Theoret. chim. Acta (Berl.) 27, 121—134 (1972)

Open Shell CNDO Treatments on Small and Aliphatic Radicals. Electronic Spectra and Some Ground State Properties

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Received April 10, 1972

Electronic spectra, ionization potentials and ground state geometries of nine radicals containing 3 or 4 atoms were studied by configuration interaction treatment based on SCF MO's (standard CNDO/2 and the version of Del Bene and Jaffé). SCF open shell procedures used were those developed by Roothaan and Longuet-Higgins, Pople (LHP). It appears that the LHP procedure is satisfactory; if based on the SCF MO's of Del Bene and Jaffé it gives results which agree fairly well with observed electronic spectra and first ionization potentials.

Elektronenspektren, Ionisierungspotentiale und Grundzustandsgeometrien von neun drei- und vieratomigen Radikalen wurden mit Hilfe der Konfigurationswechselwirkungsmethode mit SCF MO (CNDO/2 und Version nach Del Bene and Jaffé) untersucht. Es wurden die SCF "open-shell"-Verfahren nach Roothaan, Longuet-Higgins und Pople (LHP) benutzt. Es scheint daß das LHP-Verfahren zu zufriedenstellenden Ergebnissen führt; zusammen mit SCF-MO nach Del Bene und Jaffé ergibt sich bei Elektronenspektren und Ionisierungspotentialen befriedigende Übereinstimmung mit dem Experiment.

On a étudié les spectres électroniques, les potentiels d'ionisation et la géometrie de l'état fondamental de 9 radicaux contenant 3 ou 4 atomes par la méthode de l'interaction des configurations fondée sur les orbites moléculaires autocohérentes (standard CNDO/2 et la version de Del Bene et Jaffé). Les procédés autocohérents pour les couches ouvertes utilisés étaient ceux de Roothaan et de Longuet-Higgins, Pople (LHP). On voit que le procédé LHP est satisfaisant; dans le cas où il est basé sur les MO autocohérents de Del Bene et Jaffé, il donne des résultats qui sont en assez bon accord avec les spectres électroniques et les premiers potentiels d'ionisation observés.

In recent years the number of quantum chemical studies on conjugated radicals appears to be increasing [1], similarly as the number of *ab initio* studies on larger than biatomic radicals. The majority of semiempirical all-valence-electron open shell treatments has concerned calculations on spin densities, using the unrestricted INDO method; this topic will be disregarded in the present paper. The number of semiempirical studies devoted to other properties of radicals is still limited. The restricted open shell CNDO/2 treatment combined with configuration interaction was used to interpret the electronic spectrum of H_2NO [2]. Unrestricted methods were applied to determine the geometries of small radicals [3–12], ionization potentials [13–15], and the electronic spectrum of SO_3F [16]. Geometries and heats of formation were also studied by the recently developed "half-electron" method [17–20]. Several attempts were reported to estimate the structure of excited states by means of the open shell version of the CNDO/2 method [21–23].

The extended Hückel MO treatment of reactivity of small and aliphatic radicals and biradicals was reported by Hoffmann and co-workers [24].

The subject of this paper is the application of restricted open shell procedures (developed by Roothaan (R) [25] and Longuet-Higgins and Pople (LHP) [26]) in the frame of all-valence-electron methods. In the actual calculations, either the standard CNDO/2 parameter set [3, 27] or the one modified by Del Bene and Jaffé (DBJ) [28] will be adopted. For the NO_2 radical the INDO [29] and MINDO/2 [30] methods will also be employed. All these methods will be used to interpret the properties of radicals I-IX (Fig. 1) containing three or four atoms.

Electronic spectra of radicals I-IX represent the main field of our interest. Until now, semiempirical theoretical studies of the electronic spectra of radicals where rather rare [2, 16]. This is, of course, a very unsatisfactory state of affairs from the view-point of free radical chemistry, because the electronic spectroscopy gains its true importance [32] only if effectively combined with quantum chemical calculations.

Just as with π-electron semiempirical calculations, we think that here also one should investigate the range of properties and structural types amenable to the treatment based on a given parameter set and, more specifically, whether this parameter set gives fair agreement with both ground and excited state properties. Therefore we shall also consider heats of formation (in a later paper), molecular geometries, dipole moments, and ionization potentials.

Description of Calculations

If the procedure of Longuet-Higgins and Pople [26] is used, the $\boldsymbol{F}$ matrix elements are exactly the same as those given in the CNDO scheme for closed-shell systems [3]. The only differences concern the density matrix, which is now defined as

$$P_{\mu\nu} = \sum_{i=1}^{m-1} 2c_{i\mu}c_{i\nu} + c_{m\mu}c_{m\nu} \tag{1}$$

where m is an index of the singly occupied nondegenerate molecular orbital (SOMO), and a slightly modified expression for the total SCF energy (without core-core repulsions)

$$E = \sum_{i=1}^{m-1} \varepsilon_i + \frac{1}{2}\varepsilon_m + \frac{1}{2}\sum_{\mu}\sum_{\nu} P_{\mu\nu}H^c_{\mu\nu} - \frac{1}{4}J_{mm}, \tag{2}$$

where ε_i and $H^c_{\mu\nu}$ are orbital energies and core matrix elements, respectively, and J_{mm} is the Coulomb repulsion integral for the SOMO:

$$J_{mm} = \iint \varphi_m(1)\,\varphi_m(2)\frac{e^2}{r_{12}}\varphi_m(1)\,\varphi_m(2)\,d\tau_1\,d\tau_2\,. \tag{3}$$

Further, if

$$\varphi_m = \sum_{\varrho} c_{m\varrho}\chi_{\varrho},$$

we obtain

$$J_{mm} = \sum_{\mu}\sum_{\nu} c^2_{m\mu}c^2_{m\nu}\gamma_{\mu\nu}, \tag{4}$$

where $\gamma_{\mu\nu}$ is the electronic repulsion integral in terms of AO.

