules, that a similar iterative method does not always lead to improvements in the wave functions but some better tendency is found for molecule ions.

In this paper, a somewhat different procedure is proposed for solving an iterative EH equation with the intention of improving the above-mentioned weak points of the usual EH treatment. In the method, tentatively called a variable electronegativity extended Hückel (VEEH) method, the valence state ionization potentials (VSIP) are taken to be quadratic functions of the effective nuclear charge Z_p, just like the case of the π-electron SCF treatment (VESCF for example). We first apply the method to a pilot molecule, CO, in order to see whether the calculated charge distribution is reasonable, then to the series of oxocarbon anions. Overall comparison of the EH method with different basis sets and the VEEH method will be made in regard to the electronic structures of the oxocarbon anion series together with that of carbon monoxide.

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2) Japan Society for the Promotion of Science Postdoctral Fellow.

3) K. Sakamoto and Y. J. I'Haya, *Theor. Chim. Acta*, **13**, 220 (1969), called Part I of this series.

4) K. Sakamoto and Y. J. I'Haya, *J. Amer. Chem. Soc.*, **92**, 2636 (1970), called Part II of this series.

5) K. Sakamoto, K. Ikegami, and Y. J. I'Haya, *Reports of the University of Electro-Communications*, **28**, 95 (1970).

6) Although Skujins and Webb observed a new absorption band at 3.99 eV with $\varepsilon=87$, they did not refer to its assignment; S. Skujins and G. A. Webb, *Spectrochim. Acta*, **25A**, 917 (1969).

7) M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

8) R. Hoffmann, *ibid.*, **39**, 1397 (1963); **40**, 2047, 2474, 2480, 2745 (1964).

9) L. C. Cusachs, *ibid.*, **43**, S157 (1965); L. C. Cusachs and J. W. Reynolds, *ibid.*, **43**, S160 (1965).

10) D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **44**, 1865 (1966); D. G. Carroll and S. P. McGlynn, *ibid.*, **45**, 3827 (1966).

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Method of Calculation

In the EH calculations, the following three basis sets are used for the sake of comparison: (a) Slater-type orbitals (STO) in which the orbital exponent ζ is determined by Slater's rule, (b) the free-atom-ζ single-ζ STO's,[13,14] (c) the free-atom-ζ double-ζ STO's.[13,15] Within the framework of the EH method, the diagonal matrix elements H_{pp} are chosen to be the negative of the VSIP, *i.e.* $H_{pp}=-I_p$. The values of I_p's are taken from Pritchard's paper[16] and are assumed to be constant throughout the whole calculation. The off diagonal matrix elements H_{pq} are assumed to take the form

$$H_{pq} = (K/2)(H_{pp}+H_{qq})S_{pq},\ K = 1.75 \qquad (1)$$

The reason for this is as follows. The alternative formula assumes $K=2-|S_{pq}|$, *i.e.*

$$H_{pq} = [(2-|S_{pq}|)/2](H_{pp}+H_{qq})S_{pq} \qquad (2)$$

and both Eqs. (1) and (2) have been used successfully.[8,9] To check which formula is more favorable, both equations are applied to preliminary calculations of the oxocarbon anions. In Tables 1 and 2 are illustrated the results for $(C_4O_4)^{2-}$ obtained when the free-atom-ζ single-ζ basis set is used. As these tables show, the electronic distributions and excitation energies are not very much dependent on the assumption of which formula is used. Similar results are obtained for other oxocarbon anions. Therefore, Eq. (1) is chosen hereafter in this paper only for its simpler form.

