Theoret. chim. Acta (Berl.) 11, 271—273 (1968)

Relationes

The Electronic Properties of Conjugated Ions. II*

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Received May 24, 1968

The calculations presented here demonstrate the relative importance of the "excess charge" effect for energy calculations, and its lack of importance for spin density calculations, in conjugated ions and radicals.

In a previous paper [1], the π electronic spectra of the dinegative ions of several polyacenes were calculated, using several current π electron SCF (self consistent field) methods. The agreement with experiment left much to be desired, and appeared to be worse for the dinegative ions than for the mononegative ones. This suggests that the formal parameters involved in the π electron calculations should be allowed to vary with effective charge.

To test this hypothesis, we have re-examined the π electronic spectra of the dinegative ions of several conjugated hydrocarbons using a Brown-Heffernan [2] treatment. Thus, the integrals involved were allowed to vary with effective charge as the iteration for self consistency proceeded.

For first row atoms, the effective nuclear charge Z_i is given by

$$Z_i = N_i - 1.35 - 0.35\,(\sigma_i + 2R_{ii}) \tag{1}$$

in the notation of [3]. The valence state Ionisation Potential W_i is given by

$$W_i = 3.715\,Z_i^2 - 16.183\,Z_i + 13.933\,. \tag{2}$$

One center coulomb integrals were calculated according to

$$\gamma_{ii} = -0.195\,Z_i^2 + 7.223\,Z_i - 10.573 \tag{3}$$

and two center coulomb integrals were calculated by the method of Nishimoto and Foster [4]. As these integrals differ slightly from those used in [1], a "standard" calculation was also performed by holding the integrals constant throughout the calculation, for purposes of comparison.

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* Part 1 is considered to be Ref. [1].

Results

Butadiene dinegative ion provides a simple test-case for the energy calculations, and in Table 1 we present the one body density matrices for the two calculations. The changes in electron density are fairly small, the overall effect of the calculation being to "smear out" the charge. However, on performing configuration interaction calculations including all singly excited states the energies of the excited states are seen to be significantly different (Table 2). This difference is due principally to the different values of $-W_i$ for the charged atoms, although the different values of γ_{ij} also adds to this effect. Unfortunately, the dinegative ion of butadiene has not been observed spectroscopically, and so Table 2 also contains the results for naphthalene, biphenyl and anthracene dianions, together with the experimental results, where known. The energy levels calculated using the iteration for the SC α's are in better agreement with experiment than both those calculated without using the iteration, and than the results presented in Part 1, although the agreement with experiment is still not completely satisfactory. The calculations do, however, show that the "excess charge" effect is important in calculations of this kind. Similar conclusions also exist for the electronic spectra of the mononegative ions.

Table 1. *One body density matrices for butadiene dinegative ion*

j \ i	1	2	3	4
1	.8743	.2169	−0.2169	.1257
	.8486	.2297	−0.2297	.1513
2		.6256	.3743	−0.2169
		.6513	.3487	−0.2297

The upper figures are the results without iteration for self consistent parameters.

Table 2. *Calculated transition energies (eV). Allowed transitions only. Transition moments in brackets*

Molecule	Without iteration	With iteration	Experimental data	
Butadiene^{2-}	4.143 (1.1065)	3.6618 (2.5172)		
	9.368 (0.1226)	9.1180 (0.2423)		
Naphthalene^{2-}	2.959 (1.1998)	2.7006 (1.0178)	2.23	Ref. [5, 6]
	3.502 (1.0197)	3.2682 (1.1141)		
	5.123 (3.7713)	4.8121 (4.2938)	4.27	
	6.637 (0.6103)	6.5363 (0.6593)		
Anthracene^{2-}	2.359 (3.2974)	2.1420 (3.0146)	2.11	Ref. [5, 7]
	3.298 (0.9243)	3.0939 (0.9863)	3.07	
	4.534 (5.3716)	4.2831 (6.9923)	3.84	
	5.815 (0.01031)	5.6092 (0.0074)		
Biphenyl^{2-}	1.0297 (0.1340)	0.8279 (0.1500)		
	2.9389 (5.8685)	2.8431 (5.9213)		
	5.1967 (0.2222)	5.0405 (1.0625)		
	5.2101 (0.9313)	5.0585 (0.2094)		
	6.7421 (1.9627)	6.6115 (2.0422)		

Since the π electron density does not appear to be too greatly modified, it is probable that properties which depend only on electron density should not be greatly affected. In particular, the spin density distribution in naphthalene mononegative ion has been recalculated, and the results are presented in Table 3.

These spin density distributions were calculated by a method described previously [8], except that the Configuration Interaction was performed *exactly*, the exact lowest eigenvalue and eigenvector, y of the CI matrix A being found by the iteration [9]

$$\underline{y}^{(r+1)} = \underline{y}^{(r)} - \alpha_r [A \underline{y}^{(r)} - \mu_r \underline{y}^{(r)}]$$

where μ_r is the Rayleigh Quotient

$$\mu_r = \frac{\underline{y}^{(r)+} \underline{A} \, \underline{y}^{(r)}}{\underline{y}^{(r)+} \, \underline{y}^{(r)}}$$

in standard notation.

The spin densities are seen to be almost identical (Table 3).

Table 3. *Naphthalene mononegative ion*

Position	Spin density			
	I	II	III	IV
1	.0589	.0357	.0574	.0347
2	.1910	.2426	.1926	.2415
3	.0000	−0.0563	.0000	−0.0525

I: no CI, no iteration for SC parameters
II: CI, no iteration for SC parameters
III: no CI, iteration for SC parameters
IV: CI, iteration for SC parameters

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