In the Roothaan method the F matrix is expressed in the form

$$F_{\mu\nu} = H^c_{\mu\nu} + 2J_{C,\mu\nu} - K_{C,\mu\nu} + 2J_{0,\mu\nu} - K_{0,\mu\nu} + (D_T B)_{\mu\nu} + (B D_T)_{\mu\nu} - B_{\mu\nu} . \tag{5}$$

Elements of the matrices contributing to the F matrix in the CNDO approach are easily derived from those given by Adams and Lykos [33] for a π-electronic case:

$$J_{C,\mu\mu} = \sum_A D_{C,AA} \gamma_{AB} , \qquad \mu \in B , \tag{6}$$

$$K_{C,\mu\nu} = D_{C,\mu\nu} \gamma_{AB} , \qquad \mu \in A, \nu \in B , \tag{7}$$

$$J_{0,\mu\mu} = \sum_A D_{0,AA} \gamma_{AB} , \qquad \mu \in B , \tag{8}$$

$$K_{0,\mu\nu} = D_{0,\mu\nu} \gamma_{AB} , \qquad \mu \in A, \nu \in B , \tag{9}$$

$$J_{C,\mu\nu} = J_{0,\mu\nu} = 0 , \qquad \mu \neq \nu , \tag{10}$$

$$B_{\mu\nu} = 2\alpha J_{0,\mu\nu} - \beta K_{0,\mu\nu} , \tag{11}$$

$$D_{C,AA} = \sum_\mu{}^A D_{C,\mu\mu} , \tag{12}$$

$$D_{0,AA} = \sum_\mu{}^A D_{0,\mu\mu} , \tag{13}$$

$$D_{C,\mu\nu} = \sum_k c_{k\mu} c_{k\nu} , \tag{14}$$

$$D_{0,\mu\nu} = f \sum_m c_{m\mu} c_{m\nu} , \tag{15}$$

$$D_{T,\mu\nu} = D_{C,\mu\nu} + D_{0,\mu\nu} . \tag{16}$$

Here $k, m, \mu\nu, AB$ are indices which run over closed-shell and open-shell molecular orbitals, atomic orbitals, and atoms, respectively. The definitions of the various terms in Eqs. (5)–(16) are the same as those given in the original papers [3, 25, 33]. All approximations involved and semiempirical parameters adopted are either the CNDO/2 ones [3, 27] or those due to Del Bene and Jaffé [28]. In the latter we employed the following modification: we use the Mataga-Nishimoto approximation for two center repulsion integrals rather than that of Pariser and Parr. From the trends in CNDO/2 parameters we tentatively chose for boron and fluorine the following parameters in the computational scheme of Del Bene and Jaffé: $\gamma_{BB} = 10.2$ eV; $\beta^0_B = -15$; $\gamma_{FF} = 13.9$ eV; $\beta^0_F = -55$. INDO and MINDO/2 calculations closely follow the original papers [29, 30]. The geometries assumed are given in Fig. 1.

Assuming the same molecular geometry and the same MO's for both the parent ($R^{(n-1)+}$) and ionized (R^{n+}) systems, the first ionization potential can in the SCF approach (Longuet-Higgins and Pople or Roothaan) be expressed [34] as

$$-I_m = E(R^{(n-1)+}) - E(R^{n+}) = \varepsilon_m - \tfrac{1}{2} J_{mm} \tag{17}$$

where m is the index for the singly occupied MO in a radical; ε_m and J_{mm} were defined before (cf. Eqs. (2) and (3)). Eq. (17) can be called an extension of the Koopmans' theorem to radicals.

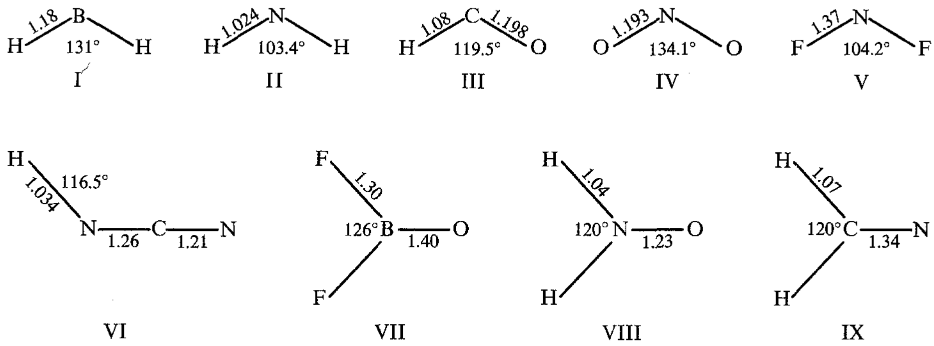

Fig. 1. Small radicals under study and geometries assumed
For radicals I–V, VI (in part), and VII experimental geometries were considered [31, 46]

For an electron removal from lower MO's the situation is more complicated because either an α-spin electron or a β-spin electron can be removed. Hence the ionized system formed can be in a singlet or a triplet state. Within the framework of the Longuet-Higgins and Pople method, the following expressions for higher ionization potentials were derived:

$$-I_i^S = \varepsilon_i - \tfrac{3}{2} K_{im}, \tag{18}$$

$$-I_i^T = \varepsilon_i + \tfrac{1}{2} K_{im}, \tag{19}$$

where

$$K_{im} = \iint \varphi_i(1)\, \varphi_m(2) \frac{e^2}{r_{12}} \varphi_m(1)\, \varphi_i(2)\, d\tau_1\, d\tau_2\,. \tag{20}$$

Assuming a singlet ionized system, the relation (18) holds, while for a triplet system Eq. (19) is valid. In the frame of the Roothaan method the following expressions hold

$$-I_i^S = \varepsilon_i - \tfrac{5}{2} K_{im}, \tag{21}$$

$$-I_i^T = \varepsilon_i - \tfrac{1}{2} K_{im}\,. \tag{22}$$

It is noteworthy that the difference in the ionization potentials I_i^S and I_i^T of the radical is equal, in the SCF approach, to the difference in transition energies, ${}^1\Delta\varepsilon_{i\to m}$ and ${}^3\Delta\varepsilon_{i\to m}$, in the ionized system

$$I_i^S - I_i^T = {}^1\Delta\varepsilon_{i\to m} - {}^3\Delta\varepsilon_{i\to m} = 2K_{im}\,. \tag{23}$$

