

Studies in Molecular Structure. I. Scope and Summary of the Diatomic Molecule Program*

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INTRODUCTION

THE coming of age of the digital computer and its impact on the field of molecular structure has recently been variously characterized as "disastrous to theoretical chemistry" and as "the means which will enable modern structural chemistry to become less of an art and more of a science." Insofar as the digital computer provides the means for critical calculations upon which theoretical concepts may be justified, tested, or based, the author is inclined toward the latter point of view; insofar as the use of a digital computer might blunt one's critical faculties and stunt the free play of his scientific imagination, reducing his research to little more than calculations for the sake of calculations, he agrees with the former estimate. Obviously a wide middle ground exists where the digital computer, intelligently used as a research instrument, can quickly provide the theoretical chemist with accurate results to an illuminating but complex critical calculation. Properly used, the numerical experiment can be as much of an aid and stimulus to the theoretical chemist as a well thought out and executed physical experiment.

The whole framework of modern structural chemistry, especially the present-day understanding of concepts such as bond order, bond length, charge density, conjugation, hyperconjugation, and resonance, which have become the everyday household words of the chemist and which provide an uneasy (because inadequate) basis for his present understanding of chemistry in relation to structure, may benefit from a reevaluation based upon accurate *a priori* quantum mechanical calculations. Motivated by these considerations a program of study of simple diatomic molecules was begun by this Laboratory. Simple diatomics were selected because of limitations at the time imposed by methods available for computing integrals and by computer size. Furthermore, computational methods needed (and continue to need) thorough testing and development, and a wealth of experimental data for comparison exists for diatomic molecules. Again, from simple diatomics much can be learned at the outset which is expected to have relevance to more complicated systems.

The program was undertaken with two ultimate goals in view: (1) a more quantitative understanding of diatomic systems which may provide a basis for the

understanding of larger molecules, thereby (2) clarifying the relationship of structure to chemical processes.

The point of view which has been adopted in the work has been:

Go as far by calculation as is reasonably possible, guided by chemical and physical intuition and computer economics, without introducing empirical schemes or data.

To date the work has been largely developmental. The molecular wave functions in limited LCAO-MO-SCF single-determinantal approximation tabulated in a following paper constitute the initial systematic accumulation of accurate data of the project. Utilization of these data in chemical problems has already begun and the results will go far to establish the validity and/or utilizability of the single-determinantal STO- ζ approximation. (Comparative discussion of types of approximation of AO's and MO's is given by R. S. Mulliken in this issue.¹)

Realization of the ultimate goals of the program requires (1) better understanding of the relation of chemical processes to structure on the basis of accurate *a priori* quantum mechanical calculation, and (2) development and perfection of mathematical techniques and approximations.

A knowledge of proper methods to calculate accurate wave functions which are (1) relatively simple in mathematical form, (2) accessible to chemical interpretation and conceptualization, (3) applicable to molecules of any size and extensible to the solid state would constitute a major advance in the field of molecular structure. Undoubtedly, the critical factor upon which the value of any method depends is the criterion for accuracy which is established. At the moment, methods exist which meet all three criteria. They are, however, not yet adequate for chemists who want reliable estimates of dissociation energies.

I. DETAILS OF CALCULATIONS

The first phase of the program at LMSS consisted in the systematic accurate calculation of ground state single-determinantal wave functions in LCAO-MO-SCF approximation (a limited STO- ζ approximation: see Mulliken's article¹) for most of the diatomic molecules of the first row which have a closed-shell ground state. The calculations were made for each molecule at its equilibrium internuclear distance, utilizing only

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¹ R. S. Mulliken, *Revs. Modern Phys.* **32**, 232 (1960), this issue.

inner- and valence-shell STO's, with three different choices of orbital exponent for the latter: (1) Slater ζ 's, (2) best atom ζ 's, and (3) best limited MO ζ 's. (See the Glossary in Paper II of this series² for terminology.) This phase has been completed for all the hydride and homopolar diatomics; best limited MO ζ 's have yet to be determined for the heteropolar molecules CO, LiF, and BF.

