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Localized Molecular Orbitals for CO_2 and CO_3^{2-}. A Comparison of Localization Types and a Comment on Isoelectronic Structures

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Abstract: Four sets of localized molecular orbitals are reported for carbon dioxide and the carbonate ion: orbitals found using the criterion of Edmiston and Ruedenberg, the criterion of Boys, and both criteria with an imposed σ–π separation. Although the wave functions which were used were obtained at the minimum basis set level, all but one of the localizations show six (fractional) LMO's associated with carbon. The exception is the complete ER localization for CO_2, for which either four or eight (fractional) LMO's are associated with carbon, depending on the criterion used for including a center as a principal contributor to an LMO. A compact notation for describing LMO structures is presented. The localization results are compared with isoelectronic structures, including those containing bridge bonds.

It has long been known[2] that the delocalized canonical molecular orbitals (CMO's) of molecular orbital theory could be transformed into more localized sets without changing the total wave function. In some cases at least, the localized molecular orbitals correspond to the electron pairs of the Lewis[3] theory. It was also recognized[4] that in highly conjugated systems difficulties might arise; the localized molecular orbitals (LMO's) might be ill-defined, might be inherently delocalized, or might give results at odds with chemical intuition.

While considerable attention has been paid to LMO patterns in the aromatic compounds[5] in organic chemistry and the boron hydrides and the related carboranes[6] in inorganic chemistry, relatively little attention has been paid to the LMO description of simple molecules which are resonance stabilized. Difficulties are anticipated in the interpretation of LMO structures of resonance stabilized molecules because there is no single valence bond structure to which the LMO structure is expected to correspond. Here we present the LMO description of CO_2 and the CO_3^{2-} ion and investigate the interpretation in the adjacent paper.[7]

The Edmiston-Ruedenberg[8] (ER) and Boys[9] criteria for localization are two of the most widely used localization criteria. It was felt that these two methods might handle the resonance problem in CO_2 and CO_3^{2-} differently, as was found to be the case. The ER and Boys criteria have previously been compared in their application to various small molecules,[10] where resonance problems were not expected to be particularly great, and for a number of electron deficient compounds.[6b,d] The ER and Boys criteria tend to treat the mixing of σ and π orbitals differently; the latter criterion usually mixes σ and π orbitals to produce bent or τ bonds, while the former occasionally fails to mix σ and π orbitals.[6b,11]

Localizations may be carried out on selected subsets of the MO's, if desired. When programmed efficiently, computation times for the ER and Boys localizations go as N^5 and N^3, respectively, where N is the number of MO's to be localized.[6b] The expedient of omitting inner shells and dividing the CMO's into σ and π sets which are localized separately is therefore an attractive one, although the imposition of a σ–π separation may lead to a different localization than would otherwise have been obtained.[12] We term a localization using all occupied orbitals a complete localization and a localization performed on σ and π MO's separately a σ–π localization. Since resonance in CO_2 and CO_3^{2-} is primarily a feature of the π system, the localization of σ and π orbitals separately offers a way to examine systems which have inherently delocalized orbitals. Moreover, since the ER and Boys criteria treat the problem of σ–π separation differently, it is of interest to compare the ER and Boys LMO's when σ–π separation is imposed.

Methods

Molecular wave functions were generated by Stevens' ab initio program[13] using minimum basis sets of Slater-type orbitals and by the PRDDO method.[14] The latter is an efficient approximate SCF method which is comparable in accuracy to minimum basis set ab initio calculations.[14,15] Slater exponents were used in all cases, and experimental geometries[16] have been employed.

