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Basis Functions for *Ab Initio* Calculations*

LELAND C. ALLEN†

Department of Physics, University of California, Berkeley 4, California

AND

ARNOLD M. KARO

Lawrence Radiation Laboratory, University of California, Livermore, California

I. INTRODUCTION

THIS article gives a compilation and basis function analysis of existing *ab initio* molecular eigenfunctions. Our review pertains to that body of the literature in which a direct solution of the Schrödinger equation is attempted, and especially that part which we believe offers the greatest opportunity for extension to the complicated molecules of chemical interest. The specific content of the article is frankly devoid of a connection with chemically significant problems. It is important for a future review to develop this connection, and it should be done in a more empirical framework than we have used.

By *ab initio* we imply: First, consideration of all the electrons simultaneously. Second, use of the exact nonrelativistic Hamiltonian (with fixed nuclei),

$$\mathcal{H}=-\tfrac{1}{2}\sum_{i}\nabla_i^2-\sum_{i,a}\frac{Z_a}{r_{ia}}+\sum_{i>j}\frac{1}{r_{ij}}+\sum_{a,b}\frac{Z_aZ_b}{r_{ab}}; \qquad (1)$$

the indices i, j and a, b refer, respectively, to the electrons and to the nuclei with nuclear charges Z_a and Z_b. Third, an effort should have been made to evaluate all integrals rigorously. Thus, calculations are omitted in which the Mulliken integral approximations or electrostatic models have been used exclusively. These approximate schemes are valuable for many purposes, but present experience indicates that they are not sufficiently accurate to give consistent results in *ab initio* work. Some three- and four-center calculations are included, however, where such procedures were the only available means of obtaining certain integrals. While not imposed as a restriction on our listings, it is nevertheless true that all of the calculations have been carried out with nuclei fixed. In other words, no problems involving more than three particles in which vibronic interactions are important or where the mass of the negative particles is significant with respect to the nuclear masses (e.g., mesonic molecules) have been treated *ab initio*.

In addition to the preceding restrictions, we have limited the survey to molecular wave functions that involve more than two electrons and employ one-electron basis orbitals. Although two-electron problems comprise a large part of our detailed knowledge of electronic systems, a full treatment of this subject would be a review in itself, and the points we wish to bring out here become important primarily for molecules with more than two electrons. Actually the limitation to systems of more than two electrons essentially implies the use of one-electron basis orbitals, since only one or two quite specialized and apparently not readily generalizable calculations explicitly include r_{ij} in the wave function for more than two electrons.

In the mid-thirties a number of rigorous applications of quantum theory to simple molecular systems were made by several investigators, principally James, Coolidge, Knipp, and Coulson. However, it is not incorrect to state that the major effort in *ab initio* work dates from the Shelter Island Conference in 1951. At that conference there was a great deal of discussion on the evaluation of two-electron molecular integrals and considerable optimism for the early realization of extensive results, at least for the diatomic case. In the conference summary the question was asked, "Are Slater atomic orbitals really the best orbitals to use as a basis for molecular calculations?" The dearth of calculations made it impossible to discuss the question at that time; but now, at the Boulder Conference, sufficient data have been accumulated to give an answer. Nearly a decade has elapsed because only very recently have we had a rapid means for obtaining large numbers of integrals over the wide range of parameters required for practical basis function experimentation.

As in 1951, it is still true that the most rapid advances in the next year or two are to be expected in the diatomic case. This follows directly from the present existence of highly efficient digital computer programs for two-center integrals. These have been devised by Boys at Cambridge University, Nesbet at Boston University, Roothaan and co-workers at the University of Chicago, Switendick and Corbató at the Massachusetts Institute of Technology, and Harris at the University of California, Berkeley.[1] More than half of these have been written for commercial machines of which there are many copies. Besides the two-center

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† National Science Foundation Postdoctoral Fellow and staff member Materials Research Laboratory, OMRO, Watertown, Massachusetts.

[1] This work is reported at greater length elsewhere in this issue of *Reviews of Modern Physics*, and further discussion is inappropriate here.

integral programs, several of the groups have prepared programs such as the transformation of integrals to the SCF basis set and the Roothaan scheme, which are applicable to any molecular problem.

In undertaking the review just outlined, we would also like to call attention to the recent article by Kotani, Mizuno, Kayama, and Yoshizumi in the *Annual Review of Physical Chemistry* [9, 245 (1958)]. Their paper includes a discussion of semiempirical theories as well as *ab initio* work and thus has a greater breadth than we have attempted. It is certainly the reference which is most pertinent and closely related to our survey.

II. METHODS OF CONSTRUCTING MOLECULAR WAVE FUNCTIONS

(a) Non-AO Methods

The construction of non-AO wave functions has proceeded along two lines. Both methods essentially attempt to exploit more fully spatial geometry in special classes of molecules than would be possible in a strict AO treatment.

The first of these is the use of an elliptical coordinate system, and the most extensive effort along this line has been made by Harris and Taylor on small diatomic molecules. In addition to the use of natural coordinates, Harris seeks to minimize the number of required configurations by relaxing the constraints that the orbitals be orthogonal and filled in pairs. This technique, coupled with computer programs for varying the nonlinear parameters automatically, is very likely the most efficient scheme for diatomic molecules with from three to six or eight electrons. For larger diatomic molecules the greater importance of the atomic singularities and the rapidly increasing complexity introduced by the relaxation of the orbital constraints appear to limit the usefulness of the method.

The other non-AO proposal has been for the use of a single coordinate origin for all basis functions. Because of high symmetry and light surrounding atoms, molecules like the central hydrides are especially suited to this scheme. A good example is the encouraging work of Saturno and Parr[2] on CH_4. Another illustration is Allen's calculation of HF. Because this molecule is also a hydride and has a large positive dipole moment, the fluorine center was chosen as the coordinate origin. The principal idea behind one-center treatments is that the simplicity of having only one-center integrals to evaluate more than compensates for a larger basis set and higher l values. The use of a single coordinate origin seems justified for cases such as those cited in the foregoing or for various arrangements of two or three hydrogen atoms, but it is difficult to imagine a widespread generalization of this technique.

