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13. Pentazole (HN_5) has the fingerprints of a metastable molecule since even though it offers a perfectly logical, even aromatic electronic structure, it is unknown experimentally.

We subjected HN_5 to theoretical analysis. At the correlated level we find that for the reaction, $2\text{HN}_5 \rightarrow 5\text{N}_2 + \text{H}_2$ ΔE is -129.1 kcal/mol resulting in an I_{sp} of 346 as a monopropellant. Considering that derivatives of the basic structure should be made to stabilize the pentazole ring, we can consider some which will be quite energetic (examples include nitropentazole, and a bipentazole analogous to biphenyl and possibly a dinitramine pentazole $(\text{O}_2\text{N})\text{N}-\text{N}_5$, and numerous metal, MN_5 structures, where M could be Li e.g.). The prospects for actually making and using pentazoles is promising.

Several recent methodology developments have been accomplished in this project. These methods, mostly unique to our effort, make it possible to perform high-level, accurate correlated calculations on much larger potential metastable species than was previously possible. These include the following: (1) Direct product decomposition approach to the full use of Abelian symmetry in coupled-cluster and MBPT applications. (2) Restricted open-shell Hartree Fock (ROHF) based CC and MBPT methods. (3) Analytical first derivatives (i.e. gradient) for open-shell CC/MBPT methods.

Final Report
Metastability in Molecules
AFOSR-89-0207

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Chemical and Atmospheric Sciences

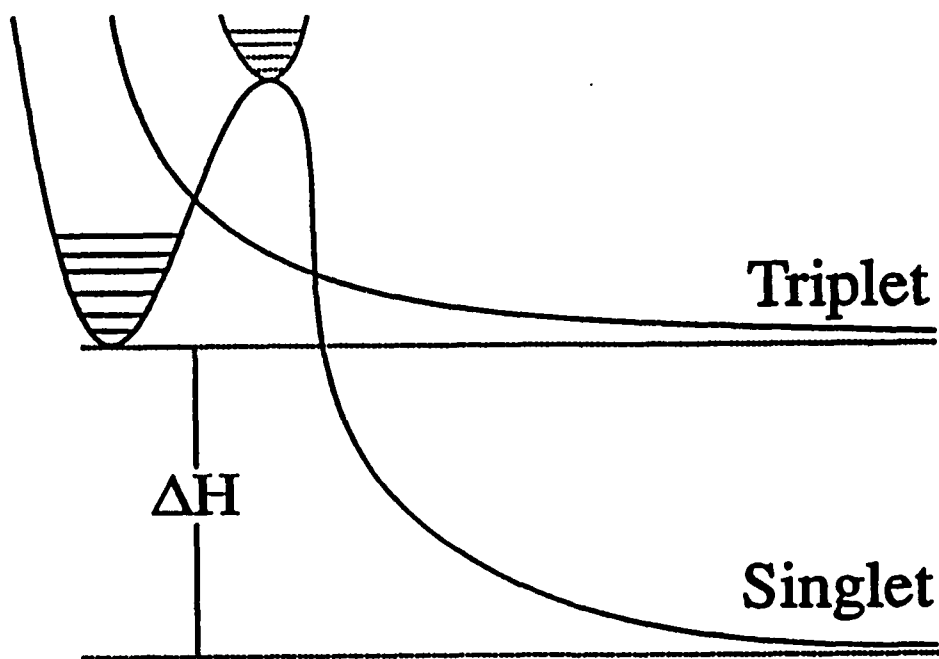
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Introduction

Among the most interesting topics in chemistry is metastability in molecules. Besides telling much about the chemical bond, it offers the potential for identifying molecules that can have important applications from high energy propellants to laser sources [1]. Molecular metastability may be achieved in two predominant ways. First, we can speak of "geometric" metastability. By this term we mean some orientation of the atoms in a molecule that is generally not known experimentally, but that has stability as measured by it being a local minimum on the potential energy surface (PES) for that collection of atoms. The global minimum on the PES will be lower, preferably very much lower if we hope to store large amounts of energy into the metastable form. Clearly we would have to have an activation barrier sufficiently high that separates our metastable form from other minima and particularly the global minimum so that we can trap a significant number of molecules into the metastable structure. Such a generic reaction path plot is shown in Fig. 1,



If the barrier ΔE_A is too low or if significant tunneling can occur, there might be an inadequate lifetime for the metastable state. Alternatively, if there are lower lying states that offer decomposition as does the triplet state shown in Fig. 1, then spin-orbit or non-Born-Oppenheimer effects can cause a curve crossing again jeopardizing the lifetime of the metastable state. Thirdly, some transients can rapidly react in a bimolecular manner, causing a short lifetime for the species. In brief, to know if a geometrically metastable molecule might be synthesized, we need much detailed information about its potential energy surfaces.

The second type of metastability would be to trap a molecule in an electronic excited state. This is commonly achieved when a closed shell, singlet molecule is excited in some way to a triplet excited state, e.g. Such a state is forbidden by spin selection rules from decaying to

the ground state, in the approximation when spin-orbit and other spin dependent terms are not included in the Hamiltonian for the system. This leads to phosphorescence and in the absence of collisions, an unusually long lifetime for the excited state of $\sim 10^{-1}$ to 10s. When the excited state has the same symmetry as the ground state fluorescence will typically occur within $\sim 10^{-4}$ s. Provided we can form a geometrically metastable molecule, we can always attempt to further trap the molecule into an excited state of some appreciable lifetime, making the two ways of achieving metastability additive.

Since metastable molecules cannot be easily formed and studied using conventional experimental approaches, predictive quantum chemistry methods have an essential role in characterizing such metastable species. In order to identify high energy molecules worthy of synthesis, at a sufficient level of approximation, which today usually requires the substantial inclusion of electron correlation, quantum chemistry can provide the following:

1. Determination of critical points (minima and transition states) on a PES using analytical gradients (first derivatives).
2. Detailed prediction of molecular structures (i.e. bond lengths and angles) at the minima.
3. Evaluation of activation barriers at the transition states and associated lifetimes.
4. Unambiguous characterization of the critical points on PES as minima, maxima, or saddle-points (i.e. transition states) by evaluating the Hessian (second derivative) matrix.
5. Prediction of heats of reaction of various potential metastable forms.
6. Predictions of vibrational spectra, frequencies and intensities, for experimental identification and interpretation.
7. Determination of excited state energy surfaces, electronic excitation energies for UV/vis spectra interpretation, and associated lifetimes.
8. Identification of other electronic states that can affect stability of metastable species.