The implementation of the ER and Boys criteria has been reviewed.[6b,17] The ER criterion requires that the LMO's maximize the self-repulsion energy,

$$J = \sum_i \langle \phi_i\phi_i | 1/r_{12} | \phi_i\phi_i \rangle \qquad (1)$$

whereas the Boys criterion requires that the LMO's minimize the orbital self-extension

$$I = \sum_i \langle \phi_i\phi_i | r_{12}^2 | \phi_i\phi_i \rangle \qquad (2)$$

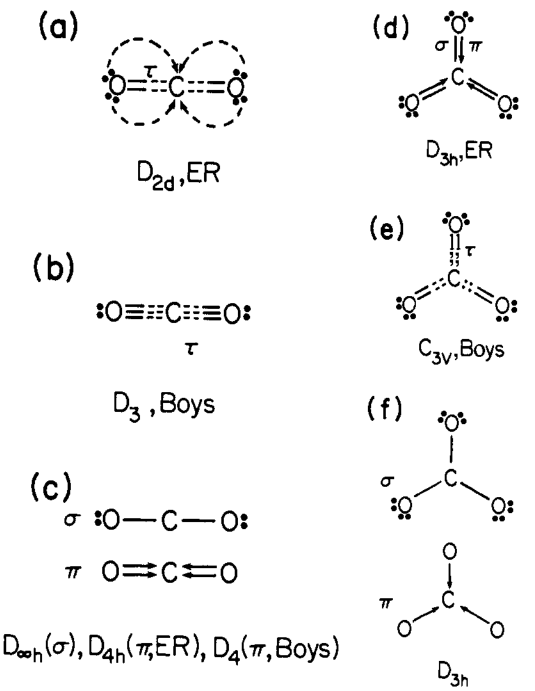


Figure 1. Edmiston-Ruedenberg and Boys localized molecular orbital structures for CO_2 and CO_3^{2-}; (a) and (d), ER localizations; (b) and (e), Boys localizations; (c) and (f), ER or Boys localizations with imposed σ-π separation. The symmetry of the set of the LMO's is indicated. See Table III for the line notation.

or, equivalently, maximize the sum of squares (SOS) of distances of the orbital centroids from an arbitrarily defined origin:

$$\mathrm{SOS} = \sum_i [\langle \phi_i | \vec{r} | \phi_i \rangle]^2 \tag{3}$$

Maximization of the SOS also ensures that the sum of squared intercentroid distances is maximized.[6b]

All four types of localization (i.e., complete ER, complete Boys, σ-π ER, and σ-π Boys) are reported here for CO_2 and CO_3^{2-}. For convenience, the ER localizations employ ab initio wave functions, and the Boys localizations utilize PRDDO wave functions. Several direct comparisons of ab-initio-ER with PRDDO-ER localizations and of ab-initio-Boys with PRDDO-Boys localizations for CO_2 and CO_3^{2-} have shown that the differences in the localizations are to be attributed to differences in the localization criteria rather than to differences in the starting wave functions.

Carbon Dioxide. The CMO's of carbon dioxide transform according to the irreducible representations of the $D_{\infty h}$ point group and are quite delocalized in the sense that ten of the eleven occupied CMO's extend the length of the molecule. Apart from the carbon inner shell, which is essentially localized already, six occupied CMO's have significant contributions from the carbon atomic orbitals. All of the CMO centroids necessarily lie on the central carbon. Table I lists the CMO eigenvalues and symmetry types, and Table II summarizes the results for the four types of localization. These results are also displayed in Figure 1 using a notation (Table III) developed for depicting relative contributions to two- and three-center LMO's (cf. ref 6c). The symbolism is compact, and no additional (e.g., resonance) structures need be written.

The LMO structure from the complete ER localization (Figure 1) superficially resembles one of the equivalent Lewis double-bond structures for CO_2.[18] In addition to the expected inner-shell orbitals on carbon and oxygen, each oxygen possesses two lone-pair orbitals (Figure 2a) and is connected to carbon via two bent, or τ, bond orbitals (Figure 2b). The double-bond and lone-pair orbitals to a given oxygen define mutually perpendicular planes, and the two sets of double bond orbitals also define perpendicular planes. The τ bonds are quite polar, the Mulliken populations[19] on oxygen and carbon being 1.26 and 0.74 e, respectively. In addition, the lone pairs have significant delocalized tails which cause the lone-pair orbitals to lean into the space between the atomic centers (Figure 2a). A Mulliken population analysis assigns 1.79 and 0.18 e to oxygen and carbon, respectively, in each lone pair. This delocalization of the ER lone pairs is, of course, required to preserve the cylindrical symmetry of the molecular charge distribution.

