Fig. 7; the horizontal line indicates the classical vibrational "sweep" of the zero-point vibration.

We also explored to some extent the possibilities of superposition of configurations using wave functions defined by Eqs. (1)–(3) with $\mu=0$ and also introduced $\pi_g\pi_g'$ and $\pi_u\pi_u'$ terms as discussed previously. Virtually the same calculation was carried out by Hagstrom[16]; his results are in excellent agreement with ours. In Table XVI we compare some of the more important results of these computations with those obtained with the SCF function and with the wave functions which contain r_{12} explicitly.

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[16] S. Hagstrom (unpublished).

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Self-Consistent Field Atomic and Molecular Orbitals and Their Approximations as Linear Combinations of Slater-Type Orbitals*

R. S. MULLIKEN

Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago 37, Illinois

GLOSSARY OF GENERAL TERMS AND SYMBOLS[1]

Orbital: An adjective used as a noun and introduced as a brief term meaning "one-electron orbital wave function," that is, either an eigenfunction of a one-electron Schrödinger equation or an approximation thereto.[2] It is the nearest quantum mechanical counterpart to the electron orbit of Bohr theory. The practice of referring to "one-electron orbitals," in other words, "one-electron one-electron orbital wave functions" should be discouraged. Could one have a two-electron one-electron orbital wave function?

Spinorbital: This was introduced as a brief term[2] meaning "one-electron wave function including spin." The frequent practice of referring to it as two words "spin orbital" is confusing, suggesting different meanings from that intended. To better indicate the pronunciation, the spelling could perhaps be changed to "spinnorbital."

AO: Central field atomic orbital [cf. Eq. (1)] or, in molecular contexts, sometimes a linear combination (hybrid) of these.

MO: Molecular orbital.

SCF: Self-consistent field.

SCF AO or MO: Cf. Eqs. (1) and (2).

CI: Configuration interaction.

STO: Slater-type orbital [cf. Eq. (3)].

ζ = orbital exponent: The variable parameter in any STO [cf. Eq. (3)].

LC–STO MO: Linear combination of STO's (not necessarily all alike in l but all alike in m or λ) to approximate an MO.

Free-atom MO, free-atom ζ: Terms used in describing LCAO–MO's to indicate that the AO's or the AO ζ values used are the AO's or the ζ's which are suitable (Slater ζ's and AO's) or optimal (best simple AO's) in describing the AO's of free atoms.

LCAO–MO's: MO's approximated by linear combinations of free-atom *or of modified* AO's; since the latter in turn are approximated by LC–STO forms, LCAO MO's in general are most conveniently considered as LC–STO forms.

INTRODUCTION: USES AND LIMITATIONS OF SELF-CONSISTENT FIELD WAVE FUNCTIONS

EVERY exact atomic or molecular wave function must conform to one of the group-theoretical species (taking into account both spin and orbital characteristics) of the appropriate symmetry group. For light atoms and molecules it is sufficient for many purposes to use wave functions in which spin-orbit interaction is neglected, so that each wave function has a definite spin quantum number and a definite orbital species (L, S coupling case for atoms, and the analogous case for molecules).

An exact wave function even of the L, S or L,S-like type does *not* correspond to a single-electron configuration, and exact wave functions are perhaps most convergently represented by linear combinations of

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* This work was assisted by a grant from the National Science Foundation.

[1] Tables I and II contain a proposed classification and terminology for various *specific* types of LC–STO approximations to SCF AO's and MO's.

[2] R. S. Mulliken, J. Chem. Phys. **23**, 2005 (1955), Sec. II.3(b).

terms involving not atomic or molecular orbitals but products of powers and exponentials of one single coordinate at a time (cf. the Hylleraas form for the He atom and the James-Coolidge form for H_2 using the interelectronic distance r_{12} as one coordinate, but note that the use of r_{ij} as a coordinate has not been shown to be practicable except for 2-electron or perhaps at most 3-electron systems).

