# DIE FILE UN



89 9 12 052

# DESTRUCTION NOTICE

Destroy this report when it is no longer needed. DO NOT return it to the originator.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commerical product.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

1a. REPORT SECURITY CLASSIFICATION Unclass if ied       1b. RESTRICTIVE MARKIP Unclass if ied         2a. SECURITY CLASSIFICATION AUTHORITY       3 DISTRIBUTION AUAL Approved for puunlimited.         2b. DECLASSIFICATION NOOWNGRADING SCHEDULE       unlimited.         4 PERFORMING ORGANIZATION REPORT NUMBER(S)       5 MONITORING ORGANIZATION BRL-TR-3044         6a. NAME OF PERFORMING ORGANIZATION Laboratory       6b. OFFICE SYMBOL (If applicable)       7b. NAME OF MONITOR SLOBA-IB         6c. ADDRESS (City, State, and ZIP Code)       7b. ADDRESS (City, State, Aberdeen Proving, Ground, MD. 21005-5066       9. PROCUREMENT INSTR CRGGAMIZATION         8b. ADDRESS (City, State, and ZIP Code)       8b. OFFICE SYMBOL (If applicable)       9. PROCUREMENT INSTR PROGRAM         8c. ADDRESS (City, State, and ZIP Code)       10. SOURCE OF FUNDING (If applicable)       9. PROCUREMENT INSTR PROGRAM         8c. ADDRESS (City, State, and ZIP Code)       10. SOURCE OF FUNDING (If applicable)       9. PROCUREMENT INSTR PROGRAM         8c. ADDRESS (City, State, and ZIP Code)       10. SOURCE OF FUNDING (If applicable)       9. PROCUREMENT INSTR PROGRAM         8c. ADDRESS (City, State, and ZIP Code)       10. SOURCE OF FUNDING (If applicable)       9. PROCUREMENT INSTR PROGRAM         11. CUEL (INCLUME & SCURTY, Claudity, M., Gallo*, Michael J. Pagle**       10. SOURCE OF FUNDING (If applicable)       10. SOURCE OF FUNDING (If applicable)         12. PERSONAL AUTHOR(S) (Georgre F. Adams, Mary M. Gallo*, Michael J. Pag		Form Approved OMB No. 0704-0188
2a. SECURITY CLASSIFICATION AUTHORITY       3 Distribution (avail Approved for puunlimited.         2b. DECLASSIFICATION (DOWNGRADING SCHEDULE       unlimited.         4 PERFORMING ORGANIZATION REPORT NUMBER(S)       5 MONITORING ORGAN         8c. NAME OF PERFORMING ORGANIZATION (f) applicable)       5 MONITORING ORGANIZATION (f) applicable)         8c. NAME OF PERFORMING ORGANIZATION (f) applicable)       7a NAME OF MONITOR         8c. ADDRESS (Gry, State, and ZIP Code)       7b ADDPESS (Gry, State, and ZIP Code)         Aberdeen Proving Ground, MD 21005-5066       9 PROCUREMENT INSTR         8c. ADDRESS (Gry, State, and ZIP Code)       10 SOURCE OF FUNDING (SPONSORING ORGANIZATION (f) applicable)         8c. ADDRESS (Gry, State, and ZIP Code)       10 SOURCE OF FUNDING (SPONSORING ORGANIZATION (f) applicable)         8c. ADDRESS (Gry, State, and ZIP Code)       10 SOURCE OF FUNDING (SPONSORING ORGANIZATION (f) applicable)         8c. ADDRESS (Gry, State, and ZIP Code)       10 SOURCE OF FUNDING (SPONSORING (f) and (f) applicable)         11eth Mitching Secure (f) Argonal (f) and (f) applicable)       10 SOURCE OF FUNDING (f) applicable)         8c. ADDRESS (Gry, State, and ZIP Code)       10 SOURCE OF FUNDING (f) applicable)         11eth Mitching Secure (f) and (f) and (f) applicable)       10 SOURCE OF FUNDING (f) applicable)         11eth Mitching Secure (f) and (f) and (f) applicable)       10 ADDRESS (Gry, State, and ZIP Code)         11eth Mitching Secure (f	INGS	
20. DECLASSIFICATION / DOWINGRADING SCHEDULE       Approved for puunlimited.         4. PERFORMING ORGANIZATION REPORT NUMBER(S)       5. MONITORING ORGANIZATION REPORT NUMBER(S)         5. NAME OF PERFORMING ORGANIZATION US Army Ballistic Research Laboratory       5. DEFICE SYMBOL (# applicable)         7. NAME OF PERFORMING ORGANIZATION SLOBERS (Gry, State and ZIP Code)       7. NAME OF MONITOR         8. NAME OF FUNDING / SPONSORING CASSING (F), State and ZIP Code)       8. DEFICE SYMBOL (# applicable)       9. PROCUREMENT INSTR         8. NAME OF FUNDING / SPONSORING CASSING (Gry, State, and ZIP Code)       8. DEFICE SYMBOL (# applicable)       9. PROCUREMENT INSTR         8. ADDRESS (Gry, State, and ZIP Code)       10. SOURCE OF FUNDING (* MONITOR)       8. DEFICE SYMBOL (# applicable)       9. PROCUREMENT INSTR         8. ADDRESS (Gry, State, and ZIP Code)       10. SOURCE OF FUNDING (* MONITOR)       8. DEFICE SYMBOL (# applicable)       9. PROCUREMENT INSTR         8. ADDRESS (Gry, State, and ZIP Code)       10. SOURCE OF FUNDING (* MONITOR)       8. DEFICE SYMBOL (* ADDRESS (Cry, State, and ZIP Code)         11. ELEMENT NO       5. COMP (* ADDRESS (Cry, State, and ZIP Code)       10. SOURCE OF FUNDING (* MONITOR)         12. PERSONAL AUTHOR(S)       6. COLORED (* MONITOR)       10. SOURCE OF FUNDING (* MONITOR)         12. PERSONAL AUTHOR(S)       7. ELEMENT NO       14. DATE OF REPORT (* MONITOR)         13. TYPE OF REPORT      13. TIME COVERD (* MONITOR)	LABILITY OF REPORT	r r
4       PERFORMING ORGANIZATION REPORT NUMBER(5)       5       MONITORING ORGANIZATION         BRL-TR-3044       6a. NAME OF PERFORMING ORGANIZATION       6b. OFFICE SYMBOL       7a       NAME OF MONITOR         Ga. NAME OF PERFORMING ORGANIZATION       6b. OFFICE SYMBOL       7a       NAME OF MONITOR         Laboratory       5LCBR-1B       7b       ADDPESS (City, State, and ZIP Code)       7b       ADDPESS (City, State, and ZIP Code)         Aberdeen Proving Ground, MD       21005-5066       9       PROCUREMENT INSTR         Ba. NAME OF FUNDING/SPONSORING       8b. OFFICE SYMBOL       9       PROCUREMENT INSTR         CADDRESS (City, State, and ZIP Code)       10       SOURCE OF FUNDING FORGARM       PROF         8c. ADDRESS (City, State, and ZIP Code)       10       SOURCE OF FUNDING FORGARM       PROF         11       EXTENSIVE STATION       8b. OFFICE SYMBOL       9       PROCUREMENT INSTR         12       EXTENSIVE STATION       8b. OFFICE SYMBOL       10       SOURCE OF FUNDING FORGARM         13a. TYPE OF REPORT       Fish Mary M. Gallo*, Michael J. Paye**       13a. TYPE OF REPORT       13b. TIME COVERED FOR State of PREPORT (VERTATION, MOLTER PROF         14       COSATI CODES       18       SUBJECT TERMS (Continue on reverse if acc the formation, Molter-Ples         17       COSATI CODES	ublic release	; distribution
BRL-TR-3044         6a. NAME OF PERFORMING ORGANIZATION US Army Ballistic Research Laboratory       6b. OFFICE SYMBOL (If applicable)       7a. NAME OF MONITOR         6c. ADDRESS (City, State, and ZIP Code)       7b. ADDPESS (City, State, Aberdeen Proving Ground, MD. 21005-5066       7b. ADDPESS (City, State, CAGALIZATION         8a. NAME OF FUNDING/SPONSORING CAGALIZATION       8b. OFFICE SYMBOL (If applicable)       9. PROCUREMENT INSTR CAGALIZATION         8c. ADDRESS (City, State, and ZIP Code)       10. SOURCE OF FUNDING PROF ELEMENT NO 61102A       10. SOURCE OF FUNDING PROF ELEMENT NO 61102A         8c. ADDRESS (City, State, and ZIP Code)       10. SOURCE OF FUNDING PROF ELEMENT NO 61102A       10. SOURCE OF FUNDING PROF ELEMENT NO 61102A         1 <sup>1</sup> EXTLE (MICHOR SERVICE CODE)       10. SOURCE OF FUNDING PROF ELEMENT NO 61102A       10. SOURCE OF FUNDING PROF ELEMENT NO 61102A         1 <sup>1</sup> EXTLE (MICHOR SERVICE CODE)       13b. TIME COVERED FROM	NIZATION REPORT N	UMBER(S)
