30. *Non-empirical Molecular-orbital Calculations on Benzene: The Scale Parameter Z.*

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As a guide to the reliability of calculations on other conjugated molecules, the energies of the lower π-electron levels of benzene have been computed by Goeppert-Mayer and Sklar's [1] method over a wide range of Z. As with ethylene,[2] the Z-dependence is so marked that the calculated energies can have but slight intrinsic quantitative significance in the absence of any properly defined procedure for the precise scaling of the wave functions. Four approximate methods for evaluating three- and four-centre integrals have been examined systematically and found to diverge badly when $Z < 3$.

Not without misgivings, Goeppert-Mayer and Sklar [1] adopted Zener's [3] value ($Z = 3{\cdot}18$) of the " effective nuclear charge " [2] of carbon ($1s^22s^22p^2\ {}^3P$) as the scale parameter in their molecular-orbital calculations on benzene, which have served as the basis of almost all subsequent non-empirical [4] studies on the π-electron energy levels of hydrocarbon molecules.

Despite the recent developments in electronic computing techniques, it is now clear that the many-sided problem of determining an optimum value of Z, altogether insuperable in 1938, is likely to await a solution for some time. In order to establish a reliable procedure for the scaling of molecular-orbital wave functions in calculations simplified by the use of the Hückel π-electron approximation [5]—if this is possible—it will almost certainly be necessary, as we have suggested elsewhere,[2,6] to carry out model computations in which the approximation is abandoned, *i.e.*, in which the σ electrons are considered explicitly along with the π electrons.

Until this exceedingly difficult undertaking can be accomplished, the interpretation of the numerical results of non-empirical molecular-orbital calculations is bound to be largely a matter of subjective judgement: there is always the danger of mistaking the properties of a set of simultaneous equations for those of the π-electron system which they purport to represent.

There being thus no well-defined procedure for determining the appropriate values of the scale parameter(s) to use in a Goeppert-Mayer–Sklar calculation, the computed energies can have little quantitative meaning unless they can be seen to be insensitive to small changes in Z in the neighbourhood of whatever the arbitrarily selected value(s) may be. Unfortunately, as we now show, both state energies and, to a lesser extent, excitation energies are rapidly varying functions of Z.

In completing an investigation [7,8] of some of the approximations which have to be adopted in antisymmetrized molecular-orbital calculations, we have had occasion to compute the core-attraction energies and the electron-repulsion energies of the lower π-electron states of benzene over a wide range of Z. In addition, we have evaluated the kinetic energies so as to make use of the opportunity of studying the Z-dependence of the total π-electron energies. The results are examined below from the two points of view just mentioned.

Approximations for Three- and Four-centred Integrals.—Using the symbols a, b, c, d, e, f to represent both the normalized atomic $2p\pi$ orbitals and also (as subscripts)

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[1] Goeppert-Mayer and Sklar, *J. Chem. Phys.*, 1938, **6**, 645; Sklar and Lyddane, *ibid.*, 1939, **7**, 374; Parr and Crawford, *ibid.*, 1948, **16**, 526, 1049; Roothaan and Parr, *ibid.*, p. 1001.

[2] Stewart, *Proc. Phys. Soc.*, in the press.

[3] Zener, *Phys. Rev.*, 1930, **36**, 51.

[4] Coulson and Jacobs, *Proc. Roy. Soc.*, 1951, *A*, **206**, 287.

[5] Altmann, *Proc. Roy. Soc.*, 1951, *A*, **210**, 327, 343.

[6] Stewart, *Proc. Phys. Soc.*, in the press.

[7] Stewart, *J.*, 1959, 70.

