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Linear Combination of Hybrid Orbitals: Cyclobutane as Test-Case*

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Hybrid-based molecular orbitals are constructed for puckered cyclobutane, and used subsequently in a configurational-interaction process. The bent-bond structure, diagonal interaction and excited states of the molecule are discussed.

Key words: Cyclobutane, hybridization in ~ – Hybrids, linear combination of ~ – Saturated organic compounds, MO treatment of ~

1. Exposition

Successes of the pi-electron approximation [2, 3], and its having stood confrontations with all-valence and all-electron results [4], suggest that separability [5, 6] might be exploited in other contexts also. In fact, certain molecular characteristics of *saturated* organic compounds have been considered in sole terms of C–C hybrids [7, 8]. Later work, however, took also account of C–H hybrids and hydrogen 1*s*-orbitals [8, 9] so that no theory, analogous in conception and aim to pi-electron methods, could evolve.

Another consequence of pi-electron achievements was that certain semiempirical techniques [6, 10], originally developed in connection with unsaturated molecules, were adapted to the saturated [11], with concomitant replacement of pi-AO's by hybrids. Such attempts, however, were overshadowed by the advent of all-valence and all-electron LCAO techniques [12], and never pursued far.

Despite the power of nonempirical LCAO methods, and the possibility to reformulate results in terms of hybridization [14], there are reasons [15] not to abandon the semiempirical construction of MO's by linear combination of hybrid orbitals[1]. For one thing, hybridization is firmly linked with concepts that chemistry has developed over the years [16], and even a qualitative LCHO theory could bridge MO formulations with classical thought [17]. For another, the computation of vacuum-ultraviolet spectra by LCAO-MO is still – despite the recurrence to reparametrized semiempirical methods [18, 19] – far from satisfactory [20]; a parametrized LCHO-MO, because of its different point of departure, provides an alternative way [1, 11] to meet the problem.

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* "Multi-Conformational Compounds", part IX. For part VIII, see Ref. [1].

[1] Hereafter abbreviated LCHO-MO. A former denotation [9], LCVO (V for Valence), is now misleading.

It should be convenient to examine the LCHO-MO approach in two stages, starting with saturated molecules that mimic, in certain respects, the unsaturated. Practically, these comprise three- and four-membered ring-compounds, where the construction of hybrids leads to "bent" bonds [21]. Here one may safely assume that certain properties of interest (conjugation, transmission of conjugation, spectral bands in the not too-far ultraviolet) depend mainly on the carbon frame [17], and attempt a "carbon-centered" description, in formal analogy and technical reliance on "pi-centered" methods. In the second stage, the technique would be extended to more general systems, by including additional hybrids and valence orbitals. The separation of the basis set needs therefore concern only the first operational step.

In previous work, we have developed a general approach to nonplanar unsaturation [22, 23], and considered cyclopropane [17] and cyclopropylketones [1]; here we examine further the first stage of the proposed analysis. To do this, we turn to cyclobutane, which presents two types of novelty [24]. First, it is puckered, and its investigation leads to a variety of geometrical dependencies. Second, the HCH-angle may be less than tetrahedral (~108° [25]), and C-hybridization in C–C smaller than 3 [24] – in contrast with the better-known case of cyclopropane (HCH ~ 114° [26]), where 3 is exceeded [17]. Still, the spectra of these two – wherein a portion might be definitely ascribed to carbon-frame transitions [27] – are quite similar [28].

Various aspects of cyclobutane structure (mainly of the hypothetical planar molecule) have been discussed by other authors. Extended-Hückel [50], CNDO/2 [24, 51], and nonempirical calculations [51], have been described, as well as overlap [53, 54] and independent-systems approaches [27]; a Walsh-type analysis has also been given [55]. Our efforts here, however, are oriented in a new direction: the adaptation of pi-electronic techniques – and their objectives – to the four-membered ring-system. In what follows, we outline our scheme and analyze results for puckered cyclobutane. We use the same geometry as before [24], namely, $r(\mathrm{CC}) = 1.548$ Å, C–C hybridization $sp^{2.86}$, molecular puckering 18°. Deviations from these values do not affect the results significantly. HCH-tilting [25] does not affect the carbon-centered construction, and need not concern us here.