In the VEEH method, the values of the matrix elements are modified by new Z_p's at each stage of the iteration process. The values of Z_p for $2s$ and $2p$ valence orbitals of carbon and oxygen are determined by

$$Z_p = N_x - 1.35 - 0.35M_x \qquad (3)$$

where N_x stands for the atomic number of atom x contributing pth orbital, and M_x is the atomic population of atom x determined by Mulliken's population analysis.[17] A new M_x is estimated from the previous one, M_x*, by the following equation[18]

$$M_{x\ \mathrm{input}} = M^*_{x\ \mathrm{input}} - \lambda(M^*_{x\ \mathrm{input}} - M^*_{x\ \mathrm{output}}) \qquad (4)$$

with a constant λ, the steepest decent parameter, which value is taken to be 0.1 in this paper. Being assumed the quadratic dependence on Z_p, the VSIP's for $2s$ and $2p$ orbitals of carbon and oxygen are obtained as shown in Table 3. These quadratic formulae are determined from atomic spectroscopic data[16,19-23] for the corresponding iso-electronic series by least squares method, as usual. The whole iteration process is continued until the total gross atomic population (atomic population) remains constant within the limits of 0.01. Such convergence was obtained by fifteen iterations, on the average. The computations used a double precision (18 places) routine.[24]

TABLE 1. AO POPULATION OF $(C_4O_4)^{2-}$ BY DIFFERENT PARAMETER K IN EH METHOD WITH BASIS SET (b)[a]

Atom	AO	$K=1.75$	$K=2-\lvert S_{pq}\rvert$
C	$2s$	1.01	0.99
	$2p_x$	0.74	0.75
	$2p_y$	0.74	0.75
	$2p_z$	0.61	0.62
O	$2s$	1.78	1.83
	$2p_x$	1.87	1.84
	$2p_y$	1.87	1.84
	$2p_z$	1.89	1.88

a) See the text.

TABLE 2. LOWEST EXCITATION ENERGIES OF $(C_4O_4)^{2-}$ BY DIFFERENT PARAMETER K IN EH METHOD CALCULATED WITH BASIS SET (b)[a]

Transition	$K=1.75$	$K=2-\lvert S_{pq}\rvert$
$\pi\rightarrow\pi^*$	4.16	4.38
$\sigma\rightarrow\pi^*$	3.53	3.63
$\sigma\rightarrow\sigma^*$	20.52	19.08

a) See the text.

TABLE 3. Z_p DEPENDENCE OF IONIZATION POTENTIAL I_p[a]

Iso-electronic Series and Atomic Valence State	AO	a_0	a_1	a_2
C: $(B^-,C,N^+,O^{+2},F^{+3})$	$2s$	3.5563	−5.8864	2.6669
$(2s)\ (2p)\ (2p)\ (2p)$	$2p$	3.3668	−7.6466	0.5758
O: $(N^-,O,F^+,Ne^{+2},Na^{+3})$[b]	$2s$	3.4060	−6.9846	−4.2390
$(2s)\ (2p)^2\ (2p)^2\ \underline{(2p)}$	$2p$	0.1055	15.2424	−53.8253

a) $I_p=a_0Z_p^2+a_1Z_p+a_2$.
b) I_p of the underlined $2p$ orbital.

Both EH and VEEH methods are first applied to a pilot molecule, CO, to examine which procedure is more preferable in regard to the prediction of the electronic states of heteroconjugated molecules. Afterwards we apply the methods to the three oxocarbon anions whose bond lengths are given in the previous paper.[4]

Results and Discussion

The calculated MO energies of CO are listed in Table 4. For comparison, the results obtained by the

13) The terminology is shown in Mulliken's paper; *Rev. Mod. Phys.*, **32**, 232 (1960).
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24) The calculations were carried out using a HITAC 5020E computer at the computer center of the University of Tokyo.

Table 4. Orbital energies of CO calculated by various methods (eV)[a]

MO's and their symmetry	EH			VEEH	Non-empirical[c]	CNDO/1[d]	observed[e]
	basis (a)	basis (b)	basis (c)[b]				
6σ (a_1)	44.11	49.64	46.21	43.83	23.47	13.64	
2π (e_1)	−9.37	−9.13	−7.94	−10.27	6.12	5.38	
5σ (a_1)[f]	−14.68	−14.52	−13.19	−14.82	−13.74	−17.35	−14.01
1π (e_1)	−18.27	−18.32	−18.52	−17.10	−16.61	−20.87	−16.51
4σ (a_1)	−20.66	−20.72	−21.23	−20.44	−20.66	−24.67	−19.72
3σ (a_1)	−37.21	−37.26	−37.29	−34.93	−41.76	−45.44	

a) The observed bond length (1.128 Å) is used (D. B .Neumann and J. W. Moskowitz, *J. Chem. Phys.*, **50**, 2216 (1969)).
b) See the text.
c) Ref. 26.
d) Ref. 25.
e) Ref. 27.
f) The highest occupied MO.