Combining the above with more qualitative theoretical considerations, such as what decomposition products are allowed by symmetry; and what kinds of bonding patterns can be expected to result in viable metastable structures; can provide a microscope that allows a penetrating study of a variety of possible metastable molecular forms that could not be investigated experimentally. Furthermore, we can investigate situations like the interactions of atoms in a host lattice, an area of little experimental information. All our work is made possible by formulating and implementing state-of-the-art *ab initio*, correlated quantum chemical methods based upon coupled-cluster (CC) theory [2-8] and its finite-order many-body perturbation theory (MBPT) [3,4,9] approximations. Many of the newest methods in this area have just been developed in the last three years of this project.

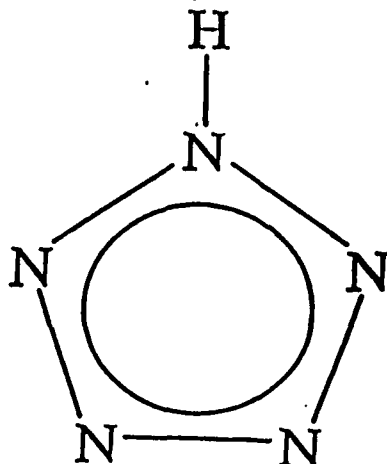
Largely under AFOSR support, we have been developing CC/MBPT methods since the mid seventies [3,4]. These methods are recognized to be among the most accurate available in quantum chemistry [3]. In the last three years under this grant, we have further added to the theory and made a new implementation [10] into a highly efficient program system to provide powerful CC/MBPT tools for analytical derivatives relating to nuclear displacement

(i.e. gradient and hessian matrices) [11,12], which are essential to locating critical points and predicting vibrational spectra including that for open-shell systems. We have formulated and succeeded in fully incorporating Abelian symmetry into our newest CC/MBPT methods [10]. All of these recent developments have been implemented into a general purpose computer program (Advances Concepts in Electronic Structure II, i.e. ACES II) to evaluate energies and analytical gradients at various MBPT [11] and CC levels [12,13]. The timings in ACES II offer a quantum jump in efficiency compared to other widely available programs like GAUSSIAN 90 that provide some of the same many-body methods. But even more significantly, many of the capabilities of ACES II are unique. Having the analytical derivatives themselves is only part of the problem, however. We must also have efficient search techniques to locate minima and especially saddle points to minimize the number of expensive gradient steps required for systems with several degrees of freedom. We have also incorporated several such approaches into ACES II, in hopes of making searches, particularly transition state searches, routine. We also require second derivatives analytically, or as numerical differences of gradients, to characterize critical points as minima or transition states [11].

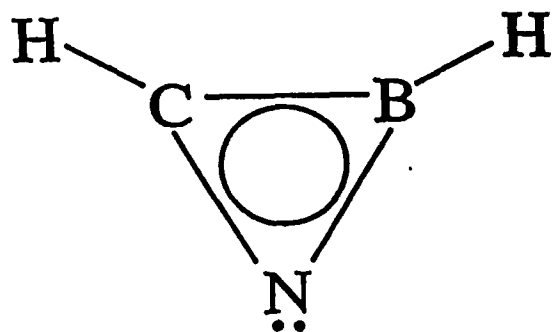
Furthermore, we include in this report several new methodological developments which will enable us to better describe metastable species.

Metastable Molecules

To date, the successes of our effort for the HEDM program, both methodological and in terms of metastable molecule chemistry have been many. Considering the latter first, recognizing the prospects for highly energetic metastable species based upon nitrogen, we initiated our study of a variety of such potential molecules. These included N_3H_3 , which is isoelectronic with the well-known species ozone, cyclopropane and propene; tetrahedral N_4 which is isovalent with P_4 or As_4 , and is forbidden by symmetry from decaying to ground state N_2 molecules; octahedral N_8 , isoelectronic with cubane and similarly forbidden from direct decomposition to N_2 ground state; pentazole



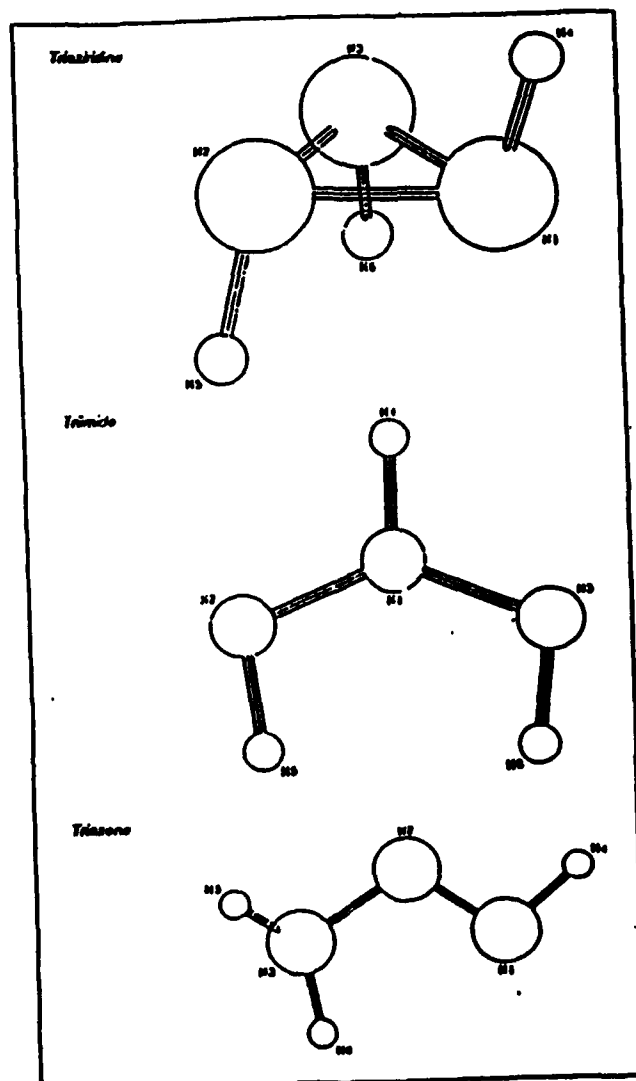
which is a cyclic aromatic structure isovalent to furan; and the analogues of the cyclopropenyl cation,



In each case we obtained some very interesting results.

In the case of N_3H_3 [14] we obtained the structures shown in Fig. 2, that consist of a triazene form, analogous to propene, a triimide analogous to ozone, and a completely cyclic triaziridine form analogous to cyclopropane.

Figure 2



Each of these was found to contribute a metastable minimum on the global N_3H_3 potential energy surface at the *ab initio* SCF and when electron correlation (DZP-MBPT(2)) was included. The minima were fully characterized by calculation of the Hessian (second derivative matrix) analytically at the MBPT(2) level [15], which also provided the IR spectra of these unknown molecules. At this level of approximation the vibrational frequencies are normally within 5% of experiment and the intensities typically to within about 20%. I might add, the character of a critical point on an energy surface can change depending upon whether electron correlation is included. E.g. the experimentally observed C_{2v} form of SiC_2 [16] is not a minimum at the SCF or GVB level, but is at the MBPT(2) level [17], so this is a critical test for every potential metastable molecule.