2. Integrals

In extension of previous treatments of cyclopropane [17] and cyclobutane [24], we consider the puckered conformation of the latter (Fig. 1) and denote by χ_i a hybrid, say on carbon A,

$$\chi_i = (1+\lambda_i^2)^{-\frac{1}{2}}(s_A + \lambda_i p_A); \tag{1}$$

s_A and p_A are here, respectively, the 2s and an appropriately-oriented 2p-type STO on A, and λ_i^2 is the hybridization index. One has

$$\sum_{i \in A} [1/(1+\lambda_i^2)] = 1$$

and, if monocentric hybrids are to be orthogonal, also

$$\cos \tau_{ij} = -1/\lambda_i \lambda_j$$

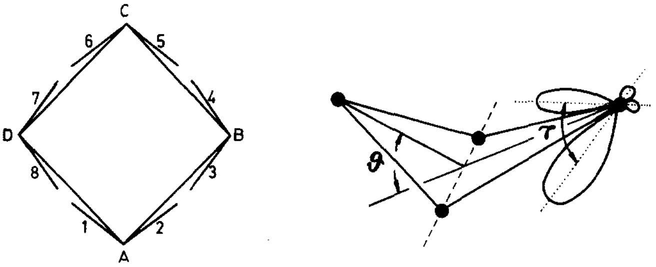

Fig. 1a and b. Cyclobutane. a Numbering of apices and C–C hybrids, b Puckering (θ) and interhybrid (τ) angles

Table 1. Integrals over χ-orbitals[a]

	$[r(\mathrm{CC}) = 1.548\,\text{Å};\ \theta = 18°]$	
I	(11, 11)	11.108
	(11, 22)	8.496
	(11, 33)	7.429
	(11, 44)	7.033
	(11, 55) = (11, 66)	6.043
II	(11, 12)	0.369
	(12, 12)	0.810
III	(11, 34)	− 0.046
	(11, 56)	0.221
	(12, 33)	− 0.027
	(12, 34)	0.003
	(12, 56)	0.040

[a] Numbering as in Fig. 1; values given in eV.

where τ_{ij} is the interorbital angle [29]. Assume that $C \rightarrow H$ hybrids are collinear with C–H axes, and take the two $C \rightarrow C$ hybrids, $A \rightarrow B$ and $A \rightarrow D$, in plane ABD. Then, λ_i^2 and the direction of χ_i are fixed for all hybrids by the puckering θ and the angle HCH. Equation (1) can therefore be reformulated in any local coordinate system, so that hybrid overlaps and bielectronic integrals are immediately expressible as sums of integrals over STO's[2].

Overlap integrals (ss), ($s\sigma$), ($\sigma\sigma$), and ($\pi\pi$) are computed [30] with Slater's exponent, 1.625. As dictated by Eq. (1), they are combined to yield hybrid overlaps $(\chi_i \chi_j)$, which serve [22] to compute β-integrals, through $\beta = kS$. Here, k must depend on λ; extrapolated from previous results ($k = -10.14$ for pure $2p$ [22], -9.70 for $\lambda^2 = 3.69$ [17]), it is

$$k = 2.064/(1 + \lambda^2) - 10.14\,.$$

As for the bielectronic integrals, we neglect polycentric terms, and retain (ss, ss), (ss, xx), (sx, sx), (xx, xx), (xx, yy), (xy, xy) among the monocentric, (ss, ss),

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[2] Details for monocentric terms were given elsewhere [17]; the bicentric case is developed in Section 7 below.

$(ss, \sigma\sigma)$, $(ss, \pi\pi)$, $(\sigma\sigma, \sigma\sigma)$, $(\sigma\sigma, \pi\pi)$, $(\pi\pi, \pi\pi)$ among the bicentric. All are evaluated [31] with the effective exponent 0.927 [22, 32] and then combined (Section 7) to form the required bielectronic integrals over hybrids. These are conveniently grouped as in Table 1, namely: I. High-valued Coulomb-repulsion integrals; II. Mixed monocentrics, of lower values; III. The still lower mixed bicentrics. We return later to this classification.

As in the case of cyclopropane [17], the evaluation of α-integrals is here redundant. Dipole-length integrals, required in the computation of oscillator-strengths, were derived as described elsewhere [33].