The expression for the electron affinity for an uptake of one electron into the singly occupied molecular orbital (SOMO), φ_m, is given in the two open-shell methods as follows:

$$-A_m = \varepsilon_m + \tfrac{1}{2} J_{mm}\,. \tag{24}$$

Configuration interaction (CI) was incorporated into the computational scheme in the same way as in the procedure within a π-electron approach [35] and therefore its description need not be repeated here. With all radicals under study, the CI basis consists of configurations arising formally from one-electron transitions between several highest doubly occupied MO, the SOMO and several lowest vacant orbitals. The transition moments were calculated by means of the following formula (the x-component is considered):

$$\langle \varphi_i | \vec{x} | \varphi_j \rangle = \sum_A \left[\sum_\mu^A c_{i\mu} c_{j\mu} x_A + (c^A_{i,2s} c^A_{j,2p_x} + c^A_{j,2s} c^A_{i,2p_x}) \langle \chi^A_{2s} | \vec{x} | \chi^A_{2p_x} \rangle \right] \tag{25}$$

where the second term accounts for the local transitions owing to the *sp* polarization [27, 36].

Equations (1), (2), (17)–(20), (23), (24) also apply in the INDO and MINDO/2 scheme based on the open shell procedure of Longuet-Higgins and Pople.

Calculations were performed on an IBM 7040 computer by programs written by the authors.

Results

The entries in Table 1 are the SCF characteristics of radicals I-V[1] for the five lowest ionization potentials, for the first electron affinity, and for the dipole moment.

Table 2 also presents the results for radicals I-V[1]. Here the entries are results of the limited configuration interaction calculations, viz. the energy depression of the ground state (i.e. the energy difference between the LCI and SCF ground states), number of configurations, wavenumbers of maxima, logarithms of oscillator strengths, and the data on the experimentally observed positions of absorption bands [31]. On the basis of theoretical and experimental study of electronic spectra of small closed-shell systems [31, 40] and analysis of spectral data on radicals [31], it can be anticipated the Rydberg transitions in the radicals under study are irrelevant to the understanding of the nature of absorption bands located in the near infra-red, visible, and near ultra-violet regions. Therefore, we did not think it necessary to extend the ordinary AO basis set employed in all-valence-electron methods.

Discussion

First we give the results concerning the possibility of estimating molecular geometry and ionization potentials. Then the individual systems will be discussed.

Molecular geometry. We calculated the equilibrium bond lengths and valence angles for radicals I-V by the CNDO/2-LHP method. The results are compared, in Table 3, with the experimental data on the one hand, and with calculated values obtained by the unrestricted CNDO/2 method on the other hand. With systems under study the difference between the calculated and observed bond lengths amounts to about 0.02 Å. The calculated N–F bond length is about 0.1 Å too short when compared to the assumed value. This possible discrepancy is not due to deficiencies in the open shell approach, since too short N–F bond

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[1] Theoretical characteristics for the remaining radicals VI-IX are available from the authors on request.

Table 1. Ground state characteristics for radicals I–V: Ionization potentials (IP, eV), electron affinities (EA, eV), dipole moments (μ, D), and atomic charges

System		IP[a]					EA[b]	μ	Charges[c]		
		1	2	3	4	5			1	2	3
BH_2	CNDO/2-R	11.52(S)	19.39(T)	19.74(S)	24.55(T)	24.75(S)	−1.14	0.46	−0.047	−0.047	0.093
	CNDO/2-LHP	10.24(S)	19.38(T)	19.79(S)	24.55(T)	24.81(S)	0.14	0.52	−0.048	−0.048	0.096
	DBJ-LHP	10.16(S)	17.27(T)	17.55(S)	22.77(T)	23.17(S)	0.46	0.61	−0.040	−0.040	0.080
	Obs.[d]	9.8 ± 0.2	—	—	—	—	—	—	—	—	—
NH_2	CNDO/2-R	15.87(S)	17.69(T)	17.69(S)	20.33(T)	20.33(S)	−3.41	2.19	0.080	0.080	−0.160
	CNDO/2-LHP	15.87(S)	17.69(T)	17.69(S)	20.33(T)	20.33(S)	−3.41	2.19	0.080	0.080	−0.160
	DBJ-LHP	12.38(S)	14.56(T)	14.56(S)	18.07(T)	18.07(S)	0.37	2.27	0.083	0.083	−0.166
	Obs.[d]	11.4	—	—	—	—	—	—	—	—	—
HCO	CNDO/2-R	12.16(S)	18.26(T)	19.58(T)	19.58(S)	20.75(T)	−1.84	1.41	0.029	0.071	−0.100
	CNDO/2-LHP	11.98(S)	18.46(T)	19.47(T)	19.47(S)	20.75(T)	−1.64	1.28	0.019	0.092	−0.112
	DBJ-LHP	10.01(S)	14.27(T)	14.96(T)	14.96(S)	17.34(T)	1.70	1.83	0.066	0.101	−0.167
	Obs.[d]	9.88	—	—	—	—	—	—	—	—	—
NO_2	CNDO/2-R	13.82(S)	15.02(T)	15.62(T)	15.62(S)	21.82(S)	−0.12	0.92	0.413	−0.207	−0.207
	CNDO/2-LHP	13.55(S)	14.91(T)	15.67(S)	15.67(S)	20.67(S)	0.15	0.84	0.406	−0.203	−0.203
	DBJ-LHP	11.11(S)	11.52(T)	12.40(S)	12.40(T)	15.88(S)	3.15	0.80	0.417	−0.208	−0.208
	Obs.[e]	11.23	13.01	13.60	14.06	14.51	2.30 ± 0.15[f]	0.29–0.58[g]	—	—	—
NF_2	CNDO/2-R	16.66(S)	19.12(T)	19.12(S)	20.67(T)	20.67(S)	−0.89	0.10	0.229	−0.114	−0.114
	CNDO/2-LHP	16.16(S)	19.14(T)	19.14(S)	20.80(T)	20.80(S)	−0.38	0.03	0.208	−0.104	−0.104
	DBJ-LHP	12.40(S)	15.75(T)	15.75(S)	16.53(T)	16.53(S)	2.24	0.21	0.158	−0.079	−0.079
	Obs.[h]	12.10	14.60		16.38		—	—	—	—	—

[a] Calculated through (17)–(22), symbols in parentheses stand for spin multiplicity of the ionized systems.