However, a practicable approach which has been more thoroughly explored is that of using CI (configuration interaction or superposition of configurations). Here linear combinations are formed from pure-electron-configuration wave functions, constructed from AO's for atoms or MO's for molecules, and the coefficients (and in general also the internal parameters of the orbitals used) are determined by energy optimization. According to the original philosophy of CI, each configuration would be represented ideally by a carefully determined SCF wave function (or a linear combination of these in the case of degenerate states). Thus, for an accurate ground state wave function, the leading term in the CI would be the SCF wave function (or functions) of the ground state, and the smaller terms would be SCF functions of all excited states of the same species as the ground state. However, excited state SCF functions are not easily determined, and besides, convergence is slow and requires extensive inclusion of continuum SCF functions.

On the other hand, more rapid convergence can be obtained if the single-configuration wave functions of which the best linear combination is to be sought are *not* SCF functions, but are regarded merely as variation functions so chosen as to give most rapid convergence toward the exact wave function. The parameters to be varied now include both the CI coefficients and the internal parameters within each single-configuration function. These internal parameters are the same ones that are varied in seeking a close approximation to an SCF function, but in the context of CI they must, in general, be *revaried simultaneously* for all the configurations in the CI function. Such a procedure being a formidable one, it is necessary to examine very carefully the configurations used and other matters so as to approach the desired goals with maximum economy for a finite number of terms.

The foregoing considerations indicate that *accurate* SCF wave functions are not necessary as way stations on the road toward accurate wave functions. Moderately accurate SCF functions and energies, if obtainable without excessive effort, should, however, be of orientational value in seeking accurate wave functions. Further, they may be very valuable as way stations in case it should prove that *they* are practically obtainable, but that the calculation of accurate wave functions is for the present, except for systems with very few electrons, only a distantly attainable goal. In this event, if *semiempirical* rules can be obtained for the estimation of correlation energies (that is, the differences in energy between SCF and accurate wave functions) for atoms and diatomic molecules, one then can at least progress toward useful knowledge and considerable understanding of atomic and molecular energies. Such semiempirical understanding will be further illuminated by accurate theoretically determined wave functions and energies which will definitely be attainable for systems containing small numbers of electrons (for two-electron atoms and molecules, the problem has already been solved). Further, it may turn out that *some* of the atomic and molecular properties which can be computed when exact wave functions are known can also be computed with moderate accuracy from SCF wave functions.

Additional strong justification for effort devoted toward attaining moderately accurate SCF wave functions for atoms and simple molecules is to be found in the light which they can throw on the regularities of atomic and molecular structure and valence theory in terms of relatively simple single-electron-configuration concepts. This conceptual simplicity appears likely to be lost when one looks at accurate wave functions. However, conversely, this is no reason for not seeking the latter. In fact, given an accurate wave function, it will presumably not be too difficult to *project out of it* less accurate but conceptually simpler desired approximations, including SCF functions. Hence, insofar as the search for accurate wave functions is presently feasible, it *may* be wise to aim one's effort directly toward them rather than toward even moderately accurate SCF functions.

Nevertheless, our effort at Chicago (while not neglecting accurate wave functions and CI) at present emphasizes the search for good SCF wave functions, especially for molecules; at the moment, for diatomic molecules containing H, He, and/or first-row atoms. We feel that much is to be learned from SCF molecular wave functions, and recent experience has made us optimistic that these can be approximated fairly well without excessive computational effort—although we have not yet proved to what extent this hope will be justified. We also feel that molecular wave functions using good SCF MO's, not just the usual simple LCAO–MO's, *may* prove to be about as good approximations to exact molecular wave functions as SCF atomic functions are to exact atomic functions.