3. SCF – CI

Basing the C-centered treatment of cyclobutane on eight $C \to C$ hybrids, eight molecular-orbitals were constructed through the LCHO-MO-SCF procedure [17]. This comprises the iterative solution of[3]

$$(\boldsymbol{F} - E\boldsymbol{I})\,\boldsymbol{c} = 0 \qquad (2)$$

where

$$\boldsymbol{F} = \boldsymbol{H} + \boldsymbol{G}$$

$$H_{ii} = \alpha_i\,(\text{redundant}), \qquad H_{ij} = \beta_{ij},$$

$$G_{ij} = \sum_k \sum_l \left\{ [2(ij, kl) - (ik, jl)] \sum_m C_{km} C_{lm} \right\}.$$

The solving vectors are arranged as

$$\left.\begin{array}{rl} 1. & B_2 \quad \text{-----} \\ 2,3. & E \quad \text{-----}\ \ \text{-----} \\ 4. & A_2 \quad \text{-----} \end{array}\right\}\ \text{virtual}$$

$$\left.\begin{array}{rl} 5,6. & E \quad \text{-----}\ \ \text{-----} \\ 7. & B_1 \quad \text{-----} \\ 8. & A_1 \quad \text{-----} \end{array}\right\}\ \text{occupied}$$

(D_{2d} notation; cf. cyclopropane [17]. *Ab initio* results [52] suggest that inclusion of the hydrogens would interchange the virtual A_2 and E). All were included in a monoexcitation CI[4], comprising altogether sixteen singlets and sixteen triplets. The corresponding state-energies should refer to, and thus single out, the carbon-centered transitions.

The consequences of neglecting certain integrals in the CI-process may be gathered from Table 2, which confronts the first two computed singlets with their experimental [28] counterparts. One sees that intermediate neglect of

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[3] Iterations on $(\boldsymbol{F} - E\boldsymbol{S})\,\boldsymbol{c} = 0$ did not converge. Equation (2) was therefore solved instead, and its eigenvectors (which anyhow are determined by symmetry) used first to obtain bond orders, then overlap-renormalized and subjected to the population analysis [34].

[4] In preliminary work, CI was based on the renormalized vectors. Results were unsatisfactory, evidently because our parametrization [22] is not oriented towards this type of construction. A similar situation has been encountered in pi-electron work [35], but interpreted differently.

Table 2. The strong electronic absorptions of cyclobutane[a] at 8–10 eV

	All integrals	INDO	CNDO	exp.[b]
I	8.49 (146)	8.64 (143)	8.95 (138)	8.7–9.2 (139; 141)
II	9.83 (126)	9.84 (126)	9.82 (126)	9.7–9.9 (126)

[a] Values in eV (in parenthesis – nm).

[b] Energies (and λ_{max}) read from curve [28].

differential overlap (INDO, i.e., neglect of integrals belonging to group III), and even complete neglect of differential overlap (CNDO, i.e., of groups II and III), do not affect adversely the computed energies. It was found, however, that CNDO rearranges higher statefunctions and even inserts a forbidden singlet between the first two.

We therefore conclude that INDO is still, but CNDO already not, applicable in the present context.

4. Ground State

Two distinctive properties of cyclobutane are its stability to ring-fission, when compared with cyclopropane [36], and the manifestation of diagonal (across-ring) interaction [37, 38], by which it differs from larger rings. Refer to Fig. 1a for the numbering of hybrids (1–8) and apices (A–D).

Elements of the "bond order and charge" matrix are given in Table 3. Like the corresponding pi-quantities in alternant hydrocarbons [39], $(i, i) = 1$ and $(i, i + 2n) = 0$. One may note that (1, 2) is repulsive, while (1, 8) has the high value of 0.953 (maximum = 1 [40]). The C-frame of cyclobutane may thus be envisaged as consisting of four strong bonds, (2, 3), (4, 5), (6, 7), and (8, 1), cross-linked at (1, 6), (2, 5), (3, 8), and (4, 7) (Fig. 2). Detection of the latter linkages is one theoretical way to account for the diagonal interactions [(A, C) and (B, D) in Fig. 2].

Table 3. Elements of the "bond order and charge" matrix in cyclobutane ($\theta = 18°$) and cyclopropane[a]

Cyclobutane		Cyclopropane	
(1, 1)	1.	(1, 1)	1.
(1, 2)	−0.211	(1, 2)	−0.235
(1, 3)	0.	(1, 3)	0.
(1, 4)	0.047	(1, 4)	0.316
(1, 5)	0.	—	—
(1, 6)	0.211	—	—
(1, 7)	0.	(1, 5)	0.
(1, 8)	0.953	(1, 6)	0.919

[a] Ref. [17].