Although sometimes postulated as an intermediate in inorganic reactions, there is no experimental evidence for the existence of N_3H_3 . This tends to be a recurring theme in the investigation of metastable molecules. Yet, the accuracy of modern *ab initio* correlated predictions is sufficiently reliable that the molecule should be capable of synthesis at least in matrix isolation and can be identified from our predicted frequencies. Using the coupled cluster singles and doubles (CCSD) plus non-iterative triples T(CCSD) model [18] gives the results in Tables 1 and 2. Each N_3H_3 form is found to have the potential for storing a great deal of energy. Their heats of oxidation correspond to specific impulses (I_{sp}) [19] shown in Table 2 compared to 456 for liquid H_2 . Furthermore, the formation of the N_3H_3 molecule is pertinent to prospects for embedding N atoms into an H_2 lattice.

Table 1. Relative Energies of N_3H_3 Isomers at MBPT(2) Optimum Energies

Isomer	MBPT(2)	Relative Energy in kcal			
		SDQ - MBPT(4)	SdTQ - MBPT(4)	CCSD	CCSD + T(CCSD)
Triaziridine	40.96	41.21	41.43	40.84	41.24*
Triimide	13.48	20.01	15.64	20.58	17.30
Triazene	0.00	0.00	0.00	0.00	0.00

All above calculations used a DZP basis set.

* $\Delta H = 87$ kcal/mol to $N_2 + H_2$.

* $\Delta H = 104$ kcal/mol to $N_2 + NH_3$.

Table 2. Specific Impulse of Several Molecular Systems (in seconds)

$H_2 + O_2$	456 (467)*	
$N_2H_4 + N_2O_4$	324	
$N_3H_3 + O_2$	SCF	CCSD + T(CCSD)
triazine	351	347
triimide	382	365

triaziridine	399	390
$N_4(T_d)$	520*	489*
$N_8(O_h)$	559*	531 *

*The formula $265\sqrt{\Delta H/M}$ was used.

Our next effort addressed the fascinating question of whether tetrahedral N_4 (tetraazatetrahedrane) constitutes a local minima on the N_4 PES. Symmetry arguments [20] and other work [21,22] suggested as much. We did, indeed, find such a local minimum at the correlated level, characterized it via correlated second derivatives, and predicted its vibrational frequencies [23]. Although the barrier to dissociation was difficult to determine definitively, which is always the case for a Woodward-Hoffman forbidden process, since at least two configurations which differ by a double excitation should be equally important in the transition state region. Using a symmetry broken multi-reference CC method, we obtained a good estimate that the barrier was more than 50 kcal/mol. This is clearly sufficient to make the molecule experimentally observable. D. Yarkony (private communication) also tells us the spin-forbidden transition to a triplet surface has a barrier of at least 30 kcal/mol further establishing tetrahedral N_4 as a viable metastable species. In establishing its existence, however, bimolecular reactions that might occur cannot be totally disregarded. We also located four other minima on the N_4 surface, including a C_{2v} and D_{2h} form that are actually even more energetic, but probably would not have as high a barrier to decomposition (see Fig. 3).

