Theoret. chim. Acta (Berl.) 23, 369—377 (1972)

Relationes

A Theoretical Study of the Heats of Formation of Some Small Molecules Using Non-Empirical Wavefunctions

A. C. HOPKINSON
Department of Chemistry, York University, Downsview, Ontario, Canada

K. YATES and I. G. CSIZMADIA
Lash Miller Chemical Laboratories, University of Toronto, Toronto 181, Ontario, Canada

Received April 13, 1971

Total energies, obtained from non-empirical LCAO–MO–SCF calculations on a series of reactions involving only closed-shell molecules and ions, have been used to calculate the heats of formation ΔH^0_{298} of a large number of small molecules. The Double-ζ basis set calculations, after empirical corrections for inadequacies in the basis set and systematic errors found in all calculations involving oxygen and carbon atoms, usually predict the heats of formation within 10 kcal/mole of the experimental value. A series of similar calculations predicts the heats of formation of some negative ions for which experimental values are either not available or are unreliable.

Non-empirical LCAO–MO–SCF calculations employing moderately large basis sets have been successfully used to predict the proton affinities of a variety of small molecules [1, 2], to obtain the standard heats of several reactions involving small molecules [3], and also to estimate the heats of hydrogenation of even larger groups of unsaturated molecules [4, 5]. The success of these studies results from the fact that both the reactants and products in all the reactions considered are *closed-shell* molecules and hence the assumption that ΔE_{corr}, the change in correlation energy in the protonation or hydrogenation reaction, is zero is not too serious an approximation. Agreement with experiment can be further improved by estimating empirically the errors introduced by (a) the approximation $\Delta E_{\text{corr}}=0$ and (b) the inadequacy of the Gaussian basis set [4].

Pople *et al.* [6] have used experimental heats of formation of several small molecules together with theoretical bond separation energies to successfully calculate heats of formation of larger molecules. In the present work a different approach has been adopted, utilising experimental heats of formation for only C_2^{2-} and O_2^{2+} (isoelectronic with N_2) and using reactions involving only molecules and ions with ground state closed-shell electronic configurations.

Elements are defined to have heats of formation of zero in their standard states at 298 °K and atmospheric pressure and the heat of formation of a molecule, ΔH^0_{298}, is the heat absorbed or released when one mole is formed from the constituent elements in their standard states. For example the heats of formation of methane, ammonia and water are estimated from the enthalpies of the following reactions:

$$\text{C (graphite)} + 2\text{H}_2\text{ (gas)} \rightarrow \text{CH}_4\text{ (gas)} \qquad \Delta H^0_{298} = -17.89\text{ kcal/mole}.$$

$$\tfrac{1}{2}\text{N}_2\text{ (gas)} + \tfrac{3}{2}\text{H}_2\text{ (gas)} \rightarrow \text{NH}_3\text{ (gas)} \qquad \Delta H^0_{298} = -11.04\text{ kcal/mole}.$$

$$\tfrac{1}{2}\text{O}_2\text{ (gas)} + \text{H}_2\text{ (gas)} \rightarrow \text{H}_2\text{O (gas)} \qquad \Delta H^0_{298} = -57.80\text{ kcal/mole}.$$

These equations illustrate the difficulties encountered in calculating heats of formation from molecular orbital theory. Only for the formation of ammonia, in which all the reactants and products are closed-shells, can the calculated ΔE be expected to give a good correlation with experimental results. In the formation of methane the carbon atom has an open-shell configuration and all the other species closed-shells resulting in a different number of electron pairs in the reactants and product. This results in a difference in correlation energy, which is difficult to estimate. In order that such difficulties over correlation energy differences would be eliminated the reaction sequence was converted to one containing only closed-shell species

$$\tfrac{1}{2}\text{C}_2^{2-} + \tfrac{3}{2}\text{H}_2 + \text{H}^+ \rightarrow \text{CH}_4 .$$

The *experimental* heats of formation of the proton [7] and the diacetylide ion [8] (Table 1) were then added to the total energy of the reactants (as calculated by MO theory). This number was subtracted from the total energy calculated for methane and a correction made for the zero point energies to give ΔE^0_0.