Ga NAME OF PERFORMING ORGANIZATION US Army Ballistic Research Laboratory       Gb OFFICE SYMBOL (# applicable)       7a NAME OF MONITOR         Ballistic Research Laboratory       SLCBR-IB       7b ADDPESS(City, State, and ZIP Code)       7b ADDPESS(City, State, and ZIP Code)         Ba. NAME OF FUNDING/SPONSORING CARGALIZATION       Bb. OFFICE SYMBOL (# applicable)       9 PROCUREMENT INSTR DOCUREMENT INSTR CARGEARM       9 PROCUREMENT INSTR DOCUREMENT INSTR DOCUREMENT INSTR CARGEARM       9 PROCUREMENT INSTR DOCUREMENT INSTR DOCUMENT INSTR		
Laboratory       SLCBR-IB         6c. ADDRESS (City, State, and ZIP Code)       7b ADDPESS (City, State         Aberdeen Proving Ground, MD 21005-5066       7b ADDPESS (City, State         Ba. NAME OF FUNDING/SPONSORING CASAWZATION       Bb OFFICE SYMBOL (If applicable)       9 PROCUREMENT INSTR PROCRAM ELEMENT NO 6.1102A         Bc. ADDRESS (City, State, and ZIP Code)       10 SOURCE OF FUNDING (If applicable)       10 SOURCE OF FUNDING PROCRAM ELEMENT NO 6.1102A         The EXTENSION SATURATIONS OF ATOMIZATION ENERGIES:       COMP 6.1102A       NO         AND DIRECT RESULTS       12 PERSONAL AUTHOR(S) George F. Adams, Mary M. Gallo*, Michael J. Page**       14 DATE OF REPORT (Ye. From	RING ORGANIZATION	·····
6c. ADDRESS (Gry, State, and ZIP Code)       7b       ADDRESS (Gry, State, and ZIP Code)         Aberdeen Proving Ground, MD       21005-5066         8a. NAME OF FUNDING/SPONSORING       8b. OFFICE SYMBOL (H appreable)       9       PROCUREMENT INSTR PROCEEDED         8c. ADDRESS (Gry, State, and ZIP Code)       10       SOURCE OF FUNDING (H appreable)       10       SOURCE OF FUNDING PROCRAM ELEMENT NO 61102A         11*ETTLE MORD BASES SET CALCULATIONS OF ATOMIZATION ENERGIES:       COMP         AND DIRECT RESULTS       12       PERSONAL AUTHOR(S) George F. Adams, Mary M. Gailo*, Michael J. Page**         13a. TYPE OF REPORT       13b       TIME COVERED FROM_Jan 88 TO_Feb 89       14       DATE OF REPORT (Yee Final         14       DATE OF REPORT       13b       TIME COVERED FROM_Jan 88 TO_Feb 89       14       DATE OF REPORT (Yee Final         17       COSATI CODES       18       SUBJECT TERMS (Continue on reverse if nec FIELD       BSUBJECT TERMS (Continue on reverse if nec FIELD         13A ABSTRACT (Continue on reverse if necessary and identify by block number)       We describe the results of a series of extended basis set Moll calculations on a series of first row hydrides, analysis of a obtained employing the isogyric reaction technique demonstrate perturbation theory results are virtually indistinguishable fr fourth-order calculation, for the set of the set of extended basis for the fourth-order calculation, for the set of the		
Ba. NAME OF FUNDING / SPONSORING CAGANIZATION       Bb. OFFICE SYMBOL (If appricable)       9 PROCUREMENT INSTR 9 PROCUREMENT INSTR 10 SOURCE OF FUNDING PROGRAM ELEMENT NO 61102A         Bc. ADDRESS (City, State, and ZIP Code)       10 SOURCE OF FUNDING PROGRAM ELEMENT NO 61102A       10 SOURCE OF FUNDING PROF PROM ELEMENT NO 61102A         11 SUFFENDEL SUPPROTA Final       10 SOURCE OF FUNDING PROF FROM Jan 88 TO Feb 89       10 SOURCE OF FUNDING PROF ELEMENT NO 61102A         12 PERSONAL AUTHOR(S) George F. Adams, Mary M. Gallo*, Michael J. Page**       13 TYPE OF REPORT FROM Jan 88 TO Feb 89       14 DATE OF REPORT (Ye. FROM Jan 88 TO Feb 89         15 SUPPENTARY NOTACIONES FIELD GROUP       13 SUBJECT TERMS (Continue on reverse if nec Subject TERMS (Continue on reverse if nec Statended Basis Set         17 COSATI CODES FIELD 20 DISTRIBUTION / AVAILABILITY OF ABSTRACT CONTINUE on a series of first row hydrides. Analysis of a obtained employing the isogytic reaction technique demonstrate perturbation theory results are virtually indistinguishable fr fourth-order calculation.         20 DISTRIBUTION / AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED 220 NONE OF REPORNINTED 220 DISTRIBUTION / AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED 221 ABSTRACT SECURITY CONSTRIBUTION / AVAILABILITY OF ABSTRACT 222 NAME OF RESPONSIBLE IN AVAILABILITY OF ABSTRACT 221 ABSTRACT SECURITY CONSTRIBUTION / AVAILABILITY OF ABSTRACT 221 ABSTRACT SECURITY CONSTRIBUTION / AVAILABILITY OF ABSTRACT 221 ABSTRACT SECURITY CONSTRUCTION / AVAILABILITY OF ABSTRACT 222 DISTRIBUTION / AVAILABILITY OF ABSTRACT 224 DAME OF RESPONSIBLE IN AVAILABILITY OF ABSTRACT 225 DISTRIBUTION / AVAILABILITY OF ABSTRACT 226 DISTRIBUTION / AVAILABILITY OF ABSTRACT 227	e, and ZIP Code)	
BC. ADDRESS (City, State, and ZIP Code)       10 SOURCE OF FUNDING PROGRAM ELEMENT NO 61102A         11 LILLE, (Include Security, Classification) AND DIRECT RESULTS       PROFECTION ENERGIES: COMP AND DIRECT RESULTS         12 PERSONAL AUTHOR(S) George F. Adams, Mary M. Gallo*, Michael J. Page**       13 TYPE OF REPORT Final       13b TIME COVERED FROM_lan 88 TO_Feb 89       14 DATE OF REPORT (Ye. Final         15 SUPPLEMENTARY NOTATIONS, INFORMATION ENERGIES:       14 DATE OF REPORT (Ye. From_lan 88 TO_Feb 89       14 DATE OF REPORT (Ye. From_lan 88 TO_Feb 89         16 SUPPLEMENTARY NOTATIONS, 1988 JANNAF Combustion Meeting       17       COSATI CODES       18 SUBJECT TERMS (Continue on reverse if necessary Published in Proceedings, 1988 JANNAF Combustion Meeting         17       COSATI CODES       18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)         We describe the results of a series of extended basis set Moll calculations on a series of first rest hydrides. Analysis of a obtained employing the isogyric reaction technique demonstrate perturbation theory results are virtually indistinguishable fr fourth-order calculation.         20       DISTRIBUTION / AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED       Yame As RPT       DIC USERS         21 ABSTRACT SECURITY UNCLASSIFIED/UNLIMITED       Yame As RPT       DIC USERS       21 ABSTRACT SECURITY UNCLASSIFIED/UNLIMITED	RUMENT IDENTIFICA	TION NUMBER
	IG NUMBERS	
11       EXTENSION ACTION AVAILABILITY OF ABSTRACT         20       DISTRIBUTION / AVAILABILITY OF ABSTRACT         21       DISTRIBUTION / AVAILABILITY OF ABSTRACT         220       DISTRIBUTION / AVAILABILITY OF ABSTRACT         21       DISTRIBUTION / AVAILABILITY OF ABSTRACT         220       DISTRIBUTION / AVAILABILITY OF ABSTRACT	ECT TASK NO AH43	WORK UNIT ACCESSION NO
20. DISTRIBUTION (AVAILABILITY OF ABSTRACT 21 ABSTRACT SECURITY UNCLASSIFIED/UNLIMITED SAME AS RPT DTIC USERS 228 NAME OF RESPONSIBLE IN AVIDUAL 22b TELEPHONE (Include	ear, Month, Day) 19 cessary and identify sset Perturba ler-Plesset pe atomization en >s that third- rom the result	<b>by block number)</b> tion Theory, erturbation theory nergy predictions -order ts using a full
ZZA NAME OF REPEINDING IN AVIOUAL IZZO TELEPHONE UNUDAL	CLASSIFICATION	
DR. GEORGE F. ADAMS 301-278-6	6197	SLCBR-IB-I
DD Form 1473, JUN 86 Previous editions are obsolete	SECURITY CLASSIFIC	ATION OF THIS PAGE