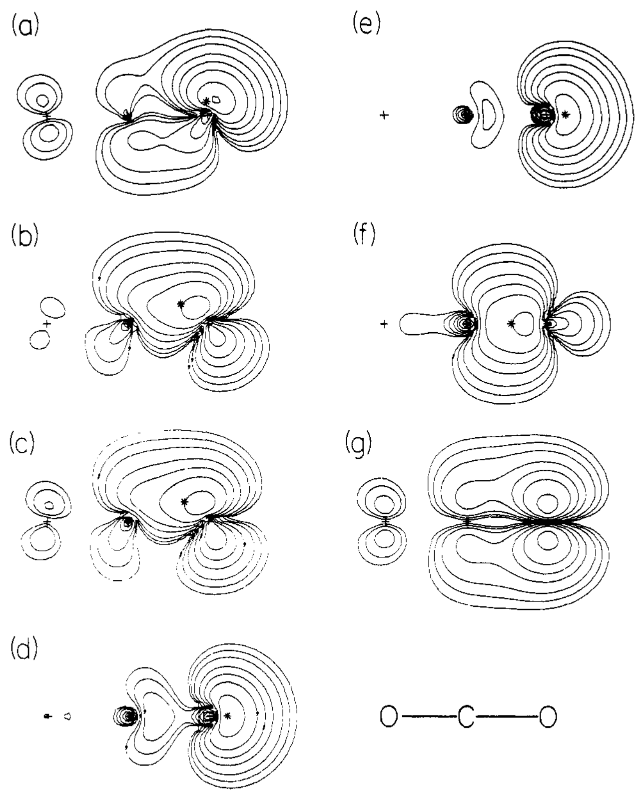


Figure 2. CO_2 LMO's. Crosses mark atomic centers; asterisks mark LMO centroids. Contour levels are 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 e/au^3 with two electrons in each LMO. The stick figure shows internuclear distances appropriate to all figure parts. See text for a description of these LMO's.

Table I. CO_2 Orbital Eigenvalues (au) and Symmetry Types

	Ab initio SCF	PRDDO SCF
	$-20.607\ 07\ A_{2u}$	$-20.597\ 09\ A_{1g}$
	$-20.606\ 72\ A_{1g}$	$-20.596\ 02\ A_{2u}$
	$-11.501\ 70\ A_{1g}$	$-11.510\ 20\ A_{1g}$
	$-1.470\ 04\ A_{1g}$	$-1.462\ 17\ A_{1g}$
	$-1.402\ 70\ A_{2u}$	$-1.399\ 62\ A_{2u}$
	$-0.689\ 43\ A_{1g}$	$-0.699\ 16\ A_{1g}$
	$-0.655\ 63$ } E_{1u}	$-0.663\ 21$ } E_{1u}
	$-0.655\ 63$	$-0.663\ 21$
	$-0.597\ 21\ A_{2u}$	$-0.589\ 21\ A_{2u}$
	$-0.399\ 07$ } E_g	$-0.405\ 79$ } E_g
	$-0.399\ 07$[a]	$-0.405\ 79$[a]
	$+0.304\ 75$[b] } E_{1u}	$+0.298\ 43$[b] } E_{1u}
	$+0.304\ 75$	$+0.298\ 43$
	$+0.502\ 25\ A_{1g}$	$+0.489\ 20\ A_{1g}$
	$+1.337\ 05\ A_{2u}$	$+1.363\ 07\ A_{2u}$
E_{SCF}	$-186.867\ 33$ au	$-186.872\ 99$ au

[a] Highest occupied molecular orbital. [b] Lowest unoccupied molecular orbital.

Table II. Localized Orbitals for CO_2

LMO	Mulliken pop.	% s character	Bond angle dev, deg[b]	% d[c]
Complete ER localization				
O inner shell (2)[a]	2.00	100		1
C inner shell (1)	2.00	100		4
O lone pair (4)	1.79	50		25
CO τ bond orbital (4)	1.26 (O)	9	60	7
Complete Boys localization	0.74 (C)	31	51	
O inner shell (2)				
C inner shell (1)	2.00	100		1
O lone pair (2)	2.00	100		2
	2.00	75		23
CO τ bond orbital (6)	1.37 (O)	9	69	11
σ–π ER localization	0.61 (C)	23	61	
O lone pair (2)				
	2.04	79		20
CO σ bond orbital (2)	1.05 (O)	30	0	3
	0.95 (C)	53	0	
CO π bond orbital (4)	1.51 (O)	0	90	13
σ–π Boys localization	0.46 (C)	0	90	
O lone pair (2)				
	2.07	82		17
CO σ bond orbital (2)	1.04 (O)	20	0	4
	0.96 (C)	57	0	
CO π bond orbital (4)	1.51 (O)	0	90	13
	0.47 (C)	0	90	