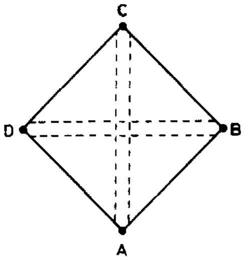

Fig. 2

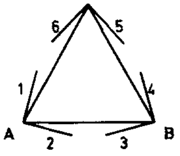

Fig. 3

Table 4. Overlap populations in cyclobutane ($\theta = 18°$)

(1, 2)	0.
(1, 3)	−0.021
(1, 4)	−0.017
(1, 5)	−0.024
(1, 6)	0.038
(1, 7)	−0.021
(1, 8)	0.765

On comparing cyclobutane bond orders with those of cyclopropane (Table 3, numbering as in Fig. 3), one notes that p_{18} is higher in the former than in the latter; this should account for the relative resistance of cyclobutane to ring-cleavage [36]. Another difference is that p_{14} is appreciable in cyclopropane, but low in cyclobutane. The capability of three-membered rings to transmit conjugation [41] can therefore be explained by vicinal interaction [(A, B) in Fig. 3], whereas a diagonal mechanism [(A, C) in Fig. 2] has to be invoked in the four-membered.

The computed overlap populations (Table 4) are repulsive or null, except for the small p_{16} and the large p_{18}. The apex-apex populations[5] take us back to Fig. 2; they are,

$$\text{at } (A, B)\text{:} \quad \sum_{i=1}^{2} \sum_{j=3}^{4} (i, j) = 0.706\,,$$

corresponding to a single bond, and

$$\text{at } (A, C)\text{:} \quad \sum_{i=1}^{2} \sum_{j=4}^{5} (i, j) = 0.027\,.$$

Another view of the electronic structure is provided by density maps[6] which, in our approach, disregard C–H bonds and refer only to the carbon frame. Consequently [cf. 42], densities computed near apices are lower than habitual

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[5] Analogous to the "reduced overlap populations" of LCAO. Users of CNDO/2 would recognize that a reduced population of ca. 0.7 represents roughly a single bond.

[6] The density map (Fig. 4) refers to the eight electrons of the carbon frame, and is scaled in elect./A^3. A: 0.020–0.039; B: 0.060–0.079; C: 0.100–0.119, etc.

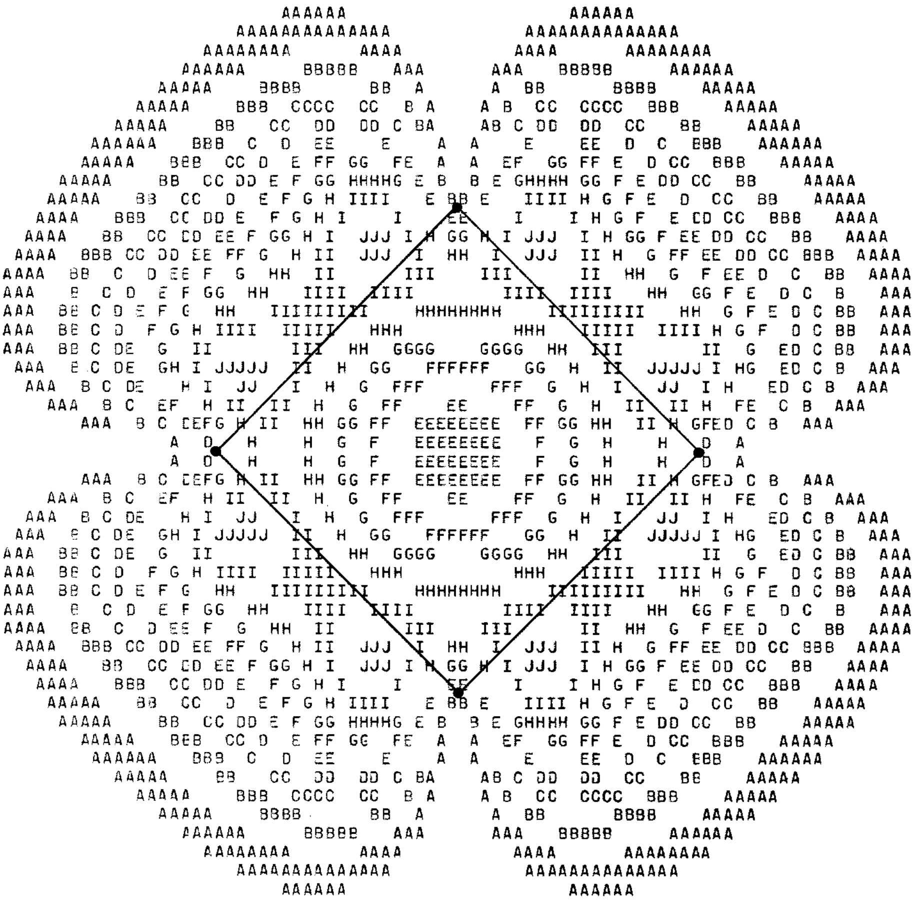
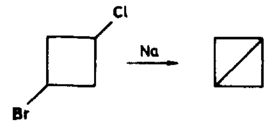


