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Configuration Interaction Calculation of the Ground State π-Electronic Angular Momenta of the Benzene Anion and Cation

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The ground state π-electronic angular momenta of the benzene anion and cation are calculated by the MC LCAO MO method which includes an optimum configuration interaction. Calculated values are $\pm 1.03\,\hbar$ for the anion and $\pm 0.74\,\hbar$ for the cation, while those obtained by the usual SCF without CI method are $\pm 1.07\,\hbar$ and $\pm 0.78\,\hbar$, respectively.

Theoretical calculations of the electronic angular momenta (therefore the magnetic dipole moments) of polyatomic molecules are becoming more and more important as rapid development in spectroscopic techniques facilitates resolving fine structures of the electronic transitions in such molecules. For non-linear axial molecules in their non-degenerate electronic states, just as linear molecules in Σ states, the electronic angular momentum is zero. This is the case for the ground state of benzene. In degenerate states, like the E_{1u} excited state of benzene and the ground states of the benzene mono-ions, the angular momentum is non-zero about the molecular symmetry axis. However, its value is not given by the well known formula, $\pm \Lambda\hbar$ ($\Lambda = 0, 1, 2, \ldots$), since there is no longer cylindrical symmetry, but is a non-integral multiple of $\hbar$. If reasonably good estimates of these electronic angular momenta are provided, they will be useful for an analysis of the rotational structure of the molecular electronic transitions and for a clear understanding of the optical and magneto-optical rotations of these molecules [1].

In this communication, we take up the benzene mono-positive and mono-negative ions as prototypes and try to calculate their ground state π-electronic angular momenta around molecular symmetry axis in their D_{6h} symmetry structures. A preliminary calculation for these ions has been carried out by Bishop and Dingle [2], in which only their ground configurations have been taken into account. We shall here examine to what extent configuration interaction (CI) has an effect on the results of such simple calculations. The wave-functions and the geometrical structures for the π-electronic ground states of these ions were taken from our previous papers [3, 4], in which we used a multi-configuration (MC) LCAO MO approach within a Pariser-Parr type π-electron approximation.

If we define a Cartesian coordinate system with its origin at the ring centre and the z-axis perpendicular to the molecular plane, the expectation value of the total electronic angular momentum around the z-axis for the ground configuration function is

$$\langle L_z \rangle = \Sigma_p \langle l_z \rangle_p \,, \tag{1}$$

where $\langle l_z \rangle_p$ is the expectation value of the analogous operator for an electron in molecular orbital (MO) p. If we assume the MO's to be linear combinations of $2p\pi$ Slater AO's centred on each nucleus, i.e.,

$$\Phi_p = (6N_p)^{-\frac{1}{2}} \sum_{j=1}^{6} \exp(2\pi i p k/6)\, \chi_k \,, \qquad p = 0, \pm 1, \pm 2, 3 \,. \tag{2}$$

$\langle l_z \rangle_p$ is easily expressed in terms of the two-centre integrals over these AO's such as

$$\langle \chi_a | l_z | \chi_b \rangle = -0.1\, i\hbar |\tan\theta| e^{-\varrho} (\varrho^2 + \varrho^3 + \varrho^4/3) \tag{3}$$

with $\varrho = ZR/2$, Z being the effective nuclear charge and R the distance between nucleus a and nucleus b. θ is the angle between the line joining either of the two nuclei and the ring centre and the x-axis, the latter being taken to be parallel with the line joining the two nuclei. Eq. (3) is in accord with that presented by Bishop and Dingle [2]. Using the well-known relations $\langle l_z \rangle_p = -\langle l_z)_{-p}$ and $\langle l_z \rangle_0 = 0$, we obtain $\langle L_z \rangle = \pm \langle l_z \rangle_2$ for the benzene anion and $\langle L_z \rangle = \pm \langle l_z \rangle_1$ for the benzene cation.

When the ground state function Ψ is approximated by an orthonormal linear combination of ground and excited configuration functions such that $\Psi = \Sigma_m A_m \Phi_m$, the expectation value of the total electronic angular momentum around the z-axis for the molecular ground state turns out to be

$$\langle L_z \rangle = \Sigma_m A_m^2 \langle L_z \rangle_m = \Sigma_{m,p} A_m^2 \langle l_z \rangle_{p,m} \tag{4}$$

instead of Eq. (1). Here $\langle l_z \rangle_{p,m}$ is the expectation value of the analogous operator for an electron in the p^{th} MO in excited state Φ_m, and the sum over p is to be taken over only occupied MO's in each state m. The off-diagonal matrix elements $\langle m | l_z | n \rangle$ all vanish due to the molecular symmetry.