In addition, the $^1\Sigma^+$ state for NH and the $^1\Sigma_g^+$ state for Be₂ (the latter at an arbitrarily chosen internuclear distance) were calculated.

Total energies, orbital energies, dipole moments, and population analyses have been computed for each of these wave functions and, except for the population analyses, they are tabulated in II.

A second group of calculations near completion consists of a potential curve and calculation of the dipole moment function for CO, and potential curves for He₂, He₂⁺⁺, and H₂ utilizing an extended basis set.

This phase of the project, utilizing the present automatic diatomic molecule computer program, will be terminated by introducing configuration interaction in most of the work described in the foregoing to assay its effectiveness in accounting for electron correlation.

Other related work on diatomic molecules, utilizing other computer programs and emphasizing methods other than the STO- ζ is Richardson's work on N₂ utilizing double- ζ AO's and Phillipson and Mulliken's calculations on H₂ and He₂ in the MO- ζ approximation. (See Mulliken¹ for the relation of these methods to the method used in the calculations reported here, namely, the STO- ζ method.) Finally, T. Itoh is investigating the interaction of two N atoms at distances greater than equilibrium.

II. COMPUTATIONAL METHODS

Footnote 10 of II gives a complete listing of papers relevant to the present computations. All conventions as regards choice of units, coordinate geometry, etc., not appearing explicitly in II can be found in previous publications cited there.

Computer Programs

The Roothaan SCF procedure³ was programmed for the Scientific Univac 1103 by A. Weiss and coupled by M. Yoshimine to the integrals program which computes all one- and two-electron, one- and two-center integrals necessary for a molecular computation.⁴ Because the calculated physical observables (total

² Bernard J. Ransil, *Revs. Modern Phys.* **32**, 245 (1960), this issue.

³ C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951); also J. F. Mulligan *J. Chem. Phys.* **19**, 347 (1951). Roothaan recently generalized the procedure to handle certain types of open-shell n -electron systems. [See C. C. J. Roothaan, *Revs. Modern Phys.* **32**, 179 (1960), this issue.] The generalized procedure has been programmed for the IBM 704 at Argonne National Laboratory and for the Scientific Univac 1103A at WADC, and is currently in use for atomic calculations.

⁴ See footnote 10 of II, p. 245, this issue.

energies, orbital energies, and dipole moments) are invariant under unitary transformation, the integrals were expressed in terms of STO's (which are nodeless and therefore not always mutually orthogonal), rather than in terms of orthogonal AO's. The final MO vectors printed out and tabulated in II are those corresponding to the STO's.

The complete molecular program is automatic. Input data consist of ζ values, internuclear distances, the desired orbital occupation, and, in the case of heteropolar molecules, a reasonable initial guess of the vectors. The computer calculates all necessary integrals, printing them as they are computed, shuffles them into proper order for use in the supermatrix, computes the one-electron H matrix, and then the two-electron G matrix utilizing the starting vectors. It then solves the usual secular equation, compares the resulting vectors with the starting set, and tests against a specified criterion for convergence. Iteration continues until this criterion is met. Whereupon the total energy, input data, and all orbital energies and vectors are printed out.

If dipole moments and population analyses are wanted, another program is read into the computer which utilizes the SCF data stored in the memory. It orthogonalizes the vectors, computes population analyses and dipole moments, and prints out pertinent intermediate data and final results. All intermediate integral data together with final SCF data are punched on paper tape and stored for future need.

An independent program begins with the kinetic energy integrals as input and computes the total kinetic energy as a check on how well the wave functions satisfy the virial theorem. Another program, near completion, will utilize the integrals and SCF data stored on tape to perform rather extensive configuration interaction.

A technique utilized in conjunction with the automatic molecular program to obtain best limited LCAO-MO's is described in some detail in the following.