Figure 3

Relative Energetics of Several N_4 Stationary Points

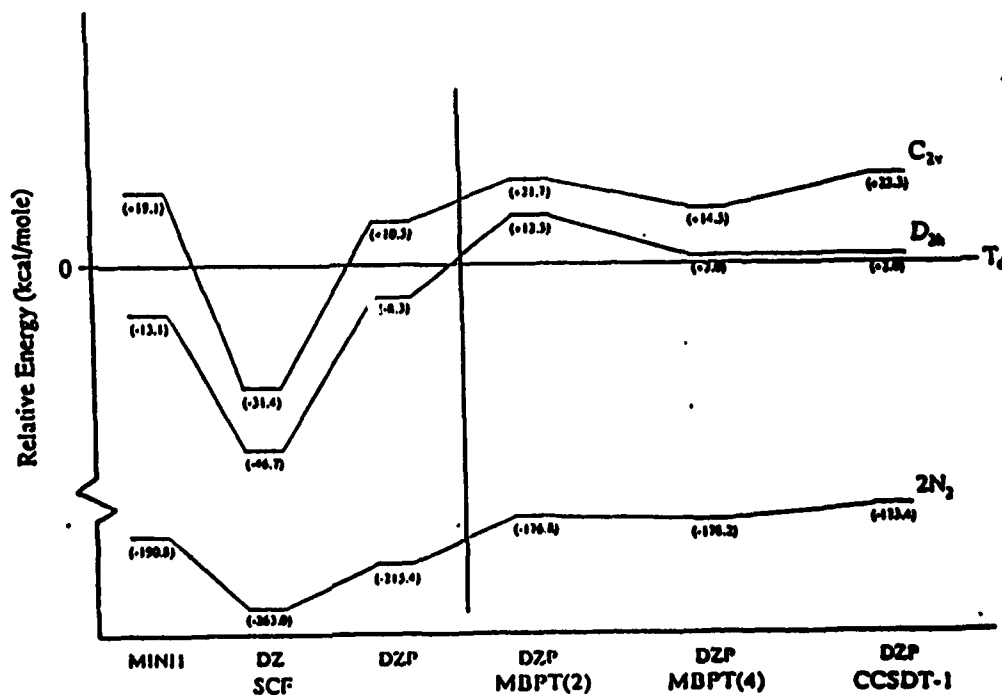
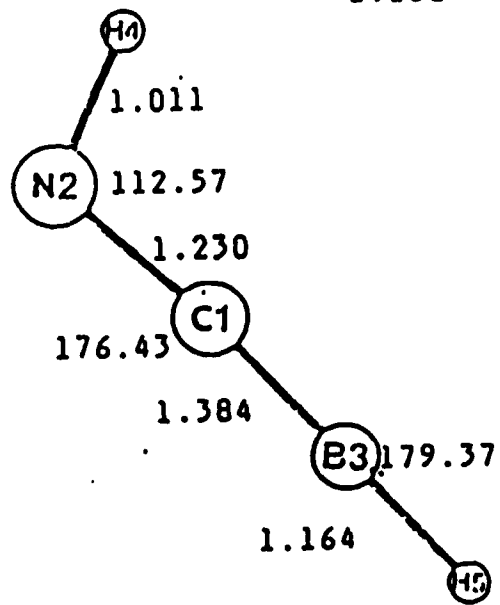
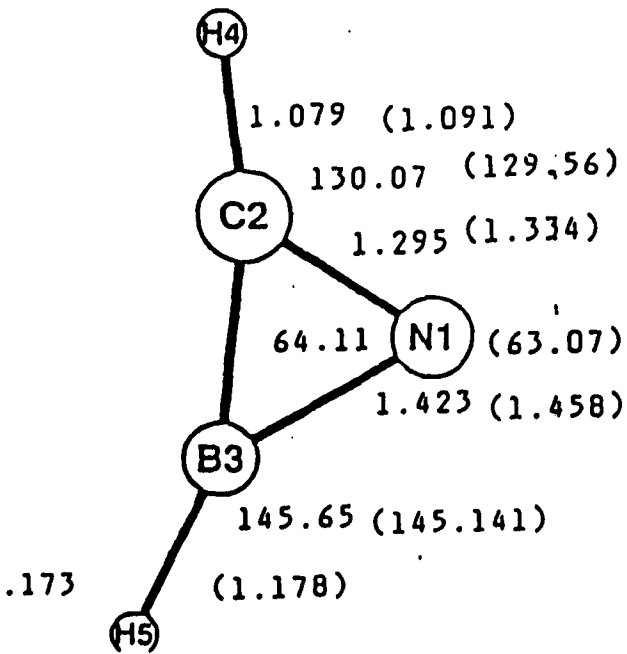
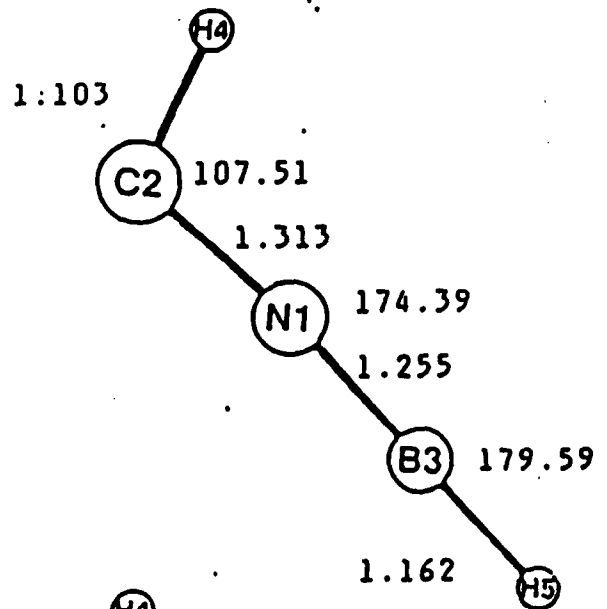
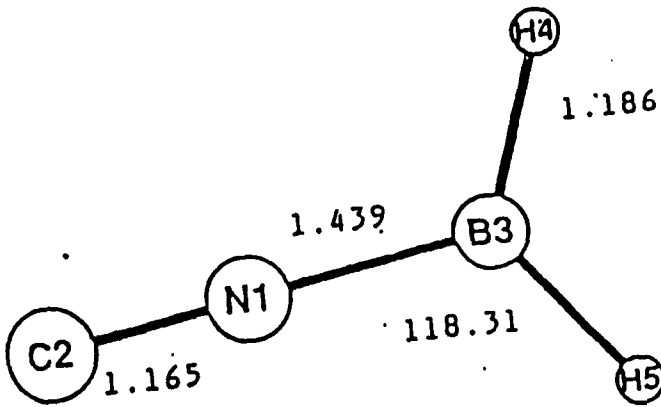
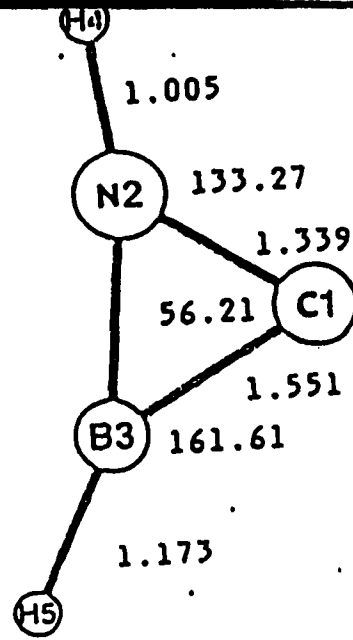
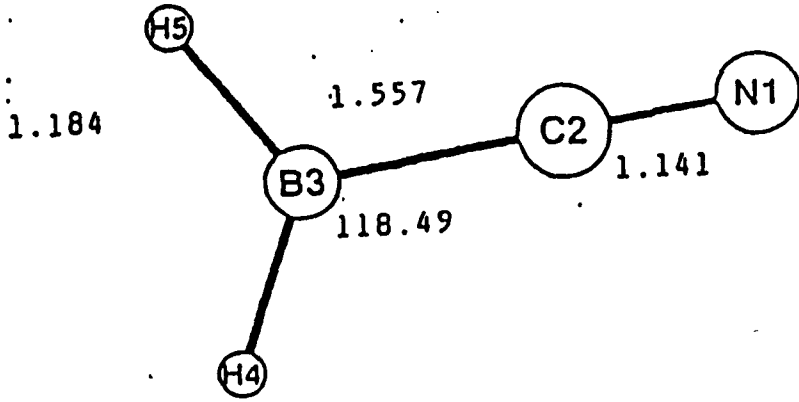
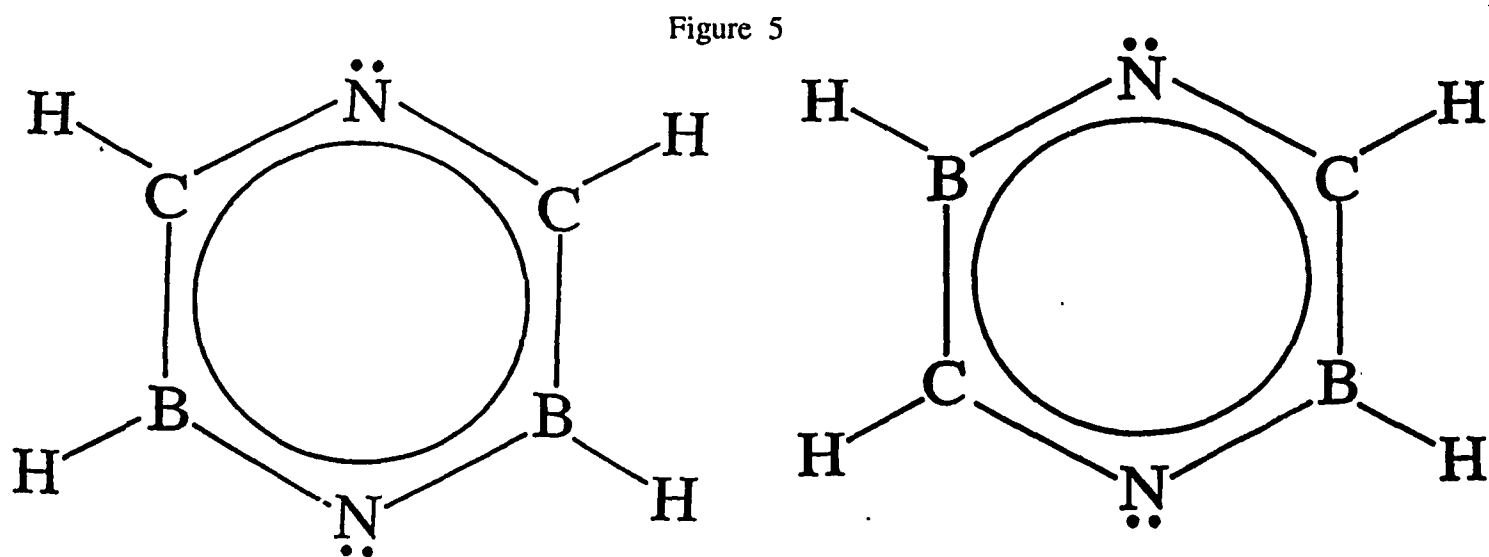