This memorandum is devoted mainly to approximating SCF AO's and MO's as linear combinations of AO's; more precisely, of STO's (Slater-type AO's). Although expansions of diatomic MO's in elliptic coordinates are also useful, and we are devoting some attention to these for the lightest molecules, we feel that LC–STO's (linear combinations of STO's) are more useful in general. In the course of reviewing recent and current work in this Laboratory, the necessity became apparent to Dr. B. J. Ransil and the writer for developing a systematic terminology to describe various different ways of choosing disposable parameters (in particular, ζ values) in constructing AO's and MO's as LC–STO's. Most of what follows is devoted to this rather annoying matter of terminology. However, it is hoped that the result is much more than a matter of terminology; namely, that it will make it easier to see the possibilities for approaching good SCF AO's and especially MO's more rapidly.

SELF-CONSISTENT-FIELD ORBITALS

Any SCF wave function is a *single-electron-configuration* approximation to the wave function of an atomic or molecular state. Further, in an SCF wave function, the SCF orbitals, which form an orthonormal set, obey the Hartree-Fock equations, or generalizations of these (cf. C. C. J. Roothaan[3a]) and minimize the energy within the constraints imposed by the single-electron-configuration requirement. The orbitals in an SCF wave function may be said to be "optimized."

These orbitals are central-field AO's in the case of an atom, or MO's conforming to the symmetry group of the equilibrium nuclear skeleton in the case of a molecule. For an atom and a diatomic molecule, respectively, they take the forms

$$\text{AO's: } R_{nl}(r)\,Y_{lm}(\theta,\phi), \tag{1}$$

Diatomic MO's:

$$F(z,\,\rho,\text{ or equivalent coordinates})\,e^{\pm i\lambda\phi}. \tag{2}$$

In (1), l and n are the azimuthal and principal quantum numbers, m is the magnetic quantum number; in (2), $\lambda=|m|$ is a characteristic quantum number for diatomic or, in general, linear-molecule MO's.

As is well known, suitable linear combinations of radially nodeless analytical forms of the type

$$S_{Nlm}(\theta,\phi)=R_{Nl}(r)\,Y_{lm}(\theta,\phi)$$

with

$$R_{Nl}(r)=\text{const}\,r^{N-1}\exp-\zeta_{Nl}r, \tag{3}$$

which may be called Slater-type functions (STO's), are useful as approximations to SCF (or other) AO's and MO's of any kind. In (3), ζ_{Nl} is known as the *orbital exponent* and may be used as a variation parameter; r is in atomic units. STO's may be designated as Ns ($1s$, $2s$, $\cdots$) if $l=0$; Np if $l=1$, Nd if $l=2$, and so on, and further distinguished in terms of λ values, e.g., $Nd\sigma$, $Nd\pi$, and $Nd\delta$ for $l=2$ with $\lambda=0$, 1, and 2, respectively. When STO's are used in constructing AO's, ζ_{Nl} is independent of m or l, but when they are used in constructing diatomic MO's, ζ may be taken different ($\zeta_{Nl\lambda}$) for different λ values; the generalization for polyatomic MO's is obvious.

Slater AO's are STO's with particular values of ζ_{Nl} specified for any particular atom with a particular electron configuration by a well-known set of simple rules given by Slater, and used as radially nodeless approximations to AO's.

In a broad program foreshadowed in an earlier paper by Roothaan,[3b] SCF orbitals can be conveniently approximated as LC–STO's whose *coefficients* and *orbital exponents* can be determined by energy-variation methods. The desired approximations can be approached increasingly closely by using an increasingly well-chosen variety and/or increasing number of STO's in approximating each SCF AO or MO. A large part of the recent and continuing effort of this Laboratory has been devoted to a comprehensive search for the most suitable sets of STO's and of the best ζ values for these to effect adequate convergence with a minimum number of terms. (Prior to and concomitant with this effort, extensive work has been done on methods of computing the numerous energy integrals required in evaluating the energy of any wave function using the type of approximation just indicated and of carrying out the required variation procedures.)

Because of the confusing variety of ways in which a limited set of STO's and their ζ values can be selected, especially in constructing MO's, a brief descriptive classification and nomenclature is given here, first for AO's, then for MO's.