### TABLE OF CONTENTS

# I. INTRODUCTION .5 II. METHODS .5 III. RESULTS .7 IV. DISCUSSION .9 ACKNOWLEDGEMENTS .11 REFERENCES .13 DISTRIBUTION\_LIST .15

3



Page

### I. INTRODUCTION

With the development of software efficiently implementing quantum chemical techniques that employ energy gradient and Hessian data, and the concurrent increase of access to modern supercomputers, systematic studies of molecular structures and properties have become routine. Recently, several groups have reported efforts to compute accurate values of molecular heats of formation. Pople and coworkers described a study of first-row hydrides using full fourth-order perturbation theory with a variety of basis sets.<sup>1</sup> In the same proceedings, Binkley and Frisch described results of perturbation theory studies of bond dissociation energies for a series of first-row diatomics.<sup>2</sup> The results described in these papers indicated that fourth-order perturbation theory calculations using extended basis sets provided generally excellent results for sigma-bonded systems, with less accurate results obtained for multiply bonded systems.

Subsequently, Page, et al., used a similar approach to evaluate the dimerization energy of borane.<sup>3</sup> There were systematic differences among these studies that should be noted. Binkley and Frisch computed equilibrium structures using third-order perturbation theory, whereas the other calculations used structural parameters predicted at the Hartree-Fock level. Page, et al., employed an extended basis set when computing the energy, while the other authors approximated this extended basis set by assuming that the effects of individual basis set extensions were additive. Related to these efforts to predict molecular energies accurately, Handy and coworkers have published a series of papers that attempt to evaluate the success of various levels of theory in predicting the properties of molecules.4,5,6 Those computations all employed extended basis sets in order to isolate the effect of theoretical method from the effect of basis set deficiencies. This note describes the effects on computed atomization energies of variation in the theoretical model used to analyze extended basis set results. In particular, we focus on differences obtained when one uses either the isogyric analysis employed by Pople, et al.,<sup>1</sup> or the direct method of computation used in our previous reports.<sup>3,7</sup> We also describe the application of isogyric analyses at several orders of perturbation theory.