Finally, Bingel (1)[3] recently has given the expansion of the molecular wave function in terms of the eigenfunctions of the united atom. For small separations the expansion depends on the internuclear distances, the united-atom charge density and its radial gradient at the origin. Although no calculations have yet been reported, this approach may prove to be a valuable adjunct to LCAO calculations at small internuclear distances. (In their review Kotani et al. use the term "united-atom orbitals" to refer to the type of basis functions mentioned both in this paragraph and the one preceding.)

(b) AO Methods

The valence bond and the LCAO molecular orbital schemes are the two general methods which form a natural framework for the use of AO's. In the valence bond method, as supplemented by configuration interaction (CI), the molecular wave function is expanded as a number of determinantal functions, each of which corresponds to a molecular system built up from definite states of the free atoms. The linear coefficients of this set of determinantal functions are obtained by energy minimization. When relatively few configurations can give a good result, this is an efficient method and is the procedure most used in early work.

On the other hand, the molecular orbital method is an approach to a molecular Hartree-Fock solution. In practice, the Roothaan procedure is the most useful technique for constructing the molecular orbital solution. The molecular orbitals are expanded as a finite set of specified basis functions with energy-determined linear coefficients, and when expressed in matrix form, this scheme is ideally suited for use with digital computers. Experience has shown that the molecular orbital state determined in this manner gives moderately good results for molecules at their equilibrium separations. This fact, together with the computational advantages of the Roothaan scheme, has led to the recent ascendancy of this procedure over all others for constructing molecular wave functions. (The notation, SCF LCAO-MO, has now become standardized for this type of calculation.) As is well known, configurations arising from one- and two-orbital substitutions in this single molecular-orbital determinant must be added to make the treatment equivalent to the valence bond method described in the preceding paragraph.

Assuming that one is able to carry out the necessary integrations, the central problem becomes the choice of AO's. By far the largest number of existing calculations have employed single exponential AO's. (Mulliken has introduced at the conference the designation and abbreviation, Slater Type Orbital—STO.) Except for symmetry considerations, basis orbital choice is then reduced to a specification of the three nonlinear param-

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[2] Saturno and Parr have employed nonintegral principal quantum numbers in their single exponential basis functions.

[3] References are listed in the Bibliography at the end of the article.

eters, n, a, and l, in $r^n e^{-ar} Y_l^{|m|}(\theta,\varphi)$. Rules for obtaining these have been given by Slater (2), Pauling (3), Zener (4), Roothaan (5), Duncanson and Coulson (6), and Morse, Young, and Haurwitz (7). The lists given by Duncanson and Coulson, and Morse et al. are slightly more complicated than the others; e.g., the 2s function is constructed from two exponentials with the parameters of the second term differing somewhat from those for the 1s function. The results of our survey appear to indicate, however, that all of these various rules for choosing nonlinear parameters lead to almost the same total molecular energies.

In addition to STO's, Gaussian and Hartree-Fock AO's have been used for a few molecules, and a detailed comparison is given in later sections.

(c) Configuration Interaction

Many of the calculations we have tabulated include a limited configuration interaction. The results uniformly show a small energy lowering of the order of 1 ev, and this slow convergence has led to much discouragement concerning the utility of the configuration interaction method. Typical of current work is the limited CI treatment of HF. Six excited MO configurations are formed by allowing promotion of all but the 1σ electrons into the more energetic 4σ MO. (The two-electron integral problem is so severe that, in general, only those configurations have been considered whose Hamiltonian matrix elements may be formed from the same integrals over the original basis functions needed for the single lowest configuration.) This can give only very limited freedom in describing electron correlation, and in the HF example, at least some type of δ and φ MO's should be available for CI.

Fortunately, almost all of the problems in configuration interaction can be investigated by resorting to free-atom calculations. Some of the most thorough work has been performed by Boys on Be, F^-, Ne, and Na^+ (8, 9). Considerable insight has also been gained from such a simple system as helium, and this serves as a good example. Taylor and Parr (10), Green et al. (11), Löwdin and Shull (12, 13), Holøien (14), and Nesbet and Watson (15), have all made studies on He with methods applicable to molecules with more than two electrons. The last calculation considered ten single exponential basis functions (with l values from 0 to 3) formed into 20 configurations. The choice of nonlinear parameters was the principal problem, and the significant result was that all functions should have the same radial maxima. This is in sharp contrast to the successive spreading out of the maxima with higher l values, or with increase in the number of radial nodes, which is characteristic of solutions for the central-field problem.

A new scheme for picking configuration-interaction orbital parameters has been suggested by Boys. He introduces "exclusive orbitals" and "oscillator orbitals," defined by externally imposed auxiliary conditions, that may lead to a more rapid convergence of the configuration interaction. Boys has also described some "correlation functions" through which he hopes to make a separate calculation for part of the correlation energy. These functions may contain explicit dependence on r_{ij}, but they are also functions for which the necessary integrals may be computed readily.[1]

III. TABULATION OF *AB INITIO* CALCULATIONS

Table I (16–74) lists the calculations that we have found in the literature, technical reports, and through private communication. There are approximately eighty calculations, three-fourths of which are for diatomic molecules. The structure of the table reflects the emphasis on basis orbitals and our belief that this is the central problem around which future development will take place. Our table lacks completeness for three-electron systems. There are so many of these that only a representative sampling of more recent work has been included.

(a) Other Computed Molecular Quantities

The total molecular energy and the dipole moment, both especially characteristic of the molecular wave function, have been tabulated in separate columns. Quadrupole moments, ionization potentials, polarizabilities, quadrupole coupling constants, etc., are all listed in a single column because so few results are available. The *Annual Review of Physical Chemistry* article by Kotani et al. and a paper by Karplus[1] survey values computed for these quantities. For example, rather good agreement with experiment is obtained for the $\langle r^2 \rangle$ part of the magnetic susceptibility of H_2O by using a molecular-orbital wave function with STO's, while the same type of wave function yields poor results for quadrupole coupling constants in O_2 and NO.

(b) Binding Energies

Present calculations are limited to atoms from the first row of the periodic table, and to a crude first approximation, they yield simply a fixed percentage ($\sim$99 to 99.5) of the total observed energy. Binding energies, however, for nearly all molecules are much less than 0.5% of the total energies, and it is possible to compute almost any value through a choice of basis functions that yield a relatively poor free-atom energy. The few calculations that obtain a total molecular energy lower than the *experimental* separated-atom energies are restricted to the class of small molecules with small total energies. For these reasons, binding-energy results have been relegated to the "other quantities computed" column.