[a] Number of equivalent LMO's. [b] Angle between hybrid atomic orbital in center a and the a–b internuclear axis. [c] Percent delocalization (cf. ref 11).

Table III. Mulliken Atomic Populations on Center A in Two- and Three-Center LMO's

Symbol[a]	Two-center LMO's	Three-center LMO's
⟶ A	0.15–0.25	0.15–0.25
⟶ A	0.25–0.50	0.25–0.35
‐‐‐‐ A	0.50–0.75	0.35–0.50
—— A	≥0.75	≥0.50

[a] The line symbol is drawn from the LMO centroid to atom A.

Table IV. CO_3^{2-} Orbital Eigenvalues (au) and Symmetry Types

Ab initio SCF		PRDDO SCF	
−19.566 67	A_1'	−19.558 06	A_1'
−19.566 64	E'	−19.557 80	E'
−19.566 64		−19.557 79	
−10.641 67	A_1'	−10.655 26	A_1'
−0.657 83	A_1'	−0.655 86	A_1'
−0.500 95	E'	−0.512 93	E'
−0.500 95		−0.512 92	
+0.049 84	A_1'	+0.049 28	A_1'
+0.118 34	A_2''	+0.099 29	A_2''
+0.148 01	E'	0.152 95	E'
+0.148 01		+0.152 95	
0.383 51	E'	+0.376 49	E'
+0.383 51		+0.376 49	
+0.389 76	A_2'	+0.381 20	A_2'
+0.405 44	E''	+0.400 43	E''
+0.405 44[a]		+0.400 43[a]	
+1.033 77[b]	A_2''	+1.024 96[b]	A_2''
+1.428 36	A_1'	+1.422 26	A_1'
+1.610 49	E'	+1.609 71	E'
+1.610 49		+1.609 72	
E_{SCF} = −260.773 59 au		−260.810 55 au	

[a] Highest occupied molecular orbital. [b] Lowest unoccupied molecular orbital.

Both the shape of the lone pair (Figure 2a) and the nonnegligible (0.18 e) Mulliken population on carbon suggest that this "lone pair" could be classified as a very polar two-center LMO.

The results for the complete Boys localization (Figure 1) are quite different and rather unorthodox from the standpoint of the Lewis theory. Each oxygen has a single lone pair directed along the internuclear axis (Figure 2d) and is connected to carbon by three bent (τ) bond orbitals (Figure 2c). The latter have Mulliken populations of 1.37 and 0.61 e on oxygen and carbon, respectively. The two sets of τ orbitals are not correlated (i.e., no relative orientation such as staggered or eclipsed is preferred), for the SOS (eq 3) is invariant to any unitary transformation which simply results in a rotation of the τ-orbital centroids about the internuclear axis. The sum of the τ-orbital densities is, of course, cylindrically symmetric. Interestingly, the ER and Boys τ-bond orbitals for CO_2 (Figures 2b and 2c) are quite similar in appearance, even though there are four of the former and six of the latter.

The ER and Boys σ–π localizations are similar to one another (Table II). Each, however, is quite different from either of the complete localizations, though the axial lone-pair orbitals do closely resemble the lone-pair orbitals obtained in the complete Boys localization. There is one significant difference between the ER and Boys σ–π localizations: in the former the two sets of π-bond orbitals are eclipsed, in the latter the two sets of π bonds are not correlated (cf. the complete Boys localization). The π orbitals are quite polar, but the σ LMO's are essentially nonpolar. Figures 2e, 2f, and 2g show the σ–π Boys results for a lone pair, a σ LMO, and a π LMO, respectively.

