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Canonical Configurational Interaction Procedure

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FOR several years the only available method of obtaining approximations of unlimited accuracy to many-electron wave functions has been the use of linear combinations of Slater determinants as variational functions, the method frequently known as configurational interaction. This method has the characteristic that by choosing different sets of what we call the predetor functions, in terms of which the determinants are defined, the same answer can be expressed in an infinity of different ways. This flexibility has more disadvantages than advantages, and it would be a gain if a unique specification of the predetor functions could be found to express wave functions in their briefest form. Restriction to such a specification would also facilitate the comparison of different approximations to the same wave function, in place of the present situation where it can be difficult to identify two different ways of recording the same function. It would permit a comparison between different approximations at the simpler level of the three-dimensional functions. If a specification corresponding to the valency structure could be found, it would also permit the chemical implications of complicated calculations to be assessed more easily.

Here such a method of choice of the predetor functions is proposed. In addition to the advantages given in the foregoing the first test gives the impression that these may approximate to the chemically invariant orbitals discussed in the preceding paper.[1] This choice of the predetor functions is made after a single Slater determinant of minimum energy has been found and involves only the matrix elements of the dipole moment in an operation which is simple compared with the calculation as a whole.

The method discussed here is restricted to those electronic stationary states in which at least a crude approximation can be obtained in the form of a single Slater determinant in which each spatial orbital is occupied twice with opposite spins. Two criteria are used to choose the single-electron functions. The first, for the occupied orbitals, specifies that their centroids of charge be as far apart as is consistent with orthonormality. These have tentatively been called exclusive orbitals. Such a set of orbitals have been calculated for formaldehyde, and they correspond closely the chemical picture of the valency structure. The transformation of the remaining one-electron functions is chosen so that they provide the maximum facility for representing the correlation of the electronic movement. The actual criterion is that they maximize the dipole moment matrix elements between the exclusive orbitals and some associated orbitals which we propose to call oscillator orbitals. These definitions are set out mathematically in the following, but it is worth noting that they are not dependent on the use of any particular type or number of primary expansion functions. Indeed, if an infinite set of functions were used, corresponding to a full Hilbert space, the definitions would specify a perfectly definite system of orbitals. If in a practical calculation, only a small number of functions are used, each orbital can only approximate to its final value, but each orbital found has a definite orbital to which its approximation can be discussed. This provides the useful possibility of comparing orbital with orbital between approximate calculations based on different primary expansion functions.

To proceed with the precise formulation, let

$$\Phi_1 = \mathcal{A}\, \phi_1'\alpha\, \phi_1'\beta\, \phi_2'\alpha\, \phi_2'\beta \cdots \tag{1}$$

be a Slater determinant for which

$$\phi_i' = \sum_j X_{ij}\eta_j, \tag{2}$$

and in which the energy can be reduced no further by altering the coefficients X_{ij}. The η_j denote the whole set of primary three-dimensional expansion functions in terms of which all functions of the calculation are expressed. The ϕ_i' could be obtained by solution of the equations given by Roothaan, or other methods of obtaining an equivalent determinant could be used.

Let ϕ_r be a further orthonormal set of linear combinations of the ϕ_i', that is, functions satisfying

$$\phi_r = \sum_i A_{ri}\phi_i', \tag{3}$$

where $(\phi_r|\phi_t) = \delta_{rt}$. Let the centroids of charge of these be

$$R_{i\alpha} = (\phi_i|r_\alpha|\phi_i). \tag{4}$$

Then the exclusive orbitals are defined to maximize

$$\prod_{i>j} \left[(R_{ix}-R_{jx})^2 + (R_{iy}-R_{jy})^2 + (R_{iz}-R_{jz})^2\right] \tag{5}$$

for all variations of A_{ri} satisfying the preceding conditions. It is seen that this is a method of allowing the orbitals to separate as much as possible. Other names such as separate or repulsive did not seem particularly apposite, and exclusive was chosen as the nearest description of the tendency of the orbitals to separate as much as possible from each other.