A similar problem was encountered in estimating the heat of formation of water. One of the reactants, oxygen molecule, is a ground state triplet and this again results in correlation energy problems. In this case the following all closed-shell molecules process was used:

$$\tfrac{1}{2}\text{O}_2^{2+} + \tfrac{3}{2}\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}^+ .$$

Again a correction term, the difference between half the experimental [9] heat of formation of O_2^{2+} (Table 1) and that of the proton, was added to the energy difference calculated from the total energies of the reactants and products. After correction for the change in zero point energy in the reaction, this then gave a value for ΔE^0_0 for the formation of water from its elements.

These ΔE^0_0 values can be converted into heats of formation (ΔH^0_{298}) by addition of several small correction terms. Firstly ΔE^0_0 is converted to ΔE^0_{298} by calculating the differences in translational energy ($\tfrac{3}{2}RT$ per molecule) and rotational energy (RT for a linear molecule, $\tfrac{3}{2}RT$ for a non-linear molecule) between the products and

Table 1. *Experimental heats of formation of ions used in theoretical calculations of ΔH^0_{298} (kcal/mole)*

Ion	Experimental ΔH_f	Refs.
H^+	365.11 (0 °K)	[7]
C_2^{2-}	222.0 (298 °K)	[8]
O_2^{2+}	862.18 (298 °K)	[9]

Table 2. *Reaction sequences and correction terms used in theoretical calculations of ΔH^0_{298} (kcal/mole)*

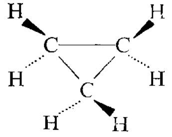
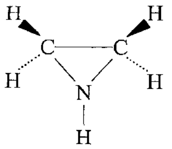
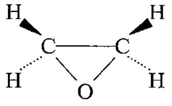
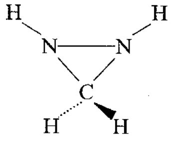
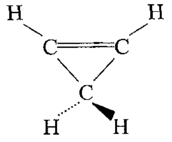
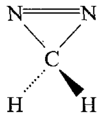
Ion or molecule	Zero point energy	Closed-shell reaction for formation	ΔE_{vib}	ΔE_{rot}	ΔE_{trans}	$RT\Delta n$	Total correction term
N^{3-}	0	$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow N^{3-} + 3H^+$	−10.98	−1.180	1.77	1.18	− 9.21
NH^{2-}	4.39[a]	$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH^{2-} + 2H^+$	− 6.59	−0.590	0.885	0.59	− 5.70
NH_2^-	11.93[a]	$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_2^- + H^+$	0.94	−0.590	0	0	+ 0.35
NH_3	20.53[b]	$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$	9.51	−0.295	−0.59	−0.59	+ 8.03
O^{2-}	0	$\frac{1}{2}O_2^{2+} + \frac{3}{2}H_2 \rightarrow O^{2-} + 3H^+$	−10.98	−1.18	1.77	1.18	− 9.21
OH^-	5.02[a]	$\frac{1}{2}O_2^{2+} + \frac{3}{2}H_2 \rightarrow OH^- + 2H^+$	− 5.96	−0.590	0.885	0.59	− 5.07
H_2O	12.93[b]	$\frac{1}{2}O_2^{2+} + \frac{3}{2}H_2 \rightarrow H_2O + H^+$	1.95	−0.295	0	0	1.65
F^-	0	$\frac{1}{2}F_2 + \frac{1}{2}H_2 \rightarrow F^- + H^+$	− 3.70	−0.590	0.885	0.59	− 2.81
HF	5.84[b]	$\frac{1}{2}F_2 + \frac{1}{2}H_2 \rightarrow HF$	2.10	0	0	0	2.10
CH_4	27.12[b]	$\frac{3}{2}H_2 + H^+ + \frac{1}{2}C_2^{2-} \rightarrow CH_4$	16.13	−0.295	−1.77	−1.18	12.91
C_2H_2	16.19[b]	$C_2^{2-} + 2H^+ \rightarrow C_2H_2$	12.81	0	−1.77	−1.18	9.86
C_2H_4	30.82[b]	$C_2^{2-} + 2H^+ + H_2 \rightarrow C_2H_4$	21.22	−0.295	−2.655	−1.77	16.50
CO	3.08[b]	$\frac{1}{2}C_2^{2-} + \frac{1}{2}O_2^{2+} \rightarrow CO$	− 0.31	0	0	0	− 0.31
HCO^+	8.16[a]	$\frac{1}{2}C_2^{2-} + \frac{1}{2}O_2^{2+} + H^+ \rightarrow HCO^+$	1.69	−0.295	0.4425	−0.59	1.25
CN^-	2.51[a]	$\frac{1}{2}N + \frac{1}{2}C_2^{2-} \rightarrow CN^-$	− 0.25	0	0	0	− 0.25
HCN	9.73[b]	$\frac{1}{2}N_2 + \frac{1}{2}C_2^{2-} + H^+ \rightarrow HCN$	6.34	0	−0.885	−0.59	4.86
CH_2O	16.13[b]	$\frac{1}{2}C_2^{2-} + \frac{1}{2}O_2^{2+} + H_2 \rightarrow CH_2O$	6.53	−0.295	−0.885	−0.59	4.76
C_2H_6	45.26[b]	$C_2^{2-} + 2H_2 + 2H^+ \rightarrow C_2H_6$	29.44	−0.885	−3.54	−2.36	22.65
N_2H_4	27.31[b]	$N_2 + 2H_2 \rightarrow N_2H_4$	11.49	−0.885	−1.77	−1.18	7.65
H_2O_2	12.43[b]	$O_2^{2+} + 2H_2 \rightarrow H_2O_2 + 2H^+$	− 3.39	−0.885	0	0	− 4.27
$HCONH_2$	29.25[b]	$\frac{1}{2}C_2^{2-} + \frac{1}{2}O_2^{2+} + \frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow HCONH_2$	14.88	−0.885	−1.77	−1.18	11.04
HCOOH	20.46[b]	$\frac{1}{2}C_2^{2-} + O_2^{2+} + \frac{3}{2}H_2 \rightarrow HCOOH + H^+$	6.09	−0.885	−0.885	−0.59	3.73
HCOF	12.93[b]	$\frac{1}{2}C_2^{2-} + \frac{1}{2}O_2^{2+} + \frac{1}{2}F_2 + \frac{1}{2}H_2 \rightarrow HCOF$	5.84	−0.295	−0.885	−0.59	4.07
	49.90[b]	$\frac{3}{2}C_2^{2-} + \frac{3}{2}H_2 + 3H^+ \rightarrow C_3H_6$	34.49	−0.885	−4.425	−2.95	26.23