Figure 4



Using the same type of symmetry argument, the N_8 (octaazacubane) species [22,24] was similarly identified and characterized by second derivatives. In a large triple zeta double polarization basis (TZ2P) the energy storage at the CCSD level for N_4 and N_8 is respectively 190.6 and 449.9 kcal/mol resulting in I_{sp} 's of 489s and 531s (Table 2). Both exceed the $H_2 + O_2$ reference value of 467s. N_8 , in particular, is close to the "revolutionary" goal of 600s. We also looked at the benzene analog, N_6 , in this paper and supported it not being a local minimum at the correlated level.

In the case of the $NBCH_2$ molecule, six local minima are found [25], that correspond to the variety of ways the atoms can be attached (see Fig. 4). Although not as energetic as N_4 or N_8 , these are still relatively energetic species. Additional pertinence lies in their relevance to the possible local structures that might occur when embedding N, C or B atoms in a H_2 lattice. Furthermore, the dimers of these isomers lead to natural cyclic structures like



that would be potentially of great interest. We propose to study such dimer structures in the next year of this research program.

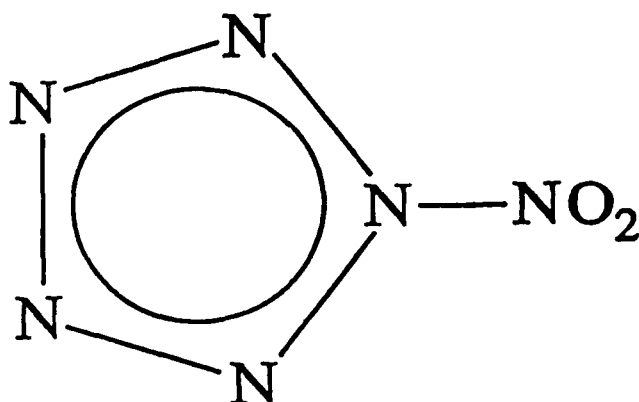
The above nitrogen based species are energetic, chemically fascinating, and experimentally completely unknown. Consequently, synthesis in sufficient quantity to use as a fuel might be difficult to achieve. We have to recognize that even a well-known molecule like O_3 , cannot yet be used as an alternative to O_2 in an actual fuel [26], even though it offers a greater heat of oxidation. This fact, and our interest in providing new, but realistic high energy fuel prospects, has led us to pentazole based molecules. This work, which is unusually promising, has just begun. We are currently making a theoretical study of pentazole derivatives and it will remain one of our major directions for the next year of this program.

Pentazole (HN_5) has the fingerprints of a metastable molecule since even though it offers a perfectly logical, even aromatic electronic structure, it is unknown experimentally. However, unlike N_4 and N_8 , derivatives of HN_5 like phenyl pentazole have been synthesized. The history of this molecule is intriguing. Attempts to synthesize it go back to 1910 [27], and a AgN_5 is actually reported in 1915 by Lipschitz [28]. Immediately thereafter, this synthesis is disputed

in the strongest possible terms by Curtius, et al. [29] who said, "A repetition of Lipschitz's experiments has shown that all his observations and the theoretical conclusions drawn from them are erroneous and that there is no formation of pentazoles." Several further attempted syntheses were not successful until 1957, when Huisgen and Uzi wrote a paper entitled, "Pentazoles I. The Solution of the Classical Problem of Organic Nitrogen Chemistry" [30]. This paper reports a phenyl pentazole derivative. Several other such derivatives have been made, but HN_5 has never been synthesized.

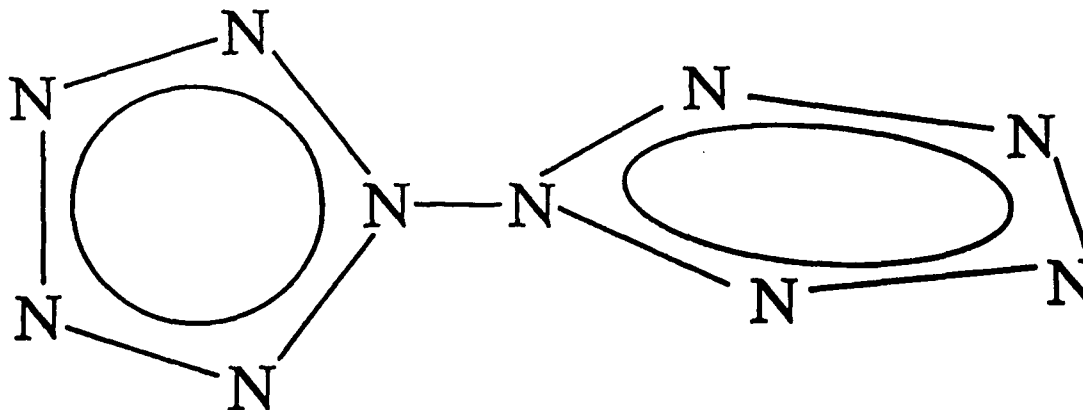
We subjected HN_5 to theoretical analysis. At the correlated level we find that for the reaction, $2\text{HN}_5 \rightarrow 5\text{N}_2 + \text{H}_2$, ΔE is -129.1 kcal/mol resulting in an I_{sp} of 346 as a monopropellant. Considering that derivatives of the basic structure should be made to stabilize the pentazole ring, we can consider some which will be quite energetic (examples include nitropentazole,