(c) Approximate Calculations

As stated in the Introduction, we have omitted from the tabulation all calculations deviating appreciably

TABLE I. Compilation and summary of *ab initio* calculations.

Molecule	Reference	Method	Basis functions[a]	No. of configurations in CI	% total energy (single determinant)	% total energy (single determinant +CI)[b]	Dipole moment (debyes)[b,c]	Other computed molecular quantities[b]	Remarks
H_3	16	SCF LCAO-MO	STO (S)	···	93.03	···	···	$D_e=1.17$ (4.47) ev $E_{\mathrm{act}}=1.81$ (0.43) ev $r_e=2.0$ a.u.	Linear nuclear configuration. H_3 approximated from SCF procedure for H_3^-.
H_3	17	LCAO-MO	STO (V)	21–35	···	98.14 (21)	···	$D_e=3.48$ (4.47) ev (21) $r_e=1.779$ a.u. (21) $E_{\mathrm{act}}=0.65$ (0.43) ev (21)	Nine nuclear configurations.
H_3	18	LCAO-MO	STO (V)	20	···	97.39 (20)	···	$r_e=1.93$ a.u. (20) $D_e=3.14$ (4.47) ev (20)	Five 1*s* hydrogenlike orbitals with centers equally spaced on line of nuclei.
H_3	19	SCF LCAO-MO	STO (V)	3	···	95.95 (3)	···	$r_e=1.84$ a.u. (3) $D_e=2.49$ (4.47) ev (3)	Variable shifting parameter used.
He−He	20	SCF LCAO-MO	STO (S)	···	···	···	···	I (He) $=24.39$ (24.58) ev $E_{\mathrm{van\ d.\ Waals}}=5.82\times10^{-4}$ (9.25×10^{-4}) ev	He_2^+ potential curve obtained with $D_e=2.07$ (2.5) ev, $r_e=2.27$ (2.06) a.u.
He−He	21	VB	Elliptic (V)	2	···	···	···	···	Complete variation of orbital parameters. Experimental and calculated values differ by 24 ev.
H_2+H_2	22	SCF LCAO-MO	STO (S)	···	···	···	···	···	Rectangular nuclear configuration found unstable.
H_3^-	23	VB	STO (S)	2	···	···	···	$D_e=1.78$ ev (2) $r_e=2.25$ a.u. (2)	Linear symmetrical configuration. Many-center integral approximations are compared.
H_4	24	LCAO-MO	STO (S)	6	···	···	···	$D_e=0.44$ ev (1) $D_e=2.26$ ev (6)	Linear nuclear configuration; complex stable w.r.t. 4H and unstable w.r.t. $2H_2$.
		SCF LCAO-MO	STO (S)	1	···	···	···	$D_e=1.49$ ev (1)	
H_4	25	SCF LCAO-MO	STO (S)	···	···	···	···	$D_e=2.11$ ev $r_e=2.1$ a.u.	Four linear nuclear configurations; complex stable w.r.t. 4H and unstable w.r.t. $2H_2$.
LiH	26	Variational	STO (S) + Elliptic	11	···	98.90 (11)	···	$D_e=1.82$ (2.52) ev (11)	STO's for Li 1*s* electrons. Valence electrons treated by James-Coolidge type expansion with r_{12} terms omitted.
LiH	27	VB	STO (S)	20	98.37	98.85 (20)	−6.04 (6)	$E_1-E_0=3.18$ (3.66) ev (6) $I=7.52$ ev	Four sets of orbital exponential parameters.
LiH	28	VB	STO (DC)	6	···	98.86 (6)	−6.31 (6)	$D_e=1.66$ (2.52) ev (6)	
LiH	29	Variational	STO (S) + Elliptic	10	···	98.90 (10)	−5.57 (10)	···	Orbital parameter variation; r_{12} terms omitted.
LiH	30	VB	STO (S)	10	···	98.93 (6)	−5.61 (6)	···	Four sets of orbital exponential parameters. $2p_\sigma$ on hydrogen introduces hydrogen atom polarization.
LiH	31	SCF LCAO-MO	STO (V)	···	98.75	···	−5.92	$D_e=1.41$ (2.52) ev	Complete variation of orbital exponential parameters.
LiH	32	VB	Hartree-Fock	6	98.61	99.03 (6)	−6.05 (6)	$D_e=1.62$ (2.52) ev (6) $r_e=3.24$ (3.01) a.u. (6) $\omega_e=1212$ (1406) cm^{-1} (6) $T_e=2.66$ (3.286) ev (6)	Nine internuclear distances; excited Σ^+ state evaluated.
LiH	33	SCF LCAO-MO	Hartree-Fock	6	98.83	99.03 (6)	−6.05 (6)	Equivalent to preceding calculation	Equivalent to preceding calculation.
LiH[d]	21	VB	Elliptic (V)	4	99.19	99.61 (4)	···	$D_e=1.30$ (2.52) ev (1) $D_e=2.21$ (2.52) ev (4)	Complete variation of orbital parameters.

[a] A further classification of the STO's is given in parenthesis: (S), orbital exponents adopted with or without modification from Slater's rules (2); (V), orbital exponents in the molecule determined by energy minimization; (DC), orbital exponents tabulated by Duncanson and Coulson (6); (MYH), orbital exponents tabulated by Morse, Young, and Haurwitz (7); (R), orbital exponents tabulated by Roothaan (5).

[b] Following the computed number, the experimental value and the number of configurations in the CI are given in parentheses. Where possible, computed values are given for the experimental internuclear distance.

[c] The sign of the dipole moment is relative to the heavier atom taken to be at the origin of coordinates.

[d] Evaluated at 3.2 a.u.

[e] Evaluated at 5.63 a.u.

[f] Evaluated at 5 a.u.

[g] Evaluated at 6.01 a.u.

[h] Corrected by R. K. Nesbet (cf. reference 58).

[i] *f* terms included.

[j] Evaluated at $r=\infty$.

[k] Apex atom positive.