Fig. 4. Planar cyclobutane. Ground state densities

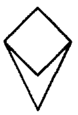
[e.g. 14]. For simplicity, consider the unpuckered molecule: our carbon-centered mapping (Fig. 4) renders noticeable the bent-bond structure and stresses the accumulation of charge *within* the ring. It is this internal charge that links diagonally-oriented carbons (Fig. 2).

Two-dimensional density maps for puckered structures – cut perpendicular to the C_2-axis – resemble Fig. 4 closely. It follows that the main effect of puckering on the electronic field is to stretch, into the third dimension, the bent bonds and diagonal interactions of Fig. 4.

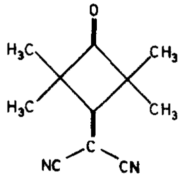
A host of experimental observations may now be rationalized. First should be mentioned 1,3-eliminations [38] where the formation of a diagonal bond, e.g. I → II, transforms cyclo- to bicyclo-butanes. The detection in NMR of long-range proton-proton splittings [43] provides another instance. The coupling constant is known to augment with puckering [44] and, in one case (III) of a particularly strong effect, the molecular structure indicates *per se* that interaction is conveyed through internal charge [45]. Thirdly, the diagonal interaction



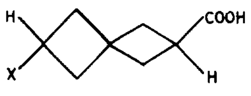
I II



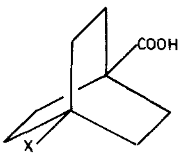
III



IV



V



VI

affects the ultraviolet spectrum of quite a number of cyclobutanes, among which IV may be cited [37]. One is even tempted to propose a *double* diagonal interaction in 6-substituted spiro[3.3]heptane-2-carboxylic acids(V), where pK_a's obey a Hammett-type regularity [46]; other mechanisms cannot however be excluded, for larger-ring acids, such as VI, manifest analogous trends [47].

It was instructive to compare the LCHO-MO density (Fig. 4) with the density of the basis hybrids, before combination to form molecular orbitals. In the latter case, the charge within the ring is attenuated and this is compensated outside by an extensive region of low charge. The difference between the two distributions has a negative region, going from the apices outwards. Therefore, the process of LCHO-MO amounts to bringing-over of charge from infinity to the inner confines of the ring.

5. Excited States

We know of three recordings [27, 28, 48] and one theoretical analysis [27] of cyclobutane spectrum. According to the analysis, two transitions are ascribable to the carbon-frame: the first, at ca. 64.5 kK (≡ 155 nm), is predicted to be forbidden, and the second, doubly-degenerate and allowed, is expected at ca. 77.6 kK (129 nm). What one actually observes is a weak progression based on 52.5 kK (190 nm) – almost certainly a forbidden Rydberg series [48] – followed by *two* strong absorptions, at 72.0 kK (139 nm) and 79.5 kK (126 nm).