Figure 6



and a bipentazole analogous to biphenyl

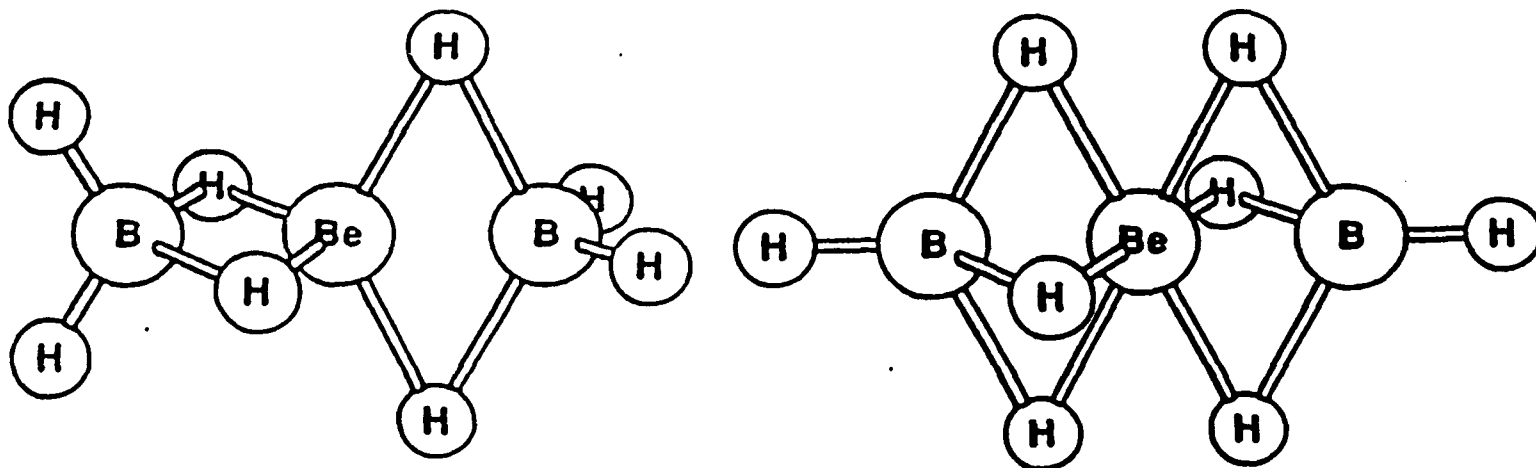
Figure 7



and possibly a dinitramine pentazole $(\text{O}_2\text{N})\text{N}-\text{N}_5$, and numerous metal, MN_5 structures, where M could be Li e.g.. The prospects for actually making and using pentazoles is promising.

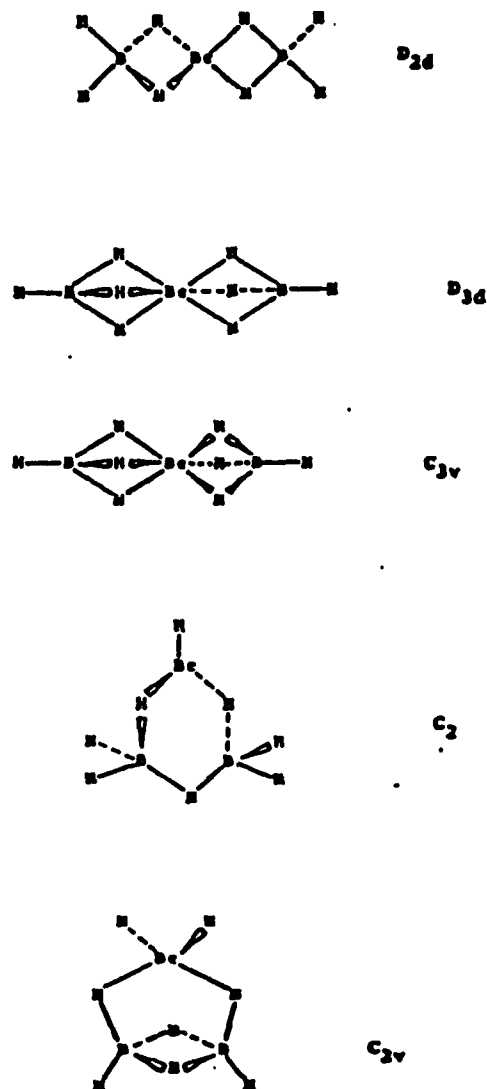
Similarly guided by realistic synthetic prospects, we have also considered other types of high energy molecules that involve Al, B and Be. The primary reason for investigating such species is the observation that the heat of formation of molecules containing electron deficient atoms like B and Be is exceptional. In fact, $\text{Be}(\text{BH}_4)_2$, shown in Fig. 8,

Figure 8



has one of the highest heats of combustion known, -592 kcal/mol. Although known for 50 years, this molecule's structure has been the subject of controversy throughout that period [31]. Some of the structures supported by different, conflicting experiments are shown in Fig. 9.

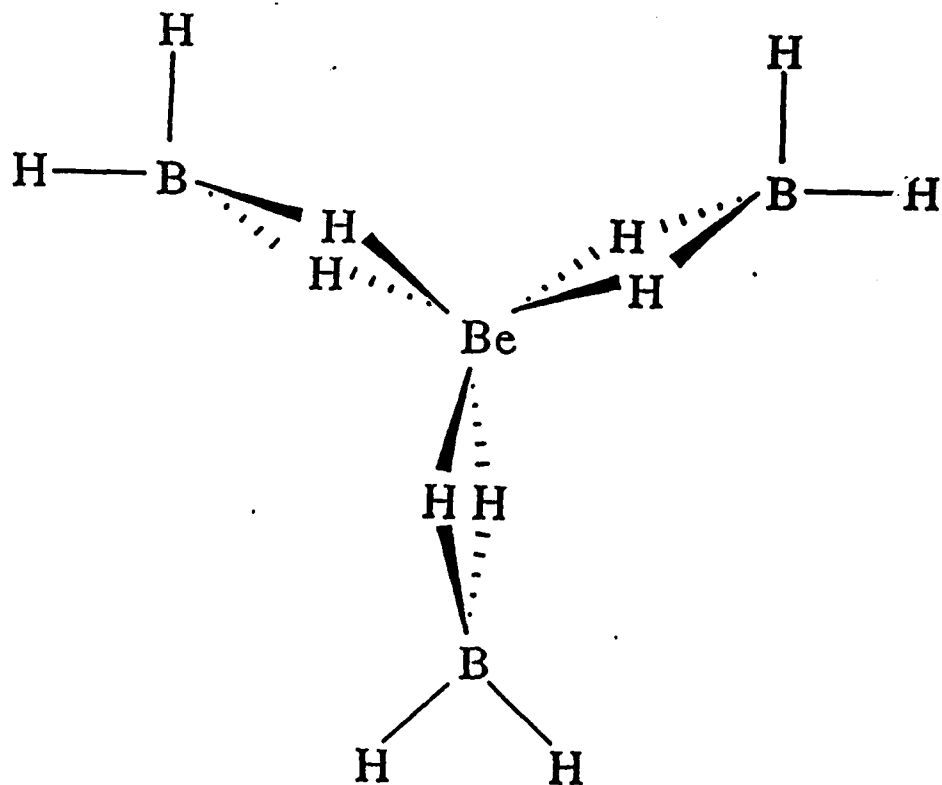
Figure 9



We have already extensively studied $\text{Be}(\text{BH}_4)_2$ and based upon making accurate predictions of vibrational spectra with correlated methods [32], we were able to show the gas phase IR spectra consisted of the D_{3h} and D_{2d} forms, of which the former triply bridged form solely remained after matrix isolation. There is still a discrepancy with the apparent observation that the molecule has a dipole moment, since neither the D_{3h} or D_{2d} structure can have one; but we attribute this observation to experimental error. Current predictions of the NMR spectra [33] for the $\text{Be}(\text{BH}_4)_2$ support our conclusions of the structure.

