368. *The Zero Differential Overlap Approximation in Molecular-orbital Calculations.*

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The reliability of the zero differential overlap approximation [1-4] has been tested under conditions of widely varying bond length and effective nuclear charge in non-empirical molecular-orbital calculations of electron-repulsion energy in the ground state and the lower excited states of ethylene and hydrogen. The use of the approximation appears to be (*a*) expedient in otherwise intractable computations on $2p\pi$-electron systems (provided these do not go much beyond the limits of sophistication set by Goeppert-Mayer and Sklar [5]); (*b*) inadmissible in $1s\sigma$ systems; [3] and (*c*) hazardous in any systems on which exploratory tests are lacking.

THE forbidding aspect of antisymmetrized molecular-orbital calculations on the stationary states of molecules with numerous valency electrons is due chiefly to the tedium of the trivial and reiterative operations involved in the expansion and evaluation of the electron-repulsion integrals. As a means of eliminating the major part of this computational work (at least in $2p\pi$-electron systems), and so removing the barrier to calculations on molecules of any but the most modest size,* Pariser and Parr [1-3] suggested the use of their zero differential overlap approximation.

So promising a simplification in technique warrants rigorous examination. As a first step, we have shown [4] (simply by isolating the electron-repulsion terms in the computed π-electron energies of ethylene and benzene) that in calculations restricted to the observed C–C distances (R_e) and to the conventional [5] value of the so-called " effective nuclear charge " of carbon ($Z = 3{\cdot}18$), the use of Pariser and Parr's approximation is fully justified, if only because the errors which it introduces are dwarfed by the lamentable disparities [6] which still exist between the calculated and the observed energies of unsaturated hydrocarbon molecules.

Several considerations suggest, however, that a non-empirical calculation in which a single value of Z is used for the ground state and each of the excited states is as unlikely to be successful in a molecular system as in an atomic system (cf. Hurley [7]). For this reason, and because of the possible development of some recent work by Phillipson and Mulliken,[8] it seems desirable to ascertain the effects of variations in Z (and, collaterally, in R) on the reliability of the zero differential overlap approximation.

Results for ethylene (treated as a two-electron system [9]) and for hydrogen are now presented. Because of complicating features in many-electron systems, the extension of the preliminary work [4] on benzene will be considered elsewhere. The zero differential overlap approximation breaks down [3] in the calculation of the " vertical " excitation energies of the hydrogen molecule: one of our objects is to investigate whether the approximation is any more successful at the larger values [10] of R_e appropriate to the excited states. (All errors vanish, of course, as R approaches ∞.)

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* The twelve-centre, twelve-electron system of diphenyl represents the limit to which complete calculations of electron-repulsion energy have yet been carried (Stewart, *J.*, 1958, 4016).

[1] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466.
[2] *Idem, ibid.*, p. 767.
[3] Parr and Pariser, *ibid.*, 1955, **23**, 711.
[4] Stewart, *J.*, 1959, 70.
[5] Goeppert-Mayer and Sklar, *J. Chem. Phys.*, 1938, **6**, 645; Sklar and Lyddane, *ibid.*, 1939, **7**, 374; Parr and Crawford, *ibid.*, 1948, **16**, 1049; Crawford and Parr, *ibid.*, 1949, **17**, 726.
[6] Parr, Craig, and Ross, *ibid.*, 1950, **18**, 1561; Moffitt and Scanlan, *Proc. Roy. Soc.*, 1953, *A*, **218**, 464; 1953, *A*, **220**, 530.
[7] Hurley, *J. Chem. Phys.*, 1958, **28**, 532.
[8] Phillipson and Mulliken, *ibid.*, p. 1248.
[9] Parr and Crawford, *ibid.*, 1948, **16**, 526.
[10] Herzberg, " Spectra of Diatomic Molecules," Van Nostrand, New York, 1950.

Pariser and Parr's Two Approximations.—As well as the zero differential overlap approximation,[1] we have examined a second approximation suggested by Parr and Pariser [3] (the " Mulliken–Parr–Pariser approximation "). In the zero differential overlap approximation all integrals involving overlap between the orbitals of non-identical atoms are disregarded (including, in many-centre systems, all three- and four-centre integrals). The Mulliken–Parr–Pariser approximation is much less drastic, and is an extension to two-centre " ionic " (" hybrid ") and exchange integrals of Mulliken's [11] well-known formula for expanding three- and four-centre integrals in terms of one- and two-centre Coulomb integrals.

