

LCAO—MO—SCF Calculations on LiH Using Gaussian Basis Set

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we believe that CO_2 should always be considered as a possible trapping site in solid organic solutions unless special precautions have been taken to remove it. The failure of Skelly, Hayes, and Hamill¹⁶ to get a narrow resonance in γ -irradiated 3-MP is possibly due to a very efficient degassing procedure. It is important to emphasize the striking similarity between the CO_2^- signal in 3-MP and the ESR signal reported in MTHF. Saturation curves obtained in 3-MP closely follow those obtained in γ -irradiated MTHF.¹¹ However, the present work cannot exclude the possibility that the similarity is coincidental.

Some comments are possible on the structure of CO_2^- . Since in 3-MP, CO_2^- is in a less perturbing environment than in sodium formate, it is believed that

the isotropic ^{13}C hyperfine splitting constant given here is more representative of the free CO_2^- molecule than the value obtained by Ovenall and Whiffen.¹⁸ Using the splitting (122 G) at the peaks (the zero of the first derivative) of the $^{13}\text{CO}_2^-$ resonance,²¹ one obtains a value of -0.32 for the coefficient of the carbon $2s$ atomic orbital in the $4a_1$ molecular orbital. This compares to -0.38 obtained by Ovenall and Whiffen from a splitting of 167 G. Simulation of the spectrum, using the sodium formate results as a guide, might well give the anisotropy constants necessary for determining the OCO angle.

²¹ Even though CO_2^- is not rotating in this system, the nature of the anisotropies seen in sodium formate suggests that this magnitude for the splitting is close to the isotropic value.

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LCAO-MO-SCF Calculations on LiH Using Gaussian Basis Set*

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A series of calculations was carried out on LiH using Gaussian-type functions (GTF) to approximate the Hartree-Fock (HF) molecular orbitals in an LCAO expansion. Scaled orbital exponents on Li and optimized exponents on H were used. The calculated values approached the Hartree-Fock limit asymptotically very well. These encouraging results certainly justify the recent use of GTF's on small organic molecules.

DIATOMIC molecules seem appropriate to test the features as well as limitations of Gaussian wavefunctions because in several cases exact analytic wavefunctions using Slater-type orbitals (STO's) as basic functions have been obtained with such an accuracy that they are considered to reach the Hartree-Fock (HF) limit. Hydrogen fluoride has been previously studied by Harrison¹ and the lithium hydride molecule has been selected as the object of this investigation.

Previous results on other chemical systems^{2,3} indicated that the best results were arrived at when the basis set was improved by the addition of both s and p -type functions. Four different basis sets were used in each of which both Li and H atoms were improved simultaneously by the use of more and more functions. The improvement of the Li atom followed the trend: $3s+1p^z$, $5s+2p^z$, $7s+3p^z$ and $9s+5p^z$, while the improve-

ment on the H atom was $2s+0p^z$, $3s+1p^z$, $4s+2p^z$, $4s+3p^z$. This choice resulted in basis sets of equal increment ($N=6, 11, 16$, and 21) yet it made possible the use of orbital exponents reported previously for elements of the second period⁴ and for hydrogen.⁵ The orbital exponents used in the above four basis sets are summarized in Table I.

Calculations were performed at a number of interatomic distances. Results are therefore presented in two ways: first as a function of basis set size and second as a function of the interatomic distance. For comparison previous calculations carried out by Kahalas and Nesbet,⁶ by Ransil⁷ using STO's, and by Karo⁸ using HFO's are included. Interatomic distances are given in Bohr atomic units ($1 \text{ a.u.} = 0.52917 \text{ \AA}$) and energy values are quoted in Hartree atomic units ($1 \text{ a.u.} = 27.21 \text{ eV} = 627.46 \text{ Kcal/mole}$). Computations

* Presented at the Alberta Symposium on Quantum Chemistry on Aug. 26, 1965. Detailed program of the Symposium has been published in *Chem. Can.* **17**, 80 (1965).

¹ M. C. Harrison, *J. Chem. Phys.* **41**, 499 (1964).