Table 2 (continued)

Ion or molecule	Zero point energy	Closed-shell reaction for formation	ΔE_{vib}	ΔE_{rot}	ΔE_{trans}	$RT\Delta n$	Total correction term
	42.56[b]	$C_2^{2-} + \frac{1}{2}N_2 + \frac{3}{2}H_2 + 2H^+ \rightarrow C_2NH_5$	28.18	−0.885	−3.54	−2.36	21.39
	35.09[b]	$C_2^{2-} + \frac{1}{2}O_2^{2+} + \frac{3}{2}H_2 + H^+ \rightarrow C_2OH_4$	20.71	−0.885	−2.655	−1.77	15.40
	36.22[b]	$\frac{1}{2}C_2^{2-} + N_2 + \frac{3}{2}H_2 + H^+ \rightarrow CN_2H_4$	21.84	−0.885	−2.655	−1.77	16.53
	34.21[b]	$\frac{3}{2}C_2^{2-} + \frac{1}{2}H_2 + 3H^+ \rightarrow C_3H_4$	26.05	−0.295	−3.54	−2.36	19.84
	20.15[b]	$\frac{1}{2}C_2^{2-} + N_2 + \frac{1}{2}H_2 + H^+ \rightarrow CN_2H_2$	11.99	−0.295	−1.77	−1.18	8.745
$CH_2{=}\overset{+}{N}{=}\overset{-}{N}$	19.21[b]	$\frac{1}{2}C_2^{2-} + N_2 + \frac{1}{2}H_2 + H^+ \rightarrow CN_2H_2$	11.05	−0.295	−1.77	−1.18	7.80
CO_2	7.28[b]	$\frac{1}{2}C_2^{2-} + O_2^{2+} + \frac{1}{2}H_2 \rightarrow CO_2 + H^+$	− 0.88	−0.590	0	0	− 1.47

[a] Ref. [1]. [b] Ref. [4].

reactants. Then ΔH^0_{298} can be obtained from the equation $\Delta H^0_{298} = \Delta E^0_{298} + RT\Delta n$ where Δn = (the number of product molecules) − (number of reactant molecules). These correction terms for all the molecules and ions, along with the reaction sequences used to estimate ΔE^0_0 and the zero point energy, are given in Table 2.