### IT. METHODS

We report a series of Moller-Plesset perturbation theory calculations on small molecules. These calculations employ large atomic centered basis sets for the expansion of the molecular orbitals, beginning with the 6-311G basis designed for use with correlation theory methods.<sup>8</sup> This basis is augmented by including diffuse functions, s-type for hydrogen and both s- and p-type for the first row atoms. Additionally three sets of functions in the first polarization space and one set in the second polarization space are added for each atom. For the largest molecule studied, diborane, the total number of basis functions is 186. Perturbation theory calculations were performed using the GAUSSIAN82 computer programs<sup>9</sup> for structures optimized at the SCF level using the well-known double zeta plus polarization basis set.<sup>10</sup>,<sup>11</sup> Structures for those compounds characterized by open-shell wavefunctions were computed using merestricted Hartree-Fock wavefunctions. Harmonic frequencies were also computed using SCF methods with the DZP basis. Results are reported for all three  $B_1$  hydrides and diborane, as well as water, ammonia, hydroxyl radical, carbon monoxide, boron oxide, BO, and methane. The atomization energies of the compounds are evaluated in two ways. One technique computes directly the difference between the sum of the energies of the constituent atoms and the molecule's energy. That is, we compute the energy for the process,

 $AH_n \rightarrow A + nH$ .

Alternately, we evaluate the energy using the isogyric technique described by Pople, et al., in Reference 1. In this case, energies relative to that of the hydrogen molecule are computed using reactions for which the number of unpaired spins is conserved. This is equivalent to conserving the number of electron pairs among the species involved in the comparison. Knowing the number of unpaired electrons for a particular atomic ground state enables one to write isogyric comparisons with molecular hydrogen. For the BH molecule, one has,

 $BH + H \rightarrow B + H_2$ .

Assuming that theory can predict the energy of a reaction producing an atom plus hydrogen molecule(s), then the precisely known value of the dissociation energy for the  ${\rm H_2}^{12}$  can be used to give the value of  ${\rm D_e}$  for the molecule of interest.

Our computations differ from those of Pople, et al., in several ways. The theoretical energies used in their analysis were obtained by improving the results of energies computed using fourth-order Moller-Plesset theory with the 6-311G\*\* basis set. Initially, they estimated a correction to the correlation energy by using an extrapolation method that estimates the contribution made by orders of perturbation greater than four. The extrapolation procedure produced atomization energies that differed little from the fourth-order results. In some cases, agreement with experiment was poorer, an indication that the main source of error was the incompleteness of the basis set used to desribe the molecular orbitals. Additionally, the fourth-order perturbation theory calculations ignored the energy contribution due to excitations of the electrons in the 1s core of the first row atoms. Most of our calculations do not make this approximation, but neither do we employ the extrapolation procedure to estimate the energy contribution obtained, perhaps, at higher orders of perturbation theory.

The basis set improvements in Reference 1 were evaluated incrementally; the effects of adding diffuse functions, polarization functions, and functions in the second polarization space were assumed to be additive. In the present case, all calculations are done with the extended basis set. Pople, et al., concluded that the addition of diffuse functions and second polarization functions had marked effects on the atomization energy calculation, but the effects of the first polarization functions were primarily equal for the atoms and the molecules.<sup>1</sup> If the effects of the basis set extensions were truly orthogonal, those results should closely mimic the data described here. Since it is unlikely that there is no cooperative effect, our approach should lead to slight differences with the incremental results. In addition to the full fourth-order perturbation theory calculations, the diborane calculations were performed using the frozen core approximation. In order to obtain an indication of the effect of this approximation on the computed atomization energy, we have computed energies for several species using both a full perturbation theory calculation and the frozen core approximation. In addition, we have included the third-order perturbation theory results for each species. We anticipate the application of lower order perturbation theory results for larger molecules using semiempirical correction factors. Our goal here is to provide data on the application of this more approximate level of theory using extended basis sets.

### III. RESULTS

We summarize the results of the perturbation theory calculations in Table 1. Our experience with the boranes indicated that extended basis set calculations yielded atomization energy predictions at third-order that were nearly equal to the full fourth-order perturbation theory predictions. With the data presented in this table, w can compare the third-order and fourthorder results over a larger class of compounds.

Molecule	Hartree-Fock	MP 3	SDTQ-MP4	SDTO-MP4(FC)
Н	-0.49981	-0.49981	-0.49981	
В	-24.53108	-24.60644	-24.61167	-24.59308
С	-37.69025	-37.79163	-37.79638	-37.77642
N	-54.39889	-54.52976	-54.53302	-54.51173
0	-74.80934	-74.98919	-74.99316	-74.97094
<b>н</b> <sub>о</sub>	-1.13275	-1.17027	-1.17178	
в́́н	-25.12930	-25.23876	-25.24484	
BHo	-25.75976	-25.87763	-25.88193	
BH2	-26.39969	-26.55272	-26.55784	-26.53676
CH <sup>2</sup>	-40.21259	-40.45285	-40.46095	-40.43767
NH2	-56.21978	-56.49086	-56.50067	-56.47654
най	-76.05931	-76.35067	-76.36215	-76.33811
oĤ	-75.41932	-75.65542	-75.66215	
B0	-99.55687	-99.89308	-99.91786	
$()_{2}$	-149.67687	-150.14865	-150.17612	
в <sup>2</sup> н <sub>6</sub>	-52.83425	-53.13056		-53.14242

### Table 1. Electronic Energy Results (Hartrees)

Table 2 contains the data on all ten molecules studied. Both direct and isogyric predictions are reported for each molecule. In every case, the isogyric computation of the atomization energy, scaling with the known atomization energy of the hydrogen molecule, predicts a larger atomization energy than does the direct method of computation. The difference between the direct and isogyric comparison is equal to a multiple of the difference between the calculated atomization energy of the hydrogen molecule and the known value that we employ in our scaling. Data comparing the results of full fourth-order atomization energy predictions with those obtained using third-order perturbation theory are presented in Table 3. Both direct and isogyric results are considered. The MP3 results preserve the energy difference between the direct and isogyric methods, although the magnitudes are greater than those obtained using the fourth-order data. For the hydrogen containing molecules, the energy differences between the third- and fourth-order results are not dramatically large, nor is the direction of the energy change constant. For the BO and  $O_2$ molecules, on the other hand, the energy differences are large. Since neither molecule's atomization reaction can be described in terms of the breaking of a series of sigma bonds, it is not surprising that the reduced treatment of electron correlation provided at the MP3 level leads to so different a result than the full MP4 calculation. Triple-excitation diagrams that occur first at fourth-order, are required to describe the dissociation of these multiplybonded systems.