Carbonate Ion. The CMO's of CO_3^{2-} transform according to the irreducible representations of the D_{3h} point group. The centroids for six of the occupied CMO's reside at the molecular center, while those for the five pairs of occupied E orbitals are symmetrically disposed about the center. Eight of the occupied CMO's, including the carbon inner-shell CMO, have large contributions from the carbon atomic orbitals. The eigenvalues and symmetry types for the CMO's are listed in Table IV.

Table V. Localized Orbitals for CO_3^{2-}

LMO	Mulliken pop.	% s character	Bond angle dev, deg[b]	% d[c]
Complete ER localization				
O inner shell (3)[a]	2.00	100		1
C inner shell (1)	2.00	100		4
O lone pair (6)	1.95	37		13
CO σ bond orbital (3)	1.01 (C)	43	6	9
	1.00 (O)	5	10	
CO π bond orbital (3)	1.71 (O)	26	81	12
	0.26 (C)	0	90	
Complete Boys localization				
O inner shell (3)	2.00	100		0
C inner shell (1)	2.00	100		2
O lone pair (6)	1.98	43		13
CO τ bond orbitals (6)	1.33 (O)	7	60	12
	0.66 (C)	32	42	
σ–π ER localization				
O lone pair (6)	1.99	46		11
CO σ bond orbital (3)	1.02 (C)	43	0	9
	0.99 (O)	10	0	
CO π bond orbital (3)	1.63 (O)	0	90	13
	0.34 (C)	0	90	
σ–π Boys localization				
O lone pair (6)	1.99	46		10
CO σ bond orbital (3)	1.02 (O)	10	0	10
	0.98 (C)	46	0	
CO π bond orbital (3)	1.62 (O)	0	90	14
	0.35 (C)	0	90	

[a] Number of equivalent LMO's. [b] See footnote b in Table II. [c] Percent delocalization (cf. ref 11).

Table VI. CO_2 LMO Coefficients over Slater Atomic Orbitals

Atomic orbital	Localization and orbital						
	Complete ER		Complete Boys		σ–π Boys		
	Lone pair	Bond pair	Lone pair	Bond pair	Lone pair	σ bond pair	π bond pair
C1s	−0.016 91	0.048 16	0.049 25	0.056 46	0.034 35	0.109 16	0.0
C2s	0.173 88	−0.273 28	−0.282 15	−0.215 34	−0.225 77	−0.409 72	0.0
C2p$_z$	0.106 09	−0.254 51	−0.178 81	−0.188 28	−0.125 98	−0.350 08	0.0
C2p$_x$	0.217 95	0.184 22	0.0	0.314 58	0.0	0.0	0.086 32
C2p$_y$	−0.162 53	0.247 14	0.000 01	0.118 55	0.0	0.0	0.402 58
O1s	0.062 87	0.041 12	−0.154 71	0.053 41	−0.164 25	0.077 35	0.0
O2s	−0.682 24	−0.215 13	0.937 24	−0.231 29	0.986 48	−0.256 69	0.0
O2p$_z$	−0.339 19	0.337 82	0.524 62	0.251 25	0.453 38	0.508 97	0.0
O2p$_x$	0.470 65	0.341 10	0.0	0.626 32	0.0	0.0	0.171 87
O2p$_y$	−0.350 96	0.457 61	0.000 01	0.236 03	0.0	0.0	0.801 52
O1s	0.002 49	−0.002 70	−0.007 17	−0.003 77	−0.005 63	−0.007 11	0.0
O2s	−0.015 21	−0.013 02	0.028 85	0.000 19	0.026 90	−0.001 42	0.0
O2p$_z$	−0.029 83	0.026 35	0.053 81	0.022 54	0.044 28	0.049 30	0.0
O2p$_x$	−0.132 43	−0.055 23	0.0	−0.139 82	0.0	0.0	−0.038 37
O2p$_y$	0.098 74	−0.074 09	0.0	−0.052 69	0.0	0.0	−0.178 93

The complete ER localization (Figure 1d) yields four inner shells, two lone-pair orbitals on each oxygen (Figure 3a,b), three C-O σ-bond orbitals (Figure 3c), and three polar C-O π-bond orbitals (Figure 3d). The Mulliken charge on oxygen, −0.65 e (PRDDO value), closely matches the charge of $-2/3$ e predicted by simple valence-bond treatments.[20] Despite the terminology, however, the "π-bond orbitals" have little more population on carbon (0.26 e) than that found for the complete ER "lone pairs" in CO_2 (0.18 e). The LMO populations and other localization results are summarized in Table V.