LC-STO AO's

Every SCF free-atom AO [cf. Eq. (1)] evidently can be approximated by a linear combination of a set of STO's all having a common factor $Y_{lm}(\theta,\phi)$. We have therefore to consider only the characteristics of the radial factor. In an SCF AO, this factor has n-l-1 nodes and n-l loops. Since STO's are radially nodeless, the necessary nodes (in case $n>l-1$) must be supplied by forming LC–STO's with coefficients not all alike in sign. Table I, which is self-explanatory, contains a classification of LC–STO AO's into types. For each type, the AO's may be optimized, giving the closest approach possible to SCF AO's within the limitations imposed by the use of a finite set of STO's, by varying the coefficients and the ζ's, using Roothaan's SCF equations.

LCAO MO's

If an MO is approximated by a linear combination of AO's, and each of the latter in turn by an LC–STO form, the result is an LC–STO MO. Such an MO form may be regarded either as an LCAO or directly as an LC–STO. In the simplest and most familiar LCAO MO forms, using one AO per atom and this approximated by a single STO, the two viewpoints coincide. More general MO expressions containing a larger number of LC–STO terms may be regarded as useful and flexible variational forms without regard to their relationship to AO's.

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[3] (a) C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960), this issue; (b) **23**, 69 (1951).

TABLE I. Approximation of SCF AO's as LC-STO AO's.[a]

A. Simple AO's

In these, each of the $n-l$ loops which are present in the radial factor $R_{nl}(r)$ of the SCF AO [cf. Eq. (1)] which is to be approximated is represented by a single STO. These STO's [cf. Eq. (3)] have values of N running from $n-l$ up to n. Simple AO's are the simplest LC-STO approximations which have the correct number of nodes. Simple AO's fall into several types depending on how the ζ values of the STO's are chosen.

(*a*) *Orthogonalized Slater AO's*

A Slater AO is a single STO whose ζ is chosen according to Slater's rules. It is used to represent the *outermost loop* of a simple AO. By orthogonalizing a set of Slater AO's, a set of LC-STO's of the "simple AO" type is obtained.

(*b*) *Single-ζ AO's*

These have a single ζ for all STO's of all AO's of the same l but a different ζ for STO's of different l. The ζ's are chosen so as to minimize the energy of the given state of the given atom. For example, in an electron configuration $1s^2 2s^2 2p^2$, one has

AO LC-STO

$$1s \approx 1s(\zeta)$$
$$2s \approx 2s(\zeta) - \lambda 1s(\zeta)$$
$$2p \approx 2p(\zeta').$$

(*c*) *Hydrogenic AO's*

Solutions of the 1-electron central-field Schrödinger equation; these are a special case with $\zeta = Z/n$ for all the STO's of any AO.

(*d*) *Best simple AO's*

In the most general type of simple AO's, ζ is optimized for each STO separately. For example,

AO LC-STO

$$1s \approx 1s(\zeta)$$
$$2s \approx 2s(\zeta') - \lambda 1s(\zeta'')$$
$$2p \approx 2p(\zeta''').$$

Usually, however, ζ'' is taken equal to ζ for simplicity. In either case, λ is chosen to make $2s$ orthogonal to $1s$.

B. Multiple-ζ AO's

The outermost loop (and in general also others) is represented by more than one STO of the *same form* but different ζ. For example,

AO LC-STO

$$2s \approx a_1 2s(\zeta') + a_2 2s(\zeta'') - \lambda 1s(\zeta)$$
$$2p \approx b_1 2p(\zeta''') + b_2 2p(\zeta'''').$$

The approximate AO's in this example may be called double-ζ AO's.