Computational Details

The LCAO–MO–SCF calculations in this study employed two extensive basis sets of Gaussian functions, the Double ζ set [10] and Huzinaga's 106/4 set [11]. The majority of the total energies for the product molecules were taken from earlier publications [1, 4]. Those of the remainder and of the reactants were computed on an IBM-7094-II computer using an extensively modified POLYATOM system [12] and an IBMOL-II program [13]. These are given in Table 3.

Table 3. *Calculated total energy and zero-point energy (both in hartrees) for reactants and hydrocarbons*

Ion or molecule	Double ζ	Huzinaga	Zero point
H_2	− 1.1266[b]	− 1.1266[a]	0.0099[b]
C_2^{2-}	− 75.2945	− 75.3413	0.0054[c]
N_2	−108.8695[b]	−108.9047	0.0054[b]
O_2^{2+}	−148.0663	−148.1047	0.0054[c]
F_2	−198.6932[b]	−198.7374	0.0020[b]
CH_4	− 40.1822[b]	− 40.1871	0.0432[b]
C_2H_4	− 78.0052[b]	—	0.0491[b]
C_2H_2	− 76.7919[b]	—	0.0258[b]
N^{3-}	− 53.0324	− 53.2117[a]	—
NH^{2-}	− 54.4376	− 54.5076[a]	0.007[a]
NH_2^-	− 55.4782	− 55.5009[a]	0.019[a]
O^{2-}	− 74.2741	− 74.3619[a]	—
OH^-	− 75.3451	− 75.3756[a]	0.008[a]
F^-	− 99.4065	− 99.4197[a]	—
CN^-	− 92.2516	—	0.005[a]
HCO^+	−112.9000	—	0.013[a]

[a] Ref. [1].
[b] Ref. [4].
[c] Assumed the same as that of the isoelectronic N_2 molecule.

Results and Discussion

Preliminary calculations, using small sets of basis functions showed, as in other studies [1, 5] that the computed heats of formation are too large but converge on the experimental value as the size of the basis set is increased. The results obtained from calculations using the extensive sets of basis functions are given in Table 4 along with the experimentally determined values. Although there are only a few molecules upon which to base a comparison, the Huzinaga basis set (without contraction) gives a slightly better correlation with experimental data than the Double-ζ calculations. Both sets of calculations predict the heats of formation of molecules (but not ions) to be too exothermic by about 40 kcal/mole for each oxygen atom in the product molecule and about 13 kcal/mole for each carbon atom. This systematic error could be caused by changes in correlation energy in the reaction sequence used to estimate the heat of formation. However, after allowing a correction factor of 7 kcal/mole per hydrogen added in each reaction sequence to allow for the inadequacy of the Double-ζ basis set [4], good agreement was found between the predicted and experimental heats of formation of the molecules not involving carbon and oxygen atoms. This re-emphasises that correlation energy changes are not very large in reactions involving only molecules with closed-shells and suggests that the majority of the systematic error is caused by (a) inaccurate experimental values for ΔH^0_{298} for O_2^{2+} and C_2^{2-}, (the former value, in particular, is suspect as the two values in the literature vary by 1.1 eV [9, 14]), (b) poor estimates of E_{vib}, the change in zero-point energy caused by estimating C_2^{2-} and O_2^{2+} to have the same zero-point vibrational energy as the isoelectronic N_2 molecule, (c) partly by using ΔH^0_{298} values for C_2^{2-} and O_2^{2+} instead of the required ΔH^0_0 values, and (d) assuming the bond length of C_2^{2-} and O_2^{2+} to be the same as those of C_2 and O_2.

This last source of error was eliminated for the Double-ζ calculations by carrying out a bond length optimization for the two ions. The optimum bond lengths taken from Fig. 1 were found to be 1.032 Å for O_2^{2+} and 1.297 Å for C_2^{2-}, compared with experimental values of 1.2074 Å [14] and 1.3117 Å [15] for O_2 and C_2 respectively. The major difference is for O_2^{2+} where the bond length is considerably shorter than that for O_2, the loss of two antibonding electrons producing an ion with a triple bond. The corresponding minimum total energies