Table 2. MP4 Predictions of Atomization Energies (Units: Hartrees)

	Full	MP4	Frozen Core	MP4
Molecule	Direct	Isogyric	Direct	Isogyric
вн	0.13336	0.13566		
BH	0.27064	0.27294		
BH2	0.44674	0.45134	0.44425	0.44884
сн,	0.66233	0.66923	0.66201	0.66891
NH	0.46822	0.47512	0.46538	0.47228
н <sub>л</sub> о	0.36937	().37397	0.36755	0.37215
∩หื	0.16918	0.17148		
BO	0.31303	0.31523		
0.2	0.18980	0.19210		
в <sup>2</sup> н <sub>6</sub>			0.95740	0.96660

Table 3. Comparison of MP3 and MP4 Atomization Energies (Units: H)

	SDTO-MP4		MP 3	
Molecule	Direct	Isogyric	Direct	Isogyric
вн	0.13336	0.13566	0.13251	0.13632
BHo	0.27064	0.27294	0.27157	0.27538
BH3	0.44674	0.45134	0.44685	().45447
CH	0.66233	0.66923	0.66198	0.67341
NH3	0.46822	0.47512	0.46167	0.47310
H2Ó	0.36937	0.37397	0.36186	0.36948
OĤ	0.16918	0.17148	0.16642	0.17023
BO	0.31303	0.31533	0.29745	0.30126
02	0.18980	().1921()	0.17027	0.17408

### IV. DISCUSSION

Handy and coworkers in a series of publications investigated the effect of the level of correlation energy on the prediction of molecular structures and spectroscopic properties.<sup>4,5,6</sup> Most of these studies used an extended basis set similar to that employed in this work. In each case, the rationale is that the extended basis set removes at least one variable from the analysis of the results; additional basis set improvements will have scant effect. We assume that this is so in our calculations. While we have not set out to determine the convergence of the perturbation sequence with respect to the atomization energy predictions, we can comment on that based upon the thirdorder perturbation theory results.

The most obvious characteristic of these calculations is the systematic difference in predicted atomization energy that occurs at each level of theory investigated. Isogyric analysis always predicts a larger atomization energy than does a direct computation, with the difference between the methods increasing as the completeness of the theoretical treatment of correlation is reduced. This must occur, since the magnitude of the correction factor increases as the level of sophistication of correlation energy calculation is reduced.

It is also true that the full fourth-order perturbation theory atomization energies always exceed the frozen core results. The differences are generally small, a consequence of the fact that all the cases for which we can compare numbers involve a single first-row atom. In addition, our frozen core predictions are always equal to or greater than the predictions given by Pople, et al., for the same molecules. These differences are primarily due to the difference in hydrogen atom basis sets used in the two sets of calculations.

As discussed previously, the difference between the direct calculation of the atomization energy and the isogyric prediction is a multiple of the difference between the computed energy for the hydrogen molecule and the exact value. Thus, the correction factor for the BH molecule is one-third that of the methane molecule. To evaluate the results of the calculations, we compare the atomization energy predictions to those given in Reference 1. Those authors evaluated zero-point energy contributions using the best vibrational frequency data available at that time. There are cases, especially for the BH, molecule, the experimental numbers for both frequency and heat of formation are clearly incorrect. These empirically derived data, along with the results of our calculations and the frozen core data of Pople, et al., are summarized in Table 4. Note that the full MP4 calculations using the isogyric method of analysis overestimates the empirical atomization energy in every case but one, the BH<sub>2</sub> molecule. Our value for BH<sub>3</sub> is higher than that derived in a recent experimental study.<sup>14</sup> That report assigns a  $\rm D_0$  value of 265.3 kcal/mole, from which we derive a D\_ equal to 280.6 kcal/mole, using our previously reported zero point energy.<sup>3</sup> Our direct computation of the atomization energies tend to be close to the frozen core results, and are always lower than the experimental values, except for the BH molecule. In this case, there is reason to question the accuracy of the theoretical result. Both the BH molecule and the boron atom have low-lving excited states that are the consequence of double excitations. The perturbation theory techniques used in this study do not accurately account for the energy

contribution due to these excited states. Curtis and Pople have described a technique for computing corrections due to higher-order perturbation theory terms,<sup>15</sup> and they have demonstrated the application of the technique in a study of small boron compounds.<sup>16</sup> That analysis leads to a reduction by several kcal/mole of the atomization energies originally reported in Reference 1.

Since the magnitudes of the energy differences between theory and experiment are so small it is not possible to assign the "correct" value, except in the case of  $BH_2$  for which the empirical value is known to be incorrect.

	SDTQ-	-MP4			10
Molecule	Direct	Isogyric	MP 3	$SDTO-MP4-FC^{1}$	Experiment <sup>13</sup>
BH	83.7	85.1	85.5	85.3	82.8
BH <sub>2</sub>	169.8	171.2	172.8	168.5	196.2
BH	280.3	283.2	285.2	280.9	280 •6 <sup>14</sup>
Снд	415.6	419.8	422.5	419.9	419.8
NH3	293.8	298.1	296.9	296.2	297.3
най	231.8	234.7	231.8	230.9	232.2
о́Я	106.2	107.6	106.9	105.5	106.6

Table 4. Theoretical and Experimental Atomization Energies (kcal/mole)

Finally, we consider results of the isogyric analysis with the thirdorder perturbation theory results. As noted above, this technique fails utterly when applied to multiply bonded systems. In the case of the hydrides, however, the large basis set predictions are in reasonable agreement with the full fourth-order results. In every case, the corrected third order results exceed the atomization energy predictions of the direct calculations and the frozen-core calculations. There is not a systematic difference between the third-and fourth-order isogyric results, however. While admitting that the test set is small, we must conclude that the third-order perturbation theory calculations do provide surprisingly reasonable values for the signa bonded molecules. Certainly, a more thorough evaluation of the application of extended basis set third-order results for signa bonded systems seems warranted, since the computational advantages of this lower level of theory are substantial. The recent description of Carter and Goddard of an excellent prediction of the methylene singlet-triplet splitting obtained using an extended basis set with the computationally efficient GVB method  $^{1/2}$ also indicates the potential benefits of this genre of quantum chemical technique.

### ACKNOWLEDGEMENTS

This work was supported, in part, by the United States Air Force Astronautics Laboratory. Conversations with Dr. L.A. Curtiss, Argonne National Laboratory were most helpful, and we thank him for his assistance.