C. Extended AO's

Outermost loop (and in general also others) is represented by more than one STO including STO's of higher n than for the SCF AO being approximated. For example,

AO LC-STO

$$2s \approx a_1 2s(\zeta') + a_2 3s(\zeta') + \cdots - \lambda 1s(\zeta)$$
$$2p \approx b_1 2p(\zeta'') + b_2 3p(\zeta'') + \cdots.$$

The added higher-n STO's may also be taken with different ζ values than for the main STO, but the improvement obtained thereby though appreciable is not large. For example,

AO LC-STO

$$2p \approx b_1 2p(\zeta'') + b_2 3p(\zeta''') + \cdots.$$

D. Multiple-extended AO's

Approximations B and C, when each is extended to increasing numbers of terms, converge toward the same limit. Approximation B probably converges faster, but the variation procedure is less simple than for C. A judicious selection of terms from both B and C may prove to be best according to Roothaan's recent experience with light atoms. Thus, the multiple-extended type of LC-STO AO may be of especial importance.

[a] Throughout, it is to be kept in mind that the set of SCF AO's considered are mutually orthogonal and their approximations as LC-STO MO's are to be kept likewise.

Nevertheless, it is often useful in classifying LC–STO MO's to think of them first as LCAO MO's, whose AO's are then approximated as LC–STO AO's. However, it is then very important to keep in mind that the coefficients and ζ values in the LC–STO AO's used to build an LCAO MO *must, in general, be revaried* if one is to obtain the best approximation to a desired SCF MO. In other words, good free-atom AO's (i.e., SCF AO's or approximations to these) *cannot, in general,* be used without modification to construct good simple LCAO approximations to SCF MO's. However, in special cases (in particular, nonbonding closed-shell MO's), free-atom AO's may be suitable without much modification.

A characteristic feature of good LCAO–MO's is AO *hybridization,* that is, entrance into any LCAO of AO's, hence STO's, differing in l. For either atom in a diatomic molecule, AO's which have different l but the

TABLE II. Approximation of SCF MO's as LC-STO MO's.[a]

General features of LC-STO MO classification

LC-STO MO's can be classified under essentially the same four headings as AO's (simple, multiple, extended and multiple-extended). This classification, as in the AO case, describes the *number* and *kind* of STO's used. LC-STO MO's can *also* be classified under three headings of a *different* kind which has no analog for AO's. Both kinds of classification are used below, simultaneously, but with priority for the *second* kind because of its special importance.

1. Free-atom-ζ MO's

LC-STO MO's with the ζ values in the STO's taken equal to those for the same STO's in free-atom AO's (cf. Table I). This makes ζ the same for any one STO in every MO where it appears, in addition to specifying a particular (free-atom) value of ζ.

A. Free-atom-ζ simple MO's

By simple MO's are meant LC-STO MO's all containing just *one* STO *for each radial loop of every valence-shell* AO of correct symmetry (e.g., of every valence-shell σ AO in the case of a σ, σ_g, or σ_u MO), for every atom in the molecule; or (as an equivalent alternative description) all containing one STO *representing the outer loop of every valence-shell and every inner-shell* AO of correct symmetry, for every atom. The following, *if free-atom values* of the indicated ζ's are used, are examples of free-atom-ζ simple MO's:

$$\mathrm{N}_2\begin{cases} m\sigma_g\,(m=1\text{–}3):\; c_{m1}[1s_a(\zeta_1)+1s_b(\zeta_1)]+c_{m2}[2s_a(\zeta_2)+2s_b(\zeta_2)]+c_{m3}[2p\sigma_a(\zeta_3)+2p\sigma_b(\zeta_3)],\\ n\sigma_u\,(n=1,\,2):\; c_{n1}[1s_a(\zeta_1)-1s_b(\zeta_1)]+c_{n2}[2s_a(\zeta_2)-2s_b(\zeta_2)]+c_{n3}[2p\sigma_a(\zeta_3)-2p\sigma_b(\zeta_3)],\\ 1\pi_u:\; d[2p\pi_a(\zeta_3)+2p\pi_b(\zeta_3)]; \end{cases}$$

$$\mathrm{CH}\begin{cases} m\sigma\,(m=1\text{–}3):\; c_{m1}1s_{\mathrm{C}}(\zeta_1)+c_{m2}2s_{\mathrm{C}}(\zeta_2)+c_{m3}1s_{\mathrm{H}}(\zeta_3)+c_{m4}2p\sigma_{\mathrm{C}}(\zeta_4),\\ 1\pi:\; 2p\pi_{\mathrm{C}}(\zeta_4). \end{cases}$$

(*a*) *Best atomic-ζ simple MO's*
Here ζ values as for the best simple AO's [cf. Table I, Sec. A(a)] are used.