Table 5. AO and atomic populations of CO calculated by various methods

			EH			VEEH	Non-empirical[b]	CNDO/1[c]
			basis (a)	basis (b)	basis (c)[a]			
AO-population	C	$2s$	1.44	1.43	1.37	1.47	1.66	1.70
		$2p_\sigma$	1.09	1.10	1.17	1.20	0.93	1.09
		$2p_\pi$	0.24	0.26	0.33	0.51	0.62	0.62
	O	$2s$	1.71	1.70	1.69	1.63	1.86	1.70
		$2p_\sigma$	1.77	1.77	1.77	1.69	1.54	1.51
		$2p_\pi$	1.76	1.74	1.67	1.49	1.38	1.38
Atomic population	C		3.00	3.04	3.19	3.69	3.83	4.03
	O		7.00	6.96	6.81	6.31	6.17	5.97

a) See the text.
b), c) See footnotes c and d of Table 4.

CNDO/1[25] and a non-empirical LCAO-SCF[26] are included. The occupied MO energies calculated by the EH and the VEEH methods are rather close to those computed by the non-empirical SCF method, and also to observed values,[27] compared with those of the CNDO/1 calculation.

The AO population and the atomic population of CO calculated by various methods are compared in Table 5. The charge tends to delocalize in going from basis (a) to basis (c) in the EH method. When the VEEH approximation is applied the charge distribution gets closer to that calculated by the non-empirical SCF method. The dipole moments of CO, including the atomic polarization term,[25] are calculated to be 2.86, 2.58, and 1.59 Debyes, respectively, for three basis sets (a), (b), and (c) in the EH method, all in the sense of C^+O^- polarity. On the other hand, the VEEH method yields a dipole moment 0.22 Debye, the polarity being C^-O^+. This explains well the observed sign and magnitude of the dipole moment of CO.[28] From the above, the following points are noteworthy. (1) The MO energies and charge distributions produced by the VEEH approach are pretty close to those obtained by a non-empirical SCF calculation, and the calculated dipole moment is in accord with the observed value. (2) In the EH method, the charge distributions and orbital energies are hardly influenced by suitable choices of basis functions.

In Table 6 are shown the calculated orbital energies and their symmetries of three oxocarbon anions, $(C_4O_4)^{2-}$, $(C_5O_5)^{2-}$, and $(C_6O_6)^{2-}$. Only the results obtained by the EH method with basis (a) are listed, since the data for those calculated with bases (b) and (c) and also by the VEEH method are not very much different from the entries in Table 6. In particular, in the EH calculation the energies of the occupied MO's

Table 6. Orbital energies calculated from EH method with STO basis set (eV)[a]

$(C_4O_4)^{2-}$		$(C_5O_5)^{2-}$		$(C_6O_6)^{2-}$	
Energy	Symmetry	Energy	Symmetry	Energy	Symmetry
15.04	e_u	9.74	a_2'	7.80	e_{1u}
5.30	a_{2g}	9.08	e_1'	−4.14*	b_{2g}
−4.67*	b_{1u}	−5.60*	e_2''	−7.38*	e_{2u}
−9.45*	e_g	−10.79*	e_1''	−11.55*	e_{1g}
−12.86†	b_{1g}	−13.15†	e_2'	−12.78†	a_{2g}
−13.26*	a_{2u}	−13.23*	a_2''	−13.17*	a_{2u}
−14.94	e_u	−16.24	e_1'	−14.00	e_{2g}
−17.88	a_{1g}	−17.77	a_2'	−16.88	e_{1u}

a) Asterisk denotes π-MO's and others correspond to σ-MO's. Dagger denotes the highest occupied MO's.

25) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segel, *ibid.*, **43**, S136 (1965).
26) H. Brion and C. Moser, *ibid.*, **32**, 1194 (1960).
27) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.
28) B. Rosenblum and A. H. Nethercot, Jr., *J. Chem. Phys.*, **27**, 828 (1957).

are not affected so much by the starting basis functions, just as in the case of CO. In both EH and VEEH calculations, it is found that each highest occupied MO of the anions is made up of a linear combination of $2p_x$ and $2p_y$ AO's centered on all the carbon and oxygen atoms and does not contain a $2s$ character.[29] Therefore these highest occupied MO's are characterized to be not a so-called lone-pair orbital but a σ-type orbital. Furthermore, it is found that the charge flows from oxygen to carbon in the EH method, while in the VEEH method the situation is reverse and the degree of delocalization increases. On the other hand, the second highest occupied and the lowest and the second lowest vacant MO's are all clearly specified to be of pure π-characters.[30]

TABLE 7. LOWER EXCITATION ENERGY FOR OXOCARBON ANIONS (eV)

Molecule	Transition	EH basis (a)	EH basis (b)	EH basis (c)[a]	VEEH	Obsd.
$(C_4O_4)^{2-}$	$\pi\rightarrow\pi^*$ E_u	3.81	4.16	5.19	2.41	4.60
	E_u	8.59	9.62	11.85	6.72	
	$\sigma\rightarrow\pi^*$ E_g	3.41	3.53	3.44	2.18	3.81[b]
	A_{1u}	8.19	8.99	10.10	6.49	
	$\sigma\rightarrow\sigma^*$ B_{2g}	18.16	20.52	21.76	16.12	
	E_u	27.90	31.60	32.05	23.80	
$(C_5O_5)^{2-}$	$\pi\rightarrow\pi^*$ E_1'	2.45	2.67	3.44	1.39	3.40
	E_2'	7.63	8.52	10.55	5.85	
	$\sigma\rightarrow\pi^*$ E_1''	2.37	2.30	1.70	1.28	
	E_1''	7.55	8.15	8.81	5.75	
	$\sigma\rightarrow\sigma^*$ E_1'	22.23	24.80	26.19	19.16	
$(C_6O_6)^{2-}$	$\pi\rightarrow\pi^*$ E_{1u}	1.62	1.76	2.35	0.82	2.56
	E_{2g}	5.79	6.40	8.02	4.11	
	$\sigma\rightarrow\pi^*$ E_{1g}	1.24	1.07	0.27	0.69	
	E_{2u}	5.40	5.71	1.53	3.97	
	$\sigma\rightarrow\sigma^*$ E_{1u}	20.58	22.85	24.53	18.35	

a) See the text.
b) Ref. 5.

The lower excitation energies for the anions, being assumed to be orbital energy differences, are given in Table 7. The $\sigma\rightarrow\pi^*$ excitation energy of $(C_4O_4)^{2-}$, 3.41 eV, which corresponds to an electron excitation from the highest occupied (σ-type) to the lowest vacant (π-type) orbital, is in good accord with our observed value, 3.81 eV.[5] The overall agreement with the experimental $\pi\rightarrow\pi^*$ excitation energies is fairly good in the EH treatment; specifically the method with the use of basis (c) is the best.

As for the VEEH treatment, the calculated $\pi\rightarrow\pi^*$ and $\sigma\rightarrow\pi^*$ excitation energies of $(C_4O_4)^{2-}$ are qualitatively consistent with the experimental conclusion that the $\pi\rightarrow\pi^*$ excitation energy is larger than the $\sigma\rightarrow\pi^*$ one. However, the $\pi\rightarrow\pi^*$ excitation energies predicted by the VEEH method for other anions are too low to be compared with the corresponding observed values. This can not be understood at present, but will be improved by the inclusion of electronic repulsion.[31]