² S. S. Seung, M. C. Harrison, and I. G. Csizmadia (to be published).

³ I. G. Csizmadia, M. C. Harrison, B. T. Sutcliffe (to be published).

⁴ I. G. Csizmadia, M. C. Harrison, J. W. Moskovitz, and B. T. Sutcliffe (to be published). M. C. Harrison and I. G. Csizmadia *Quart. Progr. Rept. MIT-G* **49**, 78 (1963).

⁵ C. M. Reeves, *J. Chem. Phys.* **39**, 1 (1963).

⁶ S. L. Kahalas and R. K. Nesbet, *J. Chem. Phys.* **39**, 529 (1963).

⁷ B. J. Ransil, *Rev. Mod. Phys.* **32**, 250 (1960).

⁸ A. M. Karo, *J. Chem. Phys.* **30**, 1241 (1959).

TABLE I. Orbital exponents used in LiH calculations.

Type of	Li	$3s+1p$	$5s+2p$	$7s+3p$	$9s+5p$
GTF	H	$2s+0p$	$3s+1p$	$4s+2p$	$4s+3p$
N	6	11	16	21	
Atom	Type	Orbital exponents			
Li	s	0.1222	0.0581	0.0297	0.0280
Li	s	0.9700	0.2950	0.1170	0.0880
Li	s	7.6300	1.5000	0.4610	0.2770
Li	s	...	7.6300	1.8200	0.8820
Li	s	...	38.6000	7.1900	2.7700
Li	s	28.2000	8.8200
Li	s	111.0000	27.7000
Li	s	88.2000
Li	s	277.0000
Li	z	0.0068	0.0403	0.0285	0.0160
Li	z	...	0.2370	0.1480	0.0550
Li	z	0.7650	0.1880
Li	z	0.6520
Li	z	2.2600
H	s	0.2015	0.1483	0.1233	0.1233
H	s	1.3320	0.6577	0.4552	0.4552
H	s	...	4.2392	2.0258	2.0258
H	s	13.7098	13.7098
H	z	...	0.0453	0.0324	0.0247
H	z	0.1393	0.0797
H	z	0.3363

were carried out on IBM 7094 II Computer using the POLYATOM system.⁹

Figure 1 shows how the total energy calculated using GTF's approaches the value obtained by Kahalas and Nesbet using 10 or 11 STO's. When the GTF basis set is extrapolated to infinity ($N \rightarrow \infty$) with the formula $E = E_\infty + E_0 \exp(-\beta N)$, the energy value obtained

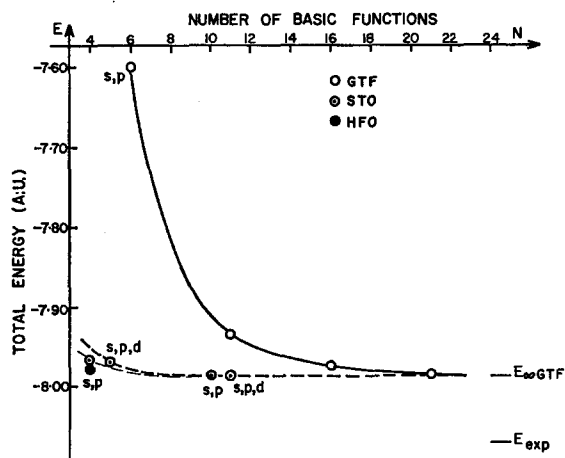


FIG. 1. The variation of total energy of LiH with the basis set size.

⁹ I. G. Csizmadia, M. C. Harrison, J. W. Moskovitz, S. S. Seung, B. T. Sutcliffe, and M. P. Barnett, "The POLYATOM System" Technical notes Nos. 36 and 40, co-operative computing laboratory, MIT (unpublished).