(*b*) *Slater-ζ MO's*
Here Slater ζ values are used [cf. Table I, Sec. A(a)].

B. Free-atom-ζ multiple-ζ MO's

By multiple-ζ MO's are meant LC-STO MO's containing the same number of *types* (as specified by N, l, λ) of STO's as simple MO's, but with some (or possibly all) STO's of the simple MO replaced each by a linear combination of two (or possibly more) STO's of the same type but differing in ζ, in the same way as for multiple-ζ AO's (cf. Table I, Sec. B). For example, the free-atom-ζ simple MO's of N_2 and CH given in Sec. 1.A of this table become free-atom-ζ multiple-ζ (here double-ζ) MO's if some or all of the individual STO's of a C or N atom are each replaced by a linear combination of a pair of like STO's with two different ζ values determined by optimizing the energy with respect to this ζ pair in a multiple-ζ AO expression for the C or N AO's.

C. Free-atom-ζ extended MO's

These differ from free-atom-ζ simple MO's in that STO's of higher than valence-shell n are added, in the same way for each atom as for extended AO's (cf. Table I, Sec. C).

D. Free-atom-ζ multiple-extended MO's

(Cf. Table I, Sec. D.)

2. STO-ζ MO's

LC-STO MO's with ζ values in the STO's optimized as follows. A single ζ is determined *for each* STO in such a way as to minimize the energy of the molecule in any particular MO electron configuration and state. Thus some of the constraints imposed on the choice of ζ values in free-atom-ζ MO's (see Sec. 1) are released, but there remains the often rather severe constraint that the same ζ is used for any one STO in every MO where it appears; this constraint is removed in MO-ζ MO's (see Sec. 3). It is regrettable that the term "STO-ζ MO's" is scarcely self-explanatory. A more nearly descriptive but still hardly self-explanatory name would be "STO-optimized-ζ MO's."

Thus in the states of N_2 with electron configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$ and in that of CH with configuration $1\sigma^2 2\sigma^2 3\sigma^2 1\pi$, the free-atom-$\zeta$ simple MO's expressions given in Sec. 1.A of this table become STO-ζ simple MO's if all the ζ's (now *four* distinct ζ's for N_2 and *five* for CH) are optimally determined for the molecule instead of being given free-atom values. It should be noted that the ζ values so determined for $2p\pi$ STO's are now different from those for $2p\sigma$ STO's; STO-ζ MO's are thus more flexible than free-atom-ζ MO's.

A. STO-ζ simple MO's

These are simple MO's, as defined in Sec. 1.A of this table, whose ζ values have been determined in the manner just described for STO-ζ MO's. The N_2 and CH examples discussed are examples of STO-ζ *simple* MO's.

B. STO-ζ multiple-ζ MO's

These are multiple-ζ MO's as defined in Sec. 1.B of this table, whose ζ values have been determined in the manner described for STO-ζ MO's.