[8] Stewart, *J.*, 1959, 1856.

their origins of co-ordinates, we may write the π-electron Hamiltonian operator, H, for benzene as follows, V being Goeppert-Mayer and Sklar's core-potential function:[1,2]

$$\mathrm{H} = -\tfrac{1}{2}\sum \nabla_i^2 + \sum(\mathrm{V}_{ai} + \mathrm{V}_{bi} + \ldots + \mathrm{V}_{fi}) + \sum\sum \frac{1}{r_{ij}}$$

$$[\text{Summations: } i = 1 \text{ to } 6;\ j = 1 \text{ to } 5;\ i > j]$$

The energies, $(\Phi|\mathrm{H}|\Phi)$, of the various π-electron states ($\Phi_0, \ldots, \Phi_4$ in our notation[9]) can be broken down into sums of products of overlap integrals and three types of energy integral over atomic orbitals, corresponding to the three summation terms in the Hamiltonian operator. Whereas the numerical values of the individual kinetic-energy integrals can be obtained quite straightforwardly, core-attraction and electron-repulsion integrals invariably require computations of considerable complexity when the integrands are functions of co-ordinates referred to more than two origins. In practice the latter integrals are always evaluated approximately in terms of one- and two-centre Coulomb integrals. If we consider typical overlap, core-attraction, and electron-repulsion integrals,

$$S_{ab} = \int ab\,\mathrm{d}\tau$$

$$(a|\mathrm{V}_a|b) = \int a\mathrm{V}_a b\,\mathrm{d}\tau$$

$$\left(ab\left|\frac{1}{r_{12}}\right|cd\right) = \int a(1)b(1)\frac{1}{r_{12}}c(2)d(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

the four approximations in common use are as defined below.

Sklar Approximation[10] (S):

$$(a|\mathrm{V}_c|b) = S_{ab}(g|\mathrm{V}_c|g)$$

$$\left(ab\left|\frac{1}{r_{12}}\right|cd\right) = S_{ab}S_{cd}\left(gg\left|\frac{1}{r_{12}}\right|hh\right)$$

[g = midpoint between a and b; h = midpoint between c and d]

Mulliken Approximation[11] (M):

$$(a|\mathrm{V}_c|b) = \tfrac{1}{2}S_{ab}\{(a|\mathrm{V}_c|a) + (b|\mathrm{V}_c|b)\}$$

$$\left(ab\left|\frac{1}{r_{12}}\right|cd\right) = \tfrac{1}{4}S_{ab}S_{cd}\left\{\left(aa\left|\frac{1}{r_{12}}\right|cc\right) + \left(aa\left|\frac{1}{r_{12}}\right|dd\right) + \left(bb\left|\frac{1}{r_{12}}\right|cc\right) + \left(bb\left|\frac{1}{r_{12}}\right|dd\right)\right\}$$

[provided not more than two of a, b, c, d are identical]

Mulliken–Parr–Pariser Approximation[8,12] (M.P.P.):

$$\left(ab\left|\frac{1}{r_{12}}\right|cd\right) = \tfrac{1}{4}S_{ab}S_{cd}\left\{\left(aa\left|\frac{1}{r_{12}}\right|cc\right) + \left(aa\left|\frac{1}{r_{12}}\right|dd\right) + \left(bb\left|\frac{1}{r_{12}}\right|cc\right) + \left(bb\left|\frac{1}{r_{12}}\right|dd\right)\right\}$$

[without the above restriction]

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[9] Stewart, *J.*, 1958, 4016.

[10] Sklar, *J. Chem. Phys.*, 1939, **7**, 984; A. London, *ibid.*, 1945, **13**, 396.

[11] Mulliken, *J. Chim. phys.*, 1949, **46**, 497; Rüdenberg, *J. Chem. Phys.*, 1951, **19**, 1433.

[12] Parr and Pariser, *J. Chem. Phys.*, 1955, **23**, 711.