(E_∞) is slightly lower than the best STO value. This series of calculations was carried out at 3.02 a.u. interatomic separation. The energy values obtained with GTF are summarized in Table II in comparisons with previously obtained figures using numerical H.F. atomic orbitals⁸ as well as STO's.⁶

Results obtained with different interatomic distances are summarized in Table III and Fig. 2. The potential curves were obtained by fitting parabolas $E = E_0 + 1/2k(R-R_0)^2$ to the three lowest points. This was done with the assumption that close to the minimum the real potential curve and the parabola will osculate. It is easy to see that the calculations made with GTF approximate rather well the results of the best STO

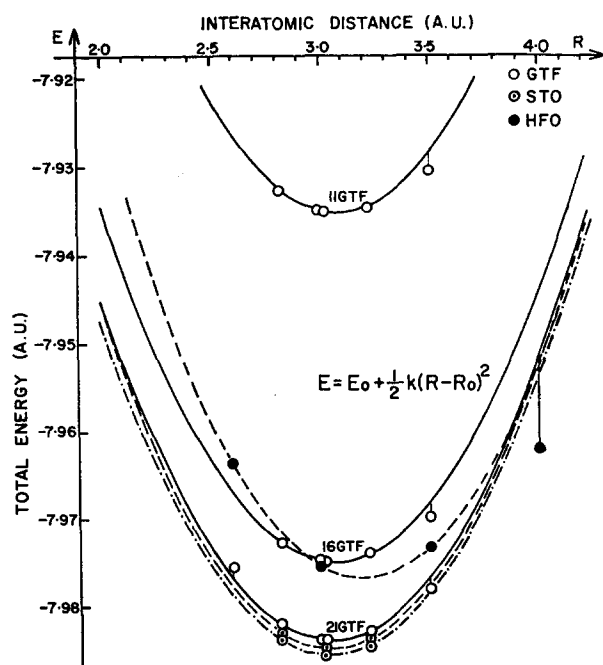


FIG. 2. The variation of total energy of LiH with the interatomic distance.

calculations at other distances besides the equilibrium separation. The parameters (E_0 , R_0 , k) characteristic for the harmonic oscillator are tabulated in Table IV and their change with the size of the basis set (N) is shown on Fig. 3. It appears that all the three calculated constants (E_0 , R_0 , k) converge to values similar to those obtained by STO's, but somewhat away from the experimental figures. Obviously in the energy value the difference is due mostly to the electronic correlation which is beyond the Hartree-Fock approach. As far as R_0 and k are concerned it is not obvious whether the wavefunction, the selected harmonic potential or the selection of the interatomic distances is responsible for the deviation.

The variation of dipole moment with the size of the basis set is summarized in Table V and Fig. 4. It seems

TABLE II. Total energy^a of LiH ($R=3.02$ a.u.) calculated with GTF's, STO's, and HFO's.

Type of AO	GTF (s, p)					Extrapolated value
N	6	11	16	21	∞	
E_{calc}	-7.600948	-7.935485	-7.975159	-7.984206	-7.986878 ^b	
Type of AO	HFO (s, p)	STO (s, p)	STO (s, p, d)	STO (s, p)	STO (s, p, d)	
N	4 ^c	4	5	10	11	
E_{calc}	-7.975811	-7.969016	-7.970022	-7.985366	-7.985970	

^a $E_{\text{exp}} = -8.0703$ a.u.^b E_{∞} .^c Calculated at $R=3.00$ a.u.

TABLE III. Total energy variation with interatomic distance of LiH.

Type of AO's	GTF (s, p)	GTF (s, p)	GTF (s, p)	HFO (s, p)	STO (s, p)	STO (s, p, d)
N	11	16	21	4	10	11
R (a.u.)	Total energy (a.u.)					
2.60	-7.975677	-7.963730
2.82	-7.933010	-7.973050	-7.982405	...	-7.983538	-7.984260
3.00	-7.935391	-7.975093	-7.984172	-7.975811
3.02	-7.935484	-7.975159	-7.984206	...	-7.985366	-7.985970
3.22	-7.934942	-7.974427	-7.983169	...	-7.984320	-7.984872
3.50	-7.930776	-7.970162	-7.978540	-7.973882

TABLE IV. Harmonic-oscillator parameters of LiH.