Table I.—*Continued.*

Molecule	Reference	Method	Basis functions[a]	No. of configurations in CI	% total energy (single determinant)	% total energy (single determinant +CI)[b]	Dipole moment (debyes)[b,c]	Other computed molecular quantities[b]	Remarks
BeH^+	27	VB	STO (S)	10	···	98.98 (10)	···	$E_1-E_0=5.22$ (5.40) ev (6)	Two sets of orbital exponential parameters.
BeH	34	SCF LCAO-MO	STO (S)	···	99.41	···	···	$D_e=2.75$ (2.22) ev $r_e=2.51$ (2.54) a.u. $I=8.43$ (8.1) ev	Four internuclear distances. Be 1*s* not mixed in forming MO's.
Li_2^+ [e]	35	VB	STO (S)	···	···	···	···	$D_e=0.304$ (1.30) ev	
		Variational	STO (S) + Elliptic	8	···	···	···	$D_e=0.49$ (1.30) ev (1) $D_e=1.24$ (1.30) ev (8)	STO's for Li 1*s*. Valence electrons treated by James-Coolidge type expansion with r_{12} terms omitted.
Li_2	36, 37	VB	STO (S)	2	99.00[g]	99.00(2)	···	$D_e=0.27$ (1.05) ev (2) $r_e=6.01$ (5.049) a.u. $q'=0.0040$ a.u.	Integrals evaluated in polar or elliptical coordinates. Three internuclear distances. Orbital variations for 2*s*.
		Variational	STO (S) + Elliptic	18	···	99.11 (18)	···	$D_e=0.51$ (1.05) ev (18) $q'=-0.0030$ a.u. (18)	STO's for Li 1*s* electrons. Valence electrons treated by James-Coolidge type expansion with r_{12} terms omitted.
Li_2 [f]	38	LCAO-MO	STO (S)	···	98.82	···	···	$D_e=-0.3$ (1.05) ev	Li 1*s* not mixed in forming MO's; orbital exponential parameters varied.
Li_2	39	SCF LCAO-MO	STO (MYH)	···	99.02	···	···	$D_e=0.33$ (1.05) ev $I=4.91$ ev $E_1-E_0=2.30$ (1.895) ev $Q(Li_2)=-0.17$ a.u.	
Li_2	40	LCAO-MO	STO (S)	8	98.88	99.11 (8)	···	$D_e=0.77$ (1.05) ev (8) $Q(Li_2)=19.46$ a.u. (8) $q'=0.0016$ a.u. (8)[e]	Three sets of orbital exponential parameters and three internuclear distances. Excited states obtained from ground state secular equation.
		SCF LCAO-MO	STO (S)	···	98.95	···	···	$D_e=0.124$(1.05) ev $Q(Li_2)=22.31$ a.u.	
Li_2	31	SCF LCAO-MO	STO (V)	···	98.98	···	···	$D_e=0.15$ (1.05) ev	Complete variation of orbital exponential parameters.
BH	41	SCF LCAO-MO	STO (S)	···	99.17	···	0.99	$D_e=1.80$ (3.14) ev	
BH	17	LCAO-MO	STO (S)	23	···	99.34 (23)	···	$D_e=1.50$ (3.14) ev (23) $r_e=2.33$ (2.33) a.u. (23)	Scale factor variation. Three internuclear distances.
BH	42	VB	STO (S)	13	99.11	99.36 (13)	···	$D_e=1.46$ (3.14) ev (1) $D_e=2.22$ (3.14) ev (13)	Hybridization introduced in single determinant calculation. Excited states evaluated.
BH	31	SCF LCAO-MO	STO (V)	···	99.21	···	1.58	$D_e=2.07$ (3.14) ev	Complete variation of orbital exponential parameters.
CH^+	43	SCF LCAO-MO	STO (S)	···	99.20	···	···	$D_e=0.9$ (3.77) ev	Excitation energies computed.
CH	43	SCF LCAO-MO	STO (S)	···	99.16	···	0.93	$D_e=1.2$ (3.64) ev $I=11.1$ (11.1) ev	Excitation energies computed.
CH	44	VB	STO (S) and Hartree-Fock	8	···	···	···	$D_e=2.51$ (3.64) ev (8) $\omega_e=3400$ (2900) cm^{-1} (8) $r_e=2.00$ (2.12) a.u. (8)	Five internuclear distances. Orthogonality between C 1*s* and H 1*s* assumed. C 1*s* not mixed in forming MO's. One-center integrals from Hartree-Fock AO's. Two-center integrals from Slater AO's. Excited states obtained from ground state secular equation.
		SCF LCAO-MO	STO (S) and Hartree-Fock	12	···	···	1.97 (1)	$D_e=2.27$ (3.64) ev $D_e=2.95$ (3.64) ev (12) $\omega_e=3100$ (2900) cm^{-1} (12) $r_e=2.06$ (2.12) a.u. (12) $I=12.7$ (11.1) ev	
Be_2	31	SCF LCAO-MO	STO (V)	···	···	···	···	···	Complete variation of orbital exponential parameters. Total energy computed.
NH	43	SCF LCAO-MO	STO (S)	···	99.14	···	0.90	$D_e=0.5$ (4.01)ev $I=11.8$ ev	Excitation energies computed.
NH	45	SCF LCAO-MO	STO (S) and Hartree-Fock	···	···	···	1.24	$D_e=1.40$ (4.01) ev	Cf. remarks for CH (reference 44). N 1*s* not mixed in forming MO's. Excited states obtained from ground state secular equation.
NH	46	SCF LCAO-MO	STO (S)	···	99.16	···	0.91	$D_e=0.50$ (4.01) ev	Separate SCF calculation for *d* $^1\Sigma^+$ state. Other excited states obatined from ground state secular equation.
NH	31	SCF LCAO-MO	STO (V)	···	···	···	2.01	···	Complete variation of orbital exponential parameters. Total energy computed.