TABLE 1. *Calculated energies* (ev *) *of the lower π-electron configurations of benzene.*

$ZR_o/2$		1·5	2·0	2·5	3·0	3·5	4·0	4·5	5·0	5·5
Z		1·14	1·52	1·89	2·27	2·65	3·03	3·41	3·79	4·17
					Kinetic energy.					
Configuration										
Gd. ($^1A_{1g}$)		31·14	48·08	67·74	91·32	120·29	156·05	199·64	251·62	312·07
Exc. (B_{1u}, B_{2u}, E_{1u})		36·58	55·42	76·89	102·11	132·42	169·09	213·07	264·92	324·75
					Core-attraction energy (*hydrogen-like* 2*s orbital*).					
Con-fign.	Approxn.									
Gd.	S.	−297·52	−339·08	−368·06	−392·19	−415·81	−440·92	−468·23	−497·73	−529·20
	M.	−324·57	−356·08	−378·33	−398·30	−419·34	−442·91	−469·32	−498·32	−529·54
Exc.	S.	−307·89	−346·25	−374·36	−398·63	−422·58	−447·84	−475·01	−504·07	−534·85
	M.	−322·93	−357·08	−381·52	−403·12	−425·24	−449·34	−475·82	−504·51	−535·10
					Core-attraction energy (*nodeless* 2*s orbital*).					
Con-fign.	Approxn.									
Gd.	S.	−286·30	−327·54	−356·72	−381·20	−404·97	−429·95	−456·86	−485·68	−516·15
	M.	−312·03	−343·59	−366·34	−386·85	−408·21	−431·75	−457·84	−486·22	−516·46
Exc.	S.	−296·30	−334·38	−362·76	−387·41	−411·51	−436·62	−463·38	−491·76	−521·60
	M.	−310·55	−344·72	−369·57	−391·63	−413·97	−437·98	−464·11	−492·16	−521·82
					Electron-repulsion energy.					
Con-fign.	Approxn.									
$^1A_{1g}$	S.	63·86	78·66	90·34	99·42	106·51	112·23	117·06	121·34	125·31
	M.	69·87	83·52	93·76	101·65	107·94	113·18	117·71	121·81	125·64
	M.P.P.	69·90	83·32	93·45	101·36	107·80	113·24	118·02	122·33	126·34
	z.d.o.	71·64	84·73	94·47	102·05	108·23	113·51	118·18	122·43	126·39
$^1B_{1u}$	S.	70·70	81·41	91·88	100·67	107·90	113·95	119·23	124·02	128·53
	M.	66·91	82·23	93·16	101·60	108·47	114·30	119·47	124·20	128·68
	M.P.P.	69·05	82·59	93·01	101·36	108·31	114·30	119·66	124·57	129·18
	z.d.o.	71·62	84·76	94·64	102·47	109·02	114·75	119·93	124·72	129·27
$^1B_{2u}$	S.	67·16	79·66	90·79	99·78	106·92	112·71	117·62	121·96	125·96
	M.	68·04	82·47	92·96	101·07	107·60	113·07	117·82	122·09	126·06
	M.P.P.	69·01	82·46	92·73	100·84	107·49	113·12	118·06	122·49	126·58
	z.d.o.	71·68	84·84	94·64	102·28	108·51	113·83	118·52	122·79	126·77
$^1E_{1u}$	S.	69·40	82·09	93·44	102·73	110·24	116·43	121·75	126·49	130·89
	M.	69·78	84·90	95·94	104·48	111·37	117·16	122·23	126·82	131·12
	M.P.P.	71·34	85·32	95·99	104·42	111·35	117·26	122·48	127·23	131·65
	z.d.o.	72·60	86·40	96·83	105·04	111·78	117·56	122·68	127·36	131·73
$^3B_{1u}$	S.	67·18	78·91	89·49	98·03	104·74	110·10	114·54	118·37	121·82
	M.	67·11	81·57	91·87	99·64	105·75	110·73	114·95	118·65	122·02
	M.P.P.	68·88	82·10	92·03	99·72	105·86	110·94	115·29	119·12	122·59
	z.d.o.	71·55	84·49	93·95	101·15	106·88	111·64	115·76	119·42	122·78
$^3B_{2u}$	S.	70·36	80·97	91·28	99·87	106·84	112·58	117·48	121·85	125·88
	M.	66·31	81·51	92·37	100·69	107·36	112·92	117·74	122·05	126·04
	M.P.P.	69·01	82·46	92·73	100·84	107·49	113·12	118·06	122·49	126·58
	z.d.o.	71·68	84·84	94·64	102·28	108·51	113·83	118·52	122·79	126·77
$^3E_{1u}$	S.	68·77	79·94	90·39	98·95	105·79	111·34	116·01	120·11	123·85
	M.	66·71	81·54	92·12	100·17	106·56	111·83	116·34	120·35	124·03
	M.P.P.	68·95	82·28	92·38	100·28	106·67	112·03	116·67	120·81	124·59
	z.d.o.	71·62	84·66	94·29	101·72	107·70	112·74	117·14	121·10	124·77
					Total π-electron energy (*hydrogen-like* 2*s orbital*).					
Con-fign.	Approxn.									
$^1A_{1g}$	S.	−202·52	−212·34	−209·97	−201·45	−189·01	−172·64	−151·54	−124·76	−91·83
	M.	−223·57	−224·47	−216·83	−205·33	−191·11	−173·68	−151·97	−124·89	−91·83