Wave Functions and Energies.—For a symmetrical two-centre system of two electrons, the simplest molecular-orbital wave functions [12] forming an orthogonal set can be expanded as follows (in order of increasing energy):

	Symmetry	
	Group $D_{\infty h}$	Group D_{2h}
$^1\Psi_{++} = \frac{1}{2}(1 + S)^{-1}(ab + ba + aa + bb)$	$^1A_{1g}$	^1A_g
$^3\Psi_{+-} = 2^{-\frac{1}{2}}(1 - S^2)^{-\frac{1}{2}}(ab - ba)$	$^3A_{1u}$	$^3B_{1u}$
$^1\Psi_{+-} = 2^{-\frac{1}{2}}(1 - S^2)^{-\frac{1}{2}}(aa - bb)$	$^1A_{1u}$	$^1B_{1u}$
$^1\Psi_{--} = \frac{1}{2}(1 - S)^{-1}(ab + ba - aa - bb)$	$^1A_{1g}$	^1A_g

The corresponding electron-repulsion energies are:

$$
\begin{aligned}
{}^1\mathcal{U}_{++} &= (1 + S)^{-2}(\tfrac{1}{2}C_0 + \tfrac{1}{2}C + 2L + A) \\
{}^3\mathcal{U}_{+-} &= (1 - S^2)^{-1}(C - A) \\
{}^1\mathcal{U}_{+-} &= (1 - S^2)^{-1}(C_0 - A) \\
{}^1\mathcal{U}_{--} &= (1 - S)^{-2}(\tfrac{1}{2}C_0 + \tfrac{1}{2}C - 2L + A)
\end{aligned}
$$

S, C, L, and A are Kopineck's [13] symbols (with subscripts removed) for the overlap, Coulomb, ionic, and exchange integrals; C_0 denotes the one-centre Coulomb integral. The effects of the approximations we have examined are:

Mulliken–Parr–Pariser: $L = \frac{1}{2}S(C_0 + C)$, $A = \frac{1}{2}S^2(C_0 + C)$;
Zero differential overlap: $S = 0$, $L = 0$, $A = 0$.

In states represented by the wave functions $^1\Psi_{++}$ or $^1\Psi_{--}$ (but not orthonormal linear combinations of these functions) the two approximations happen to be equivalent.

Results.—In Table 1 are listed the energies of repulsion between the two π electrons of ethylene, calculated both precisely and approximately over wide ranges of Z and R, each parameter being in turn fixed and varied. The corresponding figures for hydrogen are given in Table 2. In each case the choice of constant values of Z may be regarded as arbitrary.

Ethylene. The two approximations work very well in calculations on the ground state of ethylene, leading at worst to errors of 0·15 ev (only 0·05 ev for $Z \sim 3{\cdot}2$ and $R \sim R_e$); they are rather less satisfactory for the excited state ($^1\Psi_{--}$) in which they are equivalent.

In the states where the two approximations diverge ($^3\Psi_{+-}$, $^1\Psi_{+-}$), the zero differential overlap approximation is, as would be expected, the cruder. That it is indeed useless at very short bond lengths is of little practical importance, for molecular-orbital wave functions based on linear combinations of primitive atomic orbitals are bound in any case to break down when $R \ll R_e$; the approximation may be used fairly safely when $ZR/2 > 4{\cdot}0$. [This requirement is not necessarily fulfilled in the calculation of " vertical " excitation energies: the (unknown) optimum values of Z for the excited states may well be significantly less than 3·18.]

Hydrogen. Although the zero differential overlap approximation is very satisfactory

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

[12] Longuet-Higgins, *Proc. Phys. Soc.*, 1948, **60**, 270.

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

in the calculation of the ground-state electron-repulsion energy of hydrogen (astonishingly so in the neighbourhood of R_e), it is manifestly too rough to be used for the excited states,[3] even at the relatively large equilibrium H–H distance observed[10] in the lowest $^1A_{1u}$ state: it is thus valueless in the calculation of excitation energies. The Mulliken–Parr–Pariser approximation is far more trustworthy, except in the $^1\Psi_{--}$ state.

TABLE 1. *Ethylene: Electron-repulsion energy* (ev*).

