Discussion on Conjugated Systems

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SNYDER: Professor A. F. Saturno of the University of Tennessee, Dr. H. W. Joy of Oak Ridge National Laboratory, and I have made computations to evaluate Dewar's split p-orbital (SPO) method. The split p-orbital (SPO) wave function derived from the single determinant det $\{2p_z\bar{2}p_z\}$ corresponding to the singlet state in which a single $2p_z$ orbital is doubly occupied, correlates the electronic motion so that the electrons always occupy opposite lobes of the $2p_z$ orbital. This SPO singlet wave function may be written as $2^{-\frac{1}{2}}[-\det\{2p_z\bar{2}p_z\} + \det\{|2p_z| \ |\bar{2}p_z|\}]$ and is the lowest energy linear combination of this pair of degenerate two-electron determinants. The energy improvement is 5.95 eV when the $2p_z$ orbital exponent is Zener's value of 3.18 for carbon. In this two-electron context, the triplet function det $\{2p_z|2p_z|\}$ is degenerate with the SPO singlet.

In order to test the persistence of this qualitative picture when occupied sigma core orbitals are explicitly included, we have performed analogous rigorous computations on the $1s^2 2s^2 2p_z^2$ nonstationary state of carbon, using corresponding determinants det $\{1s\bar{1}s2s^*\bar{2}s^*2p_z\bar{2}p_z\}$ and det $\{1s\bar{1}s2s^*\bar{2}s^*|\bar{2}\bar{p}_z| \ |2p_z|\}$ which include occupied $1s$ and $2s^*$ core orbitals appropriate for a carbon atom. The lowest energy singlet linear combination is found to be almost entirely composed of the first determinant and corresponds to a conventional rather than an SPO wave function. Variational addition of the second determinant lowers the energy by only 0.07 eV. The triplet determinant det $\{1s\bar{1}s2s^*\bar{2}s^*2p_z|2p_z|\}$ is of 2.5 a.u. higher energy than the lowest singlet. These results are due to the kinetic energy increase of $|2p_z|$ upon proper orthogonalization to the doubly occupied $1s$ and $2s^*$ orbitals of the core. We have examined an analogous computation in which a more realistic core of three doubly occupied sp^2 hybrids is employed. We estimate an energy improvement of 0.35 eV upon addition of the corresponding second determinant.

While these calculations do not support the SPO method as stated for this one-center problem, it is possible that computations with other basis functions will suggest vertical correlation of pi electronic motion. [A. F. Saturno, H. W. Joy and L. C. Snyder, J. Chem. Phys. (to be published, 1963)].

CUSACHS: While Snyder and colleagues were making their elegant calculations, I was in Spain and concerned with the problem of explaining the objection to an organic chemist, so I was restricted to a calculation done on the back of an envelope.

The "split p" orbital for one electron has the energy of a regular orbital. However, when other electrons are present in the molecule, it is necessary to take into account the nonorthogonality to the $1s$ and $2s$ functions. If $\bar{p}$ is the "split p" orbital, the wave function used must be $\bar{p} = C_p(\bar{p}) + C_{1s}(1s) + C_{2s}(2s)$, where the C's are determined so that $\bar{p}$ is normalized and orthogonal to the others.

The kinetic energy is defined in terms of an integral

$$\text{KE} = -\tfrac{1}{2}\int \Psi^{+}\nabla^{2}\Psi dV \ ,$$

which cannot be used in this case, since the "split p" function has a discontinuity in its first derivative halfway through the range of the angular variables, making the ∇^2 term infinitely discontinuous so that we cannot evaluate the integral. As pointed out by Hirschfelder and Nazaroff, we can still transform to an equivalent form

$$\text{KE} = +\tfrac{1}{2}\int (\nabla\Psi^{+})\cdot(\nabla\Psi)dV + \text{boundary term}.$$

The boundary term is zero if the wave function satisfies the boundary conditions requiring it and its first derivative to be continuous. If there is only the "split p" orbital it is also zero because the p orbital is valid, a factor in the term happens to be zero. But when we use the orthoganalized function alone, the s parts are not zero and the boundary term is important; with Slater orbitals I calculate 12 eV/electron. The "split p" orbital, in a molecule, then has a very large kinetic energy which more than cancels the improvement on the electron repulsion term, so that it is not an improvement.

Furthermore, the "split p" orbital is not really a p orbital; it is probably better regarded as a $(2s)$ since it is like the off-center s orbitals used for hydrogen in molecules by Gurney and Magee and by Hurley, which were less satisfactory than the ordinary ones.