Type of GTF	Li $3s+1p^z$ H $2s+0p^z$	$5s+2p^z$ $3s+1p^z$	$7s+3p^z$ $4s+2p^z$	$9s+5p^z$ $4s+3p^z$	
N	6	11	16	21	
k (mdyn/Å)	1.4085	1.1745	1.1065	1.1044	
R_0 (a.u.)	3.0443	3.0840	3.0684	3.0469	
E_0 (a.u.)	-7.600975	-7.935639	-7.975242	-7.984232	

Type of AO	HFO (s, p)	STO (s, p)	STO (s, p, d)	Experimental
N	4	10	11	...
k (mdyn/Å)	1.1783	1.1189	1.0920	1.026
R_0 (a.u.)	3.1990	3.0472	3.0418	3.015
E_0 (a.u.)	-7.977310	-7.985392	-7.985986	-8.0703

TABLE V. Dipole moment^a of LiH ($R=3.02$ a.u.) calculated with GTF's, STO's and HFO's.

Type of GTF	Li $3s+1p^z$ $2s+0p^z$	$5s+2p^z$ $3s+1p^z$	$7s+3p^z$ $4s+2p^z$	$9s+5p^z$ $4s+3p^z$	Extrapolated value
N	6	11	16	21	∞
μ_z (debye)	-5.9179	-6.0929	-6.0139	-6.0079	-6.0074

Type of AO	HFO (s, p)	STO (s, p)	STO (s, p, d)	STO (s, p)	STO (s, p, d)
N	4 ^b	4	5	10	11
μ_z (debye)	-6.52	-5.932	-6.003	-5.831	-5.888

^a $\mu_{\text{exp}} = -5.882$.^b Calculated at $R=3.00$ a.u.

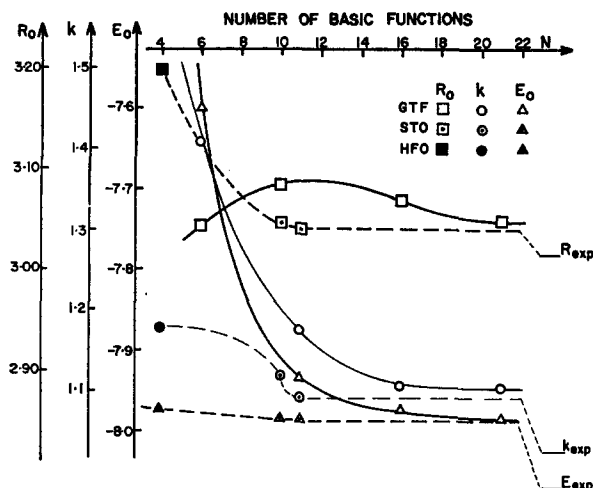


FIG. 3. The variation of harmonic parameters of LiH with the basis set size.

likely that the inclusion of a d orbital in the STO basis set makes a systematic improvement of the dipole moment regardless of the number of s and p orbitals used. It may be anticipated therefore, that the inclusion of d -type function in the GTF basis set would also change the calculated dipole moment towards the experimental value. The best μ calculated however, is quite close to the experimental one for practical purposes. This best μ value is quite satisfactory if one compares it to the figures obtained by 4HFO and 5STO basis sets. The variation of dipole moment with internuclear separation is shown on Fig. 5 and the numerical values are summarized in Table VI. The values included in this diagram were obtained with the best basis set (21GTF). Unfortunately no information is available on the change of μ with R when an STO wavefunction is used. As R increases however, the energy (E) converges to the sum of the energy of the two ionic species Li^+ and H^- (ionic dissociation). It may be expected therefore that the dipole moment (μ) will converge to the ionic model (dashed line) at large R values. This seems to be more likely with the 21GTF than in the case of 4HFO's.

TABLE VI. Dipole moment^a of LiH calculated with s , p HFO's, and GTF's.