[b] Calculated through (24).

[c] Numbering of positions corresponds to the order of atomic numbers.

[d] Ref. [31]. – [e] Ref. [37]. – [f] Ref. [38]. – [g] Ref. [39]. – [h] Ref. [13].

Table 2. Electronic spectra of radicals I–V

System	Method	Depr.[a]	CI-basis[b]	Wavenumbers (10^{-3} cm^{-1}) and logarithms of oscillator strengths					
				$\tilde{\nu}_1$	$\log f_1$	$\tilde{\nu}_2$	$\log f_2$	$\tilde{\nu}_3$	$\log f_3$
BH_2	CNDO/2-R	−0.003	18	8.01	−2.23	58.67	−2.08	70.55	−1.33
	CNDO/2-LHP	−0.009	18	8.01	−2.23	58.60	−2.08	70.45	−1.32
	DBJ-LHP	−0.026	18	7.96	−2.24	61.22	−1.94	72.76	−1.83
	Obs.[c]	—	—	11.6–15.6	—	—	—	—	—
NH_2	CNDO/2-R	0	18	21.95	−2.14	60.04	forbidden	70.75	−1.68
	CNDO/2-LHP	0	18	21.95	−2.14	60.04	forbidden	70.75	−1.68
	DBJ-LHP	0	18	22.60	−2.09	65.09	forbidden	79.13	−1.59
	Obs.[c]	—	—	11.1–23.3	—	—	—	—	—
HCO	CNDO/2-R	−0.122	39	20.44	−2.23	49.02	−1.50	52.64	−2.41
	CNDO/2-LHP	−0.153	39	20.66	−2.23	49.85	−1.48	53.21	−2.37
	DBJ-LHP	−0.047	39	15.08	−2.42	35.98	−2.70	36.70	−1.49
	Obs.[c]	—	—	11.6–21.7	—	24.4–38.5	—	—	—
NO_2	CNDO/2-R	−0.241	39	16.61	−3.88	17.90	forbidden	19.16	−2.39
	CNDO/2-LHP	−0.231	39	16.83	−2.92	17.52	forbidden	17.87	−2.32
	DBJ-LHP	−0.034	39	11.41	−2.11	12.08	forbidden	13.00	−3.21
	Obs.[c]	—	—	—		10.0–31.2			
				$\tilde{\nu}_4$	$\log f_4$	$\tilde{\nu}_5$	$\log f_5$	$\tilde{\nu}_6$	$\log f_6$
				37.58	forbidden	42.87	forbidden	64.51	−1.31
				36.55	forbidden	43.58	forbidden	63.46	−1.21
				23.16	forbidden	30.51	forbidden	55.14	forbidden
				$\tilde{\nu}_1$	$\log f_1$	$\tilde{\nu}_2$	$\log f_2$	$\tilde{\nu}_3$	$\log f_3$
NF_2	CNDO/2-R	0.000	33	42.85	−2.10	54.03	−1.82	57.51	forbidden
	CNDO/2-LHP	−0.115	33	41.07	−2.10	55.48	−1.80	58.92	forbidden
	DBJ-LHP	−0.075	33	38.48	−1.98	63.81	forbidden	69.97	−1.27
	Obs.[c]	—	—	35.7–42.5		—	—	—	—

[a] Doublet ground state energy depression (eV).

[b] Number of configurations (A, B, C_α, C_β) taken into account; one-electron promotions between the highest occupied, singly occupied, and the lowest unoccupied MO's were considered.

[c] Ref. [31].

Table 3. Calculated and experimental bond lengths and angles

System	l Θ	CNDO/2-LHP	CNDO/2-UHF[a]	Exp.[b]
BH_2	Å	1.179	—	1.18
	[°]	136.3	136.6	131
NH_2	Å	1.064	—	1.024
	[°]	106.1	107.3	103.4
NO_2	Å	1.189	—	1.1934
	[°]	138.7	137.7	134.1
NF_2	Å	1.227	—	1.37[c]
	[°]	105.8	102.5	104.2
HCO	C–H	1.109	—	1.08
	C–O	1.220	—	1.198
	[°]	131.7	—	119.5

[a] Ref. [3]. – [b] Ref. [31]. – [c] Assumed.

lengths are also predicted[2] for closed-shell systems [41]. Estimated valence angles are in all five cases higher than the observed values; the average deviation is 5°. Unfortunately, this deviation is systematic. The later experimental data [42] on the valence angle of III are in better agreement with the theory. A recent ab initio calculation yielded the value 130° [43].

Ionization potentials. Table 1 summarizes the calculated and observed first ionization potentials of radicals I-V. The DBJ-LHP values are in a fair agreement with the experimental data (the average error amounts to about 0.4 eV). As with closed shell systems, the estimated ionization potentials are too high if the repulsion integrals are calculated analytically (CNDO/2-LHP, CNDO/2-R, cf. Table 1). It is noteworthy that, with the systems under study, the extended Hückel energies of SOMO, being near (deviations lesser than 1 eV) to the $\varepsilon_m^{SCF} - \frac{1}{2} J_{mm}$ terms (DBJ-LHP procedure), give fair estimates of the observed first ionization potentials. Since the extended Hückel theory entirely disregards electron spin, it is inherently incapable of giving even qualitative estimates of higher ionization potentials of radicals.