Quadratic Minimization Procedure

Minimization of the total energy simultaneously with respect to all of the orbital exponents was done in a manner which avoided the brute force approach of varying each ζ independently along a selected grid of values. The latter procedure is costly, and because economical use of machine time is a critical consideration, a minimization procedure was developed based upon a Maclaurin's expansion about an arbitrary zero point near a minimum.⁵

Assuming the ζ 's to be independent variables, the total energy $E(\zeta_1, \zeta_2, \dots, \zeta_n)$ at the minimum may be expanded about an arbitrary point near the minimum

⁵ Suggested by Professor C. C. J. Roothaan.

E_0 as follows:

$$E_i = E_0 + \sum_i (\partial E / \partial \zeta_i)_0 \Delta \zeta_i + \frac{1}{2} \sum_i \sum_j (\partial^2 E / \partial \zeta_i \partial \zeta_j)_0 \Delta \zeta_i \Delta \zeta_j + \dots \quad (1)$$

Define minimum total energy as that for which

$$\partial E / \partial \zeta_i = 0. \quad (2)$$

By insertion in (1), we obtain the equation

$$(\partial E / \partial \zeta_i) + \sum_j (\partial^2 E / \partial \zeta_i \partial \zeta_j) \Delta \zeta_j = 0 \quad (3)$$

or, in matrix notation,

$$\begin{pmatrix} \partial E / \partial \zeta_1 \\ \partial E / \partial \zeta_2 \\ \dots \\ \dots \\ \partial E / \partial \zeta_n \end{pmatrix} = - \begin{pmatrix} \partial^2 E / \partial \zeta_1^2 & \partial^2 E / \partial \zeta_1 \partial \zeta_2 & \dots \\ \partial^2 E / \partial \zeta_2 \partial \zeta_1 & \partial^2 E / \partial \zeta_2^2 & \\ \dots & \dots & \\ \dots & \dots & \\ \dots & \dots & \\ \dots & \dots & \partial^2 E / \partial \zeta_n^2 \end{pmatrix} \begin{pmatrix} \Delta \zeta_1 \\ \Delta \zeta_2 \\ \dots \\ \dots \\ \Delta \zeta_n \end{pmatrix} \quad (4)$$

where the increment vector $(\Delta \zeta_i)$ is the unknown to be determined.

The elements of the vector $(\partial E / \partial \zeta_i)$ after some algebraic development are given by

$$\partial E / \partial \zeta_i = [E(\zeta_1 \dots \zeta_i + \Delta \zeta_i \dots \zeta_n) - E(\zeta_1 \dots \zeta_i - \Delta \zeta_i \dots \zeta_n)] / 2 \Delta \zeta_i, \quad (5)$$

and so on. Similarly, the elements for the square matrix $(\partial^2 E / \partial \zeta_i \partial \zeta_j)$ are given by

$$\partial^2 E / \partial \zeta_i^2 = \frac{E(\zeta_1 \dots \zeta_i + \Delta \zeta_i \dots \zeta_n) - 2E(\zeta_1, \zeta_2, \dots, \zeta_n) + E(\zeta_1 \dots \zeta_i - \Delta \zeta_i \dots \zeta_n)}{\Delta \zeta_i^2},$$

$$\partial^2 E / \partial \zeta_i \partial \zeta_j = \frac{E(\zeta_1 \dots \zeta_i + \Delta \zeta_i \dots \zeta_j + \Delta \zeta_j \dots \zeta_n) - E(\zeta_1 \dots \zeta_i + \Delta \zeta_i \dots \zeta_n) - E(\zeta_1 \dots \zeta_j + \Delta \zeta_j \dots \zeta_n) + E(\zeta_1, \zeta_2, \dots, \zeta_n)}{\Delta \zeta_i \Delta \zeta_j}, \quad (6)$$

etc.

A set of ζ 's and an appropriate variational increment are chosen and the appropriate energy values computed. [Two independent parameters require 6 energy calculations; three, 10; in general, n independent parameters require $\frac{1}{2}(n+2)(n+1)$ energy calculations to solve (4).]