Surprisingly, the ER LMO centroids show only C_{3v} symmetry, even though the total electron density has, of course, D_{3h} symmetry. Thus, the centroids for the lone pairs (Figure 3b) and localized σ orbitals (Figure 3c) lie to one side of the molecular plane, while those for the π orbitals (Figure 3d) are displaced compensatingly toward the other side. As a result, the ER localized structure is intermediate between a description having a polar π bond and two lone pairs on each oxygen and a description having three lone pairs on each oxygen. In some respects, the distortion of the ER LMO's in the carbonate ion parallels that of the ER LMO's found in planar NH_3.[21]

The complete Boys localization also yields four inner-shell orbitals and two lone-pair orbitals on each oxygen (Figure 3e). However, there are now two equivalent bent (τ) bond orbitals to carbon from each oxygen (Figure 3f), rather than a σ–π pair. As might be expected, the six LMO's have much larger populations on oxygen (1.33 e) than on carbon (0.66 e).

The ER and Boys σ–π localizations are very similar to one another. Table V summarizes the results, and Figures 3g, 3h, and 3i show a σ–π localized Boys lone pair, σ orbital, and polar π orbital, respectively. Both localizations clearly reflect the D_{3h} symmetry, as does the complete Boys localization.

Table VII. CO_3^{2-} LMO Coefficients over Slater Atomic Orbitals

Atomic orbital	Localization and orbital							
	Complete ER			Complete Boys		σ–π Boys		
	Lone pair	σ bond pair	π bond pair	Lone pair	Bond pair	Lone pair	σ bond pair	π bond pair
C1s	0.007 32	−0.055 26	−0.000 86	−0.018 78	−0.059 16	0.012 93	−0.088 12	0.0
C2s	−0.088 04	0.396 43	−0.023 55	0.117 30	0.270 47	−0.090 95	0.396 61	0.0
C2p$_z$	0.114 20	0.046 06	−0.318 25	0.0	−0.259 20	0.0	0.0	−0.366 57
C2p$_x$	−0.078 46	0.441 03	0.002 12	0.107 92	0.287 92	−0.077 61	0.420 95	0.0
C2p$_y$	0.099 19	−0.000 13	0.000 37	0.108 69	−0.000 00	0.108 34	−0.000 01	0.0
O1s	−0.059 81	−0.036 46	−0.048 50	0.098 35	−0.052 68	−0.101 52	−0.063 48	0.0
O2s	0.619 00	0.125 49	0.469 57	−0.679 73	0.196 62	0.696 13	0.180 10	0.0
O2p$_z$	0.283 98	0.094 09	−0.768 26	0.0	−0.612 70	0.0	0.0	−0.866 51
O2p$_x$	0.254 12	−0.553 00	0.114 61	−0.324 61	−0.358 52	0.286 53	−0.550 58	0.0
O2p$_y$	0.685 60	−0.000 17	0.002 74	0.685 39	−0.000 01	0.685 49	−0.000 05	0.0
O1s	0.003 79	0.004 58	−0.000 14	0.009 25	0.006 02	0.005 75	0.008 59	0.0
O2s	−0.047 24	−0.037 14	0.004 79	−0.069 62	−0.033 93	−0.047 73	−0.046 85	0.0
O2p$_z$	−0.044 22	−0.008 14	0.116 01	0.0	0.096 89	0.0	−0.0	0.137 02
O2p$_x$	−0.037 08	−0.076 21	−0.007 88	−0.065 29	−0.063 10	−0.027 26	−0.092 00	0.0
O2p$_y$	0.045 25	0.022 42	0.002 68	0.046 21	0.011 55	0.036 83	0.018 18	0.0
O1s	−0.005 04	0.004 60	−0.000 14	−0.005 01	0.006 02	−0.008 55	0.008 59	0.0
O2s	0.060 33	−0.037 30	0.005 17	0.044 00	−0.033 94	0.065 85	−0.046 85	0.0
O2p$_z$	−0.047 31	−0.008 34	0.115 93	0.0	0.096 89	0.0	0.0	0.137 02
O2p$_x$	0.059 65	−0.076 16	−0.007 22	0.019 96	−0.063 10	0.058 27	−0.092 00	0.0
O2p$_y$	0.058 43	−0.022 23	−0.002 46	0.034 64	−0.011 55	0.044 65	−0.018 18	0.0

