A Remark on the Goeppert-Mayer and Sklar's Theory on the Excited States of Benzene

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Of the numerous theoretical procedures which have been proposed to elucidate the electronic states of benzene, the most outstanding is the so-called GMS-method (Goeppert-Mayer and Sklar's method), though it is in many respects open to criticism. Despite the effort of London(1) and Mulliken(2) to improve the method, the fundamental deficiency of the theory still remains, especially as it concerns the singlet-triplet transitions. In a preceding paper we have reported that benzene shows an absorption band at 5200 Å, which has been overlooked by

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(1) A. London, *J. Chem. Phys.*, **13**, 396 (1945).

(2) R. S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

earlier workers. The purpose of the present paper is to achieve, applying the principle of the GMS-method and taking duly into account the newly discovered absorption band, a more satisfactory agreement of the theory with experimental data. It may be stated in advance that our trial also proved to be far from successful, but its presentation here may be relevant, since it seems to have revealed the limit of applicability of the GMS-method.

To begin with, a correction had to be made in the values of integrals used by Goeppert-Mayer and Sklar⁽³⁾, which was taken from the Bartlett's table of molecular integrals. We calculated these values by using equations derived by Kotani⁽⁴⁾ and Parr and Crawford⁽⁵⁾, which gave results coinciding satisfactorily with each other. This agreement may indicate the validity of the recalculated values. Applying the corrected values, the energy differences between the ground level and the excited levels were calculated according to the GMS-method.

For the sake of simplicity, we shall omit here the procedures of calculation and only show the result in Table 1, in which the energy differences are given in e. v. unit.

Table 1

	$^3B_{1U}$	$^3E_{1U}$	$^3B_{2U}$	$^1B_{2U}$	$^1B_{1U}$	E_{1U}
corrected values	0.7	1.3	1.9	3.8	4.3	6.6
uncorrected values	1.5	2.2	3.0	5.0	5.8	8.0

As is indicated by the figures in the table, our corrected values yielded results which are rather in worse agreement with experiments than in the case of the original calculation by Goeppert-Mayer and Sklar. Our calculation gives lower values for all energy levels, and especially so for the triplet states.

The most prominent characteristics of the calculation by GMS-method is that the energy levels can be calculated, though with rather crude approximation, almost absolutely; that is to say, with no parameters and empirical data except those concerning the C-C distance and the effective nuclear charge. Since, however, this method gives such a poor agreement with experiment as shown above, it seems worth while to introduce a parameter in the calculation in order to get better quantitative agreement with the experiment.

In the above calculation, the C-C distance was taken to be $r=1.39$ Å. which was based on the experimental data on benzene. It is, therefore, unreasonable for us to take the value of the C-C distance as a parameter. On the other hand, the effective nuclear charge was chosen to be $Z=3.18$, a value which was obtained by Zener⁽⁶⁾ on the basis of a variational calculation minimizing the energy of the ground state of one carbon atom. There is, however, no evidence that the value of Z fitted for the atomic state must be the same as the value for the molecular state. It is to be supposed that the 2p electron cloud of a carbon atom is deformed in the benzene molecule on account of various kinds of interaction. Considering these points, it seems pertinent to take the effective nuclear charge as a parameter. Calculation was made taking the figures 2.28, 3.04, 3.18 and 3.80 as the value of Z. These values were chosen only for the sake of easiness of calculation. The result of the calculation is shown in Fig. 1, in which the height of energy levels is plotted against the values of Z, and the dotted lines show the height of energy levels determined from experiments.

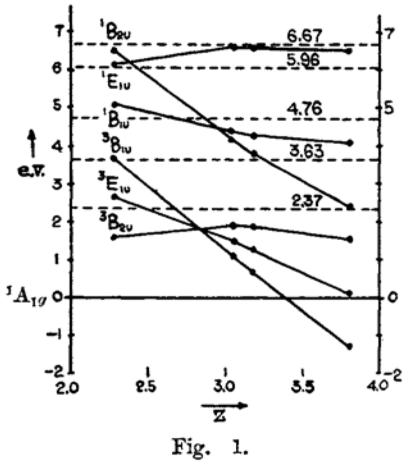

Fig. 1.

It is obvious from this figure that the increase of the value of Z causes the height of energy levels to be lowered, although the heights of $^1E_{1U}$ and $^3B_{2U}$ are not altered profoundly. The heights of excited levels at $Z=3.80$ are not reasonable, because they are too low; equally unreasonable is the result at $Z=2.28$, which does not agree with experiments even qualitatively. Contrary to our expectation, a comparatively better result was obtained at $Z=3.18$, the value that has been used in the original work of Goeppert-Mayer and Sklar. As will

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(3) M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

(4) M. Kotani, *Proc. of the physico-mathematical Soc. of Japan*, 20, extra No. (1938); **22**, extra No. (1940).

(5) Parr and Crawford, *J., Chem. Phys.* **16**, 1049 (1948).

(6) Zener, *Phys. Rev.*, **36**, 51 (1930).

be seen from these results, our trials to get more satisfactory results than the already obtained one have, on the whole, proved to be quite unsuccessful. The failure we have experienced may show that for attaining satisfactory results we have to improve fundamentally the method of approximation itself.

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