TABLE I.—*Continued.*

Molecule	Reference	Method	Basis functions^a	No. of configurations in CI	% total energy (single determinant)	% total energy (single determinant +CI)^b	Dipole moment (debyes)^{b,c}	Other computed molecular quantities^b	Remarks
OH	47	VB	Hartree-Fock	10	99.24	99.40 (10)	2.29 (3)	D_e =1.04 (4.58) ev (10)	
		SCF LCAO-MO	Hartree-Fock	6	99.39	99.41 (6)	2.66 (1)	D_e =1.25 (4.58) ev (6)	Three internuclear distances.
OH	43	SCF LCAO-MO	STO (S)	···	99.06	···	0.92	D_e =0.8 (4.58) ev I =10.8 (13.16) ev	Excitation energies computed.
NH_2	45	SCF LCAO-MO	STO (S) and Hartree-Fock	···	···	···	1.9	D_e =4.2 ev I =14.16 (11.05) ev Equil. bond angle =105°	Cf. remarks for NH (reference 45). Variation w.r.t. bond angle. Two-electron three-center integrals approximated.
CH_3	58	SCF LCAO-MO	Approx SCF AO's	···	···	···	···	D_e =11.78 (12.7) ev I =12.04 (9.95) ev	Orthogonality between C 1*s* and H 1*s* assumed. C 1*s* not mixed in forming MO's. C 3*s* determined variationally. 3*s* exchange and two-electron three- and four-center integrals approximated. Excitation energies computed.
B_2	49	SCF LCAO-MO	STO (S)	···	99.10	···	···	D_e =0.17 (3.67) ev	Three internuclear distances. Excited states obtained from ground state ($^3\Sigma_g^-$) secular equation.
HF	50	VB	STO (S)	6	···	98.95 (2)	1.13 (1.74) (2)	D_e =1.03 (6.08) ev (2)	
		VB	STO (DC)	6	···	99.00 (6)	0.93 (1.74) (6)	D_e =1.96 (6.08) ev (6)	
HF	43	SCF LCAO-MO	STO (S)	···	98.95	···	0.87 (1.74)	D_e =1.1 (6.08) ev I =12.6 (15.77) ev	
HF	51	SCF LCAO-MO	STO (S)	7	98.96	98.99 (7)	0.69 (1.74) (7)	D_e =2.12 (6.08) ev (7) I =12.7 (15.77) ev I =15.5 (17.0) ev	
HF	52	SCF LCAO-MO	Hartree-Fock	7	99.44	99.46 (7)	1.84 (1.74) (7)	D_e =2.11 (6.08) ev (7) r_e =2.0 (1.7328) a.u. (7) I =17.31 (15.77) ev I =19.4 (17.0) ev	Five internuclear distances.
HF	31, 53	SCF LCAO-MO	STO (V)	···	99.01	···	1.49 (1.74)	D_e =2.42 (6.08) I =12.8 (15.77) ev I =16.2 (17.0) ev	Complete variation of orbital exponential parameters.
HF	54	One-center	STO (V)	···	99.42	···	2.28 (1.74)	D_e =1.59 (6.08) ev	*s*, *p*, and *d* orbitals on *F* center. *f* orbitals included in later calculation.
H_2O	55	SCF LCAO-MO	STO (S)	3	99.13_3	99.13_5 (3)	1.52 (1.84) (1)	D_e =7.7 (10.06) ev (1) I =11.79 (12.6) ev I =13.20 (14.5) ev I =18.55 (16.2) ev Equil. bond angle =120° (105°) (1)	Variation with respect to bond angle. Most three-center integrals approximated.
H_2O	17	LCAO-MO	STO (S)	30	···	99.08 (30)	···	D_e =5.81 (10.06) ev (30) r_e =1.95 (1.81) a.u. (30) Equil. bond angle =96° (105°) (30)	Seven nuclear configurations. Force constants computed.
NH_3	45	SCF LCAO-MO	STO (S) and Hartree-Fock	···	···	···	1.97 (1.46)	D_e =8.6 (12.47) ev I =13.14 (10.25) ev Equil. bond angle =108° (106.8°)	Cf. remarks for NH and NH_2 (reference 45). Two-electron three- and four-center integrals approximated. Barrier energy =0.4 (0.25) ev.
NH_3	56	SCF LCAO-MO	Hartree-Fock	13	99.43	99.46 (13)	1.82 (1.46)	D_e =10.3 (12.47) ev (13) I =14.0 (11.0) ev I =19.3 (17.0) ev	Two nuclear configurations. Barrier energy =3.97 (0.25) ev.
NH_3	57	SCF LCAO-MO	STO (S)	···	99.17	···	1.49 (1.46)	D_e =9.00 (12.47) ev I =9.94 (11.0) ev I =16.20 (17.0) ev	
NH_4^+	58	Variational spherical model	STO (V)	···	···	···	···	r_e =1.84 a.u.	Total energy computed.
CH_4	58	Variational spherical model	STO (V)	···	97.06	···	···	r_e =1.98 (2.041) a.u.	
CH_4	59	SCF MO spherical model	Hartree	···	97.43^h	···	···	D_e = −5.44 (∼20) ev $\chi = -33.2\times10^{-6}$ (-12.2×10^{-6}) emu $\alpha = 7.6\times10^{-24}$ (2.5×10^{-24}) cm^3	Exchange neglected.
CH_4	60	SCF MO spherical model	Hartree-Fock	···	97.18	98.86^i	···	···	*f* terms included for perturbation calculation.

