

#### 14. An Examination of Some Approximations in Antisymmetrized Molecular-Orbital Calculations.

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A numerical study of some of the arbitrary simplifications adopted in "non-empirical" calculations on the energy levels of hydrocarbon  $\pi$ -electron systems indicates that (a) the customary approximations for three- and four-centre potential-energy integrals agree reasonably well *inter se*, and calculations on many-electron systems are thus probably not subject to significantly greater error than calculations on two-electron systems; (b) the analytical form of the carbon 2s wave function is not critical; (c) considerable uncertainty is introduced by the use of the  $W_{2p}$  approximation,

$$\int \phi_b(T + V_a)\phi_a d\tau \sim W_{2p} \int \phi_b \phi_a d\tau$$

APART from the problems arising from the essential inflexibility of the molecular wave functions,  $\Psi$ , and the incompleteness of the Hamiltonian operator,  $H$ , "non-empirical" calculations on the energy levels of the  $\pi$ -electron systems of unsaturated or aromatic hydrocarbons are always beset by uncertainties resulting from the use of a number of arbitrary procedures (some inescapable) in the evaluation of the matrix elements  $\int \Psi^* H \Psi d\tau$ .

In an attempt to assess the relative importance of the last source of error, a purely numerical study has been made of three possible difficulties: (a) recourse to approximate methods for evaluating three- and four-centre integrals; (b) the lack of any simple criterion for determining the optimum form of the carbon 2s wave function; (c) the adoption of the questionable  $W_{2p}$  approximation. Kinetic energies ( $\mathcal{K}$ ), electron-repulsion energies ( $\mathcal{U}$ ), and core-attraction energies ( $\mathcal{V}$ ) have been considered separately; for purposes of illustration the antisymmetrized molecular-orbital (ASMO) calculations of Parr and Crawford<sup>1</sup> on ethylene and of Goepfert-Mayer and Sklar<sup>2,3</sup> on benzene have been chosen. No allowance has been made for configuration interaction or for  $\sigma$ - $\pi$  exchange; and the original Goepfert-Mayer-Sklar technique<sup>2</sup> has been modified only in the ways indicated explicitly below.

The conventional value of 3.18 has been assigned to  $Z$  in the exponential factor,  $\exp(-Zr/2)$ , of the carbon 2s and 2p atomic wave functions. This value of the "effective nuclear charge" cannot be justified, and it is doubtless quite unsuitable in a molecular calculation; but there is at present no tolerably simple quantum-mechanical means of obtaining a better estimate. However, the  $Z$ -dependence of the results presented here has been tested (paper in preparation), and, except where the contrary is specified, it may be understood that the conclusions derived from an examination of Tables 1 and 2 hold good over a wide range of  $Z$  and  $R$  ( $1 \leq ZR/2 \leq 6$ ),  $R$  being the C-C internuclear distance in Bohr radii.

*Ethylene (Table 1).*—Ethylene is the only molecule in which the electron-repulsion energy can be evaluated without resort to simplifications not fundamental to the Hückel  $\pi$ -electron approximation or the Goepfert-Mayer-Sklar procedure. It is thus most appropriate for an examination of Pariser and Parr's<sup>4</sup> "zero differential overlap" (z.d.o.) approximation, in which all integrals representing overlap between different atoms and all electron-repulsion integrals other than one- and two-centre Coulomb integrals are disregarded. It is clear from Table 1 that the enormous saving of computational effort which results (especially in more complex molecules) is fully justified. The maximum

<sup>1</sup> Parr and Crawford, *J. Chem. Phys.*, 1948, **16**, 526.

<sup>2</sup> Goepfert-Mayer and Sklar, *ibid.*, 1938, **6**, 645; Sklar and Lyddane, *ibid.*, 1939, **7**, 374; Parr and Crawford, *ibid.*, 1948, **16**, 1049.

<sup>3</sup> Stewart, *J.*, 1958, 4016.

<sup>4</sup> (a) Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767; (b) Parr and Pariser, *ibid.*, 1955, **23**, 711.

error of 0.35 eV found in ethylene is not large in relation to the standard of accuracy attainable in ASMO calculations of excitation energies. The very close approximation to the accurately computed electron-repulsion energy of the ground state [only] persists over a wide range of  $ZR$ , and is found also in the hydrogen molecule.