TABLE 8. AO POPULATION FOR OXOCARBON ANIONS

Molecule	Atom	AO	EH basis (a)	EH basis (b)	EH basis (c)[a]	VEEH	PPP–VESCF[b]
$(C_4O_4)^{2-}$	C	$2s$	1.02	1.01	0.98	1.11	
		$2p_\sigma$	1.47	1.48	1.52	1.67	
		$2p_\pi$	0.62	0.61	0.65	0.92	0.94
	O	$2s$	1.79	1.78	1.77	1.67	
		$2p_\sigma$	3.72	3.73	3.73	3.54	
		$2p_\pi$	1.90	1.89	1.85	1.58	1.56
$(C_5O_5)^{2-}$	C	$2s$	1.03	1.03	0.99	1.12	
		$2p_\sigma$	1.44	1.45	1.50	1.65	
		$2p_\pi$	0.51	0.52	0.57	0.91	0.93[c]
	O	$2s$	1.79	1.78	1.77	1.67	
		$2p_\sigma$	3.73	3.74	3.74	3.56	
		$2p_\pi$	1.89	1.88	1.83	1.49	1.47[c]
$(C_6O_6)^{2-}$	C	$2s$	1.03	1.03	1.00	1.11	
		$2p_\sigma$	1.43	1.44	1.48	1.64	
		$2p_\pi$	0.46	0.47	0.51	0.91	0.92
	O	$2s$	1.79	1.78	1.77	1.68	
		$2p_\sigma$	3.74	3.75	3.75	3.57	
		$2p_\pi$	1.88	1.87	1.82	1.43	1.41

a) See the text.
b) Under the approximation of Pariser-Parr equation for two-center electronic repulsion integral and of including all the terms for resonance integral.
c) Ref. 3.

The results of the AO population analysis are given in Table 8. The overall charge distribution obtained by the EH method is not very much dependent on starting basis functions as before. Comparing the VEEH method with the EH method, the former yields more delocalized picture for electrons than the latter does. Furthermore, the former computes the π-type AO populations (indicated as $2p_\pi$ in Table 8) very close to the π-electron densities calculated by a Pariser-Parr type π-electron approximation (see the last column

TABLE 9. ATOMIC BOND POPULATION FOR OXOCARBON ANIONS AND CARBON MONOXIDE

Molecule	Bond	EH basis (a)	EH basis (b)	EH basis (c)[a]	VEEH
$(C_4O_4)^{2-}$	C–C	0.93	0.95	0.96	0.87
	C–O	0.64	0.65	0.65	0.94
$(C_5O_5)^{2-}$	C–C	0.94	0.96	0.98	0.90
	C–O	0.65	0.67	0.68	0.95
$(C_6O_6)^{2-}$	C–C	0.91	0.93	0.94	0.90
	C–O	0.66	0.68	0.70	0.96
CO	C–O	1.11	1.15	1.24	1.44

a) See the text.

29) The highest occupied MO of $(C_5O_5)^{2-}$ contains a small amount of $2s$ component.

30) That is, σ-MO's levels are embedded between π-MO's levels. Indeed, such a behavior is noted for many aromatic substances, for example benzene.[8]

31) A study on the electronic structures of the same anion series by means of a semi-empirical VESCF method including all valence electrons has just been completed and will be submitted for publication in the future.

of Table 8). The effective σ-type AO populations, that is, ratios of the $2s$ and $2p_\sigma$ AO populations, do not change from anion to anion and from method to method, and are approximately $2s^{1.0}\ 2p_\sigma^{1.5}$ for the carbon atom and $2s^{1.0}\ 2p_\sigma^{2.0}$ for the oxygen atom.

In Table 9 are presented the results of the atomic bond population analysis for the three anions and CO. It is found that the atomic bond population for CO is always larger than those for the C–O bonds of the anions, irrespective of the method of calculation. This is consistent with the observed fact that the bond length in CO (1.128 Å) is shorter than any C–O bond length in the three anions (1.259—1.262 Å).

The values of VSIP's produced at the final stage of iteration in the VEEH method are considerably different from the constant values used in the EH method. For example, with regard to the carbon atom of $(C_4O_4)^{2-}$, the quantity obtained from the VEEH method is greater than that used in the EH method, by 1.7 eV for $2s$ AO's and by 1.5 eV for $2p$ AO's. As for the oxygen atom, the former is less than the latter, the differences being 6.5 and 4.0 eV for $2s$ and $2p$ AO's, respectively. A similar conclusion is also obtained in other two anions.