Unlike a previous suggestion [27] that these two are due to the Jahn-Teller splitting [49] of the 77.6-state, our calculations (Table 5) characterize them as *distinct* singlet-singlet transitions, allowed both but of different symmetry. The first (calc. 143 nm, B_2) is represented by an extensive mixture of configurations

Table 5. Electronic spectrum of cyclobutane

Type	Energy	λ	f	Experimental
				Fine structure of low extinction[a] up to 152 nm
$^1B_2$	8.64	143	0.018	$\lambda_{max} = 141$ nm, $\varepsilon = 6480$
^3E	9.25	134	—	fine structure up to 130 nm
$^3B_2$	9.76	127	—	
^1E	9.84	126	0.859	$\lambda_{max} = 126$ nm, $\varepsilon = 11250$
$^3A_2$	10.09	123	—	fine structure from 122 nm
$^1A_2$	10.17	122	0.005	
$^1B_1$	10.51	118	0.012	

Type: D_{2d}-representation and multiplicity; Energy: transition energy (eV), as calculated for the puckered molecule in the INDO approximation; λ: corresponding wavelength (nm); f: computed oscillator strength; Experimental: outline of the absorption curve in Ref. [28].

[a] Probably a forbidden Rydberg series [27].

which renders its energy even lower that that of the corresponding triplet. Numbering molecular orbitals as in Section 3, it is

$$0.33[(5\to 2)+(6\to 3)]+0.44[(6\to 2)-(5\to 3)]+0.63(7\to 4)-0.08(8\to 1).$$

The next (calc. 126 nm, E) is indeed degenerate, being formed by combination of (5→4) and (6→4). Some fine structure, revealed in the absorption curve between the two [28], may be attributed to the occurrence of triplets.

The 126-band is, by both measurement and theory, the most prominent in the carbon-frame region of the spectrum. Its density map indicates that bent bonding and diagonal interaction are conserved during excitation. Yet, the negative regions in the difference-density map are much more extensive than in the ground state; excitation, therefore, is accompanied by a contraction of charge.

Higher computed absorptions invade the CH-range [27] and are less significant.

6. Concluding Remarks

When applied to the carbon-skeleton of cyclobutane, the LCHO-MO technique provides a quantitative characterization of excited states, and a qualitative understanding of the ground state, without recourse to any new *ad hoc* parametrization.

Our method has now been tested on cyclopropane [17], all conformations of cyclopropyl ketones [1], and cyclobutane. Its generalization to more complicated small-ring systems, unsubstituted and substituted, is immediate; for the sake of economy, it would have to be based on Eq. (2), and the INDO approximation (Section 3) adopted throughout. Results pertaining to this wider domain will be reported elsewhere.

7. Appendix

Development of Bicentric Integrals over Hybrids as Sums of Integrals over Atomic Orbitals

In the particular case of cyclobutane, let λ^2 be the $C \rightarrow C$ hybridization index, θ the angle of puckering, τ the interhybrid angle (Fig. 1), and denote

$$N = (1+\lambda^2)^{-\frac{1}{2}} \text{ (normalization factor)}$$

$$\xi = \cos(\theta/2),\ \zeta = \sin(\theta/2),\ \varrho = \cos(\tau/2),\ \omega = \sin(\tau/2),$$

$$A = (1+\xi^2)^{-\frac{1}{2}},\ B = \xi\varrho + \omega,\ C = \xi\varrho - \omega,$$

$$D = \varrho + \omega\xi,\ E = \varrho - \omega\xi,$$

$$F = \zeta\varrho,\ G = \xi\varrho.$$

Also denote by s_i, x_i, etc., a (2*s*), ($2p_x$)–AO, etc., on apex *i*. Hybrids are now reformulated [cf. Eq. (1), Section 2] as follows.

a) Neighbours:

$$\chi_1 = N\{s_1 + \lambda[\sqrt{2}AB\zeta x_1 + \sqrt{2}By_1 + AEz_1]\}$$

$$\chi_2 = N\{s_1 + \lambda[\sqrt{2}AC\zeta x_1 + \sqrt{2}Cy_1 + ADz_1]\}$$

$$\chi_3 = N\{s_2 + \lambda[-\sqrt{2}AC\zeta x_2 + \sqrt{2}Cy_2 + ADz_2]\}$$

$$\chi_4 = N\{s_2 + \lambda[-\sqrt{2}AB\zeta x_2 + \sqrt{2}By_2 + AEz_2]\};$$

b) Next-neighbours:

$$\chi_1 = N\{s_1 + \lambda[Fx_1 + \omega y_1 + Gz_1]\}$$

$$\chi_2 = N\{s_1 + \lambda[Fx_1 - \omega y_1 + Gz_1]\}$$

$$\chi_5 = N\{s_3 + \lambda[Fx_3 - \omega y_3 + Gz_3]\}$$

$$\chi_6 = N\{s_3 + \lambda[Fx_3 + \omega y_3 + Gz_3]\}.$$

Taking account of symmetry, all required integrals may now be written down, e.g.,

$$\begin{aligned}(\chi_1\chi_1, \chi_5\chi_5) = N^4\{&(ss, ss)\\ &+ 2\lambda^2[G^2(ss, \sigma\sigma) + (\omega^2 + F^2)(ss, \pi\pi)]\\ &+ \lambda^4[G^4(\sigma\sigma, \sigma\sigma) + 2G^2(\omega^2 + F^2)(\sigma\sigma, \pi\pi)\\ &+ (\omega^4 + 2\omega^2F^2 + \varrho^2F^2)(\pi\pi, \pi\pi)]\}\\ = (\chi_2\chi_2&, \chi_6\chi_6) = (\chi_3\chi_3, \chi_7\chi_7), \quad \text{etc.,}\end{aligned}$$

where (*ss*, *ss*), etc., is a shorthand for $(s_1 s_1, s_3 s_3)$, etc.

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References

1. Meyer, A. Y., Muel, B., Kasha, M.: J. Mol. Spectr. **43**, 262 (1972)
2. Static properties: Kutzelnigg, W., Del Re, G., Berthier, G.: Fortschr. Chem. Forsch. **22**, 1 (1971)
3. Dynamic properties: Woodward, R. B., Hoffmann, H.: The conservation of orbital symmetry. Weinheim: Verlag Chemie 1970. See also Ref. 2, p. 119
4. Pullman, A., Bergmann, E. D., Pullman, B. (Eds.): Quantum aspects of heterocyclic compounds in chemistry and biochemistry. The Second Jerusalem Symposium. Jerusalem: Israel Academy 1970, p. 9
5. Lykos, P. G., Parr, R. G.: J. Chem. Phys. **24**, 1166 (1956)
6. Parr, R. G.: The quantum theory of molecular electronic structure. New York: Benjamin 1963
7. Sandorfy, C., Daudel, R.: Compt. Rend. Acad. Sci. (Paris) **238**, 93 (1954)
8. Sandorfy, C.: Can. J. Chem. **33**, 1337 (1955)
9. Fukui, K.: In: Sinanoğlu, O. (Ed.): Modern quantum chemistry, the Istanbul lectures. New York and London: Academic Press 1965. Vol. I, p. 49
10. Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953)
11. Katagiri, S., Sandorfy, C.: Theoret. Chim. Acta (Berl.) **4**, 203 (1966)
12. Pople, J. A.: Ref. 13, p. 17. See also the discussion, p. 34
13. Daudel, R., Pullman, A. (Eds.): Aspects de la chimie quantique contemporaine. Paris: Editions du CNRS 1971
14. Newton, M. D., Schulman, J. M.: J. Am. Chem. Soc. **94**, 767, 773 (1972)
15. For various points of view, see: Berthier, G.: Ref. 13, p. 49; the discussion, ibid., p. 67; Pozzoli, S. A., Rastelli, A., Tedeschi, M.: J. Chem. Soc., Faraday II, 256 (1973); Meaume, M.-T., Odiot, S., Brigot, N.: Compt. Rend. Acad. Sci. (Paris) **272**, 591 (1971)
16. Randić, M., Maksić, Z. B.: Chem. Rev. **72**, 43 (1972)
17. Meyer, A. Y.: Theoret. Chim. Acta (Berl.) **22**, 271 (1971)
18. Del Bene, J., Jaffé, H. H.: J. Chem. Phys. **48**, 4050 (1968)
19. Salahub, D. R.: Theoret. Chim. Acta (Berl.) **22**, 330 (1971), and previous papers in the series; Brabant, C., Salahub, D. R.: Theoret. Chim. Acta (Berl.) **23**, 285 (1971); Mullen, P. A., Orloff, M. K.: Theoret. Chim. Acta (Berl.) **23**, 278 (1971)
20. Giessner-Prettre, C., Pullman, A.: Theoret. Chim. Acta (Berl.) **13**, 265 (1969); Giessner-Prettre, C.: Ref. 13, p. 45
21. Coulson, C. A., Moffitt, W. E.: Phil. Mag. **40**, 1 (1949)
22. Meyer, A. Y., Kesten, Y.: Theoret. Chim. Acta (Berl.) **20**, 352 (1971), and preceding papers in the series
23. Meyer, A. Y., Yinnon, H.: Tetrahedron **28**, 3915 (1972)
24. Pasternak, R., Meyer, A. Y.: J. Mol. Struct. **13**, 201 (1972)
25. Meiboom, S., Snyder, L. C.: J. Chem. Phys. **52**, 3857 (1970)
26. Diehl, P., Khetrapal, C. L.: In: Diehl, P., Fluck, E., Kosfeld, R. (Eds.): NMR – Basic principles and progress, Vol. 1. Berlin: Springer-Verlag 1969, p. 62
27. Raymonda, J. W., Simpson, W. T.: J. Chem. Phys. **47**, 430 (1967)
28. Sandorfy, C.: In: Sinanoğlu, O., Wiberg, K. B. (Eds.): Sigma molecular orbital theory. New Haven and London: Yale University Press 1970, p. 130
29. Coulson, C. A.: Valence, 2nd. Ed., reprinted with further corrections. Oxford: Oxford University Press 1969
30. Mulliken, R. S., Rieke, C. A., Orloff, D., Orloff, H.: J. Chem. Phys. **17**, 1248 (1949)
31. Roothaan, C. C. J.: J. Chem. Phys. **19**, 1445 (1951)
32. Berthod, H., Giessner-Prettre, C., Pullman, A.: Theoret. Chim. Acta (Berl.) **5**, 53 (1966)
33. Meyer, A. Y.: J. Chim. Phys. **69**, 112 (1972)
34. Mulliken, R. S.: J. Chem. Phys. **23**, 1833 (1955)
35. Mizuno, M., Saëki, S.: Mol. Phys. **24**, 219 (1972)
36. Coffey, S. (Ed.): Rodd's chemistry of carbon compounds, 2nd Ed., Vol. II, part A. Elsevier: Amsterdam 1967, p. 78
37. LaLancette, E. A., Benson, R. E.: J. Am. Chem. Soc. **83**, 4867 (1961)
38. LeBel, N. A.: Adv. Alicycl. Chem. **3**, 206 (1971)
39. McLachlan, A. D.: Mol. Phys. **2**, 271 (1959)
40. Trindle, C., Sinanoğlu, O.: J. Am. Chem. Soc. **91**, 219 (1969)

