INFLUENCE OF THE CHOICE
OF PARAMETERS AND GEOMETRY OF RADICALS
ON SPIN DENSITIES CALCULATED
BY THE LONGUET–HIGGINS–POPLE–LEFEBVRE METHOD
AND BY THE UNRESTRICTED HARTREE–FOCK METHOD

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From the point of view of spin distribution, the problem of choice of parameters in the semi-empirical SCF MO methods is especially important. For interpretation of an ESR spectrum it is necessary to determine correctly all splitting constants; however, in calculating the spin densities by various methods not only different values but also different ratios in various pairs of positions are obtained[1,2]. A typical example is the Longuet–Higgins–Pople–Lefebvre (LHP CI) method[3,4] and the unrestricted Hartree–Fock method with complete projection of the wave function[5] (UHF UP). In the LHP CI method the splitting constants in positions with negative spin densities are very small whereas in the UHF UP method these positions are described correctly.

A similar problem arises in choosing different parameters in the same method. It is known that the choice of the mode of calculation of two-center coulombic integrals (further: γ integrals) influences considerably the calculated overall spin distribution in radicals. The result of neglecting the real geometry of a radical is not known. Interatomic distances in ion radicals are in general different from those in corresponding neutral molecules, but these differences are calculated by the MO method from the corresponding changes in orders of π-bonds with a sufficient accuracy[6].

The present paper deals with the influence of choosing two-center coulombic integrals and core-resonance integrals (further: β-integrals) as well as of considering different interatomic distances on spin densities.

METHOD OF CALCULATION AND PARAMETERS

We shall use the LPH CI and UHF UP methods[2] with the following parameters:

a) Atomic valence state ionization potential $W_c = 0$; $\beta_{ij} = -2.39$ eV for neighbouring atoms, otherwise $\beta_{ij} = 0$. The γ integrals are calculated by the Pariser–Parr interpolation method[7] with $\gamma_{cc} = 11.13$ eV (ref.[8]).

b) As in (*a*) except for γ integrals which are calculated by the Nishimoto–Mataga interpolation method[9].

c) Interatomic distances and β integrals are calculated from bond orders[10] according to

$$r_{ij} = 1.517 - 0.18 P_{ij}, \quad \beta_{ij} = -1.90 - 0.51 P_{ij}, \tag{1}$$

where P_{ij} means element of the bond order matrix. Gamma integrals are calculated as in (*a*) or in (*b*), which cases are denoted in Tables I, II and IV as *A* and *AA*, respectively.

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[a] Experimental splitting constants in gauss units from ref.[12] except for naphthalene; [b] ref.[13].

TABLE I
Spin Densities Calculated by LHP CI and UHF UP Methods and Experimental Splitting Constants[a]

Radical	Position	a_E	LHP CI (a)	LHP CI (b)	LHP CI (c) A	LHP CI (c) AA	UHF UP (a)	UHF UP (b)	UHF UP (c) A	UHF UP (c) AA
Allyl	1	−14·38	0·522	0·535	0·522	0·535	0·545	0·573	0·548	0·575
	2	4·06	−0·045	−0·070	−0·045	−0·070	−0·090	−0·146	−0·096	−0·149
Pentadienyl	1	8·99	0·333	0·355	0·315	0·337	0·376	0·457	0·350	0·444
	2	2·65	−0·038	−0·056	−0·037	−0·056	−0·089	−0·153	−0·091	−0·153
	3	13·40	0·410	0·403	0·444	0·437	0·426	0·394	0·482	0·419
Benzyl	2	5·10	0·169	0·177	0·178	0·185	0·154	0·244	0·156	0·246
	3	1·60	−0·019	−0·029	−0·020	−0·030	−0·047	−0·123	−0·054	−0·122
	4	6·30	0·178	0·186	0·199	0·203	0·127	0·219	0·133	0·219
	7	16·40	0·557	0·572	0·520	0·542	0·716	0·650	0·727	0·659
Perinaphthenyl	1	7·30	0·186	0·195	0·187	0·195	0·213	0·264	0·207	0·261
	2	2·20	−0·021	−0·031	−0·021	−0·031	−0·058	−0·131	−0·051	−0·126
Pyrene⁻	1	4·75	0·144	0·154	0·143	0·156	0·169	0·230	0·176	0·232
	2	1·09	−0·016	−0·024	−0·016	−0·025	−0·039	−0·091	−0·044	−0·089
	4	2·08	0·092	0·090	0·088	0·087	0·086	0·072	0·082	0·069
Naphthalene±[b]	1	5·54	0·197	0·204	0·205	0·206	0·212	0·230	0·217	0·233
		4·90								
	2	2·06	0·062	0·067	0·060	0·056	0·049	0·038	0·046	0·035
		1·83								
Anthracene±	1	3·12	0·110	0·114	0·109	0·113	0·105	0·112	0·104	0·109
		2·76								
	2	1·40	0·044	0·042	0·044	0·043	0·030	0·020	0·029	0·020
		1·53								
	9	6·65	0·206	0·213	0·207	0·214	0·255	0·289	0·265	0·296
		5·41								
Naphthacene±	1	1·72	0·065	0·068	0·062	0·066	0·055	0·062	0·052	0·060
		1·55								
	2	1·06	0·031	0·030	0·031	0·030	0·018	0·010	0·017	0·007
		1·15								
	5	5·17	0·162	0·167	0·168	0·168	0·194	0·216	0·201	0·229
		4·25								