TABLE II.—*Continued.*

C. STO-ζ extended MO's

These differ from STO-ζ simple MO's in that STO's of higher than valence-shell N and l are added. For example, the following STO's would be the most important *additions* to the LC-STO MO expressions given for N_2 and CH in Sec. 1.A of this table:

$$N_2\begin{cases} m\sigma_g(m=1\text{–}3),\text{ add } c_{m4}[3s_a(\zeta_2)+3s_b(\zeta_2)]+c_{m5}[3p\sigma_a(\zeta_3)+3p\sigma_b(\zeta_3)]+c_{m6}[3d\sigma_a(\zeta_2)+3d\sigma_b(\zeta_2)], \\ n\sigma_u(n=1,\,2),\text{ add } c_{n4}[3s_a(\zeta_2)-3s_b(\zeta_2)]+c_{n5}[3p\sigma_a(\zeta_3)-3p\sigma_b(\zeta_3)+c_{n6}[3d\sigma_a(\zeta_2)-3d\sigma_b(\zeta_2)], \\ 1\pi_u,\text{ add } d_2[3p\pi_a(\zeta_4)+3p\pi_b(\zeta_4)]+d_3[3d\pi_a(\zeta_4)+3d\pi_b(\zeta_4)]\text{ to } d_1[2p\pi_a(\zeta_4)+2p\pi_b(\zeta_4)]; \end{cases}$$

$$\text{CH}\begin{cases} m\sigma(m=1\text{–}3),\text{ add } c_{m5}2s_H(\zeta_3)+c_{m6}2p\sigma_H(\zeta_3)+c_{m7}3s_C(\zeta_2)+c_{m8}3p\sigma_C(\zeta_2)+c_{m9}3d\sigma_C(\zeta_2), \\ 1\pi,\text{ add } 3p\pi_C(\zeta_5),\ 3d\pi_C(\zeta_5),\text{ and } 2p\pi_H(\zeta_6)\text{ to } 2p\pi_C(\zeta_5). \end{cases}$$

Full use of STO-ζ extended MO's obviously involves a great increase in computational effort. This effort can be diminished if the ζ's of the higher-n STO's are in most cases set equal to those of related valence-shell STO's, as has been done in a plausible way in the preceding descriptions. Only further experiment can show what are the wisest choices to obtain good results with minimum effort, but it is likely that higher-n ζ's chosen somewhat in the manner just illustrated will be satisfactory.

D. STO-ζ multiple-extended MO's

(Cf. Table I, Sec. D.)

3. MO-ζ MO's

LC-STO MO's with ζ values in general individually optimized for each STO in *each occupied* MO. A more fully descriptive name would be "MO-optimized-ζ MO's," but even this term is, regrettably, hardly self-explanatory. Full use of this method would involve much computational effort, but in simple cases (excited H_2 and repulsion curve for two He atoms)[b,c] it has proved extremely valuable. In the LC-STO simple MO expressions for N_2 and CH given in Sec. 1.A of this table, full use of this method would require nine σ_g and six σ_u MO ζ's, also one π_u ζ, in the case of N_2, and in the case of CH, twelve σ-MO ζ's and one π-MO ζ. However, nearly as good results may be expected if various judicious simplifications are made; for example, in N_2 perhaps the use of the same ζ for the $1s$ STO in *all* the MO's and another single ζ for the $2s$ and another for the $2p\sigma$ in the $1\sigma_g$ and $1\sigma_u$ MO's; but in any event, different ζ's for the σ_g than for the σ_u valence-shell MO's.

A. MO-ζ simple MO's

These are simple MO's, as defined in Sec. 1.A of this table, whose ζ values have been determined in the manner described for MO-ζ MO's. The N_2 and CH examples just discussed are examples of MO-ζ *simple* MO's.

B. MO-ζ multiple-ζ MO's

These are multiple-ζ MO's as defined in Sec. 1.B of this table, whose ζ values have been determined in the manner described for MO-ζ MO's. They are, in general, different for every STO and every MO, but in practice many simplications should be possible with little loss of accuracy.

C. MO-ζ extended MO's

These differ from MO-ζ simple MO's in that STO's of higher than valence-shell N and l are added. The possibilities and complications of this method can be appreciated by a consideration of the N_2 and CH LC-STO MO's discussed in Sec. 2.C of this table, but with different ζ values for different MO's as outlined at the beginning of Sec. 3 of this table, except for qualifications on full generality as discussed in Sec. 2.C.