Boron dihydride (I). Boron represents a positive pole in the B–H bonds. Table 4 presents, for the sake of illustration, the CNDO/2-R values for the dipole

Table 4. Calculated (CNDO/2-R) dipole moments (D) and electronic repulsion integrals (eV) for BH_2 as a function of the H–B–H valence angle (Θ in degrees)

Θ	μ	J_{33}	K_{13}	K_{23}
160	0.493	12.785	0.034	0.060
140	0.541	12.691	0.088	0.147
120	0.316	12.645	0.125	0.184
100	0.054	12.637	0.146	0.177
90	0.036	12.641	0.155	0.162

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[2] The calculations mentioned are of the INDO type, however the CNDO and INDO methods give practically the same estimations of molecular geometry, as expected on theoretical grounds (the interatomic contribution to the total energy is the same in both methods).

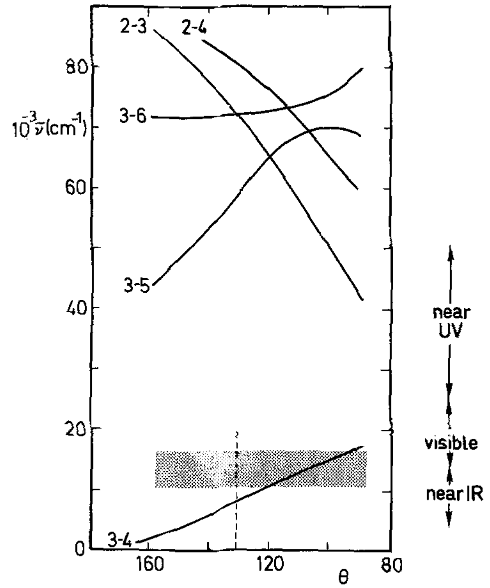

Fig. 2. Calculated CNDO/2-R transition energies in BH_2 as a function of the valence angle Θ. Main configurations (weights above 90% except 2–4) are indicated. The dotted area corresponds to the observed absorption [31]. The experimental valence angle [31] is indicated by a dashed line

moment and for the repulsion integrals J_{33}, K_{13}, and K_{23} as functions of the valence angle. The experimental dipole moment can be expected to have the value of about 0.4 D. On the basis of values of DBJ-LHP orbital energies and of repulsion integrals one can expect (Table 1) in the photoelectron spectrum three peaks in the region up to 21 eV (at 10.2, 17.3(T), 17.6(S) eV).

In the electronic spectrum only one band ($^2B_1 \leftarrow {}^2A_1$) was recorded [31], which occupies the great part of the visible region up to the near infra-red region. In spite of the great effort [31], no other band was found in the near ultraviolet. Fig. 2 presents the five lowest transition energies as a function of the valence angle. With the first four transitions the configurational mixing is insignificant. The calculation successfully interprets the first observed band as a $^2B_1 \leftarrow {}^2A_1$ transition from a singly occupied lone sp orbital to the empty $2p_z$ boron orbital, and explains why no other band was detected in the UV region.

Nitrogen dihydride (II). As is known, the SOMO is localized in the $2p_z$ AO of nitrogen [44], and therefore the value of the J_{44} integral is high. Because the coefficients in MO's φ_1, φ_2, and φ_3 standing at that AO are zero, all K_{i4} integrals in the CNDO approach vanish. Thus theoretical values for all higher ionization potentials equal the orbital energies ε_1, ε_2, and ε_3. The increase in the ionization potential on passing from BH_2 to NH_2 is understandable: in the SCF approach this increase is connected not only with the increase in J_{mm} (localized MO) but also with the decrease in the energy of SOMO.

As with the radical I, here also only one absorption band ($^2A_1 \leftarrow {}^2B_1$) was observed, its location expanding over the visible region up to the near infra-red.

The LCI calculations accord with this experimental finding (Table 2). The electronic transition is of the same type as in I, but here the lone *sp* orbital is doubly occupied and the $2p_z$ nitrogen orbital singly occupied in the ground state. The second band is predicted to lie in the vacuum ultra-violet.

Formyl radical (III). In the electronic spectrum two bands were observed [31], one in the visible ($\tilde{A} \leftarrow \tilde{X}$) and one in the ultra-violet. Herzberg pointed out [31] that it is uncertain that the lower state of the UV band is the ground state of III. However, the LCI calculations (DBJ-LHP) support the idea that both are due to excitation from the doublet ground state; in the region of the UV band (24,400–38,500 cm^{-1}) there occur two theoretical transitions (Table 2). The lowest three transitions can be characterized as follows: the first one is a 6–7 transition from a singly occupied "non-bonding" orbital to a π^* orbital, the second and third transitions are of the $\pi \rightarrow$ "n" (5–6) and "σ" $\rightarrow$ "n" (4–6) types.

Nitrogen dioxide (IV). The DBJ-LHP calculation interprets well the first ionization potential (Table 1). As none of the CNDO computational schemes employed gives reasonable results for higher ionization potentials determined by photoelectron spectroscopy [37], we also performed open shell INDO-LHP and MINDO/2-LHP calculations. Experimental [37] and MINDO/2-LHP ionization potentials are summaried in Fig. 3. The overall correspondence between