### REFERENCES

- 1. J.A. Pople, M.J. Frisch, B.T. Luke, and J.S. Binkley, "A Moller-Plesset Study of the Energetics of AH<sub>n</sub> Molecules (A = Li to F)," <u>Int. Jour.</u> <u>Quantum Chem.</u>, Vol. 17S, p. 307, 1983.
- J.S. Binkley and M.J. Frisch, "Ab Initio Determination of Band Dissociation Energies: The First Row Diatomics CO, N<sub>2</sub>, NO, O<sub>2</sub>, and F<sub>2</sub>," <u>Int. Jour. Quantum Chem.</u>, Vol. 17S, p. 331, 1983.
- 3. M.J. Page, G.F. Adams, J.S. Binklev, and C.F. Melius, "Dimerization Energy of Borane," J. Phys. Chem., Vol. 91, p. 2675, 1987.
- 4. E.D. Simandiras, N.C. Handy, and R.D. Amos, "On the High Accuracy of MP2-Optimized Geometries and Harmonic Frequencies with Large Basis Sets," Chem. Phys. Letters Vol. 133, p. 324, 1987.
- E.D. Simandiras, J.E. Rice, T.J. Lee, R.D. Amos, and N.C. Handy, "On the Necessity of F Basis Functions for Sending Frequencies," <u>J. Chem. Phys.</u>, Vol. 88, p. 3187, 1988.
- 6. I.A. Alberts and N.C. Handy, "Moller-Plesset Third Order Calculations with Large Basis Sets," J. Chem. Phys., Vol. 89, p. 2107, 1983.
- 5. R. Krishnan, J.S. Binkley, R. Seeger, and J.A. Pople, <u>J. Chem. Phys.</u>, Vol. 72, p. 650, 1980.
- 6. R.D. Amos, S.M. Colwell, N.C. Handy, P.J. Knowles, R. Nobes, J.E. Rice, and A.J. Stone, CADPAC, The Cambridge Analytic Derivatives Package, 1986.
- 7. G.F. Adams and M.J. Page, "Structures and Energies for Small Boron Compounds. One and Two Boron Compounds," BRL Technical Report in press.
- R. Kirshman, J.S. Binkley, R. Seeger, and J.A. Pople, "Self-Consistent Molecular Orbital Methods. XX. A Basis Set for Correlated Wave Functions," J. Chem. Phys., Vol. 72, p. 650, 1980.
- 9. J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Ragavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder, R.E. Seeger, and J.A. Pople, <u>GAUSSIAN-82</u>, <u>Release H</u>, Dept. of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.
- 10. S.J. Huzinaga, "Gaussian Type Basis Functions for Polyatomic Systems," J. Chem. Phys., Vol. 42, p. 1293, 1965.
- T.H. Dunning, Jr., "Gaussian Basis Functions for Use in Molecular Calculations. I. Contraction of (9s,5p) Atomic Basis Sets for the First-Row Atoms," J. Chem. Phys., Vol. 53, p. 2823, 1970.
- 12. K. Huber and G. Herzberg, <u>Constants of Diatomic Molecules</u>, Van Nostrand Reinhold, New York, 1979.

- 13. D.H. Stull and H. Prophet, Project Directors, <u>JANAF Thermochemical</u> <u>Tables</u>, 2nd Ed., US Government Printing Office, Washington, DC, NSRDS-NBS-37, Catalog Number Cl3.48:37, 1971.
- 14. B. Ruscic, C.A. Mayhew, and J. Berkowitz, "Photoionization Studies of (BH<sub>3</sub>)<sub>n</sub> (n=1,2)," <u>J. Chem. Phys.</u>, Vol. 88, p. 5580, 1988.
- 15. L.A. Curtis and J.A. Pople, "A Theoretical Study of BH<sub>0</sub> Compounds," <u>J.</u> <u>Chem. Phys.</u>, Vol. 89, p. 614, 1988.
- 16. L.A. Curtis and J.A. Pople, "Theoretical Studies of  $B_2H_5^+$ ,  $B_2H_6^+$ , and  $B_2H_6$ ," <u>J. Chem. Phys.</u>, Vol. 89, p. 4875, 1988.
- E.A. Carter and W.A. Goddard, III, "Correlation-Consistent Configuration Interaction: Accurate Band Dissociation Energies from Simple Wave Functions," J. Chem. Phys., Vol. 88, p. 3132, 1988.

### BRL MANDATORY DISTRIBUTION LIST

No of	
Copies	Organization

(Unclass., unlimited) 12 (Unclass., timited) 2 (Classified) 2

- Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station ~ Alexandria, VA 22304-6145
- 1 HQDA (SARD-TR) WASH, DC 20310-0001
- Commander US Army Materiel Command ATTN: AMCDRA-ST 5001 Eisenhower Avenue Alexandría, VA 22333-0001
- Commander US Army Laboratory Command ATTN: AMSLC-DL Adelphi, MD 20783-1145
- 2 Commander Armament RD&E Center US Army AMCCOM ATTN: SMCAR-MSI Picatinny Arsenal, NJ 07806-5000
- 2 Commander Armament RD&E Center US Army AMCCOM ATTN: SMCAR-TDC Picatinny Arsenal, NJ 07806-5000
- Director Benet Weapons Laboratory Armament RD&E Center US Army AMCCOM ATTN: SMCAR-LCB-TL Watervliet, NY 12189-4050
- Commander US Army Armament, Munitions and Chemical Command ATTN: SMCAR-ESP-L Rock Island, IL 61299-5000
- Commander US Army Aviation Systems Command ATTN: AMSAV-DACL 4300 Goodfellow Blvd. St. Louis, MO 63120-1798
- Director
   US Army Aviation Research
   and Technology Activity
   Armes Research Center
   Moffett Field, CA 94035-1099

# No of Copies Organization

- Commander US Army Missile Command ATTN: AMSMI-RD-CS-R (DOC) Redstone Arsenal, AL 35898-5010
- 1 Commander US Army Tank Automotive Command ATTN: AMSTA-TSL (Technical Library) Warren, MI 48397-5000
- Director
   US Army TRADOC Analysis Command ATTN: ATAA-SL
   White Sands Missile Range, NM 88002-5502
- (Class. only) 1 Commandant US Army Infantry School ATTN: ATSH-CD (Security Mgr.) Fort Benning, GA 31905-5660
- (Unclass. only) 1 Commandant US Army Infantry School ATTN: ATSH-CD-CSO-OR Fort Benning, GA 31905-5660
  - 1 The Rand Corporation P.O. Box 2138 Santa Monica, CA 90401-2138
  - (Class. only)
    - 1 Air Force Armament Laboratory ATTN: AFATL/DLODL Eglin AFB, FL 32542-5000
      - Aberdeen Proving Ground Dir, USAMSAA ATTN: AMXSY-D AMXSY-MP, H. Cohen Cdr, USATECOM ATTN: AMSTE-TO-F Cdr, CRDEC, AMCCOM ATTN: SMCCR-RSP-A SMCCR-MU SMCCR-MSI