RESULTS AND DISCUSSION

The calculations were performed with the use of parameters according to $(a)-(c)$ for radicals I and II. It follows from Table I that different approximations in cases (a) and (b) for γ integrals lead to considerably different spin distribution in radicals. Spin densities based on approximation (a) are smaller than those based on (b). However, in both these approximations the ratios of spin densities ϱ_1/ϱ_3 in pentadienyl and ϱ_2/ϱ_4 in benzyl calculated by the LHP CI method are obtained correctly (smaller than unity). With the UHF UP method, these ratios are inverted with respect to the corresponding ratios of measured splitting constants. Hence, it is necessary to determine correctly the interaction parameters Q and K in the Colpa–Bolton relationship[11] between splitting constants and spin densities. Their values determined by the method of ref.[2] are shown in Table II with coefficients of statistical analysis of the relationship between experimental splitting constants, theoretical parameters and spin densities. It follows from the results that when the values of the interaction parameters are chosen properly on the basis of the given method, the differences in the statistical coefficients are negligible.

allyl pentadienyl benzyl perinaphthenyl

I

naphthalene anthracene tetracene pyrene
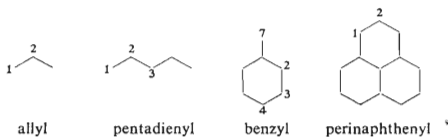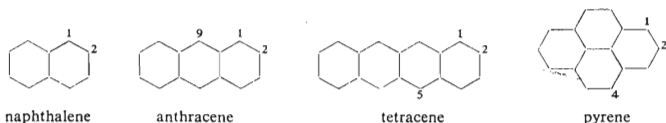
II

It was found[2] that the interaction parameters must be chosen individually in all methods of calculating the spin densities. It follows from Table II that a similar statement applies for the interaction parameters used in a single method when different approximations are used for the γ integrals.

We shall discuss the influence of chosen values for the β integrals. The value of -2.39 eV for vicinal positions and neglecting all values for nonvicinal positions is an approximation which can influence the accuracy of calculated spin densities. Based on $\beta_{cc} = -2.92$ eV for ethylene and $\beta_{cc} = -2.39$ eV for benzene[7], the dependence of spin densities on β integrals was for radicals of the first group studied with the use of various modes of calculating γ integrals. In the interval from -2 to -3 eV the influence of the β value on the spin densities is manifested only on the third decimal place, which is negligible with respect to other parameters (Table III).

The influence of different β integrals for various pairs of atoms on spin densities in hydrocarbons was also studied. Their values were calculated from Eq. (1). It is seen from Table IV that the changes of spin densities are somewhat larger than with constant β integrals, but negli-

gible against differences obtained by using different methods or different approximations for calculation of γ integrals. Similar conclusions follow from Table IV for the case where only γ integrals are changed during calculation.

TABLE II

Coefficients of Statistical Analysis of the Relationship between Experimental Hyperfine Splitting Constants, Theoretical Parameters and Spin Densities

Method			Correlation coefficient[a]	Standard deviation[a]	Q	K
LHP CI	(a)		0·984	0·832	28·61	14·37
	(b)		0·986	0·782	27·99	15·75
	(c)	A	0·986	0·799	28·66	14·06
		AA	0·989	0·682	27·98	15·81
UHF UP	(a)		0·976	1·020	27·25	12·76
	(b)		0·976	1·022	25·68	13·88
	(c)	A	0·979	0·957	26·91	12·71
		AA	0·979	0·966	25·33	13·54
LHP CI[b]	A	L^c	0·989	1·036	33·13	
	A	M^d	0·986	1·159	33·26	
	AA	L	0·991	0·942	31·44	
	AA	M	0·988	1·103	31·61	
UHF UP[b]	A	L	0·979	1·433	28·34	
	AA	M	0·975	1·560	28·95	
	AA	L	0·982	1·313	24·18	
	AA	M	0·981	1·374	24·74	

[a] Defined as in ref.[14]; [b] for radical group I, method (c); [c] only β integrals are changed during calculation; [d] only γ integrals are changed during calculation.