* A.U. = 27·210 ev.

Zero Differential Overlap Approximation[8,12–14] (z.d.o.):

$$\left(ab\left|\frac{1}{r_{12}}\right|cd\right) = 0 \text{ unless } a = b \text{ and } c = d$$

$$S_{ab} = 0 \text{ unless } a = b$$

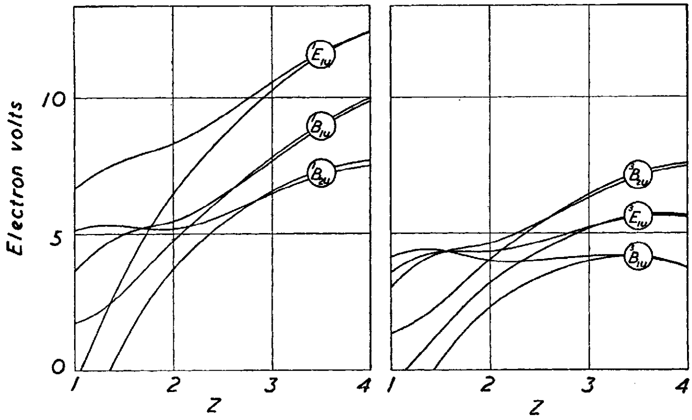
Limiting the scope of the work by considering only the states (" configurations "[4]) defined by Goeppert-Mayer and Sklar[1] (or, equivalently, by Stewart[9]), and ignoring configuration " interaction " and σ–π " exchange," we have calculated the components of the π-electron energies of benzene for $Z = 1{\cdot}13637(0{\cdot}37879)4{\cdot}16669$, *i.e.*, for $ZR_o/2 = 1{\cdot}5(0{\cdot}5)5{\cdot}5$. $R_o = 1{\cdot}397/0{\cdot}52917$ Bohr radii[15] is the *ortho* C–C bond-length.[16] In evaluating integrals over atomic orbitals we have used Kopineck's[17] and Roothaan's[18] formulæ and tables.

We have eschewed Goeppert-Mayer and Sklar's approximate relation[1,2,7]

$$(b|-\tfrac{1}{2}\nabla^2 + \mathrm{V}_a|a) \sim S_{ab}(a|-\tfrac{1}{2}\nabla^2 + \mathrm{V}_a|a) \sim S_{ab}W_{2p},$$

where a, b represent any two members of the set $a, b, \ldots, f$. This relation can patently not be treated as an identity in Z (a point sometimes overlooked).