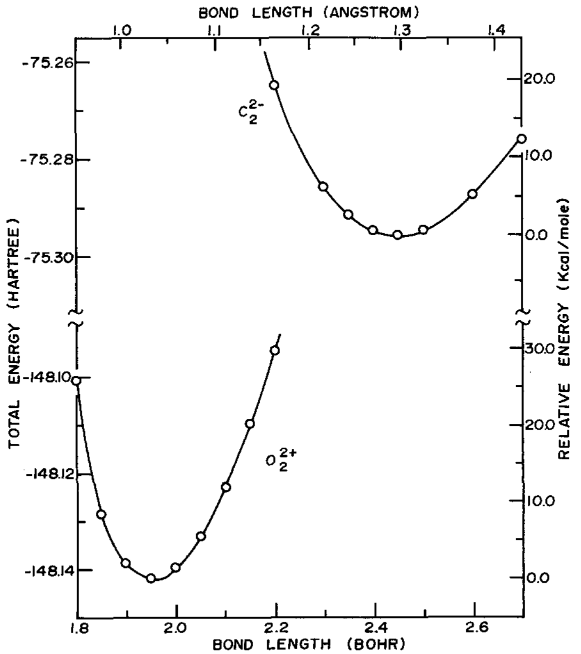


Fig. 1. Plots of calculated total energy (hartree) against bond length (Å) for the O_2^{2+} and C_2^{2-} ions

are found to be -148.1421 hartrees for O_2^{2+} and -75.2955 hartrees for C_2^{2-}. Hence the error in estimating the bond length of O_2^{2+} resulted in an error of 0.0758 hartrees in the total energy and made the estimated heats of formation of all oxygen containing compounds too exothermic by 23.79 kcal/mole per oxygen atom. The optimized total energy for C_2^{2-} resulted in a correction term of only 0.3 kcal/mole for each carbon atom in the molecule.

The computed heats of formation, after application of the correction for errors in the bond lengths of C_2^{2-} and O_2^{2+}, were still too exothermic, and were further improved by making two *empirical* corrections. Firstly, in an attempt to make up for deficiences in the Double-ζ basis set, a correction term of 7 kcal/mole [4] was used for each hydrogen molecule added in the formation reaction. Then correction terms of 16.33 kcal/mole and 12.82 kcal/mole were added for each oxygen and carbon atom respectively, thereby allowing for errors in (i) the experimental heats of formation of O_2^{2+} and C_2^{2-} and (ii) using the same vibrational energy for these ions. The corrected computed ΔH_{298}^0 values are given in the fourth column of Table 4. There is good agreement between the experimental and calculated heats of formation for the *neutral* molecules, the largest deviation being 9.00 kcal/mole for formaldehyde.

Table 4. *Heats of formation (kcal/mole)*

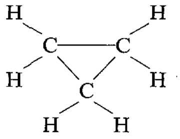
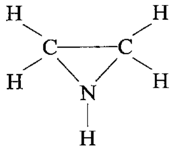
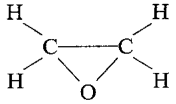
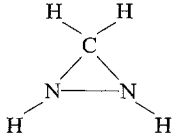
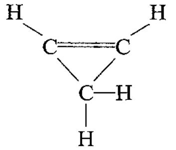
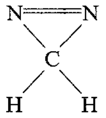
Molecule or ion	Double-ζ	Huzinaga	Corrected Double-ζ ΔH_{298}^0 value	Experimental
N^{3-}	836.80	735.29	847.30	717[b]
NH^{2-}	323.25	290.36	333.75	—
NH_2^-	41.11	37.92	51.61	−6.4, 10.6, 16.6, 18.0[b]
NH_3	− 21.45[a]	− 16.41	− 10.95	−11.04[a]
O^{2-}	236.68	193.59	287.26	215, 224, 209, 207[b]
OH^-	− 66.48	− 73.56	− 15.86	−48.4→39.3[b]
H_2O	−108.42	−105.29	− 57.80	−57.80[a]
F^-	− 37.95	− 46.26	− 34.45	−65.5[c]
HF	− 63.80[a]	− 62.94	− 64.8	−64.8[a]
CH_4	− 41.51	− 29.92	− 17.89	−17.89[a]
C_2H_2	21.98	—	48.23	54.19[a]
C_2H_4	− 29.31	—	3.84	12.50[a]
CO	− 82.99	—	− 29.75	−26.42[a]
HCO^+	143.10	—	196.34	207[d]
CN^-	4.30	—	17.42	10, 21, 81, 118[c]
HCN	12.05	—	25.17	31.2[a]
CH_2O	− 96.94	—	− 36.70	−27.7[a]
$HCONH_2$	−114.06	—	− 50.32	−50.0[a]
HCOOH	−198.04	—	− 94.19	−86.67[a]
C_2H_6	− 61.27	—	− 21.03	−20.24[a]
N_2H_4	5.52	—	− 19.52	22.75[a]
H_2O_2	−133.79	—	− 39.64	−32.53[a]
HCOF	−140.14	—	− 83.4	−90.0[a]
	− 38.58	—	11.89	12.74[a]

Table 4 (continued).