TABLE I.—*Continued.*

Molecule	Reference	Method	Basis functions[a]	No. of configurations in CI	% total energy (single determinant)	% total energy (single determinant +CI)[b]	Dipole moment (debyes)[b,c]	Other computed molecular quantities[b]	Remarks
CH_4	61	One-center	STO (V); integer-*n*	5	97.30	98.08 (5)	···	$r_e=1.93$ (2.041) a.u. (5)	Three internuclear distances. Force constants evaluated.
			STO (V); non-integer-*n*	5	97.49	98.23 (5)	···	$r_e=2.02$ (2.041) a.u. (5)	
C_2	31	SCF LCAO-MO	STO (V)	···	···	···	···	···	Complete variation of orbital exponential parameters. Total energy computed.
LiF	31	SCF LCAO-MO	STO (R)	···	98.96	···	3.43	$D_e=0.58$ (5.99) ev	
N_2	62, 63	SCF LCAO-MO	STO (S)	6	99.05	99.12 (6)	···	$D_e=1.20$ (9.90) ev (1) $D_e=3.29$ (9.90) ev (6) $I=14.82$ (15.60) ev $I=15.77$ (17.08) ev $I=19.88$ (18.72) ev $Q(N_2)=-1.87$ (± 1.11) a.u.	
N_2	31	SCF LCAO-MO	STO (V)	···	99.13	···	···	$D_e=2.61$ (9.90) ev $I=15.11$ (15.60) ev $I=14.84$ (17.08) ev $I=19.42$ (18.72) ev	Complete variation of orbital exponential parameters. Ionization potentials are not vertically corrected.
BF	31	SCF LCAO-MO	STO (S)	···	99.07	···	−2.16	$D_e=5.24$ (4.39) ev	
CO	64	SCF LCAO-MO	STO (S)	···	99.27	···	−1.00 (−0.12)	$D_e=11.2$ (11.11) ev $I=13.37$ (14.01) ev $I=15.97$ (16.58) ev $I=20.01$ (19.70) ev	C 1*s* and O 1*s* not mixed in forming MO's.
CO	31	SCF LCAO-MO	STO (S)	···	99.09	···	−0.73 (−0.12)	$D_e=5.38$ (11.11) ev $I=13.08$ (14.01) ev $I=15.87$ (16.58) ev $I=19.93$ (19.70) ev	Ionization potentials are not vertically corrected.
HCN	65	SCF LCAO-MO	STO (DC)	···	···	···	···	$I=17.3$ (13.7) ev $I=26.4$ (26.3) ev $Q(N^{14})=0.0071 \times 10^{-24}$ cm^2	C 1*s* and N 1*s* not mixed in forming MO's.
NO	66	SCF LCAO-MO	STO (S)	9	99.05	99.14 (9)	−0.50 (±0.16)	$D_e=1.7$ (6.6) ev (9) $I=9.14$ (9.25) ev (1)	Excitation energies computed.
O_2	67	LCAO-MO	Gaussian	9	···	···	···	$D_e=5.07$ (5.18) ev (9) $r_e=2.26$ (2.28) a.u. (9) $\omega_e=1503$ (1580) cm^{-1} (9)	Six internuclear distances. $^1\Sigma_g^+$ state calculated with twelve configurations.
O_2	68	LCAO-MO	STO (S)	15	99.07	99.19 (15)	···	$D_e=3.63$ (5.18) ev $Q(O_2)=-1.53$ ($\|Q\|<0.82$) a.u.	Excited states obtained from ground-state secular equation. Excitation energies computed.
		SCF LCAO-MO	STO (S)	···	99.12	···	···	$D_e=0.80$ (5.18) ev $Q(O_2)=-1.76$ ($\|Q\|<0.82$) a.u.	
Be_4	69	SCF LCAO-MO	STO (S)	···	99.22[j]	···	···	$I=8.30$ (9.33) ev[j]	Four square planar nuclear configurations. Three- and four-center integral approximations are compared.
F_2	70	VB	STO (S+DC)	···	99.16	···	···	$D_e=7.62$ (1.68) ev	Exchange interactions between *F* 1*s* on one atom and electrons of other atom are neglected. One-center integrals from Duncanson-Coulson AO's. Two-center integrals from Slater AO's. $^3\Sigma_u^+$ state calculated.
F_2	71	SCF LCAO-MO	STO (S)	6	99.10	99.14 (6)	···	$D_e=-0.23$ (1.68) ev (1) $D_e=1.96$ (1.68) ev (6) $Q(F_2)=0.169$ a.u. $I=12.33$ (15.7) ev $I=14.34$ ev $I=15.96$ ev	Excitation energies computed.
F_2	31	SCF LCAO-MO	STO (V)	···	99.10	···	···	$D_e=-0.20$ (1.68) ev $I=12.91$ (15.7) ev $I=14.86$ ev $I=16.54$ ev	Complete variation of orbital exponential parameters. Ionization potentials are not vertically corrected.
SiH_4	72	SCF MO spherical model	Hartree	···	···	···	···	$D_e=-9.52$ ev $r_e=3.10$ (2.80) a.u.	Exchange included. Total energy computed.
CO_2	73	SCF LCAO-MO	STO (S)	···	99.36	···	···	$D_e=21.46$ (16.5) ev $I=11.5$ (13.75) ev $I=17.9$ (18.0) ev $I=18.8$ (17.29) ev	1*s* orbitals not mixed in forming MO's. Many two- and three-center integrals approximated.
O_3	74	SCF LCAO-MO	Hartree-Fock	···	98.45	···	−0.25 (−0.55)[k]	$D_e=5.05$ (6.20) ev	O 1*s* not mixed in forming MO's. Excited states obtained from ground-state secular equation. Excitation energies computed.

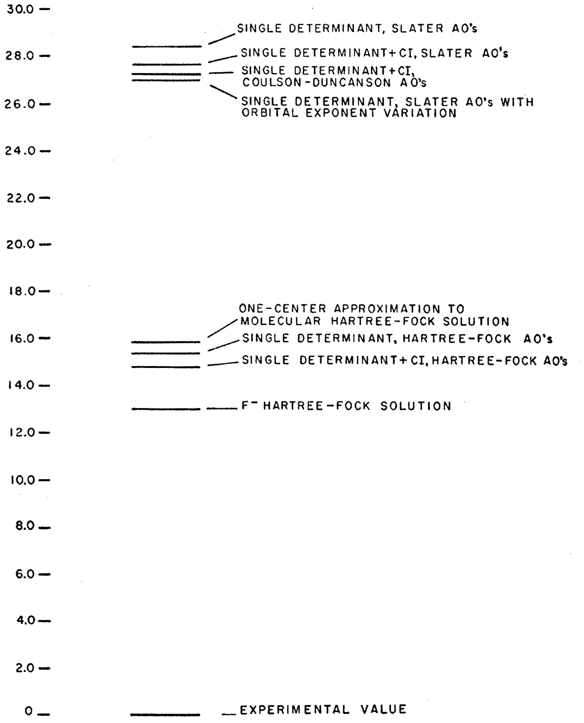

FIG. 1. Error in total energies (ev), $r_0=1.7328$ a.u.

from the *ab initio* prescription. But precisely what and how great departures may be made without causing a significant modification of results has by no means been sufficiently explored. Karo and Allen (51) and Ballinger (53) have investigated the accuracy requirements for the one- and two-electron integrals in HF. Ishiguro, Kayama, Kotani, and Mizuno (40) examined the validity of neglecting the overlap between the $1s$ orbital on one center and the $2s$, $2p$ on the other for Li_2. They also made calculations with the $1s$ collapsed into the nuclear core. In general, Ishiguro et al. found that these approximations seriously affected the prediction of molecular quantities.