This first step in the calculation provides orbitals

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[1] S. F. Boys, Revs. Modern Phys. **32**, 296 (1960), this issue.

which are localized, but the main reason for this is to be able to introduce a further set of orbitals which each interacts mainly with one exclusive orbital and enables electronic correlation to be introduced for that orbital. Use of these in higher-order Slater determinants should introduce a correlation in the probability distribution of the electrons so that they can avoid each other and so reduce the positive energy due to the electrostatic potential of two electrons.

It is easily seen that the introduction of variational functions with large matrix elements with the original orbitals for the dipole moment operator allows the electrons to have higher probabilities at opposite sides of occupied orbitals. The amount that each of these contributes can be determined by the final variational calculation. Hence, let ϕ_{ik} be functions chosen as linear combinations of the residual single-electron functions with a particular ϕ_{ik} specially related to ϕ_i, so that

$$\phi_{ik}=\sum_s \Lambda_{iks}\eta_s, \tag{6}$$

with $(\phi_{ik}|\phi_j)=0$ and $(\phi_{ik}|\phi_{jl})=\delta_{ij}\delta_{kl}$. Let

$$\Omega=\sum_i \sum_k |(\phi_i|\mathbf{r}|\phi_{ik})|^2 \tag{7}$$

be maximized. In principle, the possible values of k for each i are to be assigned to obtain the absolute maximum of Ω. These final ϕ_{ik} we call oscillator orbitals. They are limited in number by the fact that the total of the exclusive and oscillator orbitals must be equal to that of the original η_r. It is unlikely that k will have more than one value for each i in calculations at the present time, but if this should occur we favor maximizing Ω_1 for the largest set of orbitals which does not assign more than one ϕ_{ik} to each i, then maximizing Ω_2 for a largest second set with not more than one k per i, and so forth. There are probably several variants which are not very different in practice for the choice of oscillator orbitals, but it is better to leave consideration of these until more applications have been made.

It is generally recognized that the greater part of the correlation correction to the first determinant can be made by adding other determinants in which two of the orbitals are replaced by higher orbitals. Here we suggest a working level of approximation for complicated molecules, which appears as if it may include most of the correlation effects possible by use of the given primary functions. This is to include just those determinants Φ_s in the variational problem, which can be formed by replacing any ϕ_i, ϕ_j by all the corresponding pairs ϕ_{ik}, ϕ_{jl}. It is considered that such replacements by functions in the same spatial regions have the largest contributions, but trials can show whether these are sufficient in particular cases.

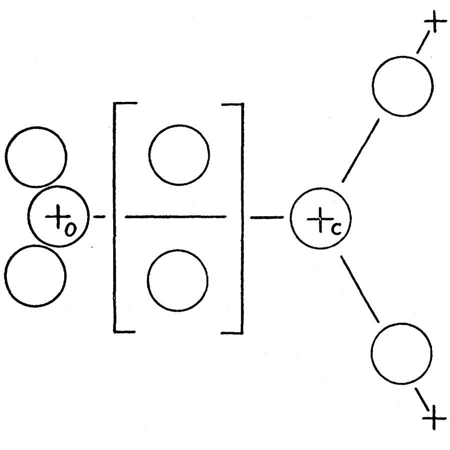

FIG. 1. Centroids of charge for the exclusive orbitals of HCHO.

Even if this limited set of determinants is not sufficient for some system, the number actually necessary is probably much lower than if an arbitrary choice of the predetor functions had been made, and also, a complete systematization has been effected since each detor can be assigned a physical significance. This may be particularly informative in the case of continuous deformations of molecules or other atomic associations, where previously the variation of the coefficient of a particular detor could not be interpreted since this could be altered by noncorresponding choices of the predetor functions.