We speculated that we could create similar molecules with exceptional heats of combustion by adding a third BH_4 group to the basic structure of beryllium borohydride with a Li counter ion, namely $\text{LiBe}(\text{BH}_4)_3$. This molecule is unknown experimentally. In preliminary studies we predicted its structure and find that the $\text{Be}(\text{BH}_4)_3^-$ anion looks like a propeller (Fig. 10)

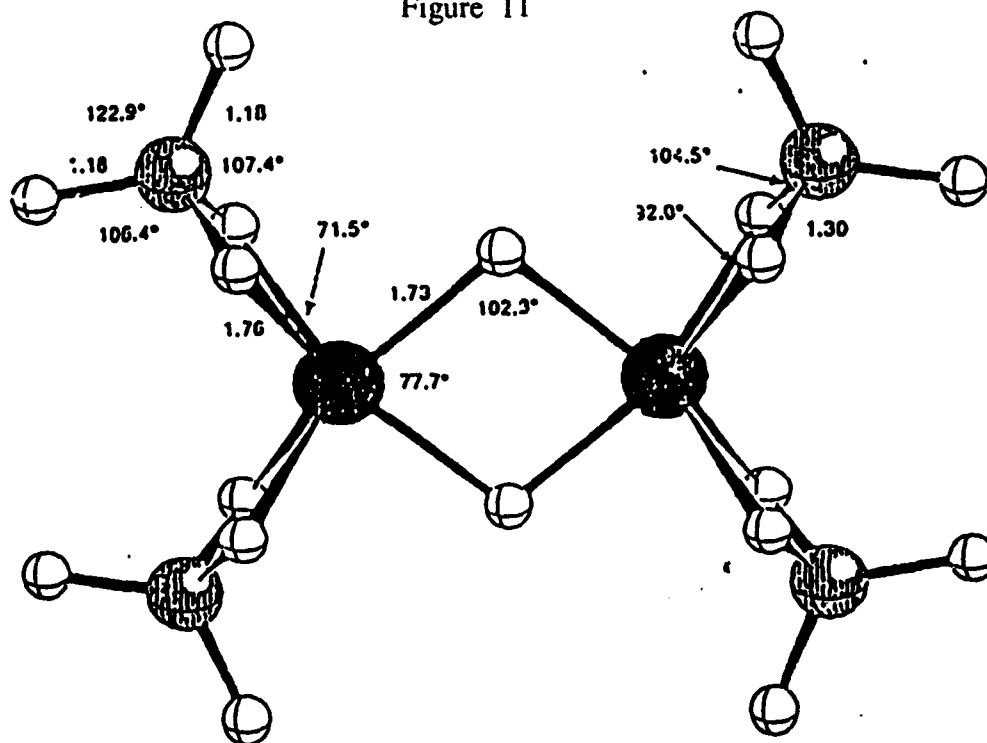
Figure 10



and finally we also predict its vibrational spectra at the MBPT(2) level. Having Be in a propellant and getting complete combustion of B are well known problems to the explosives community, but the exceptional prospects for such species as propellant molecules, perhaps as additives in cryogenic solids, still makes their investigation particularly pertinent to attempting to achieve revolutionary I_{sp} 's in realistically synthesizable structures.

Another example of a readily synthesizable high energy material is $Al_2B_4H_{18}$ which has D_{2h} symmetry (Fig. 11)

Figure 11



Besides being of interest because of its high energy, a correlated description of this molecule using a DZP basis for B and Al, and DZP for H, requires 238 contracted Gaussian functions. Not including core correlation, there are 224 active orbitals. We determined this molecule's structure at the SCF level, which is as shown in Fig. 11 above, and then determined its energy using the CCSD method implemented with symmetry in ACES II. This is the largest CCSD calculation that has been reported. The calculation requires the determination of two million cluster amplitudes. Sustaining an execution rate of 290 megaflops on the CRAY-YMP the CCSD calculation was accomplished in 1303 seconds, or about 108s per iteration. Including all steps (integrals, SCF, transformation, sorting) the total time for the calculation amounted to 2973s or about 50 minutes. The ΔH_f was determined to be +65 kcal/mol. From the CCSD energies, assuming complete combustion, the $\Delta H_{rxn} \approx -1600$ kcal/mol which corresponds to an $I_{sp} = 528$ s.

Methodological Progress

Several recent methodology developments have been accomplished in this project. These methods, mostly unique to our effort, make it possible to perform high-level, accurate correlated calculations on much larger potential metastable species than was previously possible. These include the following:

1. Direct product decomposition approach to the full use of Abelian symmetry in coupled-cluster and MBPT applications.
2. Restricted open-shell Hartree Fock (ROHF) based CC and MBPT methods.
3. Analytical first derivatives (i.e. gradients) for open-shell CC/MBPT methods

In the study of metastable species high symmetry is often important, since for such examples symmetry arguments immediately suggest the existence of barriers to decomposition. Similarly, cluster models of cryogenic solids will frequently exhibit high symmetry. Most *ab initio* quantum chemical programs that can be applied to such problems do not take advantage of point group symmetry once electron correlation is included. We developed a new approach to readily incorporate symmetry for sophisticated methods, termed the Direct Product Decomposition (DPD) [10]. This tool underlies all of our new program system, ACES II. To cite just one example, for cubane (C₈H₈) a 6-31G** basis, "quadratic" QCISD calculations (a simplified CCSD) which is the highest level of correlation available in GAUSSIAN 90, can be performed by ACES II 115 times faster than by GAUSSIAN 90, and the whole calculation, SCF, integrals, transformations, etc. 40 times faster (see Table 3). The time required in our calculation is about 9 minutes on a CRAY YMP compared to 366 minutes for GAUSSIAN 90. The obvious impossibility of performing such calculations for large molecules and basis sets with GAUSSIAN 90 is apparent.

Table 3.