(a) $Z = 3{\cdot}18$; *C–C distance varied.*

ZR/2		1·0	2·0	3·0	4·0	5·0	6·0	7·0
C–C distance † (Å *)		0·3328	0·6656	0·9984	1·3313	1·6641	1·9969	2·3297
State	Approximation ‡							
$^1\Psi_{++}$	None	16·507	15·471	14·236	13·115	12·263	11·674	11·269
	M.P.P. or z.d.o.	16·440	15·317	14·126	13·138	12·387	11·822	11·393
$^3\Psi_{+-}$	None	12·958	11·761	10·332	8·933	7·696	6·666	5·841
	M.P.P.	13·646	12·193	10·530	9·001	7·714	6·670	5·841
	z.d.o.	15·947	13·700	11·318	9·342	7·839	6·712	5·853
$^1\Psi_{+-}$	None	18·546	18·010	17·523	17·207	17·041	16·970	16·946
	M.P.P.	19·234	18·442	17·721	17·274	17·059	16·974	16·946
	z.d.o.	16·934	16·934	16·934	16·934	16·934	16·934	16·934
$^1\Psi_{--}$	None	16·356	15·356	14·372	13·454	12·676	12·044	11·542
	M.P.P. or z.d.o.	16·440	15·317	14·126	13·138	12·387	11·822	11·393

(b) *Z varied;* C–C *distance* = 1·353 Å. §

ZR/2		2·0	2·5	3·0	3·5	4·0	4·5	5·0
Z †		1·5644	1·9555	2·3467	2·7378	3·1289	3·5200	3·9111
State	Approximation ‡							
$^1\Psi_{++}$	None	7·611	9·135	10·506	11·750	12·904	14·005	15·082
	M.P.P. or z.d.o.	7·535	9·043	10·424	11·709	12·926	14·096	15·234
$^3\Psi_{+-}$	None	5·786	6·798	7·625	8·281	8·790	9·175	9·465
	M.P.P.	5·998	6·984	7·771	8·384	8·856	9·215	9·488
	z.d.o.	6·740	7·672	8·352	8·840	9·191	9·448	9·641
$^1\Psi_{+-}$	None	8·860	10·915	12·931	14·932	16·930	18·936	20·959
	M.P.P.	9·073	11·101	13·077	15·034	16·997	18·977	20·981
	z.d.o.	8·331	10·413	12·496	14·579	16·661	18·744	20·827
$^1\Psi_{--}$	None	7·555	9·141	10·606	11·964	13·238	14·442	15·591
	M.P.P. or z.d.o.	7·535	9·043	10·424	11·709	12·926	14·096	15·234

* A.U. = 27·210 ev; a_0 = 0·52917 Å (Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, 1957, App. 1).

† Arguments correspond with those of Kopineck,[13] whose numerical values of *S*, *C*, *L*, and *A* have been used.

‡ M.P.P. = Mulliken–Parr–Pariser; z.d.o. = zero differential overlap.

§ Equilibrium C–C distance in ground state (Gallaway and Barker, *J. Chem. Phys.*, 1942, **10**, 88).

Even in the ground state the zero differential overlap approximation depends for its success upon its accidental equivalence with the Mulliken–Parr–Pariser approximation, and this equivalence seems in turn to depend on the arbitrary balance between " covalent " and " ionic " contributions characteristic of single-configuration molecular-orbital wave functions (Table 3).

The sign of the error resulting from the use of the zero differential overlap approximation with the second wave function of Table 3 is important (cf. $^1\Psi_{++}$, $^1\Psi_{--}$). The approximation disturbs the optimum balance between the component configurations, thus defeating the object of a configuration-interaction calculation.

Conclusions.—The Mulliken–Parr–Pariser is clearly the safer of the two approximations, and the fact that it works equally well with wave functions as dissimilar as those of ethylene and hydrogen suggests that it might be used without undue hazard in calculations on other molecules. But it seems unlikely that any important saving of computational effort would follow from its use in many-centre systems. The present results are of interest, not because they suggest the use of the Mulliken–Parr–Pariser approximation, but because they indirectly support the use of the parent approximation[11] for three- and four-centre integrals.

In many-centre systems the zero differential overlap approximation offers an enormous

TABLE 2. *Hydrogen: Electron-repulsion energy* (ev*).