Energies of the lower π-electron configurations of benzene, calculated relative to that of the ground state. Three- and four-centre potential-energy integrals evaluated by means of the Sklar approximation (three lower curves at the left of each half of the figure) and the Mulliken approximation (three upper curves).



The results in Table 1 confirm those reported previously,[7,8] and call for little further comment. Attention must be directed, however, to the large discrepancies between the results of the various approximate calculations which arise when $Z < 3$. These affect not only the configuration energies (a matter which would perhaps not be very serious in a Goeppert-Mayer–Sklar calculation with the usual limited objectives) but also the excitation energies (see Figure).

Preliminary calculations on ethylene (Murai;[19] cf. Stewart[2]) suggest that values of

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[13] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.

[14] Mulliken, " Symposium on Molecular Physics at Nikko, 1953," p. 17.

[15] Kauzmann, " Quantum Chemistry," Academic Press Inc., New York, 1957, App. 1.

[16] Langseth and Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350.

[17] Kopineck, *Z. Naturforsch.*, 1950, **5**a, 420; 1951, **6**a, 177; 1952, **7**a, 785; Preuss, " Integraltafeln zur Quantenchemie," Springer-Verlag, Berlin etc., 1956, Vol. 1.

[18] Roothaan, *J. Chem. Phys.*, 1951, **19**, 1445; *idem*, " Tables of Two-Center Coulomb Integrals between 1s, 2s, and 2p Orbitals," Laboratory of Molecular Structure and Spectra, University of Chicago, 1955.

[19] Murai, *Progr. Theor. Phys.* (*Japan*), 1952, **7**, 345.

Z nearer 2 than 3 may be appropriate for the excited configurations. If this should prove to be a feature of general applicability and general importance in π-electron calculations, it will obviously become necessary to investigate the evaluation of three- and four-centre integrals much more thoroughly than hitherto. [Although this paper is concerned essentially with non-empirical calculations, we should emphasize the need for discretion in semi-empirical calculations in which artificially low values of Z are used.]

The differences (*ca.* 11—13 ev) between the two sets of core-attraction energies in Table 1 have, of course, no direct bearing on the choice of a $2s$ orbital of optimum form: the $2s$ orbital is represented only in the core-potential function and not in the (incomplete) molecular wave function. The calculated excitation energies are relatively insensitive to the type of $2s$ orbital used: Table 1 reveals a maximum divergence of 0·37 ev. [A hydrogen-like orbital was used in obtaining the excitation energies plotted in the Figure.]

Z-Dependence of Calculated Energies.—The variety of approximations available for the calculation of the potential-energy components makes the estimation of the total π-electron energies very arbitrary, especially at low values of Z. Using the same approximation for repulsion as for attraction energies (because this gives the least disconcerting results), we have listed the π-electron energy of the ground state in the last two rows of Table 1. It is evident that in the region around $Z = 3{\cdot}18$ a change of only 1% in Z changes the ground-state energy by about $1\frac{1}{2}$ ev, and much the same is true for the excited states: in the absence of any procedure for determining the precise value of Z, state energies have thus scarcely any quantitative significance.

We have recently [2] examined the conditions under which the variation principle may be invoked in calculations embodying Goeppert-Mayer and Sklar's application of the Hückel π-electron approximation, and it suffices here to re-affirm that the energy minima near $Z = 1{\cdot}5$ are entirely without variational significance.

The results shown in the Figure are altogether different from those which Shull and Ellison [20] obtained with the use of Goeppert-Mayer and Sklar's W_{2p} approximation. Excitation energies are necessarily much less sensitive to changes in Z than state energies, but the uncertainty which the Figure reveals is nevertheless most disquieting. While it is pleasing that the order of the energy levels is the same over the whole of the range of Z likely to be of interest, it seems very doubtful whether there can be much justification for carrying out elaborate calculations to obtain results of such slight quantitative value, or for using these results in the analysis of electronic spectra.

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[20] Shull and Ellison, *J. Chem. Phys.*, 1951, **19**, 1215.