No. Of Copies	Organization	No. Of Copies	Organization
		<u></u>	
1	Commander Armament R&D Center US Army AMCCOM ATTN: SMCAR-SCA-T, L. Stiefel Dover, NJ 07801	ì	Commander Naval Air Systems Command ATTN: J. Ramnarace, AIR-54111C Washington, DC 20360
1	Commander Armament R&D Center US Army AMCCOM ATTN: SMCAR-LC-G, L. Harris	1	Commander Naval Surface Weapons Center ATTN: J.L. East, Jr., G-23 Dahlgren, VA 22448-5000 Commander
2	Commander US Army Missile Command ATTN: AMSMI-RK, D.J. Ifshin W. Wharton		Naval Surface Weapons Center ATTN: R. Bernecker, R-13 G.B. Wilmot, R-16 Silver Spring, MD 20902-5000
	Redstone Arsenal, AL 35898	5	Commander Naval Research Laboratory
ł	Commander US Army Missile Command ATTN: AMSMI-RKA, A.R. Maykut Redstone Arsenal, AL 35898-5249		ATTN: M.C. Lin J. McDonald E. Oran J. Shnur
4	Commander US Army Research Office		Washington, DC 20375
	ATTN: R. Ghirardelli D. Mann R. Singleton R. Shaw P. O. Box 12211 Research Triangle Park, NC	1	Commanding Officer Naval Underwater Systems Center Weapons Dept. ATTN: R.S. Lazar/Code 36301 Newport, RI 02840
3	27709-2211 Commander Armament R&D Center US Army AMCCOM ATTN: SMCAR-LCA-G, D. S. Downs,	1	Superintendent Naval Postgraduate School Dept. of Aeronautics ATTN: D.W. Netzer Monterey, CA 93940
	Dover, NJ 07801	· · · · · · · · · · · · · · · · · · ·	AFRPL/CX ATTN: S. Rodgers
1	Office of Naval Research Department of the Navy ATTN: R.S. Miller, Code 432 800 N. Quincy Street Arlington, VA 22217		P. Dolan D. Konawalow M. Rosenkratz Edwards AFB, CA 93523-5000

No. Of	
Copies	Organization
4	AFRPL/DY, Stop 24 ATTN: R. Corley R. Geisler J. Levine
	D. Weaver Edwards AFB, CA 93523-5000
1	AFRPL/MKPB, Stop 24 ATTN: B. Goshgarian Edwards AFB, CA 93523-5000
3	AFOSR ATTN: J.M. Tishkoff L. Davis F. Wodarczyk
	Bolling Air Force Base Washington, DC 20332
1	NASA Langley Research Center Langley Station ATTN: G.B. Northam/MS 168 Hampton, VA 23365
4	National Bureau of Standards ATTN: J. Hastie M. Jacox T. Kashiwagi H. Semerjian US Department of Commerce Washington, DC 20234
1	OSD/SDIO/UST ATTN: L.H. Caveny Pentagon Washington, DC 20301-7100
1	Aerojet Solid Propulsion Co.

### No. Of Copies

1

2

ł

### Organization

- Applied Combustion Technology, Inc. ATTN: A.M. Varney P.O. Box 17885 Orlando, FL 32860
- Applied Mechanics Reviews The American Society of Mechanical Engineers ATTN: R.E. White A.B. Wenzel 345 F. 47th Street New York, NY 10017
- Atlantic Research Corp. ATTN: M.K. King 5390 Cherokee Avenue Alexandria, VA 22314
- 1 Atlantic Research Corp. ATTN: R.H.W. Waesche 7511 Wellington Road Gainesville, VA 22065
- I AVCO Everett Rsch. Lab. Div. ATTN: 0. Stickler 2385 Revere Beach Parkway Everett, MA 02149
- Battelle Memorial Institute Tactical Technology Center ATTN: J. Huggins 505 King Avenue Columbus, OH 43201
- 1 Cohen Professional Services ATTN: N.S. Cohen 141 Channing Street Redlands, CA 92373
- 1 Exxon Research & Eng. Co. ATTN: A. Dean Route 22E Annandale, NJ 08801
- 1 Aerojet Solid Propulsion Co. ATTN: P. Micheli Sacramento, CA 95813

No. Of Copies	Organization	No. Copi
1	Ford Aerospace and Communications Corp. DIVAD Division Div. Hq., Irvine ATTN: D. Williams	1
	Main Street & Ford Road Newport Beach, CA 92663	l
1	General Applied Science Laboratories, Inc. 77 Raynor Avenue Ronkonkama NY 11779-6649	
l	General Electric Armament & Electrical Systems ATTN: M.J. Bulman	1
	Burlington, VT 05401	4
l	General Electric Company 2352 Jade Lane Schenectady, NY - 12309	
1	General Electric Ordnance Systems ATTN: J. Mandzy 100 Plastics Avenue Pittsfield, MA 01203	1
2	General Motors Rsch Labs Physics Department ATTN: T. Sloan R. Teets Warren, MI 48090	ł
2	Hercules, Inc. Allegany Ballistics Lab. ATTN: R.R. Miller E.A. Yount P.O. Box 210	1
	Cumberland, MD 21501	,
1	Honeywell, Inc. Government and Aerospace Products ATTN: D.E. Broden/ MS_MN50-2000 600_2nd_Street_NE Hopkins, MN 55343	1

## No. Of 99

### Orgunization

- Honeywell, Inc. ATTN: R.E. Tompkins MN38-3300 10400 Yellow Circle Drive Minnetonka, MN 55343
- IBM Corporation ATTN: A.C. Tam Research Division 5600 Cottle Road San Jose, CA 95193

IIT Research Institute ATTN: R.F. Remaly 10 West 35th Street Chicago, IL 60616

- Director Lawrence Livermore National Laboratory ATTN: C. Westbrook M. Costantino B. Lengsfield N. Winter P.O. Box 808 Livermore, CA 94550
- Lockheed Missiles & Space Co. ATTN: George Lo 3251 Hanover Street Dept. 52-35/B204/2 Palo Alto, CA 94304
- Los Alamos National Lab ATTN: B. Nichols T7, MS-B284 P.O. Box 1663 Los Alamos, NM 87545
- National Science Foundation ATTN: A.B. Harvey Washington, DC 20550
- Olin Corporation Smokeless Powder Operations ATTN: V. McDonald P.O. Box 222 St. Marks, FL. 32355

No. Of Copies	Organization	No. Of Copies
1	Paul Gough Associates, Inc. ATTN: P.S. Gough 1048 South Street Portsmouth, NH 03801-5423	3
2	Princeton Combustion Research Laboratories, Inc. ATTN: M. Summerfield N.A. Messina 475 US Highway One Monmouth Junction, NJ (08852)	1
1	Hughes Aircraft Company ATTN: T.E. Ward 8433 Fallbrook Avenue Canoga Park, CA 91303	1
1	Rockwell International Corp. Rocketdyne Division ATTN: J.E. Flanagan/HBO2 6633 Canoga Avenue Canoga Park, CA 91304	1
8	Sandia National Laboratories Combustion Sciences Dept. ATTN: R. Cattolica S. Johnston P. Mattern D. Stephenson C.F. Melius D. Dandy	3
	C. Rohlfing S.J. Binkley Livermore, CA 94550	3
I	Science Applications, Inc. ATTN: R.B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364	
ł	Science Applications, Inc. ATTN: H.S. Pergament 1100 State Road, Bldg. N Princeton, NJ 08540	1