(a) $Z = 1$; H–H *distance varied.*

ZR		1·0	1·5	2·0	2·5	3·0	3·5	4·0
H–H distance † (Å *) ...		0·5292	0·7938	1·0583	1·3229	1·5875	1·8521	2·1167
State	Approximation ‡							
$^1\Psi_{++}$	None	16·077	15·224	14·333	13·492	12·754	12·142	11·656
	M.P.P. or z.d.o.	16·047	15·174	14·299	13·515	12·854	12·312	11·871
$^3\Psi_{+-}$	None	12·187	11·105	10·029	9·017	8·093	7·268	6·545
	M.P.P.	12·404	11·310	10·171	9·096	8·128	7·279	6·545
	z.d.o.	15·089	13·341	11·591	10·024	8·702	7·617	6·736
$^1\Psi_{+-}$	None	19·474	18·833	18·284	17·856	17·545	17·334	17·197
	M.P.P.	19·691	19·038	18·426	17·935	17·580	17·344	17·197
	z.d.o.	17·006	17·006	17·006	17·006	17·006	17·006	17·006
$^1\Psi_{--}$	None	16·717	15·767	14·888	14·107	13·426	12·838	12·334
	M.P.P. or z.d.o.	16·047	15·174	14·299	13·515	12·854	12·312	11·871

(b) *Z varied* §; H–H *distance constant.*

		H–H distance = 0·74166 Å §			H–H distance = 1·29270 Å §			
ZR		1·0	1·5	2·0	1·5	2·0	2·5	3·0
Z †		0·7135	1·0702	1·4270	0·6140	0·8187	1·0234	1·2281
State	Approximation ‡							
$^1\Psi_{++}$	None	11·471	16·294	20·452	9·348	11·734	13·808	15·663
	M.P.P. or z.d.o.	11·450	16·240	20·404	9·317	11·706	13·831	15·786
$^3\Psi_{+-}$	None	8·695	11·885	14·312	6·819	8·211	9·227	9·938
	M.P.P.	8·850	12·105	14·514	6·945	8·327	9·308	9·981
	z.d.o.	10·766	14·279	16·540	8·192	9·489	10·258	10·686
$^1\Psi_{+-}$	None	13·894	20·156	26·091	11·564	14·969	18·273	21·547
	M.P.P.	14·049	20·376	26·293	11·690	15·085	18·354	21·590
	z.d.o.	12·134	18·201	24·268	10·442	13·923	17·404	20·885
$^1\Psi_{--}$	None	11·927	16·874	21·244	9·681	12·189	14·437	16·488
	M.P.P. or z.d.o.	11·450	16·240	20·404	9·317	11·706	13·831	15·786

*‡ See footnotes to Table 1.

† Arguments correspond with those of Hirschfelder and Linnett (*J. Chem. Phys.*, 1950, **18**, 130), whose numerical values of S, C, L, and A (present notation) have been used.

§ Equilibrium H–H distances: 0·74166 Å in the ground state; 1·29270 Å in the lowest $^1A_{1u}$ state.[10] The corresponding optimum values of Z are 1·19 and 0·79.

TABLE 3. *Hydrogen: Ground-state electron-repulsion energy* (ev*) *for various wave functions.*

H–H *distance* = 0·74166 Å.§

Z †		0·7135	1·0702	1·4270
Wave function	Approximation ‡			
Molecular-orbital ($^1\Psi_{++}$)	None	11·471	16·294	20·453
	M.P.P. or z.d.o.	11·450	16·240	20·404
Molecular-orbital with configuration interaction	None	10·891	15·389	19·103
	M.P.P.	10·853	15·314	19·023
	z.d.o.	11·407	16·028	19·800
Valency-bond (purely " covalent ")	None	11·079	15·023	17·628
	M.P.P.	11·056	14·955	17·529
	z.d.o.	10·766	14·279	16·540

*‡ See footnotes to Table 1. †§ See footnotes to Table 2.

advantage; and, although some of the disparities in Table 1 are large enough to be disturbing, there seems to be adequate justification for the use of the approximation in calculations on the $2p\pi$ *wave functions of conjugated or aromatic molecules* which would otherwise be unrewardingly long.

It is probably undesirable, however, that the approximation should be used in non-empirical calculations embodying quasi-variational complicacies such as interacting configurations, self-consistent * orbitals, or sets of wave functions with non-uniform values of

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* In Roothaan's sense (*Rev. Mod. Physics*, 1951, **23**, 69). The term " self-consistent " (often with the odd addition of the word " field ") is now commonly used to describe essentially empirical calculations in which allowance is made for the energy of repulsion between electron distributions described by unmodified Hückel orbitals. This usage can sometimes be as perplexing to the theoretician as it must always be to the experimentalist interested in the results of quantum-chemical calculations, but not the techniques.

Z. Errors of the same order as those in $1s\sigma$ systems (Table 3) are not to be expected; but there is some danger that the zero differential overlap approximation may invalidate calculations purporting to transcend the limitations of the original Goeppert-Mayer–Sklar procedure.[5,9]

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