Discussion

Although the wave functions used were obtained at the minimum basis set level, and therefore employ only four valence orbitals on carbon and oxygen, all but one of the localizations show six LMO's associated[22] with carbon (plus the inner shell); the exception is the complete ER localization for CO_2, for which either four or eight LMO's are associated with carbon, depending on whether the oxygen "lone pairs" (Figure 2a) are classified as one-center or two-center LMO's. First row atoms which participate in more than four valence LMO's have been termed fractional centers.[7,23] Some implications of fractionality in LMO's are discussed in the adjacent paper[7] in which the apparent tension between the octet rule and localized structures associating six LMO's with carbon is resolved. Note that the resonance or fractionality problem can be isolated in the π system.

If localizations of molecular orbitals are performed to find relationships between molecular orbital theory and chemical intuition, then the complete ER LMO's for CO_3^{2-} must be regarded as unappealing. While this unusual localization for CO_3^{2-} may be rationalized as an attempt to average the three Lewis structures for CO_3^{2-}, the C_{3v} symmetry of the set of LMO shapes[24] unfortunately suggests that the molecule should be nonplanar.

Likewise the complete and σ–π Boys LMO's for CO_2 are somewhat disconsonant with chemical intuition because of the lack of correlation between opposing sets of τ or π orbitals which have a center in common.

The imposition of σ–π separation on the localizations must be regarded as a constraint,[12] but a constraint which is not out of harmony with chemical intuition. Further the imposition of σ–π symmetry has demonstrated that fractionality[7,23] or inherent delocalization[4,7] resides in the π system, whereas the σ system is quite in accord with chemical intuition. Imposition of σ–π symmetry has also demonstrated that for CO_2 and CO_3^{2-} the major difference between the ER and Boys criteria is the way in which they mix σ and π orbitals.

Boys localized molecular orbitals have previously been reported for N_3^{-} [25] and for BF_3[11a] which are isoelectronic with CO_2 and CO_3^{2-}, respectively. As might be expected, the results are similar to the complete Boys localizations reported above. Localizations carried out in this laboratory[26] confirm that for

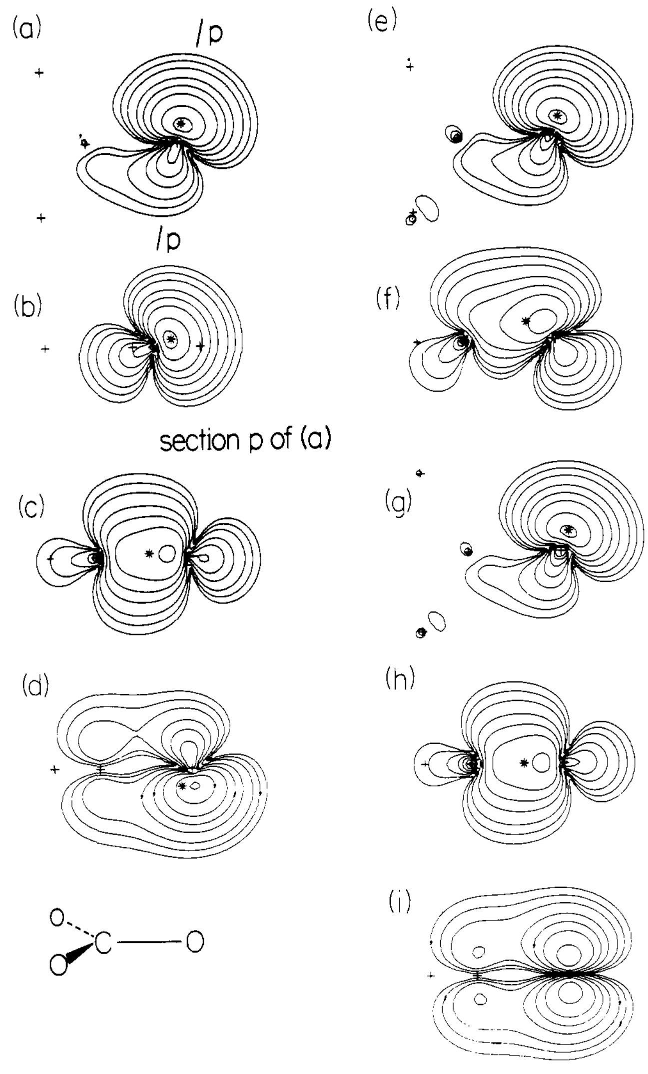
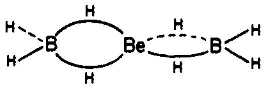