It is only recently that these concepts have been formulated and tested on HCHO, and improvements by minor modification of the definitions cannot be ruled out. Hence extensive analysis will be postponed until various issues can be examined as more examples are investigated.

The results for HCHO show a gratifying feature in a respect which was not our main aim. The centroids of the exclusive orbitals show a high correspondence with the chemists' picture of the valence structure. It is possible that these may be approximately the same as the chemically invariant orbitals discussed by Boys.[1] If later tests do show that these have an invariant character from molecule to molecule, the more elaborate procedure put forward by Boys might be avoided. There is not yet enough evidence to judge this, but if it should be so, one of the difficulties in the construction

TABLE I. Centroids of charge for the exclusive orbitals of HCHO.

	x	y	z
Ck	0	0	−0.001
Ok	0	0	−2.299
CH_1	0	1.166	0.713
CH_2	0	−1.166	0.713
On_1	0	0.526	−2.521
On_2	0	−0.526	−2.521
t_1CO	0.544	0	−1.242
t_2CO	−0.544	0	−1.242
C atom	0	0	0
O atom	0	0	−2.3
H_1 atom	0	1.732	1.0

TABLE II. HCHO eigenvector coefficients for double replacements, oscillator/exclusive.

Oscillator pair	Coefficient
Φ_1	1.0
$(CH_1)_1(CH_1)_1$	−0.076
$(t_1CO)_1(t_1CO)_1$	−0.093
$(CH_1)_1(CH_2)_1$	0.024
$(t_1CO)_1(CH_1)_1$	−0.021
$(t_1CO)_1(t_2CO)_1$	−0.090

of wave functions for larger molecules would have been simplified.

The results for HCHO are most easily seen from Fig. 1, where crosses represent the nuclei, and circles are described round the centroids of charge. The three-dimensional positions are shown by enclosing the out-of-plane circles in large square brackets to show the distances exactly above and below the CO axis. The centroids, from left to right, can be seen to correspond to the following orbitals, which are denoted by the symbols as shown: oxygen lone pairs, On_1, On_2; oxygen core, Ok, double-bond orbitals, t_1CO, t_2CO; carbon core, Ck; CH bonds, CH_1, CH_2. The coordinates are given in Table I. In Table II we give the coefficients for sufficient of the Φ_s formed by the replacement of two of the ϕ_i by ϕ_{ik}, that all the others can be seen from symmetry. Where two singlet terms could be made in a double replacement, the resultant magnitude of the linear combination given by the variational calculation is quoted. It is possible to construct only 4 oscillator functions from the residue of the 12 primary expansion functions used in this calculation. The functions found to give the maximum criterion corresponded approximately to linear polarizations along the CO and CH exclusive orbitals, and they have been denoted by adding the suffix 1 for the k value to those orbitals. All maximization processes were performed by automatic programs which adjusted two orbitals at a time.

The total energy found for the best single Slater determinant is −113.450 atomic units, and with all the simple oscillator correlation functions −113.534. This agrees roughly with the energy reductions for similar terms in atomic calculations. It is regrettable that the extention of the calculation to include oscillator functions for the oxygen lone pairs would involve considerable further work, but such results should be available in the next year or two.

In conclusion it appears that the exclusive orbitals have many of the desired properties of localized orbitals which may have been implicitly sought in earlier analyses. (See the hybrid-orbital analysis of Pauling,[2] Slater,[3] and that for equivalent orbitals by Lennard-Jones,[4] Pople, and Hall.) The exclusive orbitals give a degree of simplicity and precision to these requirements which has not previously been obtained. In addition, there is the possibility that if they remain almost unchanged from molecule to molecule, they may serve as chemically invariant orbitals. The oscillator orbitals approximately localize the electronic correlation terms and enable them to be represented in a briefer and clearer form than has been possible before.

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[2] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[3] J. C. Slater, Phys. Rev. **37**, 481 (1931).

[4] J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A197**, 1 (1949).