In order to yield non-zero values for $\langle l_z \rangle_{\pm 1}$ and $\langle l_z \rangle_{\pm 2}$ we have to start from the complex MO's (2) and repeat the MC LCAO MO calculation proposed in our previous paper [3]. Instead of doing so, we solved the CI matrices constructed from configuration functions, the ${}^2E_{2u}$ species for $C_6H_6^-$ and the ${}^2E_{1g}$ species for $C_6H_6^+$, with the MC self-consistent C–C bond distances obtained before [3, 4]. Two-types of calculations, in which

(i) $$\beta_{pq} = \beta_0 \exp[-(r_{pq} - b)/a]$$

and

(ii) $$\beta_{pq} = -\tfrac{1}{2} K S_{pq} (I_p + I_q)$$

were used for the evaluation of the resonance integrals, were carried out with the effective nuclear charges 3.192 for $C_6H_6^-$ and 3.308 for $C_6H_6^+$ [3]. This treatment is justified because the MO eigenvalues of both ions thus calculated are in accord with those obtained previously by the standard iteration precedure [3, 4] in seven significant figures.

The calculated results are summarized in Tables 1 and 2. Eighteen configuration functions included in the $C_6H_6^-$ calculation are of the same types as (but

Table 1. *Ground state angular momentum of the benzene anion*

Type of calc.	NO CI	18CI's	
Approx. for β[a]	(i) (ii)	(i)	(ii)
C–C distance (Å)[b]	1.41042	1.41249	1.41268
$\langle l_z \rangle_1$[c]	0.802_0	0.801_0	0.800_9
$\langle l_z \rangle_2$[c]	1.068_6	1.066_4	1.066_2
$\langle L_z \rangle$[c]	1.068_6	1.032_0	1.028_0

[a] See the text.

[b] Self-consistent C–C bond distances calculated by the MC LCAO MO method in Refs. [3] and [4].

[c] All in units of ± $\hbar$.

Table 2. *Ground state angular momentum of the benzene cation*

Type of calc.	NO CI	14 CI's		16 CI's	
Approx. for β[a]	(i) (ii)	(i)	(ii)	(i)	(ii)
C–C distances (Å)[b]	1.41042	1.41220	1.41203	1.41234	1.41218
$\langle l_z \rangle_1$[c]	0.777_1	0.776_2	0.776_3	0.776_1	0.776_2
$\langle l_z \rangle_2$[c]	1.015_4	1.013_5	1.013_7	1.013_4	1.013_5
$\langle L_z \rangle$[c]	0.777_1	0.739_3	0.741_4	0.738_3	0.740_4

[a, b, c] See the footnotes of Table 1.

the linear combinations of) those listed in Table 3 of Ref. [3]. Of the sixteen configuration functions for $C_6H_6^+$, which are exactly of the same types as those listed in Table 1 of Ref. [4], the last two, Ψ_{23}^{66} and Ψ_{22}^{66}, are omitted in the fourteen CI's calculation, since these two have considerably high eigenvalues.

It is seen from the tables that the value of $\langle L_z \rangle$ becomes smaller as the C–C bond distances becomes larger and as the number of configurations increases. Our tentative conclusion is that the theoretical angular momenta around the molecular axis are $\pm 1.03\,\hbar$ for the benzene anion and $\pm 0.74\,\hbar$ for the benzene cation. Bishop and Dingle [2] found $\langle L_z \rangle = \pm 1.08\,\hbar$ and $\pm 0.81\,\hbar$ for $C_6H_6^-$ and $C_6H_6^+$ using a single configuration function with $Z = 3.18$ and the C–C bond distance 1.40 Å. Since a reasonably good estimate of the electronic angular momentum is needed for a calculation of the magneto-optical rotation of molecules, the MC LCAO MO approach used in the present note is promising for such purposes. The application of this approach to the molecular excited states to yield excited state angular momenta will be investigated in a subsequent paper.

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