The digital computer program computes the vector $(\partial E / \partial \zeta_i)$ and square matrix $(\partial^2 E / \partial \zeta_i \partial \zeta_j)$ from the input array of energy values mentioned in the foregoing, $E(\zeta_1, \zeta_2, \zeta_3, \dots, \zeta_n)$, $E(\zeta_1 + \Delta \zeta_1, \zeta_2, \zeta_3, \dots, \zeta_n)$, $E(\zeta_1 - \Delta \zeta_1, \zeta_2, \zeta_3, \dots, \zeta_n)$, etc., and solves for the improved increment vector $(\Delta \zeta_i)$. Up to 10 independent parameters can be handled by the routine and an energy minimization can be quickly and economically realized as long as the ζ 's are independent and one's initial guesses lie on a parabolic surface reasonably close to the minimum.

Concerning the rapidity of minimization, the hydrides LiH, BH, NH, HF, and the homopolars Li₂, Be₂, C₂, N₂, and F₂ (four to five independent ζ 's) were well behaved. At least three complete sequences, and no more than five, were usually needed to realize ζ values reliable to the third decimal place.

Remarks on Convergence

Two isoelectronic series (N₂, CO, and BF, C₂, BeO, BN, and LiF) were marked at the outset for extensive computation because of practical interest in a few members of the series and because much can be learned about electronic properties in general, and binding in particular, by comparing isoelectromers. The calculations on the first series are well on their way to completion. But the calculations for BeO and BN failed to converge in the runs employing both Slater ζ 's and best atom ζ 's. Rather than converging, the total energies exhibited an alternating behavior and diverged to

two distinct energy values differing roughly by an atomic unit. The same behavior was also noted for a few calculations on CO and LiF whenever the ratios of the π orbital exponents attained a certain value.

Limitations of the Present Molecular Computer Program

There are a number of limitations on the computer program used for the calculations:

(1) It is subject to the comment on the accuracy of atomic integrals discussed in II.

(2) The convergence criterion was set at about 10^{-5} , that is, when two successive sets of MO coefficients agree in the fifth decimal place, iteration ceases.

(3) There is a lower limit on the ζ values which can be assigned as roughly 0.5. Below this value certain hybrid integrals lose accuracy quickly.

(4) The total energies tend to blow up in the united atom range of internuclear distance. The precise R value differs for each molecule.

TABLE I. Molecular energies (a.u.).

	Calc			Obs
	Slater LCAO-MO	Best atom LCAO-MO	Best limited LCAO-MO	
LiH	-7.96666	-7.96598	-7.96992	-8.0703
BH	-25.06210	-25.05509	-25.07460	-25.273
NH ($^1\Sigma^+$)	-54.25984	-54.27581	-54.32459	
HF	-99.47854	-99.49147	-99.53614	-100.527
Li ₂	-14.84075	-14.84111	-14.84149	-14.9944
Be ₂	-29.05645	-29.05612	-29.05825	
C ₂	-75.21122	-75.19880	-75.22381	
N ₂	-108.57362	-108.55808	-108.63359	-109.586
F ₂	-197.85686	-197.87409	-197.87694	-199.670
CO	-112.34357	-112.32604		-113.377
BF	-123.61550	-123.60373		-124.777
LiF	-106.36521	-106.38126		-107.502

TABLE II. Differences between observed and computed molecular energies (ev).