COOPE: I should like to make two points about split p orbitals:

1. The effect of orthogonalization to the core may be seen rather clearly from the expression in spherical harmonics.

$$\eta = \frac{1}{\sqrt{2}} 2p_z + \sum_{l \text{ even}} C_l R_{2p} Y_{l,0}(\theta,\varphi) = (1/\sqrt{2})2p_z + (3/8)^{\frac{1}{2}}2s' + (15/128)^{\frac{1}{2}}2d_z'2 + \cdots \; .$$

Here the normalized $s,d \cdots$ terms have the same radial dependence as $2p$. The remaining contributions are small; in fact

$$\sum_{l>2} C_l^2 = 1/128 \; .$$

Now the effect of orthogonalization to a $1s^2 2s^2$ core, as in Snyder's second calculation, is essentially to subtract out the $2s'$ term in the expansion. The subtraction is exact if the usual Slater $2s$ orbitals are used. The orthogonalized split p orbital which remains differs little from an ordinary p orbital. The small remaining correlational effect is essentially equivalent to a specified amount of configuration interaction involving d orbitals.

In simplest terms, a split p orbital is almost equivalent to an sp-hybrid. But on orthogonalization to the s-orbital, an sp-hybrid reduces to an ordinary p orbital. These remarks must be modified however in the case of a bonded carbon atom, or in Snyder's third calculation, where the core is not simply $1s^2 2s^2$.

2. With respect to Cusachs' remarks, it might be added that peculiarities in the calculation of kinetic-energy integrals disappear when account is taken of the $\delta(z)$ term in $\nabla^2 \eta$. For example, ∇^2 is Hermitian in $\langle ns | \nabla^2 | \eta \rangle$. The $\delta(z)$ singularity is, of course, associated with the fact that η is not an eigenstate of $\mathcal{L}^2$.

DEWAR: The difficulties concerning orthogonality, etc., could no doubt be met, as Mrs. Sabelli and I have pointed out, by using orbitals of SPO symmetry that are orthogonal to the core. Orbitals of this kind could be constructed in various ways. However, we feel that the main value of the SPO approach lies rather in the suggestions it gives concerning the way vertical correlation may be effectively included in Pople calculations by empirical adjustment of repulsion integrals. The difficulties concerning orthogonality also arise, as we have seen, in other treatments where correlated pi-electron functions are built up by multiplying "normal" uncorrelated functions by functions of r_{12}; one further contribution of the SPO method has been to draw attention to this difficulty by raising it in an extreme form. One might add that if electron correlation is included, then the Hückel approximation of separating sigma- and pi-electrons is no longer valid. For this reason, we feel that there is no particular virtue in so-called *a priori* treatments of pi-electrons; the possibility of treating pi-electrons separately can be established only by experiment and so any treatment based on the Hückel approximation is *ipso facto* empirical.

DE HEER: Dewar has expressed the belief that the alternant molecular-orbital (AMO) method becomes impractical for large systems. It is true that in developing this scheme much of the initial emphasis has been placed on the six-center system, benzene in particular. However, the AMO method was primarily designed to deal with large systems, where a good configuration interaction treatment is out of the question. In fact, AMO calculations on the infinite chain have already been published [R. Pauncz, J. de Heer, and P. O. Löwdin, J. Chem. Phys. **36**, 2257 (1962)] and improved calculations on large systems will be reported elsewhere in this symposium [J. de Heer, Rev. Mod. Phys. **35**, 631 (1963)].

Dewar has also expressed the belief that by neglecting differential overlap one may take care of a large portion of the "horizontal" correlation in conjugated systems. Leaving aside the question of the legitimacy of this approximation, we have carried out an AMO treatment within this framework (with the usual, much reduced, electron interaction integrals) [J. de Heer, J. Chem. Phys. **37**, 2080 (1962)] and find that the ground-state energy is improved 0.67 eV below that of the single determinant. Insofar as chemists have to be interested in energy differences of the order of 0.1 eV, this amount can hardly be considered negligible.

While the distinction "horizontal" versus "vertical" correlation is useful, we should not overlook the fact that we are thus describing two aspects of the same phenomenon. One seems hardly justified in calling the latter important and attempts to deal with the former a "waste of time." If a crude method gives better agreement with experiment than a refined one, there is something wrong which has to be further investigated even if many are willing to accept the crude results as useful "rules of thumb." On the other hand, we still frequently run into cases where we are required to take into account horizontal correlation to get even a *qualitative* understanding of the phenomenon involved. This fact has long been known to theoretical physicists and Dewar himself has given an example in the theory of conjugated systems, namely, the "first-order configuration" treatment of the uv spectra of catacondensed hydrocarbons. In this connection one should also mention the work by Lefebvre, Dearman, and McConnell on spin densities in odd alternant hydrocarbon radicals [R. Lefebvre, H. H. Dearman, and H. M. McConnell, J. Chem. Phys. **32**, 176 (1960)]. Here again, even in order to get only qualitative agreement with experiment, one has to use a wave function which allows for horizontal correlation.