SRI International ATTN: G. Smith D. Crosley D. Golden 333 Ravenswood Avenue Menlo Park, CA 94025

Organization

Stevens Institute of Tech. Davidson Laboratory ATTN: R. McAlevy, III Hoboken, NJ 07030

- Thiokol Corporation Elkton Division ATTN: W.N. Brundige P.O. Box 241 Elkton, MD 21921
- Thiokol Corporation Huntsville Division ATTN: R. Glick Huntsville, AL 35807
- Thiokol Corporation Wasatch Division ATTN: S.J. Bennett P.O. Box 524 Brigham City, UT 84302
- United Technologies ATTN: A.C. Eckbreth East Hartford, CT 06108
- United Technologies Corp. Chemical Systems Division ATTN: R.S. Brown T.D. Myers (2 copies) P.O. Box 50015 San Jose, CA 95150-0015
- Universal Propulsion Company ATTN: H.J. McSpadden Black Canyon Stage 1 Box 1140 Phoenix, AZ 85029

No. Of Copies	Organization
1	Veritay Technology, Inc. ATTN: E.B. Fisher 4845 Millersport Highway P.O. Box 305 East Ambarat NY 14051-0205
1	Brigham Young University Dept. of Chemical Engineering ATTN: M.W. Beckstead Provo, UT 84601
l	California Institute of Tech. Jet Propulsion Laboratory ATTN: MS 125/159 4800 Oak Grove Drive Pasadena, CA 91103
١	California Institute of Technology ATTN: F.E.C. Culick/ MC 301-46 204 Karman Lab. Pasadena, CA 91125
1	University of California, Berkeley Mechanical Engineering Dept. ATTN: J. Daily Berkeley, CA 94720
1	University of California Los Alamos Scientific Lab. P.O. Box 1663, Mail Stop B216 Los Alamos, NM 87545
2	University of California, Santa Barbara Quantum Institute ATTN: K. Schofield M. Steinberg Santa Barbara, CA 93106

No.	Of
Copt	les

5

### Organization

- University of Southern California Dept. of Chemistry ATTN: S. Benson C. Wittig R. Beaudet H. Reisler G. Segal Los Angeles, CA 90007
- 1 Case Western Reserve Univ. Div. of Aerospace Sciences ATTN: J. Tien Cleveland, OH 44135
- 1 Cornell University Department of Chemistry ATTN: T.A. Cool Baker Laboratory Ithaca, NY 14853
- 1 Univ. of Dayton Rsch Inst. ATTN: D. Campbell AFRPL/PAP Stop 24 Edwards AFB, CA 93523
- 1 University of Florida Dept. of Chemistry ATTN: J. Winefordner Gainesville, FL 32611
- 2 University of Florida Ouantum Theory Project ATTN: R.J. Bartlett M. Zerner Gainesville, FL 32611
- Georgia Institute of Technology
   School of Aerospace Engineering
   ATTN: E. Price
   W.C. Strahle
   B.T. Zinn
   Atlanta, GA 30332

No. Of		No. Of			
Copies	Organization	Copies	Organization		
1	University of Illinois	1	Princeton University		
	Dept. of Mech. Eng.		MAE Dept.		
	ATTN: H. Krier		ATTN: F.A. Williams		
	144MEB, 1206 W. Green St.		Princeton, NJ 08544		
	Urbana, IL 61801				
_		1	Purdue University		
1	Johns Hopkins University/APL		School of Aeronautics		
	Chemical Propulsion		and Astronautics		
	Information Agency		ATTN: J.R. Osborn		
	ATTN: T.W. Christian		Grissom Hall		
	Johns Hopkins Road		West Lafayette, IN 47906		
	Laurel, MD 20707				
		1	Purdue University		
l	University of Michigan		Department of Chemistry		
	Gas Dynamics Lab		ATTN: E. Grant		
	Aerospace Engineering Bldg.		West Lafayette, IN 4/906		
	ATTN: G.M. Faeth				
	Ann Ardor, M1 48109-2140	2	Purdue University		
	Hadana ita di Miana ta		School of Mechanical		
L	Dant of Markaniaal		Engineering ATTN: N.M. Laurendeau S.N.B. Murthy		
	Dept. Of Mechanical				
	Engineering				
	AllN: 5. Fletchet		TSPC Charree Hall		
	Muneaports, My 33437		west Larayette, IN 47906		
3	Pennsylvania State University	l Rensselaer Polytechnic Inst. Dept. of Chemical Engineering			
	Applied Research Laboratory				
	ATTN: K.K. Kuo		ATTN: A. Fontiin		
	H. Palmer		Trov. NY 12181		
	M. Micci		· · · · · · · · · · · · · · · · · · ·		
	University Park, PA 16802	1	Stanford University		
			Dept. of Mechanical		
l	Pennsylvania State University		Engineering		
	Dept. of Mechanical Engineering		ATTN: R. Hanson		
	ATTN: V. Yang		Stanford, CA 94305		
	University Park, PA 16802		, ,		
		1	University of Texas		
1	Polytechnic Institute of NY		Dept. of Chemistry		
	Graduate Center		ATTN: W. Gardiner		
	ATTN: S. Lederman		Austin, TX 78712		
	Route 110				
	Farmingdale, NY 11735	1	University of Utah		
~			Dept. of Chemical Engineering		
2	Princeton University		ATTN: G. Flandro		
	Forrestal Campus Library		Salt Lake City, UT 84112		
	ATTN: K. Brezinsky				
	I. Glassman				
	P.0. Box /10				
	Princeton, NJ (18540)				

No. Of Copies	Organization
l	Virginia Polytechnic Institute and State University ATTN: J.A. Schetz Blacksburg, VA 24061
1	Commandant USAFAS ATTN: ATSF-TSM-CN Fort Sill, OK 73503-5600
2	F.J. Seiler Research Lab (AFSC) ATTN: S.A. Shakelford J. Stewart USAF Academy, CO 80840-6528
1	Freedman Associates ATTN: E. Freedman 2411 Diana Road Baltimore, MD 21209-1525

### USER EVALUATION SHEET/CHANGE OF ADDRESS

This laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers below will aid us in our efforts.

- Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.)
- 2. How, specifically, is the report being used? (Information source, design data, procedure, source of ideas, etc.)

----

\_\_\_\_\_

3. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate.

\_\_\_\_\_

- ------

\_\_\_\_\_

4. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.)

BRL Report	Number	<u> </u>	Division Symbol	· · · · · · · · · · · · · · · · · · ·		
Check here	if desire	to be removed fr	om distribution list.			
Check here	for address change.					
Current	address:	Organization Address				



U.S. Army Ballistic Research Laboratory ATTN: SLCBR-DD-T(NEI) Aberdeen Proving Ground, MD 21005-9989