	$E_{\text{calc}} - E_{\text{obs}}$			D_e (ev)
	Slater LCAO-MO	Best atom LCAO-MO	Best limited LCAO-MO	
LiH	2.82	2.84	2.73	2.52
BH	5.74	5.93	5.39	3.14
HF	28.52	28.19	26.96	6.06
Li ₂	4.18	4.17	4.16	1.05
N ₂	27.54	27.97	25.90	9.902
F ₂	49.33	48.87	48.79	1.68
CO	28.11	28.92		11.2
BF	31.62	31.92		8.58
LiF	30.94	30.50		5.99

III. CALCULATION OF BEST LIMITED LCAO-MO'S

"Best limited LCAO-MO's" are STO- ζ MO's approximated as a linear combination of inner and valence shell STO's. Further, their orbital exponents (ζ 's) have been chosen so as to minimize the total energy. The process of optimizing the ζ 's involved computing the total energy a large number of times for various values of each ζ . Great economy was introduced with the minimization procedure discussed in the foregoing. The minimization procedure was useful

only when the energy calculated with the initial ζ 's was near the minimum and if there were no multiple minima. The latter behavior has occurred thus far only when extra-valence shell STO's were introduced for He₂, H₂, and the hydrides, work which will be published in full later. Invariably the Slater ζ 's or best-atom ζ 's were close enough initial guesses that convergence to a minimum, i.e., until there was no further change in the third decimal place of the ζ 's, could be effected in three to four passes.

Note added in proof. Sufficient experience has been gained with minimization procedure since the foregoing was submitted to indicate that perhaps too sanguine a view was taken of its efficacy in obtaining a minimum. The limitations on the procedure as stated will stand, but attaining the proper absolute minimal surface to enable the final zeroing-in is a relatively tricky business. It is now not certain that this has been achieved with Li₂ and LiH, although any further energy improvement should not be significant.

As a rule, ζ variation in the best limited LCAO-MO calculations was stopped when the fifth decimal place of the total energy settled down. In some cases this could mean two-decimal-place reliability in the ζ values, in other cases, three- and four-decimal-place reliability. Consequently, four decimals are quoted in all cases, but one should not in general try to attach too much significance to it.

Multiple Minima

The occurrence of multiple minima in the cases of He₂ and H₂ (utilizing 1s, 2s, 2p STO's) indicates that the ζ 's may not be independent parameters. Nearly as good

TABLE III. Dipole moments (debye units).

	LiH	BH	NH ($^1\Sigma^+$)	HF	CO	BF	LiF
Slater LCAO-MO	6.41 (Li ⁺ H ⁻)	0.999 (B-H ⁺)	1.54 (N-H ⁺)	0.878 (H ⁺ F ⁻)	0.730 (C-O ⁺)	2.16 (B-F ⁺)	2.94 (Li ⁺ F ⁻)
Best atom LCAO-MO	6.48 (Li ⁺ H ⁻)	1.03 (B-H ⁺)	1.68 (N-H ⁺)	1.12 (H ⁺ F ⁻)	0.592 (C-O ⁺)	1.96 (B-F ⁺)	3.43 (Li ⁺ F ⁻)
Best limited LCAO-MO	5.92 (Li ⁺ H ⁻)	1.58 (B-H ⁺)	2.01 (N-H ⁺)	1.44 (H ⁺ F ⁻)			
Experimental	1.73 (H ⁺ F ⁻)	0.118 (C-O ⁺)	...	6.6±0.3 (Li ⁺ F ⁻)

TABLE IV. Orbital energies—ionization potentials^a (ev).

	N ₂	F ₂	CO
Slater	3σ _g : -14.82	1π _g : -11.75	5σ: -13.08
Best atom LCAO-MO	3σ _g : -15.44	1π _g : -13.04	5σ: -13.79
Best limited LCAO-MO	3σ _g : -15.11	1π _g : -12.91	
Experimental	-15.60	-15.7	-14.01
Slater	1π _u : -15.77	3σ _g : -13.71	1π: -15.87
Best atom LCAO-MO	1π _u : -16.46	3σ _g : -15.15	1π: -16.66
Best limited LCAO-MO	1π _u : -14.84	3σ _g : -14.86	
Experimental	-17.08		-16.58
Slater	2σ _u : -19.88	1π _u : -15.36	4σ: -19.93
Best atom LCAO-MO	2σ _u : -20.52	1π _u : -16.71	4σ: -20.68
Best limited LCAO-MO	2σ _u : -19.42	1π _u : -16.54	
Experimental	-18.72		-19.70

^a The ionization potentials quoted here are not vertically corrected. The vertical correction for 1π_u of N₂ is appreciable; the vertical correction for F₂(1π_g) increases the quoted value slightly; for CO the vertical correction is important for 1π and appreciable (hundredths of ev) for the others.