LYKOS: Allen estimated his $2s$–$2p$ orbital exponent splitting by correcting the value of $(11|11)$ as obtained with a single Slater orbital by the correlation energy of a $2p$-electron pair. This points out a common interpretation made of the lowering of the value of the $(11|11)$ integral when computed over a Slater or HF $2p$ orbital to an empirical value of about 11 eV. The relatively large change of 4 to 6 eV, however, does not seem to be attributable to correlation energy alone.

As a matter of fact, in a paper published in J. Chem. Phys. **38**, 1447 (1963) by T. Arai and myself, the point is made that by applying the virial theorem to the ground-state solutions of the helium atom obtained by Pekeris (assumed to be exact) and by Sachs (a Hartree–Fock solution), it is found that the potential energy contribution is exactly twice the correlation energy [pointed out by P. O. Löwdin, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. II] and that most of that contribution is due to the electron repulsion correlation error. Accordingly, assuming a similar situation exists in carbon, if the exact value of (11 11) is desired (within the core-peel approximation), one should take a Hartree–Fock value of (11 11) and subtract from it *twice* the correlation energy. Using a Hartree–Fock result provided by P. Bagus and a $2p$ correlation energy estimate made by Allen, we estimate an exact value of (11 11) as 12.1 eV.

DONATH: Calculations were done on the singlet states of benzene using the Pariser–Parr Method with all singly and doubly excited configurations. The energies of the various states came out as follows (with Pariser–Parr semiempirical integrals and $\beta = -2.48$ eV):

	Pariser and Parr	This calculation	Exptl.
$^1B_{2u}$	4.9	4.66	4.71
$^1B_{1u}$	5.2	5.56	5.96
$^1E_{1u}$	7.0	7.09	6.76
$^1E_{2g}$		7.45	

In effect, the doubly excited states split the $^1B_{2u}$ and $^1B_{1u}$ in a more favorable direction. The transition f—values for the $^1E_{1u}$ are 2.4, 1.64, and 0.7 for 10 term singly excited, 55 term doubly excited and experimental values, respectively. The $^1E_{2g}$ state, which is about 33% doubly excited states, has the following bond orders:

Bonds	Bond Orders		
	$1E_{2g}^1 - 1E_{2g}^1$	$1E_{2g}^1 - 2E_{2g}^1$	$2E_{2g}^1 - 2E_{2g}^1$
$1 - 2$	0.257	0.218	0.506
$2 - 3$	0.632	-0.001	0.131
$3 - 4$	0.255	-0.216	0.508

The correlation energy for the ground state was 0.57 eV.

CUSACHS: The use of the operator $p_i \cdot p_j \cdot$ in studying the introduction of correlation in multi-electron systems, often included in large calculations on small systems, permits some striking observations. Since the quantity, $\nabla\Psi$, is of opposite parity from the original function, Ψ, $\langle \mathbf{p}_i \cdot \mathbf{p}_j \rangle$ vanishes for orbital products. Thus, functions which improve the energy while leaving the calculated expectation value of this operator zero must be regarded as improving orbital shape rather than correlating electronic motion since $p_i \cdot p_j \cdot$ is the projection of the momentum of one particle on that of the other.

It must be noted that kinetic energy as well as correlation corrections are important in the one center integrals used in semiempirical calculations. In addition, there is the possibility that transitions and, for instance, singlet-triplet separations, are seriously in error because of the failure to correct for the difference in kinetic energy between excited states.

JOY: Saturno and I, continuing our work described yesterday by Snyder, have elaborated the calculation on the $1s^2 2s^2 2p_z^2$ state of carbon ($\Psi = c_1 \det \{1s^2 2s^2 2p_z^2\} + c_2 \det \{1s^2 2s^2 |2p_z|^2\}$, $c_1 = 0.9997$, $c_2 = 0.0229$, $E = -37.506$ a.u.), by replacing the $|2p_z|^2$ function by $3s^2$, giving $c_1 = 0.9995$, $c_2 = 0.0307$, $E = -37.505$ a.u., by $3d_{z^2}^2$, giving $c_1 = 0.9988$, $c_2 = 0.0499$, $E = -37.509$ a.u., and by splitting the $2p_z^2$ function to $2p_z 2p_z^1$:

$$\Psi = \det \{1s^2 2s^2 2p_z \alpha 2p_z^1 \beta\} + \det \{1s^2 2s^2 2p_z \beta 2p_z^1 \alpha\} \text{ giving } E = -37.554 \text{ a.u.}$$