41. Montaudo, G., Overberger, C. G.: J. Org. Chem. **38**, 804 (1973)
42. Mårtensson, O., Sperber, G.: Acta Chem. Scand. **24**, 1749 (1970)
43. Fleming, I., Williams, D. H.: Tetrahedron **23**, 2747 (1967)
44. Wiberg, K. B., Barth, D. E.: J. Am. Chem. Soc. **91**, 5124 (1969)
45. Chiang, J. F., Bauer, S. H.: J. Am. Chem. Soc. **92**, 1614 (1970)
46. Liotta, C. L., Fisher, W. F., Greene, G. H., Joyner, B. L.: J. Am. Chem. Soc. **94**, 4891 (1972)
47. Holtz, H. D., Stock, L. M.: J. Am. Chem. Soc. **86**, 5188 (1964)
48. Raymonda, J. W.: J. Chem. Phys. **56**, 3912 (1972)
49. Bischof, P., Haselbach, E., Heilbronner, E.: Angew. Chem. **82**, 952 (1970)
50. Yonezawa, T., Shimizu, K., Kato, H.: Bull. Chem. Soc. Japan **40**, 456 (1967)
51. Wright, J. S., Salem, L.: Chem. Commun. 1370 (1969)
52. Wright, J. S., Salem, L.: J. Am. Chem. Soc. **94**, 322 (1972)
53. Veillard, A., Del Re, G.: Theoret. Chim. Acta (Berl.) **2**, 55 (1964)
54. Maksić, Z. B., Eckert-Maksić, M., Randić, M.: Theoret. Chim. Acta (Berl.) **22**, 70 (1971)
55. Hoffmann, R., Davidson, R. B.: J. Am. Chem. Soc. **93**, 5699 (1971)

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