Type of AO	HFO ^a	GTF	GTF	GTF	GTF
N	4	6	11	16	21
$R(\text{a.u.})$	μz (debye)				
2.60	-6.20	-5.5170
2.82	...	-5.7304	-5.8576	-5.7694	-5.7581
3.00	-6.52	-5.8984	-6.0688	-5.9897	-5.9733
3.02	...	-5.9179	-6.0929	-6.0139	-6.0079
3.22	...	-6.1284	-6.3443	-6.2648	-6.2479
3.50	-6.95	-6.4475	-6.7070	-6.6409	-6.6237

^a See Ref. 8.

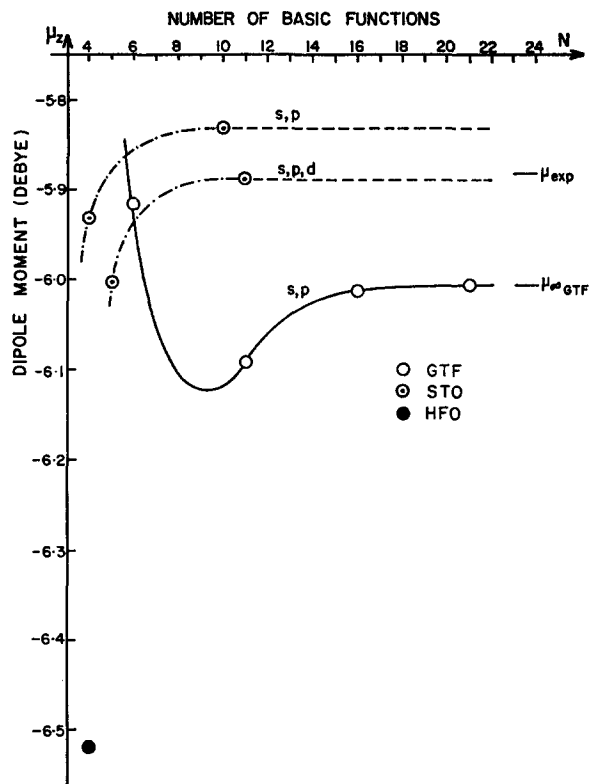


FIG. 4. The variation of dipole moment of LiH with the basis-set size.

In addition to the primary and derivative properties that belong to the molecule as a whole, some comparison has been made between the individual molecular orbitals, comparing the orbital energies of the three lowest MO's calculated. The reported and calculated values at $R=3.02$ a.u. are summarized in Table VII and shown graphically on Fig. 6 as a function of the basis set size (N). It is interesting to note that while in the case of STO wavefunction the crude basis set

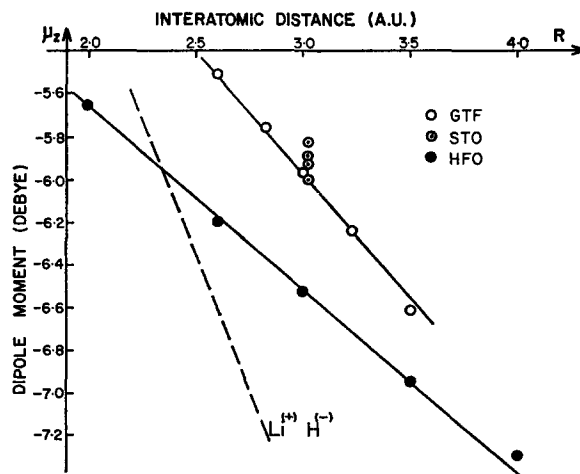


FIG. 5. The variation of dipole moment of LiH with the interatomic distance.

TABLE VII. Low-lying molecular orbital energies of LiH ($R=3.02$ a.u.).