In studying the dependence of spin densities on the geometry of radicals, we assumed that interatomic distances in ion radicals can be determined approximately from bond orders[6]. Thus, the spin densities in approximation (c) were calculated (Table II).

In approximation (c) the distribution of spin densities in radicals is generally different from that in corresponding approximations with equal interatomic distances. The deviations are, however, much smaller than those obtained in using different approximations for the calculation of γ integrals. Table II shows how these changes in the distribution of spin densities are manifested in the statistical coefficients. In all cases there is an improvement, although not considerable, in accord with experiments implying that the approximation using equal interatomic distances does not lead to a substantial error.

TABLE III

Spin Densities for Various Values of β Integrals

Radical	Position	LHP CI			
		−2 eV	−2·39 eV	−2·6 eV	−3 eV
Allyl	1	0·523	0·523	0·522	0·521
	2	−0·045	−0·045	−0·044	−0·042
Pentadienyl	1	0·330	0·333	0·336	0·338
	2	−0·039	−0·038	−0·037	−0·036
	3	0·418	0·410	0·403	0·396
Benzyl	2	0·171	0·169	0·167	0·166
	3	−0·019	−0·019	−0·018	−0·017
	4	0·182	0·178	0·176	0·174
	7	0·551	0·557	0·559	0·562
Perinaphthenyl	1	0·187	0·186	0·186	1·185
	2	−0·021	−0·021	−0·020	−0·019

TABLE IV

Spin Densities Calculated for Various Values of β and γ Integrals

Radical	Position	LHP CI (c)				UHF UP (c)			
		L^a		M^a		L		M	
		A	AA	A	AA	A	AA	A	AA
Allyl	1	0·522	0·535	0·522	0·535	0·548	0·574	0·544	0·574
	2	−0·045	−0·071	−0·044	−0·070	−0·095	−0·148	−0·089	−0·147
Pentadienyl	1	0·319	0·341	0·331	0·352	0·359	0·445	0·369	0·454
	2	−0·037	−0·056	−0·038	−0·056	−0·093	−0·153	−0·088	−0·153
	3	0·437	0·431	0·413	0·408	0·469	0·415	0·437	0·497
Benzyl	2	0·177	0·184	0·170	0·177	0·156	0·253	0·152	0·236
	3	−0·020	−0·030	−0·018	−0·028	−0·053	−0·130	−0·046	−0·117
	4	0·195	0·200	0·181	0·186	0·131	0·231	0·125	0·210
	7	0·527	0·547	0·552	0·569	0·727	0·641	0·720	0·662
Perinaphthenyl	1	0·188	0·195	0·186	0·194	0·217	0·276	0·216	0·258
	2	−0·021	−0·031	−0·021	−0·031	−0·060	−0·145	−0·060	−0·122

^{a} See Table II, foot-notes c and d.

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STEREOREGULAR POLYMERIZATION
OF BUTADIENE

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The stereoregular polymerization of butadiene takes place in the presence of heterogeneous or homogeneous catalytic systems leading to the formation of pure stereoisomers *cis*-1,4 and *trans*-1,4 polybutadiene, respectively. The homogeneous catalytic systems are of great importance both from the practical and theoretical point of view. The best homogeneous systems for the preparation of *cis*-1,4 polybutadiene are cobalt(II) bis-acetylacetonate–diethylaluminium chloride or pyridinium complex of cobaltous chloride–diethylaluminium chloride[1,2]. A homogeneous catalytic system based on the complex rhodium compounds and diethylaluminium chloride[3,4] is suitable for preparation of sterically pure *trans*-1,4 polybutadiene. Stereoregular course of polymerization of butadiene initiated by the above mentioned catalytic system is practically not influenced by reaction conditions *i.e.* by catalyst and monomer concentrations, time and temperature[2,4]. The activity of the cobalt containing system is 4 to 5 times greater than that of the rhodium system[2,4].

The simultaneous application of two compounds of different transition metals in form of a Ziegler–Natta catalyst, each being able to govern the sterical course of polymerization in a different way, has not yet been described. The purpose of this communication is to describe the stereo-