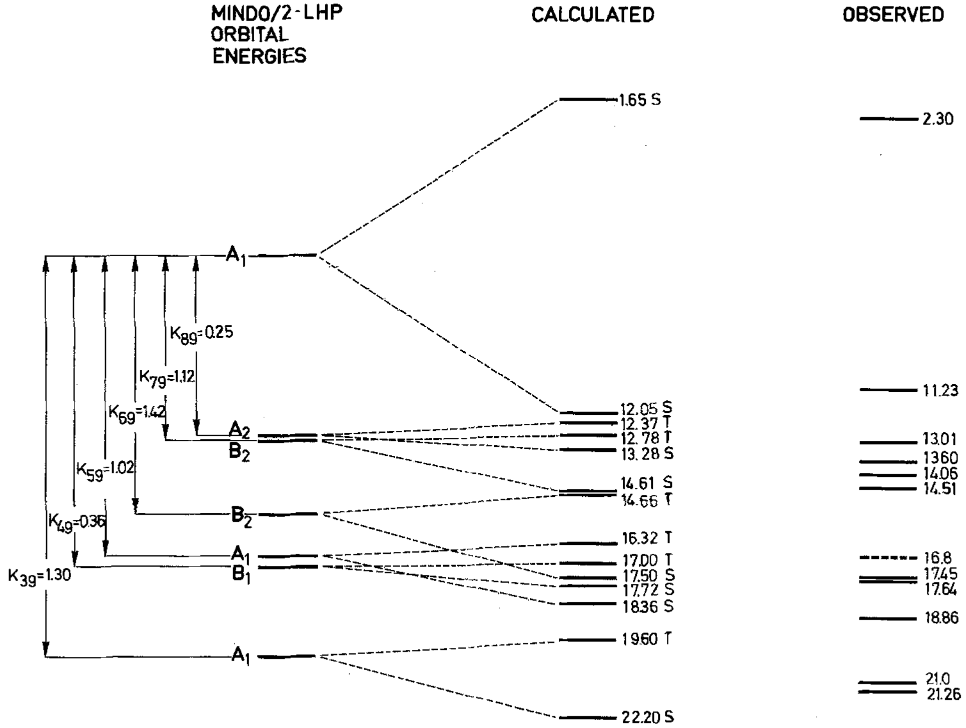

Fig. 3. Ionization potentials [37] and electron affinity [38] for NO_2. The theoretical values were calculated through Eqs. (21), (22), and (24). Values of K_{i9} exchange integrals, MO symmetries (C_{2v}), and multiplicity of states after electron removal or addition (S singlet, T triplet) are indicated

the calculated and observed potentials is fairly good, as well as that for the first electron affinity. As expected by analogy with closed shell systems, the INDO-LHP treatment gives too high values even though the agreement for the four lowest ionization potentials is reasonable.

The very nature of the absorption band of IV in the region of 10,000–31,200 cm^{-1}, its breadth and complexity, makes an analysis on this level prohibitive. It seems that this band consists of about five electronic transitions.

Nitrogen difluoride (V). From Table 1 it is apparent that a rather low dipole moment, 0.1–0.2 D, can be expected. Of the twelve MO's available, nine are doubly occupied, the tenth being the SOMO localized considerably in the nitrogen $2p_z$ AO (CNDO/2-R)

$$\varphi_{10} = 0.945\,\chi(2p_z N) - 0.230[\chi(2p_z F^1) + \chi(2p_z F^2)]\,. \qquad (26)$$

Accordingly, the value of the $J_{10,10}$ integral is very high (16.53 eV; CNDO/2-LHP). For in most of the occupied MO's the coefficient standing at the nitrogen $2p_2$ AO is zero; the exchange K_{i10} integrals accordingly mostly vanish. The DBJ-LHP values (Table 1) interpret well the photoelectron spectrum [13].

The LCI calculations lead to only one electronic transition in the UV region, in agreement with experiment [31]. The transition energy afforded by the DBJ parameter set is in quantitative agreement with the experimental value.

The observed band is interpreted as a $^2A_1 \leftarrow {}^2B_1$ transition from a σ molecular orbital (φ_9) to antibonding π molecular orbital (φ_{10}), the latter being SOMO in the ground state.

HNCN radical (VI). The calculated (DBJ-LHP and CNDO/2-LHP) dipole moment amounts to 2.5 D; the estimated value (DBJ-LHP) of the first ionization potential is 10.3 eV. Self-consistency in the CNDO/2-LHP or DBJ-LHP calculations is reached after 30 iterations; the Roothaan procedure here does not converge.

The LCI-DBJ-LHP calculation predicts a weak band ($\log f = -3.0$) in the region between the visible and infrared (11,500 cm^{-1}). The second, third, and forth transitions (31,500–33,100 cm^{-1}) can be assigned to the observed band [31] at 29,100 cm^{-1}. In the four lowest excited states the following configurations predominate (in %): 7–8 (90), 8–10 (70), 8–9 (92), and 5–8 (80). The respective molecular orbitals can be characterized as follows: φ_5 as a σ orbital, φ_7 as an orbital resembling a nonbonding π-orbital in allyl but constructed from the p_y AO's (y axis lying in the molecular plane and being perpendicular to the N–C–N direction), φ_8 as a nonbonding π-orbital (SOMO), φ_9 as an antibonding π-orbital (contructed from the p_y AO's) localized in the CN bond with the N atom being terminal, and φ_{10} as an antibonding π orbital. This implies that all these four transitions should be very weakly allowed.

BOF_2 radical (VII). The work of Mathews [45, 46] strongly suggests that F_2BO arises in the BF_3–O_2 discharge. The electronic emission spectrum exhibits two bands at 17,200 and 22,400 cm^{-1}, the second being polarized in the molecular plane perpendicularly to the molecular axis. The experimental data, however, do not exclude the possible presence of the F_2BO cation and do not afford positive evidence that both bands can be assigned to transitions from the same electronic state. The LCI calculations on the electronic spectra of VII and VII$^+$

were performed within the DBJ computational scheme, for VII using the LHP method. Given the uncertainties in the tentative parametrization for boron and fluorine, it is possible to characterize the results of calculations in a qualitative manner as follows. Probably both observed bands cannot be assigned to the F_2BO emission, because the calculation gives only one (forbidden) ${}^2B_1 \leftarrow {}^2B_2$ electronic transition (17,800 cm^{-1}) in the visible region, the next calculated one being at 36,400 cm^{-1} ($\log f = -2.05$). The closed shell calculation on $F_2BO^{\oplus}$ gives the first transition, ${}^1A_2 \leftarrow {}^1A_1$, at 8,700 cm^{-1} (forbidden), the second one, ${}^1B_2 \leftarrow {}^1A_1$, at 14,000 cm^{-1} ($\log f = -2.60$) polarized in the same manner as the short-wave observed band, and the next energy lowest transition at 31,600 cm^{-1}. These values suggest that the 22,400 cm^{-1} band observed by Mathews is due to the $F_2BO^{\oplus}$ emission and the longest-wavelength band is due to $F_2BO^{\oplus}$ and/or F_2BO first calculated transition.