TABLE V. Dissociation energies (ev).

	Calc ^a			Exptl.
	Slater LCAO- MO	Best atom LCAO- MO	Best limited LCAO- MO	
LiH	1.34	1.31	1.41	2.516
BH	1.83	1.54	2.07	3.14±0.4
FH	1.21	1.34	2.56	6.06±0.2
Li ₂	0.15	0.14	0.15	1.05
N ₂	1.19	0.55	2.61	9.902
F ₂	-0.30	-0.28	-0.20	1.68
CO	5.38	4.44		8.58±0.5
BF	5.24	4.44		11.108
LiF	0.37	0.58		5.99±0.5

^a Slater atomic energies have been used in computing the dissociation energies for the first column; best atom energies have been used for the remaining two columns. See discussion in Sec. I.

TABLE VI. Ground state atomic energies (a.u.).

	Calc ^a			Exptl. ^b
	Slater	Best atom	Hartree-Fock	
Li	-7.4176	-7.41792	-7.43272	-7.4779
Be	-14.5556	-14.55670	-14.57298	-14.6699
B	-24.495	-24.49836		-24.658
C	-37.619	-37.62239		-37.855
N	-54.2651	-54.26890	-54.39857	-54.612
O	-74.5330	-74.54036		-75.109
F	-98.934	-98.94211		-99.804

^a Single-determinantal approximation with STO's. The Slater and best-atom functions utilize inner- and valence-shell STO's. The best-atom energies are quoted from C. C. J. Roothaan, Tech. Rept. Laboratory of Molecular Study and Spectra, University of Chicago (1955). The energy values for the Slater function were calculated by the author or are quoted from M. Krauss and J. F. Wehner, J. Chem. Phys. **29**, 1287 (1958), and A. C. Hurley (to be published). The Hartree-Fock function is an analytical expansion in terms of STO's. The Hartree-Fock energy values are quoted from C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. **32**, 194 (1960), this issue; C. C. J. Roothaan, L. S. Sachs, and A. W. Weiss, *ibid.* **32**, 186 (1960), this issue.

^b Calculated from C. E. Moore, Natl. Bur. Standards (U.S.) Circ. No. 467 (1949).

energy values are obtained for H₂ if all the ζ's are set equal to one another and a variation performed.⁶ While one can only conjecture at this stage of development, this suggests that it may be necessary to perform only a limited amount of ζ variation when working with an extended basis set: STO's of like |*m*| are assigned the same value; STO's of unlike |*m*| are assigned different ζ values, the actual values to be determined by a variational procedure.

IV. DISCUSSION OF THE SUMMARY OF RESULTS

Tables I to VI document the results of the series of calculations on diatomic molecules discussed in this and the following paper.¹

Table I compares the total molecular energies calculated with three possible choices of ζ with the observed values obtained from Table VII. In all cases, ζ variation improves the total molecular energy. Table II gives an idea of the significance of this improvement: about 0.02 ev for Li₂ to 1.6 ev for N₂. The best-atom ζ's give better MO's than Slater ζ's for HF, Li₂, F₂, and LiF, molecules involving only Li and F. Table II also gives the absolute error of the computed total energies and permits comparison with the experimental dissociation energy. Although the total molecular energy is computed with an accuracy of 99% or more, the absolute error is always greater than the dissociation energy. Consequently, much greater accuracy is required in both molecular and atomic calculations before reliable dissociation energies can be expected.

Table III compares computed dipole moments with the few experimental values available. The direction of the dipole moment is given correctly in all cases where it is known, lending some credence to the remarkable prediction for BF. ζ variation markedly improves the dipole moment for HF. The predicted value for LiH lies in the expected range.