Type of GTF	Li $3s+1p^s$ H $2s+0p^s$	$5s+2p^s$ $3s+1p^s$	$7s+3p^s$ $4s+2p^s$	$9s+5p^s$ $4s+3p^s$
N	6	11	16	21
1σ	-2.3352	-2.4387	-2.4448	-2.4450
2σ	-0.2545	-0.2997	-0.3009	-0.3010
$3\sigma^*$	+0.0192	+0.0165	+0.0007	-0.0027
Type of AO	HFO (s, p) ^a	STO (s, p) ^b	STO (s, p) ^c	STO (s, p, d) ^c
N	4	4	10	11
1σ	-2.4795	-2.4470	-2.4449	-2.4445
2σ	-0.3055	-0.3035	-0.2999	-0.3001
$3\sigma^*$	+0.0059	+0.0167

^a See Ref. 8.^b See Ref. 7.^c See Ref. 6.TABLE VIII. 1σ -orbital energy variation with interatomic distance of LiH.

Type of AO	GTF (s, p)	GTF (s, p)	GTF (s, p)	HFO (s, p)	STO (s, p)	STO (s, p, d)
N	11	16	21	4 ^a	10 ^b	11 ^b
R (a.u.)	1σ -orbital energy (a.u.)					
2.60	-2.4274	-2.4638
2.82	-2.4310	-2.4365	-2.4361	...	-2.4361	-2.4355
3.00	-2.4379	-2.4439	-2.4443	-2.4795
3.02	-2.4387	-2.4448	-2.4450	...	-2.4449	-2.4445
3.22	-2.4473	-2.4539	-2.4548	...	-2.4543	-2.4540
3.50	-2.4597	-2.4670	-2.4685	-2.4936

^a See Ref. 8.^b See Ref. 6.TABLE IX. 2σ -orbital energy variation with interatomic distance of LiH.

Type of AO	GTF (s, p)	GTF (s, p)	GTF (s, p)	HFO (s, p)	STO (s, p)	STO (s, p, d)
N	11	16	21	4 ^a	10 ^b	11 ^b
R (a.u.)	2σ -orbital energy					
2.60	0.3129	-0.3146
2.82	-0.3052	-0.3069	-0.3071	...	-0.3055	-0.3058
3.00	-0.3003	-0.3015	-0.3020	-0.3055
3.02	-0.2997	-0.3009	-0.3010	...	-0.2999	-0.3001
3.22	-0.2940	-0.2952	-0.2954	...	-0.2940	-0.2942
3.50	-0.2859	-0.2870	-0.2871	-0.2931

^a See Ref. 8.^b See Ref. 6.

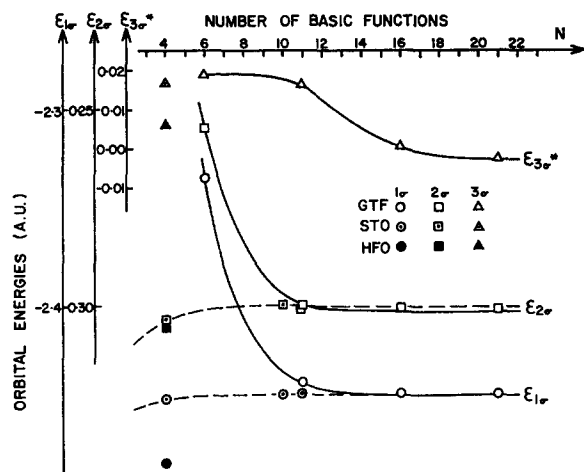


FIG. 6. The variation of orbital energies of LiH with the basis-set size.

(4STO) produces lower values than the analytic Hartree-Fock wavefunction (11STO), the tendency is directly opposite when GTF's are used. It should be mentioned that the orbital energies obtained by the extensive GTF basis set are slightly lower than the corresponding values associated with the best STO basis set. This may be considered as a feature of GTF in addition to the fact that the improvement of the occupied orbital energy is considerably faster than that of the total energy. These might be taken as encouraging signs towards the use of relatively crude GTF basis sets.

The variation of 1σ orbital energy ($\epsilon_{1\sigma}$) with R is shown in Fig. 7 and Table VIII. The lowering of the $\epsilon_{1\sigma}$ with the increase of R follows the same pattern in the cases of the two best STO and the two best GTF basis sets. The values seem to converge to the $\epsilon_{1\sigma}$ of Li^+ (-2.79 a.u.) due to ionic dissociation.