Molecule or ion	Double-ζ	Huzinaga	Corrected Double-ζ ΔH^0_{298} value	Experimental
	- 1.69	—	35.06	30.12[a]
	- 85.82	—	- 8.95	-12.19[a]
	93.10	—	116.72	—
	28.97	—	71.84	66.60[a]
	77.59	—	94.21	101.0[a]
$CH_2{=}N{=}N$	50.60	—	67.22	71.0[a]
CO_2	-184.17	—	- 87.32	-94.05[a]

[a] Ref. [4].

[b] Pritchard, H. O.: Chem. Rev. **52**, 529 (1953).

[c] Ref. 7.

[d] Pritchard, H., Harrison, A. G.: J. chem. Physics **48**, 2827 (1968).

The computed heats of formation of the ions in Table 4 also improve markedly with increases in the number of basis functions. However, from the limited data available it appears that the difference between the computed heats of formation obtained from the Double-ζ and Huzinaga basis set calculations increases rapidly with the charge on the ion and that the latter more closely reproduce the somewhat unreliable experimental values. Addition of the correction terms to the Double-ζ results did not give an improvement in the correlation with the existing experimental data as most of the computed heats of formation were already more endothermic than the experimental values and addition of the corrections made the reactions more endothermic.

In conclusion, the non-empirical calculation using the Double-ζ basis set, after correction for inadequacies in the Gaussian basis set and for the lack of sufficiently accurate experimental data on C_2^{2-} and O_2^{2+} predict heats of formation for molecules with ±9.0 kcal/mole. Agreement between computed and experimental heats of formation for ions deteriorates as the charge on the ion increases. Possible explanation for these deviations are (a) the exponents are optimised for neutral atoms not for the ions which are being studied. Perhaps exponents optimised for the Ne atom would be more appropriate for the N^{3-}, O^{2-} and F^- ions; (b) the experimental heats of formation for the negative ions are difficult to obtain and are often unreliable.

Acknowledgements. The authors wish to acknowledge the National Research Council for financial support and the Institute of Computer Science at the University of Toronto for making their computing facilities available.

References

1. Hopkinson, A. C., Holbrook, N. K., Yates, K., Csizmadia, I. G.: J. chem. Physics **49**, 3596 (1968).
2. Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Amer. chem. Soc. **93**, 808 (1970).
3. Snyder, L. C.: J. chem. Physics **46**, 3602 (1967).
4. — Basch, H.: J. Amer. chem. Soc. **91**, 2189 (1969).
5. Hehre, W. J., Ditchfield, R., Radom, L., Pople, J. A.: J. Amer. chem. Soc. **92**, 4796 (1970).
6. Radom, L., Hehre, W. J., Pople, J. A.: J. Amer. chem. Soc. **93**, 289 (1971).
7. Field, F. H., Franklin, J. L.: Electron impact phenomena and the properties of gaseous ions, New York: Academic Press Inc. Publishers 1957.
8. Vineck, G., Neckel, A., Nowotny, H.: Acta Chim. Sci. Hung. **51**, 193 (1967).
9. Daly, N. R., Powell, R. E.: Proc. physic. Soc. (London) **90**, 629 (1967).
10. Basch, H., Robin, M. B., Kuebler, N. A.: J. chem. Physics **47**, 1201 (1967).
11. Huzinaga, S.: J. chem. Physics **42**, 1293 (1965).
12. Csizmadia, I. G., Harrison, M. C., Moskowitz, J. W., Seung, S., Sutcliffe, B. T., Barnett, M. P.: The polyatom system, Tech. Notes No. 36 and 40, Co-operative Computing Laboratory, M.I.T. (unpublished). Submitted to Quantum Chemistry Program Exchange, Catalogue No. 47A.
13. Special IBM Technical Report, IBM Research Laboratory, San Jose, Calif., (1966).
14. Babcock, H. D., Herzberg, L.: Astrophys. J. **108**, 167 (1948).
15. Phillips, J. G.: Astrophys. J. **108**, 434 (1948).

Prof. Dr. A. C. Hopkinson
Department of Chemistry
York University
Downsview, Ontario, Canada