Figure 3. CO_3^{2-} LMO's. Same markings and contour levels as in Figure 2. See text for a description of these LMO's. Plane p is perpendicular to the plane of the molecule and contains the oxygen nucleus and the LMO centroid.

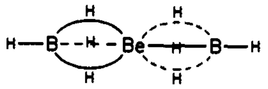
the complete Boys method at least, CO_2 and CO_3^{2-} LMO patterns are qualitatively reproduced for other isoelectronic species, which also belong to the same point group, e.g., NO_2^+ for CO_2 and NO_3^- and BO_3^{3-} for CO_3^{2-}. Species which are isoelectronic but which belong to a different point group (e.g., N_2O ($C_{\infty v}$) and CO_2 ($D_{\infty h}$)) may show different LMO patterns.[26] Likewise, F_2CO is isoelectronic with CO_3^{2-} but is not expected to show the same LMO pattern as CO_3^{2-} or BF_3.

The LMO structure of a molecule also suggests the geometries of other isoelectronic molecules which have an atomic composition capable of reflecting the symmetry of the LMO structure. Thus the complete ER LMO's for CO_2 suggest structures for isoelectronic species such as the staggered C-C and C-H bonds of allene and a structure for BeB_2H_8 (I).[27] The CO double bonds are here made into B-H-Be three-center bonds, by analogy with Longuet-Higgins' model for diborane,[28] which rests on the now well-developed theory of three-center bonds.[6a,29]



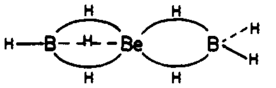
I

The complete Boys LMO's for CO_2 are consistent with an alternative structure for BeB_2H_8 (II) which is found[27a] to be only a few kilocalories above the energy of preferred conformer I on the SCF and SCF-CI energy surfaces.



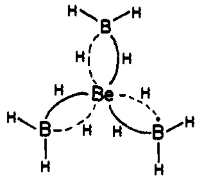
II

In structure II the bridge hydrogens are, of course, staggered with respect to one another. A third structure (III),[27] which is also close to I in energy, is a compromise between I and II. The energetic relationships between I, II, and III suggest fluxional molecular behavior with mobile protons.[27]



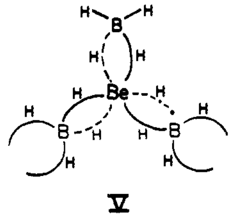
III

We note that the hypothetical $BeB_3H_{12}^-$ is isoelectronic with CO_3^{2-} and would be expected to have the structure IV.

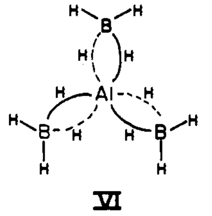


IV

Structure IV resembles the structure of the beryllium borohydride polymer (V) which is known[30] from x-ray diffraction and structure VI which has been proposed[31] for $Al(BH_4)_3$.



V



VI

Since localized molecular orbitals have been particularly successful in a systematic treatment of boron hydrides,[6] it is pleasing to note that LMO's for CO_2 and CO_3^{2-} correlate with previously published work on beryllium borohydride. The connecting link between electron deficient chemistry and nonelectron deficient chemistry is the interpretation of the bridge bond as a protonated bent bond.[28b]

Tables VI and VII, which list LMO coefficients over atomic orbitals, were added at the suggestion of a referee.

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References and Notes

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