TABLE I. *Ethylene: Composition of ground-state energy and excitation energies (eV †)*

Component ‡	2s orbital	$^1A_g$	$^1A_g - ^1A_g^*$	$^1A_g - ^1B_{1u}$	$^1A_g - ^3B_{1u}$
$\mathcal{Q}$ (accurate) .....	—	13.052	0.348	4.141	-4.204
$\mathcal{Q}$ (z.d.o.) .....	—	13.083	0.000	3.852	-3.852
$\mathcal{T}$ .....	—	58.480	28.542	14.271	14.271
$\mathcal{V}$ .....	H-like	-99.981	-13.916	-6.958	-6.958
	nodeless	-96.460	-13.457	-6.729	-6.729
$\mathcal{T} + \mathcal{V}$ .....	H-like	-41.501	14.626	7.313	7.313
	nodeless	-37.980	15.085	7.542	7.542
$\mathcal{W}$ .....	H-like	-40.660	12.300	6.150	6.150
	nodeless	-36.722	11.609	5.805	5.805

C-C bond length = 1.353 Å (Galloway and Barker, *J. Chem. Phys.*, 1942, **10**, 88).

$^1A_g$ ,  $^1A_g^*$ ,  $^1B_{1u}$ ,  $^3B_{1u}$  correspond to Parr and Crawford's  $^1\Psi_1$ ,  $\Psi_2$ ,  $\Psi_V$ ,  $\Psi_T$ .

†‡ See footnotes to Table 2.

While the use of approximation formulæ of the Mulliken type (see *Benzene* below) "almost with abandon" <sup>4b</sup> might perhaps be hazardous in some circumstances, it is easily shown that the zero differential overlap approximation is analytically equivalent in a two-electron system to an approximation in which Mulliken's formula for three- and four-centre integrals is extended to embrace two-centre exchange and ionic integrals.

In order to test the effects of a possibly poor choice of carbon 2s wave function, each of the present calculations has been carried out with the use of (i) a hydrogen-like wave function <sup>5</sup> and (ii) a function of the Slater type. <sup>6</sup> These presumably represent opposite extremes of unsuitability, (i) having a radial node much too far from the nucleus, (ii) having no radial node at all: it is thus noteworthy that the two sets of excitation energies differ by only  $\frac{1}{4}$ — $\frac{1}{3}$  eV for each electron excited. The agreement is at its worst at  $Z \sim 3$ . Inevitably, the ground-state " $\pi$ "-electronic energy (which includes a substantial  $\sigma$ - $\pi$  Coulomb contribution) is affected much more than the excitation energies.

It is conventional in ASMO calculations to assume, with Goeppert-Mayer and Sklar, <sup>7</sup> that there exists an eigenvalue  $W_{2p}$  such that

$$(T + V_a)\phi_a = W_{2p}\phi_a,$$

and hence

$$\int \phi_b(T + V_a)\phi_a d\tau = \int \phi_b W_{2p}\phi_a d\tau = \int \phi_b\phi_a d\tau \cdot W_{2p}$$

The functions  $\phi_a$  and  $\phi_b$  are carbon 2p wave functions, *hydrogen-like* in form, having their principal symmetry axes normal to the molecular plane, and their origins of co-ordinates at the nuclei of the carbon atoms  $a$  and  $b$ ;  $T$  is the kinetic-energy operator;  $V_a$  represents the potential (as specified by Goeppert-Mayer and Sklar <sup>2</sup>) of the cationic core of the carbon atom  $a$ ; and  $W_{2p}$  is a quasi-atomic parameter which I do not venture to define. (The number of non-equivalent definitions of  $W_{2p}$  is already almost equal to the number of published calculations embodying the  $W_{2p}$  approximation.) The term  $W_{2p}$  appears in the expression for the energy of each state of a homonuclear  $2p\pi$ -electron system with a coefficient equal to the number of  $\pi$  electrons, and it thus cancels out in the calculation of transition energies. [It does not follow (cf. Moser <sup>7b</sup>) that the *kinetic* energy is the same for all states.] A detailed appraisal of the  $W_{2p}$  approximation will be attempted in a later communication: it will suffice here to draw attention to the disturbingly large changes in calculated excitation energies which it brings about. While this major difficulty remains unresolved, it seems purposeless to introduce avoidable complexities into the original

<sup>5</sup> Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, 1957, App. 3.

<sup>6</sup> *Idem*, ref. 5, Ch. 10.

<sup>7</sup> Goeppert-Mayer and Sklar, ref. 2; cf. (a) Ross, *Trans. Faraday Soc.*, 1952, **48**, 973; (b) Moser, *J. Chem. Phys.*, 1953, **21**, 2098.

Goepfert-Mayer-Sklar procedure (by taking account of configuration interaction, for example, or  $\sigma$ - $\pi$  exchange).