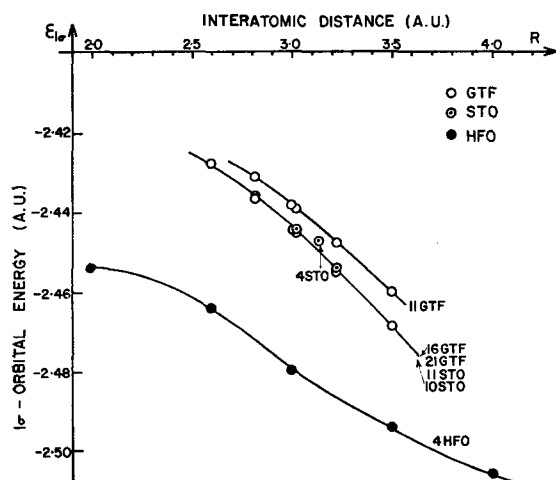


FIG. 7. The variation of 1σ orbital energies of LiH with the interatomic distance.

The variation of 2σ orbital energy ($\epsilon_{2\sigma}$) with R is shown in Fig. 8 and Table IX. The raising of the $\epsilon_{2\sigma}$ with the increase of R follows the same pattern with both STO and GTF basis set. The values seem to converge to the $\epsilon_{1\sigma}$ of $\text{H}^{(-)}$ ($+0.01$ a.u.) due to the ionic dissociation.

Although scaled orbital exponents were used on Li the match between the calculated values using extensive GTF basis set and extensive STO basis set is excellent. It may be anticipated therefore that with individually optimized exponents¹⁰ the correspondence could be brought to a level beyond any practical demand.^{11,12} In the largest basis set twice as many GTF's were used as in the analytic HF-STO-MO or five times as many as in the *minimal* Slater basis set.

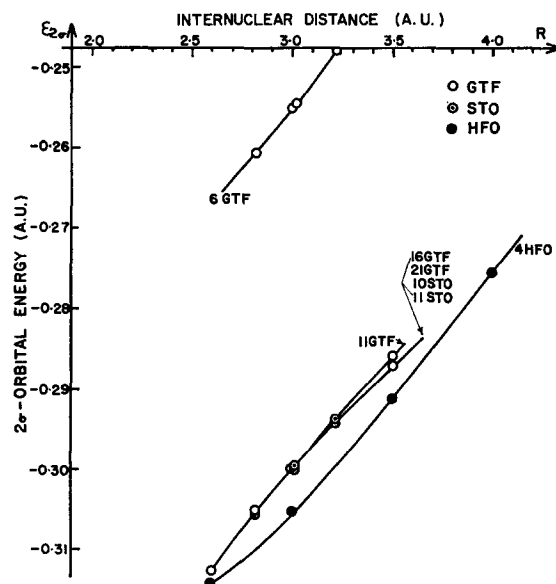


FIG. 8. The variation of 2σ -orbital energies of LiH with the inter-atomic distance.

In conclusion it seems fair to say that when a sufficient number of appropriately selected GTF's is used in *ab initio* MO calculations, the calculated properties converge towards those of the Hartree-Fock limit obtained by extended STO basis sets. There seems to be no reason to believe that this conclusion is valid for LiH or for diatomic molecules only. In fact, it is quite likely that results obtained for three, four, five, or six atomic molecules could be just as good if not better when appropriate GTF's are used in sufficient number. This may be anticipated because if a molecule consists of more than two atoms the delocalized molecular orbitals spread all over the vicinity of the atoms

¹⁰ S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

¹¹ Krauss¹² obtained in his recent calculation LiH an energy value of -7.9853745 hartrees at 3.0 Bohr internuclear separation using Huzinaga's optimized orbital exponents¹⁰ in an 18 GTF basis set.

¹² M. Krauss (personal communication).

and the expansion is more effective when the basic functions are localized at more than two centers. For all these reasons calculations on small organic molecules^{3,12-16} using GTF's are certainly justified.