The situation regarding orbital energies (Table IV)

⁶ Pointed out by V. Griffing and students. Distinct ζ variation is important for He₂ however. So far, an improvement of 3 ev has been obtained, with minimization not yet complete.

TABLE VII. Bibliography of experimental data.

	State	R_e (A)	D_0 (ev)	ω_e (ev)	D_e (ev)	E_{obs} (a.u.)
LiH	$1\Sigma^+$	1.5953 ^a	2.4288 ^d	0.1743 ^a	2.516	-8.0703
BH	$1\Sigma^+$	1.2325 ^a	3.0±0.4 ^e	(0.2933) ^a	3.14±0.4	-25.273
NH	$1\Sigma^+$	[1.045 ₅] ^a				
HF	$1\Sigma^+$	0.9171 ^a	5.8±0.2 ^e	0.5129 ^b	6.06±0.2	-100.527
Li ₂	$1\Sigma_g^+$	2.672 ₅ ^a	1.03 ^a	0.0436 ^a	1.05	-14.9944
Be ₂	$1\Sigma_g^+$	(2.0)	(0.7) ^f			
C ₂	$1\Sigma_g^+$	1.2422 ^a				
N ₂	$1\Sigma_g^+$	1.094 ^a	9.756 ^a	0.2925 ^a	9.902	-109.586
F ₂	$1\Sigma_g^+$	1.418 ^b	1.63 ^g	[0.1106] ^a	1.68	-199.670
CO	$1\Sigma^+$	1.1281 ₉ ^a	11.108 ^g	0.2690 ^a	11.242	-113.377
BF	$1\Sigma^+$	1.262 ^a	8.5±0.5 ^e	0.1735 ^a	8.58±0.5	-124.777
LiF	$1\Sigma^+$	1.51 ^a 1.525 ^c	5.95±0.5 ^e	0.0801 ⁱ 0.1124 ^e	5.99±0.5	-107.502

^a G. Herzberg, *Diatomic Molecules*, (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1955), 2nd ed.

^b D. Andrychuck, Can. J. Phys. **29**, 151 (1951).

^c G. Vidale (private communication, 1959).

^d R. Velasco, Can. J. Phys. **35**, 1204 (1957).

^e A. G. Gaydon, *Dissociation Energies*, revised edition (1953).

^f J. Drowart and R. E. Honig, J. Phys. Chem. **61**, 980 (1957).

^g R. Iczkowski and J. Margrave, J. Chem. Phys. **30**, 403 (1959).

^h G. A. Kuipers, D. F. Smith, and A. H. Nielsen, J. Chem. Phys. **25**, 275 (1956).

ⁱ J. Braunstein and J. Trischka, Phys. Rev. **98**, 1092 (1955).

is hopeful. The order of magnitude is always correct; however, ζ variation does not always give a better value, for example, $1\pi_\mu$ and $3\sigma_g$ of N₂ and $1\pi_g$ for F₂. Better approximations, for example, an extended STO- ζ treatment or the double- ζ method will very likely improve these energy values, especially for the π MO's.

The dissociation energies in Table V are listed merely to show what can be expected. Binding is obtained for all molecules except F₂. Because the dissociation energy is obtained as the difference between two large numbers which are each calculated to roughly

one percent, it cannot be accurately computed with a single-determinantal LCAO-MO-SCF function constructed exclusively from valence and inner shell AO's even with adjusted ζ values. This is certainly not new knowledge,⁷ but it is knowledge which is now sufficiently documented.

⁷ Evidence to this effect has been accumulating for years as the number of LCAO-MO-SCF calculations in the literature increased. Many of these were very helpful to the author; he is indebted to the earlier work of R. Sahni, M. Krauss, A. C. Hurley, J. F. Mulligan, L. D. Allen, C. Scherr, A. J. Freeman, and many others which was frequently relied upon for machine checks and/or which proved valuable in others ways in the course of the work.