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Zero-Field Splittings in Aromatic Triplet States

III. Naphthalene, Including Accurate Two, Three and Four Centre Integrals

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The zero-field splitting parameters D and E have been calculated for naphthalene using T.B.M. and I. R. M. wave functions, and accurate values of all significant two, three and four centre dipolar interaction integrals. Agreement with experiment is improved in the case of E, but is less satisfactory for D.

Earlier papers in this series have examined the calculation of D and E for naphthalene using different approximate triplet state wave functions, ranging from the simple two configuration wave function [1] to wave functions involving extensive configuration interaction with singly excited states [2]. The latter wave functions are based upon the extensive work of Ruedenberg [3], and give good agreement between calculated and observed triplet state energies [4]. In II, we found that these wave functions also give good agreement with the observed values of D and E.

However, these calculations used approximate values for the dipolar integrals which were evaluated by approximating each $2p_z$ orbital by a single Gaussian orbital [5]. In the present work, we have studied two improvements to the previous work; the use of accurate dipolar integrals, and the inclusion of three and four centre integrals with these same wave functions.

Karplus and co-workers [6, 7] have applied the Gaussian transform method of integral evaluation to the problem of calculating accurate dipolar interaction integrals over Slater type $2p_z$ orbitals (S.T.O.'s). Godfrey, Kern and Karplus used accurate integrals in some calculations on naphthalene using a variety of triplet wave functions which, however, were not used to evaluate the triplet energies [7].

In the present work, D and E have been calculated using the T.B.M. and I.R.M. wave functions [3, 4, 2], but using the accurate integral values of Karplus, first including all two centre integrals and finally including all three and four centre integrals with magnitude $> 10^{-5}$ a.u.

The calculations were performed on the I.B.M. 1620 II computer using a programme described previously [2]. The results are shown in the Table.

The effect of the accurate integrals compared with the approximate integrals is to reduce the theoretical D value by $\sim 3\%$ for the two centre calculations and by $\sim 6\%$ when all integrals are included. The use of single Gaussian's is thus a poor approximation, as has been emphasised previously [2, 7, 8]. Three and four centre integrals contribute significantly, as Godfrey *et al.* found [7]. However, the use of these accurate integrals increases the discrepancy between theory and experiment.

In the case of *E*, however, the present approximations result in a close agreement between observed and calculated values of *E*.

The results, and those for the energy calculations, thus indicate that the I.R.M. wave function in particular furnishes a reasonably accurate description of the triplet state. However, since these changes are small and there are several approximations in Ruedenberg's theoretical framework [3], any better agreement would be fortuitous. The discrepancies which remain may well be due to the inadequacy of the single S.T.O. representation of the carbon $2p_z$ orbitals in the M.O.'s, as indicated by the recent work of Capello and Pullman [8]. However, in view of the success of the wave functions in predicting *both* triplet state energies and *D* and *E*, it may be that σ–π interactions are responsible for the difference [9]. Further work on this topic should aim at calculating *D* and *E and* the triplet state energy using double zeta atomic orbitals [10] and extensive configuration interaction.

Table. *Zero-field splitting parameters D and E for naphthalene using different integral approximations and wave functions*

Wave function		Integral approximation			Experimental [2] values
		A	B	C	
TBM	*D*	0.0833	0.0847	0.0793	0.099
	E	−0.0110	−0.0102	−0.0117	−0.015
IRM	*D*	0.1008	0.0958	0.0901	0.099
	E	−0.0109	−0.0123	−0.0141	−0.015

A Single Gaussian approximation [5]. Two centre integrals only.
B Single S.T.O. approximation. Two centre accurate integrals only [7].
C Single S.T.O. approximation. All two, three and four centre accurate integrals [7].

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