IV. DIATOMIC LCAO CALCULATIONS

Almost all of our *ab initio* experience derives from diatomic LCAO calculations, and thus we are best able to compare various types of basis orbitals for this class of wave functions. We have chosen hydrogen fluoride as an illustration because there are many existing wave functions for this molecule and because it is sufficiently complicated to possess the principal features of larger systems.

In Fig. 1 total energies at the equilibrium internuclear separation, 1.7328 a.u., are shown relative to the experimental molecular energy. (Data from 31, 50–54, 75.) All but one of the calculations have used the Roothaan procedure as a starting point. The exception is Kastler's valence bond treatment using Duncanson and Coulson basis orbitals. However, it can be shown that, for all practical purposes, the results are equivalent to a Roothaan calculation with limited CI. The striking feature of this figure is the clustering of results into two groups separated by about a rydberg. The upper group of calculations employ STO's; the lower group, Hartree-Fock AO's. It is apparently of relatively little consequence which rules are used for choosing the nonlinear parameters in the STO's. In fact, for the best of the upper calculations, there was a variation in the molecule of all the exponential parameters in the STO's. In these calculations, CI was carried out with the same configurations (or with the equivalent set of configurations using Duncanson and Coulson AO's) for both the Hartree-Fock AO's and for the various sets of STO's. The inclusion or deletion of this in no way affects the conclusions, since at the equilibrium separation these configurations contribute less than 1 ev for both types of orbitals. The wave functions employing Hartree-Fock orbitals also were carried through for larger internuclear distances; and in this region the CI makes a far larger contribution and is necessary to obtain a potential curve that exhibits even the qualitatively correct limiting behavior.

The one-rydberg decrease in the HF molecular energy is larger than would be expected to occur in many other molecules, and the explanation is simple: single exponential basis orbitals are notoriously poor for negative ions, and for fluorine they give a large electron affinity of the wrong sign, while Hartree-Fock solutions for F and F^- give the correct sign and close to the proper magnitude (75). The polar character of HF strongly brings out this shortcoming in the STO's.

There are three other molecules with LCAO wave functions made from both Hartree-Fock AO's and STO's: LiH, NH_3, and OH. Each of these yields a lower total energy for the Hartree-Fock AO's. Total energy differences range from 0.4 ev for LiH to 7 ev for OH.

The extensive work on HF allows us to make a reasonable estimate of the true *molecular* Hartree-Fock total energy. This has been done by making a plausible extrapolation of Allen's one-center calculation and by comparing with the F^- Hartree-Fock solution. (The F^- result is shown in Fig. 1 relative to its own experimental energy.) The conclusion is that the molecular Hartree-Fock total energy lies 2 to 3 ev below the single-determinant Hartree-Fock AO value. This is significant because this energy difference would appear directly in the binding energy and give a value close to that observed experimentally. It now seems possible and highly desirable to go beyond the LCAO approximation and seek true molecular Hartree-Fock solutions through the use of the Roothaan procedure. (Direct two-dimensional numerical integration of the Hartree-Fock differential equations for two centers is still out of reach for a ten-electron system such as HF.) Here again, choice of the nonlinear parameters in the finite basis set is the major problem. The work on HF (and also LiH, NH_3, and OH) points the way to a practical procedure: since most existing digital computer programs for two-electron integrals are written for STO basis functions, a good initial guess can be obtained from those nonlinear parameters corresponding to STO fits of the Hartree-Fock AO's. Very recently Nesbet (76) has essentially done this and more for HF. Besides those parameters that represent Hartree-Fock AO's, he has added *s* and *p* orbitals on the hydrogen center and two d_σ and two d_π basis functions on the fluorine center. The total molecular energy obtained from this calculation is -99.9847 a.u. and should be within 1 to 2 ev of the molecular Hartree-Fock value. There is another and very compelling reason for emphasis on a molecular Hartree-Fock solution: It is the best wave function we can obtain and still retain clear and straightforward interpretability in terms of simple one-electron orbitals.

So far our attention has been directed toward the total energy, but we would expect the dipole moment to show similar improvement when Hartree-Fock AO's are employed. Unfortunately, present results are inconclusive. Significantly better results are found for HF, but for NH_3, STO's seem to give an anomalously good answer. For LiH and OH, experimental values are lacking. Figure 2 is a plot of the dipole moment data for HF. In Allen's one-center approach to a molecular Hartree-Fock solution, all of the functions are located on the fluorine center, and since a finite series of terms is used to represent that part of the wave function centered at the hydrogen atom, there is a tendency to overweight the ionic character of the molecule. On the other hand, lack of sufficient flexibility in the molecular orbital LCAO wave function gives rise to an incorrect slope at small internuclear separations. In spite of these shortcomings, the wave functions based on Hartree-Fock AO's yield values superior to those using STO's. The really exciting result will be the μ versus r curve for a molecular Hartree-Fock solution (augmented by the usual limited configuration interaction). Pieceing together the various parts of the curves in Fig. 2 indicates that a high degree of quantitative accuracy might be achieved. In general, calculations directed toward exploring the effect of basis function choice are especially important for the dipole moment because of its sensitivity to any change in the basis-function parameters. Ballinger (53) has computed the charge distribution in HF for Slater parameter STO's and for those parameters which minimize the molecular energy. His graphs of the two charge distributions display the sensitive nature of the dipole moment. He concludes that simple ideas attempting to relate gross charges with μ are dangerous.

Our discussion in this section concerning the greater accuracy in total energies and dipole moments, obtained with an improved basis set, certainly indicates the desirability of correlating changes in the values of other molecular quantities, such as quadrupole coupling constants, with modifications in the basis set.