D. MO-ζ multiple-extended MO's

(Cf. Table I, Sec. D.)

[a] Throughout, it is to be kept in mind that the members of any set of SCF MO's considered are mutually orthogonal, and their approximations as LC-STO MO's are to be kept likewise.

[b] See reference 4.

[c] See reference 5.

same λ can be thought of as combined to form a single hybrid AO, which is then combined (LCAO) with a suitable (hybrid or nonhybrid) AO of the other atom to form an LCAO MO.

Alternatively, we can think of such an LCAO MO as a linear combination to which, in general, each atom may contribute several nonhybrid AO's differing in l, and perhaps also in n, but of course all alike in λ. This last viewpoint appears to form the most useful basis for classifying LCAO MO's, and thereby LC–STO MO's, into types with respect to methods of choosing the component STO's in such a way as to obtain acceptable approximations to SCF MO's with minimum numbers of STO's and/or maximum computational economy. This classification into types is summarized in Table II.

TENTATIVE CONCLUSIONS ON MOST RAPIDLY CONVERGENT CHOICES OF LC-STO MO's

Most of the computations done thus far, both here and elsewhere, using LC–STO approximations to MO's, have been of the free-atom-ζ simple MO or (somewhat better) the STO–ζ simple MO type (see Table II for descriptions of types). However, a few computations have been made which indicate the possibility of radical improvements by dropping certain rather severe constraints that are inherent in LC–STO MO's limited by the two restrictions of being (a) free-atom-ζ or STO–ζ in type; (b) of the simple MO type. With reference to restriction (a), the work of Huzinaga[4] and of Phillipson and Mulliken[5] demonstrates strikingly the very great advantages of using different values for the same STO in bonding and antibonding MO's (use of MO's of MO–ζ type). With reference to restriction (b), unpublished work of J. W. Richardson indicates that the use of double-ζ (in general multiple-ζ) MO's instead of simple MO's also has great advantages; it is further evident (and there are a few calculations to support this statement) that the use of *extended* MO's instead of simple MO's should have somewhat similar though perhaps smaller advantages. It seems clear that by judicious use of MO–ζ double-ζ and/or MO–ζ extended MO's, one may reasonably hope (at the cost of considerable but not prohibitive computational effort) to obtain, with a quite moderate number of STO's, convergence toward SCF MO's.

With specific reference to the multiple-ζ method, there exist two or three computations on HF in which LCAO MO's have been constructed using SCF AO's. These have given considerably lower energies than Slater-AO and STO–ζ simple MO calculations.[6] It seems clear that the reason for this gain is that the single $2p\sigma$ and the single $2p\pi$ STO of the simple MO method have been replaced by what are essentially multiple-ζ $2p$ STO's (since a $2p$ SCF AO can be closely approximated by a linear combination of two or three $2p$ STO's with different ζ's). However, it is also clear that appreciable further improvement on the use of a free-atom SCF AO would be obtained by the use of triple-ζ or probably already by double-ζ $2p\sigma$ and $2p\pi$ STO's whose forms have been optimized *for the molecule* instead of for the atom and thus differently for $2p\sigma$ and $2p\pi$. (For the free atom, the radial factor of the SCF AO is necessarily identical for $2p\sigma$ and $2p\pi$.) In connection with the foregoing, it is worth remarking that the SCF–LCAO–MO ϵ values obtained using Slater or STO-ζ AO's, although these usually agree rather well with observed ionization potentials, are very considerably too low for the π MO's of HF and F_2 when calculated using simple MO's.[7] It seems likely that use of double-ζ MO's will yield much better agreements.

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[5] P. E. Phillipson and R. S. Mulliken, J. Chem. Phys. **28,** 1248 (1958).

[6] See A. M. Karo, J. Chem. Phys. **31,** 182 (1959) and references given there; also reference 7 for the results of recent STO-ζ calculations.

[7] B. J. Ransil, Revs. Modern Phys. **32,** 239 (1960), this issue.