It is noteworthy that the SOMO resembles a $2p$ lone pair orbital in carbonyl compounds. The calculated (CNDO/2-LHP) dipole moment amounts to 0.3 D.

Nitroxide (VIII). Besides the parent radical we also took into consideration the dimethyl derivative as the simplest dialkyl derivative. CNDO/2-LHP procedures give for the dipole moment of VIII and its dimethyl derivative the values of 3.06 and 3.48 D. These values are reasonable because the dipole moments of the N–O bonds [47] in both di-*t*-butyl- and diphenylnitroxides amount to 2.4 D, and the hydrogen atoms (methyl groups) possess a positive charge.

CI-DBJ-LHP calculations underestimate the transition energy of the band in the visible and overestimate it for the band in the ultraviolet region (Table 5). In agreement with the experimental finding [47], the theory characterizes the first transition as $n \rightarrow \pi^*$. The assignment for the second band made on experimental grounds admits, besides the $\pi \rightarrow \pi^*$ transition, the $n \rightarrow \sigma^*$ transition; according to the calculations this band is due to a $\pi^* \rightarrow \sigma^*$ transition. The calculated $\pi - \pi^*$ transition energies are 60,800 and 55,000 cm^{-1}, respectively, for VIII and its dimethyl derivative. We also employed a nonplanar geometry of H_2NO predicted by the ab initio calculation [48] ($r_{NH} = 0.99$ Å, $r_{NO} = 1.34$ Å, $\sphericalangle \text{HNH} = 116°$, out-of-plane angle 26°); the results, however, mean no improvement, the calculated first transition energy being 6,250 cm^{-1} and the second one 45,600 cm^{-1}.

Methyleneimino radical (IX). This radical arises as an intermediate in the photolysis of formalazine [49]

$$CH_2{=}N{-}N{=}CH_2 \xrightarrow{h\nu} 2\,CH_2{=}N^{\cdot} \rightarrow CH_2NH + HCN \qquad (27)$$

and its presence was proved by analyzing the ESR spectrum.

Table 5. Spectral data for nitroxides

	$\tilde{\nu}(\text{cm}^{-1})$	$\log f$	assignment	$\tilde{\nu}(\text{cm}^{-1})$	$\log f$	assignment
H_2NO (calcd.)	10,800	forbidden	$n \rightarrow \pi^*$	50,360	-1.79	$\pi^* \rightarrow \sigma^*$
$(CH_3)_2NO$ (calcd.)	12,750	forbidden	$n \rightarrow \pi^*$	52,750	-2.14	$\pi^* \rightarrow \sigma^*$
$(t\text{–}C_4H_9)_2NO$ (obs.[a])	22,000–24,500	0.9[b]	$n \rightarrow \pi^*$	~43,500	~3.5[b]	$\pi \rightarrow \pi^*$ or $n \rightarrow \sigma^*$

[a] Ref. [47]. – [b] $\log \varepsilon$.

Since there is real hope of measuring the electronic spectrum and other properties of this radical, we offer here some predictions. The dipole moment was estimated (CNDO/2-LHP) at 2.4*D* and the first ionization potential (DBJ-LHP) at 10.8 eV, the ionization being from the singly occupied MO. In agreement with a previous suggestion [50], the singly occupied orbital is approximately a nonbonding orbital localized in the $2p_y$ AO of nitrogen (the x direction along the C-N bond). The LCI-DBJ-LHP calculation gives the theoretical electronic spectrum consisting of four transitions in the visible and UV regions (17,700, 20,500, 21,200, and 37,500 cm^{-1}) which are due to almost pure 6–7, 5–7, 5–6, and 4–6 electron promotions. Only the fourth transition is allowed ($\log f = -1.91$). The first transition is of the $n \rightarrow \pi^*$ type; the next ones are of the $\pi \rightarrow \pi^*$, $\pi \rightarrow n$, and $\sigma \rightarrow n$ types.

Concluding Remark

The results obtained permit the following conclusions about the utility of various open shell treatments considered in this paper. As with conjugated radicals [51] the method of Longuet-Higgins and Pople and the Roothaan method yield similar results, the differences mostly being unimportant from the practical point of view. It appears that computational methods appropriate for interpretation of individual properties of radicals can be chosen on the basis of experience accumulated with closed shell systems [52, 53]. Thus for estimates of molecular geometry and dipole moments the standard CNDO/2 procedure is suitable, while for ionization potentials and electronic spectra the CNDO version of Del Bene and Jaffé is to be preferred.

Acknowledgements. Several FORTRAN subroutines incorporated in our program were written by Dr. P. Rosmus and Dr. J. Vojtík. Their assistance is gratefully acknowledged.