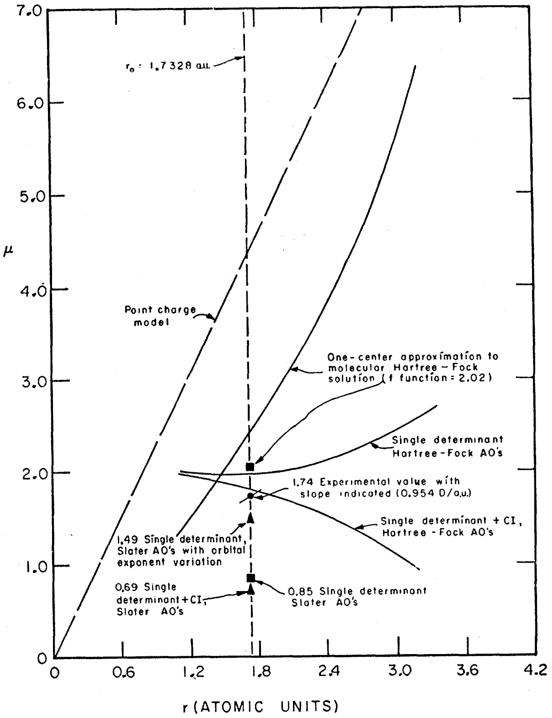

FIG. 2. Dipole moments (in debyes) for HF.

V. MORE THAN TWO CENTERS

There are approximately twenty *ab initio* calculations for molecules with more than two atoms, but there is a decided dividing line between the existing diatomic and polyatomic wave functions. Confidence in the satisfactory evaluation of the many-center two-electron integrals is very much less than for the diatomic case, and it is clearly apparent that we are in major difficulty for three- and four-center two-electron integrals.

One line of attack being pursued is the formulation and improvement of integration methods for three and four centers with STO's. Three groups, each with different techniques, are actively working on the development of efficient digital computer programs: Boys at Cambridge University expresses the STO's in a series of Gaussians and then applies his analytic many-center Gaussian formulas; Barnett at the Massachusetts Institute of Technology in using his expansion about a single center; and Roothaan and co-workers at the University of Chicago utilize an expansion in elliptic coordinates, followed by a two-dimensional numerical integration.[1]

A second approach is to re-examine and modify the basis set. STO's form natural solutions to the central-field problem and are thus efficient for describing atomic singularities in molecular wave functions. Laguerre functions are also satisfactory in this regard, and some use has been made of them. However, in no case do these functions appear to have an overwhelming advantage over STO's, and there is every indication that three- and four-center integrals will be at least as hard to evaluate as for STO's. In general, any other analytic basis function type must pay a heavy price in the number of terms necessary to represent the wave function in the region around the nuclei. One suggestion (77) has been to use a mixed basis set composed of both Gaussians and exponentials. If the individual exponential functions, or a fixed linear combination of exponential and Gaussian terms, on one center do not overlap those on another, and if only Gaussians are used to represent the bonding part of the wave function, one can then obtain the benefit of the exponentials around the nuclei without the corresponding many-center integral problem. It can be shown that the exponential part may be transformed to a Gaussian form and the analytic many-center Gaussian integral formulas applied (78). This is done at the expense of a few more terms and a relatively simple numerical integration.

Another method which seems promising at the present time is based on the revival of Boys' 1950 proposal (78) for the use of an all-Gaussian basis set. During the intervening years a number of papers reported quite discouraging results with limited sets of Gaussian orbitals, and their use was largely abandoned. However, as we have shown in Sec. IV, it has become apparent that a more elaborate basis set, regardless of its analytic form, is required for many applications. Because of this, it appears quite possible that the larger number of Gaussians required, as compared to exponentials, may be offset by the very great simplification in evaluating the two-electron many-center integrals. Finally, basis functions in the form of plane waves may be added to the Gaussian functions with very little additional increase in the labor of computing the integrals. This additional flexibility in the basis set may prove valuable in conjugated molecules and other cases where some of the electrons are free to move throughout the system (79).

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Mathematical Problems in the Complete Quantum Predictions of Chemical Phenomena

S. F. Boys

Theoretical Chemistry Department, University of Cambridge, Cambridge, England

AND

G. B. Cook

Electronic Computing Laboratory, University of Leeds, Leeds, England

1. INTRODUCTION

At present, there is only one main method which provides practical procedures for the accurate calculation of many-electron wave functions and energies. It is often referred to as the method of configurational interaction or, as we call it in this paper, the polydetor method. In using this term, we imply a general expansion of the wave function as a linear combination of Slater determinants constructed from orthonormal single electron functions, the coefficients in the expansion being determined by the Ritz variation method. Very few wave functions of this general type have been calculated, but the stage has now been reached where all the essential procedures of calculation have been programed for high-speed electronic computing machines in a fully automatic way, and many more results are to be expected.

The development of the theory given here depends on two explicit assumptions: first, the validity of Schrödinger's many-particle equation and the antisymmetry condition and, second, the sufficiency of the Born-Oppenheimer approximation in which nuclear and electronic motions are separated. The solutions are determined completely by these assumptions which are generally accepted as the basic laws for atomic and molecular structure.

It is convenient to regard the calculation of a wave function as consisting of eight distinct stages. The solutions of several of these stages have involved considerable mathematical difficulty, but each stage presents a definite problem for which the accuracy of the solution can be specified and the significance of which can be understood quite independently of the detailed method of solution. It appears certain that this multiplicity of stages and these difficulties have obscured the essentially systematic nature of the whole problem and have given the impression that there may be ambiguities where, in fact, there are none. The aim of this account is to discuss the mathematical nature of these various stages, pointing out the difficulties, and indicating techniques of solution known at present. Such an account should be useful in enabling those not working directly in this field to understand the complexities of the problem. However, more important, the scheme as given should simplify considerably future accounts of the details of solution of the different problems by enabling their relation to the whole problem to be shown.

Since this account was commenced, fully automatic solutions have been obtained for the stages not previously solved. This has made it possible to discuss with certainty the determinate nature of the whole calculation and of each stage in it. It is important to realize that the only element of choice involved in the calculation is at the stage in which the single electron functions are selected. Thereafter, the calculation is as determinate in principle as if the results for all possible selections were tabulated. The automatic solutions emphasize this beyond all doubt.

Before examining further details, let us consider pos-