*Benzene* (Table 2).—All the foregoing conclusions in respect of ethylene apply, *mutatis mutandis*, to benzene; it is only necessary to consider the simplifications invariably adopted in the evaluation of three- and four-centre integrals. In four of the six transitions

TABLE 2. *Benzene: Composition of ground-state energy and excitation energies (ev †).*

(a) *Electron-repulsion energies ( $\mathcal{U}$ )*

Approximation for three- and four-centre integrals	${}^1A_{1g}$	${}^1A_{1g} - {}^1B_{1u}$	${}^1A_{1g} - {}^1B_{2u}$	${}^1A_{1g} - {}^1E_{1u}$	${}^1A_{1g} - {}^3B_{1u}$	${}^1A_{1g} - {}^3B_{2u}$	${}^1A_{1g} - {}^3E_{1u}$
Mulliken .....	114.882	1.377	-0.024	4.193	-2.566	-0.134	-1.349
Sklar .....	113.633	1.901	0.521	4.401	-2.270	0.381	-0.944
z.d.o. ....	115.259	1.437	0.325	4.232	-2.089	0.325	-0.881

(b) *Kinetic energy and core-attraction energies*

Component ‡	2s orbital	Approximation for three-centre integrals	Ground-state energy	Excitation energy §
$\mathcal{F}$ .....	—	—	172.333	13.212
$\mathcal{V}$ .....	H-like	Mulliken	-452.511	-6.502
	H-like	Sklar	-450.977	-6.879
	nodeless	Mulliken	-441.302	-6.284
	nodeless	Sklar	-439.908	-6.630
$\mathcal{F} + \mathcal{V}$ .....	H-like	Mulliken	-280.178	6.710
	H-like	Sklar	-278.644	6.333
	nodeless	Mulliken	-268.969	6.928
	nodeless	Sklar	-267.575	6.582
$\mathcal{W}$ .....	H-like	Mulliken	-277.482	5.663
	H-like	Sklar	-275.962	5.285
	nodeless	Mulliken	-264.888	5.346
	nodeless	Sklar	-263.499	5.001

C-C bond length = 1.40 Å (Cox, *Rev. Mod. Physics*, 1958, **30**, 159).

$A_{1g}$ ,  $B_{1u}$ ,  $B_{2u}$ ,  $E_{1u}$  correspond to Stewart's  ${}^3\Phi_0$ ,  $\Phi_3$ ,  $\Phi_2$ ,  $\Phi_1$  (or  $\Phi_4$ ).

† Fundamental constants are as given by Kauzmann (ref. 5, App. 1).

‡  $\mathcal{F}$  = kinetic energy;  $\mathcal{U}$  = electron-repulsion energy;  $\mathcal{V}$  = core-attraction energy;  $\mathcal{W}$  = kinetic energy + core-attraction energy calculated with the use of the  $W_{2p}$  approximation (*i.e.*,  $\mathcal{W} \sim \mathcal{F} + \mathcal{V}$ ).

$W_{2p} = -7.889$  ev (H-like 2s orbital) or  $-6.199$  ev (nodeless 2s orbital).

§ The six states considered differ only in electron-repulsion energy: all have the same kinetic energy and the same core-attraction energy.

represented in Table 2(a) the Mulliken<sup>8</sup> and the Sklar<sup>9</sup> approximations give electron-repulsion energies differing in opposite senses from those obtained with the use of the zero differential overlap approximation: this provides further justification for the use of Pariser and Parr's very simple procedure.

The Mulliken and the Sklar approximations to the electron-repulsion energies differ from each other by as much as 0.54 ev, but the difference is reduced significantly (to 0.17 ev or less) if the potential energies of attraction and repulsion are taken together:

	${}^1A_{1g} - {}^1B_{1u}$	${}^1A_{1g} - {}^1B_{2u}$	${}^1A_{1g} - {}^1E_{1u}$	${}^1A_{1g} - {}^3B_{1u}$	${}^1A_{1g} - {}^3B_{2u}$	${}^1A_{1g} - {}^3E_{1u}$
$\mathcal{U} + \mathcal{V}$ (Mulliken) ...	-5.125	-6.526	-2.309	-9.068	-6.636	-7.851
(Sklar) .....	-4.978	-6.358	-2.478	-9.149	-6.498	-7.823

[Hydrogen-like 2s orbital. Energies in ev.]

While only an exact evaluation of the three- and four-centre integrals can settle the question finally, it seems safe to suggest that, at least for  $Z \sim 3$ , the use of the Mulliken or Sklar approximation formulae does not lead to errors of consequence.

<sup>8</sup> Mulliken, *J. Chim. phys.*, 1949, **46**, 497; Rüdénberg, *J. Chem. Phys.*, 1951, **19**, 1433.

<sup>9</sup> Sklar, *ibid.*, 1939, **7**, 984; London, *ibid.*, 1945, **13**, 396.

The results of the present study do not support Moffitt and Scanlan's<sup>10</sup> view that (when the conventional value of the effective nuclear charge of carbon is used) ASMO calculations on benzene are subject to substantially greater uncertainty than those on ethylene.

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<sup>10</sup> Moffitt and Scanlan, *Proc. Roy. Soc.*, 1953, *A*, **220**, 530.

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