References

1. For references see Zahradník, R., Čársky, P.: In: Progr. physic. org. Chem. (A. Streitwieser, Jr., R. W. Taft), submitted for publication.
2. Kikuchi, O.: Bull. chem. Soc. Japan **42**, 47 (1969).
3. Pople, J. A., Segal, G. A.: J. chem. Physics **44**, 3289 (1966).
4. Andrews, P. R.: J. molecular Structure **6**, 85 (1970).
5. Grimm, F. A., Godoy, J.: Chem. Physics Letters **6**, 336 (1970).
6. Underwood, G. R., Vogel, V. L.: Molecular Physics **19**, 621 (1970).
7. Benson, H. G., Bowles, A. J., Hudson, A., Jackson, R. A.: Molecular Physics **20**, 713 (1971).
8. Wood, D. E., Lloyd, R. V., Lathan, W. A.: J. Amer. chem. Soc. **93**, 4145 (1971).
9. Beveridge, D. L., Guth, E.: J. chem. Physics **55**, 458 (1971).
10. Kelkar, V. K., Balla, K. C., Khubchandani, P. G.: J. molecular Structure **9**, 383 (1971).
11. Boyd, R. J., Whitehead, M. A.: J. C. S. Dalton **1972**, 78.
12. Boyd, R. J., Whitehead, M. A.: J. C. S. Dalton **1972**, 81.
13. Cornford, A. B., Frost, D. C., Herring, F. G., McDowell, C. A.: J. chem. Physics **54**, 1872 (1971).
14. Cornford, A. B., Frost, D. C., Herring, F. G., McDowell, C. A.: Chem. Physics Letters **10**, 345 (1971).
15. Boyd, R. J., Whitehead, M. A.: J. chem. Soc. (A) Inorg. Phys. Theor. **1971**, 3579.
16. King, G. W., Santry, D. P., Warren, C. H.: J. chem. Physics **50**, 4565 (1969).
17. Baird, N. C., Dewar, M. J. S.: J. chem. Physics **50**, 1262 (1969).
18. Dewar, M. J. S., Haselbach, E.: J. Amer. chem. Soc. **92**, 590 (1970).
19. Haselbach, E.: Chem. Physics Letters **7**, 428 (1970).

20. Kollmar, H.: Chem. Physics Letters **8**, 533 (1971).
21. Nixon, R. N.: Molecular Physics **12**, 83 (1967).
22. Kroto, H. W., Santry, D. P.: J. chem. Physics **47**, 2736 (1967).
23. Kirby, G. H., Miller, K.: Chem. Physics Letters **3**, 643 (1969).
24. Hoffmann, R., Swaminathan, S., Odell, B. G., Gleiter, R.: J. Amer. chem. Soc. **92**, 7091 (1970).
25. Roothaan, C. C. J.: Rev. mod. Physics **32**, 179 (1960).
26. Longuet-Higgins, H. C., Pople, J. A.: Proc. physic. Soc. **68** A, 591 (1955).
27. Pople, J. A., Segal, G. A.: J. chem. Physics **43**, S136 (1965).
28. Del Bene, J., Jaffé, H. H.: J. chem. Physics **48**, 1807 (1968).
29. Pople, J. A., Beveridge, D. L., Dobosh, P. A.: J. chem. Physics **47**, 2026 (1967).
30. Bodor, N., Dewar, M. J. S., Harget, A., Haselbach, E.: J. Amer. chem. Soc. **92**, 3854 (1970).
31. Herzberg, G.: Molecular spectra and molecular structure. III. Electronic spectra and electronic structure of polyatomic molecules. New York: Nostrand Reinhold Comp. 1966.
32. Atkins, P. W., Symons, M. C. R.: The structure of inorganic radicals. Amsterdam: Elsevier Publ. Comp. 1967.
33. Adams, O. W., Lykos, P. G.: J. chem. Physics **34**, 1444 (1961).
34. Hush, N. S., Pople, J. A.: Trans. Faraday Soc. **51**, 600 (1955).
35. Zahradník, R., Čársky, P.: J. physic. Chem. **74**, 1235 (1970).
36. Giessner-Prettre, C., Pullman, A.: Theoret. chim. Acta (Berl.) **13**, 265 (1969).
37. Brundle, C. R., Neumann, D., Price, W. C., Evans, D., Potts, A. W., Streets, D. G.: J. chem. Physics **53**, 705 (1970).
38. Lifshitz, C., Hughes, B. M., Tiernan, T. O.: Chem. Physics Letters **7**, 469 (1970).
39. McClellan, A. L.: Tables of experimental dipole moments. San Francisco and London: W. H. Freeman and Comp. 1963.
40. Salahub, D. R., Sandorfy, C.: Theoret. chim. Acta (Berl.) **20**, 227 (1971).
41. Gordon, M. S., Pople, J. A.: J. chem. Physics **49**, 4643 (1968).
42. Ogilvie, J. S.: Spectrochim. Acta **23** A, 737 (1967).
43. Claxton, T. A.: Trans. Faraday Soc. **67**, 897 (1971).
44. Walsh, A. D.: J. chem. Soc. **1953**, 2266 and the following papers.
45. Mathews, C. W., Innes, K. K.: J. molecular Spectr. **15**, 199 (1965).
46. Mathews, C. W., Innes, K. K.: J. molecular Spectr. **19**, 203 (1966).
47. Forrester, A. R., Hay, J. M., Thompson, R. H.: Organic chemistry of stable free radicals. London: Academic Press 1968.
48. Salotto, A. W., Burnelle, L.: J. chem. Physics **53**, 333 (1970).
49. Kamachi, M., Kuwata, K., Murahashi, S.: J. physic. Chem. **75**, 164 (1971).
50. Brivati, J. A., Root, K. D. J., Symons, M. C. R., Tinling, D. J. A.: J. chem. Soc. (A) **1969**, 1942.
51. Čársky, P., Zahradník, R.: Collect. czechoslov. chem. Commun. **36**, 961 (1971).
52. Jaffé, H. H.: Accounts chem. Res. **2**, 136 (1969).
53. Klopman, G., O'Leary, B.: Fort. chem. Forsch. **15**, 445 (1970).

Notes Added in Proof: 1. We found in the literature further experimental data: the electron affinity 1.21 eV for NH_2 (Buchelnikova, N.S.: Usp. fiz. nauk **65**, 351 (1958)) and the first ionization potential 10.87 eV for H_2CN (Pottie, R. F., Lossing, F. P.: J. Amer. chem. Soc. **83**, 4737 (1961)).

2. The name of our Institute was changed to The J. Heyrovský Institute of Physical Chemistry and Electrochemistry.

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