BLOOR: Dewar has described a method of decreasing the computation time on calculations using the semiempirical SCF method for large pi-electron systems. This method of dropping out completely the off diagonal elements of the F matrix other than those for nearest neighbors introduces an extra and possibly undesirable empirical element into the theory. An alternative method for decreasing the computing time in semiempirical SCF calculations used by myself and Dr. P. Daykin of the British Columbia Research Council has been to carry out the diagonalization of the F matrix at each iteration only until the largest off diagonal element is one third of its original value. In addition to this device used at each iteration, we have also included Aitken's convergence formula which is similar to that used by Dr. Nesbet to be used in producing the bond density matrix for alternate iterations. By this means we have been able to carry out calculations on pi-electron systems of up to 20 pi-electrons on a relatively slow computer (IBM 1620). For example, the calculation on a 10 pi-electron molecule iterated to a stage where the charge density matrix is stable to the fourth decimal place and which includes configuration interaction between eight excited configurations can be carried out in one hour. It seems likely that a combination of Dewar's method and the one described above in which the *non* nearest neighbor interactions are not included until the orbitals are almost self-consistent to the required amount using an F matrix without the non-nearest neighbor interactions would be the most efficient for carrying out semiempirical pi-electron calculations.

HOFACKER: I would like to bring an experimental point into the discussion that might contribute to the question of the limitations of certain simple theoretical schemes used. According to A. Scheibe and coworkers [Z. Elektrochem. **54**, 403 (1950); **63**, 117, 121 (1959)] there seems to be some experimental evidence that the one-electron excited states of most aromatic hydrocarbons form Rydberg series, and the distance in energy between the first excited state and the continuum is throughout nearly the same. The latter phenomenon was extensively discussed by H. Hartmann [Z. Naturforsch. **15a**, 993 (1960)], and also by E. Ruch [Z. Naturforsch. **16a**, 808 (1961)], introducing higher atomic functions of the carbon atom into a Hückel-type LCAO scheme. However, if the suggestion of Rydberg series is supposed to be true, this would mean that the excited electron occupies a nearly central force field orbital and all approximate LCAO wave functions for excited states must be very poor, unless they include a large number of higher atomic orbitals.

BLOOR: The problem of the assignment of the Rydberg Series in benzene was first formulated before the importance of configuration interaction between excited configurations of the same symmetry was appreciated by molecular spectroscopists. For benzene there are two types of allowed Rydberg transitions, those with symmetry $^1E_{2u}$ and those with symmetry $^1A_{2u}$. The Rydberg configurations will mix with the $N - V$ configurations of the $2p$ pi MO's of the same symmetry

and will become experimentally indistinguishable from them. There are no $N - V$ configurations of A_{2u} symmetry in benzene so we should expect to find the first A_{2u} Rydberg transition in the same region as the $N - V$ transitions. It is in fact generally accepted that the intense bands in the 6.9 eV region of the benzene spectrum consist of two components one polarized in the plane of the molecule of $^1E_{2u}$ symmetry and one out of plane polarized part of $^1A_{2u}$ symmetry. The in-plane part can then be regarded as a *mixture* of $N - V$ and $N - R$ configurations of the appropriate symmetry.

The recent analysis by Wilkinson of the Rydberg bands of benzene leaves little doubt that the $^1E_{1u}$ Rydberg transition is the first member of a series given by Eq. (1).

$$\gamma_0^h = 74500 - R/(n - 0.45) \qquad n = 3,4,5\cdots \qquad (1)$$

which has a quantum defect corresponding to a p series. Attempts to correlate this assignment with transitions to particular molecular orbitals, however, have led to difficulties.

In benzene the ground state contains filled orbitals of symmetries a_{2u} and e_g^- symmetry. Excited Rydberg states may be built up from $3s$ orbitals to give MO's of symmetries a_{1g} and e_{1u} or from $3p$ orbitals when they will have symmetries a_{2u} and e_{1g}. Of the possible transitions, the only allowed transitions of $^1A_{2u}$ symmetry are members of an S series whereas the experimental assignment is to a P series. This difficulty may be overcome by using the united atom method of assigning the Rydberg excited orbitals rather than the LCAO method. On the united atom model the two orbitals built from the $3s$ AO's of carbon would have symmetries of e_{1u} and e_{1g} while the originating orbital has e_{1g} symmetry.

The out of plane polarized part of the 6.9-eV band would then be the first member of a Rydberg series given by Eq. (1) but originating in a $3d \rightarrow 4p$ transition rather than to a $3p$ as previously thought, but now the quantum defect has been effectively reduced by 1 since we are now dealing with Rydberg transitions to what is effectively a $4p$ shell.

This is in agreement with Walsh's empirical rule that the quantum defect is reduced by unity with increase of the principal quantum number of the first excited state. In answer to Hofacker's inquiry about the importance of $3p$ electrons, a calculation by J. Jacobs [Proc. Phys. Soc. (London) **A68**, 72 (1955)] has shown that they play an important role in the case of ethylene and this idea should certainly be pursued in other cases.