¹³ J. W. Moskovitz and M. C. Harrison, J. Chem. Phys. **42**, 1726 (1965).

¹⁴ J. W. Moskovitz, J. Chem. Phys. **43**, 60 (1965).

¹⁵ M. Krauss, J. Res. Natl. Bur. Std. (U.S.) **68A**, 635 (1964).

¹⁶ M. Krauss, J. Chem. Phys. **38**, 564 (1963).

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Coriolis Interaction in the ν_1 and ν_3 Fundamentals of Ozone

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(Received 4 October 1965)

The ν_1 and ν_3 vibration rotation spectrum of $^{16}\text{O}_3$ in the $9.0\text{-}\mu$ region has been analyzed. The two vibrational states are coupled through a Coriolis term, $iY_{13}\mathbf{P}_y$, and a second-order distortion term, $-X_{13}(\mathbf{P}_x\mathbf{P}_x + \mathbf{P}_y\mathbf{P}_y)$, in the Hamiltonian. The interaction has been treated by numerically diagonalizing the secular determinant for the two states with the coupling included. The effect of the interaction on the intensities has been considered and absorption contours calculated in satisfactory agreement with experiment. With the distortion parameters fixed to the ground-state values the following constants have been obtained: $\nu_1=1103.15$, $A_1=3.556$, $B_1=0.4427$, $C_1^*=0.3926$, $\nu_3=1042.09$, $A_3=3.500$, $B_3=0.4412$, $C_3^*=0.3909$, $Y_{13}=-0.46$, and $X_{13}=-0.009$ cm^{-1} . The value of the dipole-moment ratio,

$$\left(\frac{\partial M_z}{\partial Q_3}\right)_0 \bigg/ \left(\frac{\partial M_z}{\partial Q_1}\right)_0 \bigg/ Q_1,$$

is 10.0 ± 1.5 .

INTRODUCTION

STUDIES of the vibration rotation spectra of ozone have been limited despite the importance of the molecule as an atmospheric constituent. The fundamentals were first correctly assigned in 1948 by Wilson and Badger¹ from low-resolution spectra. Subsequently from rotationally resolved spectra, ν_3 was analyzed by Kaplan, Migeotte, and Neven,² ($\nu_1+\nu_3$) by Trajmar and McCaa,³ and a tentative analysis of the ν_2 band was obtained by Nexsen.⁴ The ground state has been studied by Trambarulo *et al.*,⁵ Hughes,⁶ Pierce,⁷ and Gora.⁸ In this paper we report on a detailed analysis of the ν_1 and ν_3 fundamentals.

Ozone is a planar slightly asymmetric rotor ($\kappa \approx -0.968$) of C_{2v} symmetry. The three fundamentals ν_1 , ν_2 , and ν_3 are at 1103, 701, and 1042 cm^{-1} , respectively. In the absence of interactions, ν_1 and ν_2

are Type-B bands and ν_3 an A band. Although the ν_1 fundamental is weak and overlapped by ν_3 , much of the past difficulty in assignment and analysis has resulted from the fact the spectrum does not exhibit the characteristic appearance of a B-type band. This is attributable to two vibration-rotation terms coupling the ν_1 and ν_3 states: a strong Coriolis interaction and a weaker distortion interaction. These interactions are too strong to be treated by approximate methods. They must be taken into account in the numerical diagonalization of the Hamiltonian in order to explain the intensity anomaly of the ν_1 spectrum and to obtain molecular constants interpretable in terms of the theory. Complete calculated and observed spectral contours, and tables of transition frequencies, strengths and related data are available in a separate report.⁹

EXPERIMENTAL

The absorption spectrum of ozone from 1000 to 1150 cm^{-1} was obtained with the White double-beam spectrometer.¹⁰ The ozone was prepared by passing oxygen through a silent electrical discharge, condensing the oxygen-ozone mixture in a liquid-nitrogen trap,

⁹ S. A. Clough and F. X. Kneizys, AFCRL Report, Air Force Cambridge Research Laboratories, 1965.

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