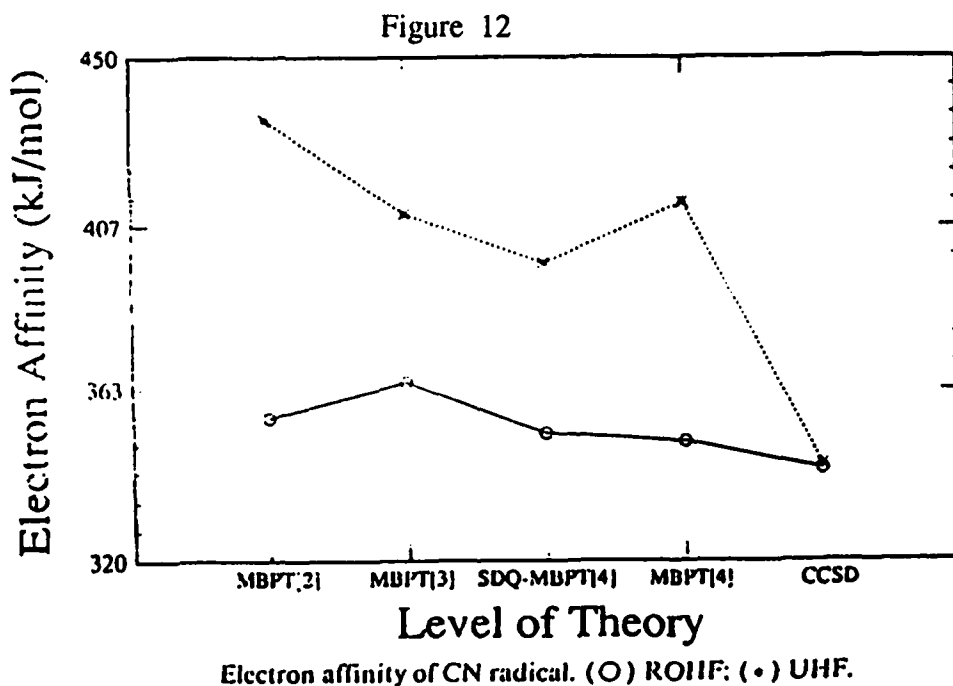
Timings(s) for QCISD calculation for cubane, 6-31G* basis set (136 basis functions, 128 molecular orbitals included in QCISD)			
	G90	ACES II	RATIO
Integrals (VMOL ^a)	799.8 s	246.9 s	3.2
SCF	1119.3	26.0	43.1
Transformation	969.1	45.6	21.3
Integral Proc.	16.0	52.0	0.3
QCISD Calculation	19037.0	168.2	115.2
QCISD Iterations	15	11	1.4
QCISD Cycle Time	1269.1	15.3	82.9
TOTAL	21941.2 s	538.7 s	40.7

^aJ. Almlöf and P. Taylor

Even more important than speed are the methods available to treat metastable molecules. In this regard, we have presented the first generally applicable ROHF-CC and ROHF-MBPT

correlated methods.. It is well known that conventional Hartree-Fock (UHF) reference functions frequently suffer from severe spin contamination. The alternative of using a restricted open-shell Hartree-Fock (ROHF) reference largely alleviates this problem, but the more complicated structures of the ROHF Fock operators makes the correlated theory difficult to formulate. We found a simple solution by formally working with a non-diagonal spin-orbital Fock operator, where all new terms are introduced naturally in any order of perturbation theory [34]. This differs from prior work of Hubac and Carsky [35]. in that we use the Møller-Plesset unperturbed Hamiltonian so there is order-by-order correspondence with the usual MBPT; an important element when open-shell points on a potential energy surface, like the separated atom limit, have to be compared with closed-shell structures. Our approach also differs from that of Wolinski and Pulay [36], in that ours is non-iterative. This makes the generalization to any order transparent.

Finally, our ROHF-MBPT approach completely eliminates the arbitrariness inherent in spin-projected MBPT(2) results [37,38]. The latter is not extensive, as required for a many-body method. Furthermore, projected techniques do not eliminate all spin-contaminants, as in our ROHF-MBPT approach. Lastly, projected MBPT(2) methods do not have natural extensions to higher orders. We, however, are already doing ROHF-MBPT(4) and analytical gradients through MBPT(3). The advantage of ROHF-MBPT over other techniques are readily shown in Figure 12, where the electron affinity of CN is plotted versus order for UHF-MBPT and ROHF-MBPT. The latter shows a very smooth convergence to the infinite-order CCSD result.



Under this grant, our next methodological development pertains to the development of analytical gradients for all levels of CC/MBPT for open- and closed-shell systems. We presented the theory for CC/MBPT analytical derivatives some years ago [39,40]. Now we have augmented the theory and implemented it into ACES II to apply to open-shell systems with unrestricted Hartree-Fock (UHF) [12], restricted open-shell Hartree-Fock (ROHF) [41], and with quasi-Hartree-Fock (QRHF) references [13]. These analytical gradient methods apply to CCSD [12],

CCSD(T) [42], QCISD [12], QCISD(T), MBPT(2), MBPT(3) and full MBPT(4) [43]. They are the only open-shell CC analytical gradients, and the only one for MBPT(4). With these tools we can search energy surfaces to locate the extremum points and transition states efficiently. Furthermore, making finite displacements of analytically computed gradients we obtain the force constant matrix for predicting IR spectra and for documenting the existence of minima and transition states.

Armed with these developments, we are in a unique position to make large scale, predictive *ab initio* studies of potential metastable molecules. Our state-of-the-art methods and programs are being provided to other AFOSR investigators for their use.

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Invited Presentations (1989–1992) Assisted by AFOSR Grant No. 89–0207

- December, 1992 — University of Virginia, Charlottesville
- November, 1992 — Workshop on Current Trends in Computational Chemistry, Jackson State University, Jackson, MS
- July, 1992 — Università Degli Studi Di Bologna, Bologna, Italy
- July, 1992 — International Academy of Quantum Molecular Sciences, Menton, France
- July, 1992 — IBM Europe Institute, Oberlech, Austria
- March, 1992 — Emory University, Atlanta — “Cherry L. Emerson Lecturer”
- December, 1991 — Air Force Non-Linear Optical Polymers Meeting, Dayton, OH
- August, 1991 — Fourth Chemical Congress of North America, New York City, NY
- June, 1991 — Workshop on Recent Developments in Electronic Structure Algorithms, Ithaca, NY
- May, 1991 — American Chemical Society Joint Central-Great Lakes Regional Meeting, Indianapolis, IN
- February, 1991 — AFOSR High Energy Density Materials Contractors Meeting, Albuquerque, NM.
- August, 1990 — Workshop on Coupled-Cluster Theory at the Interface of Atomic Physics and Quantum Chemistry, Cambridge, MA
- July, 1990 — Seventh American Conference on Theoretical Chemistry, San Diego, CA
- July, 1990 — Seventy-Third Canadian Chemical Conference, Halifax, NS
- June, 1990 — W.N. Lipscomb 70th Birthday Symposium, Cambridge, MA
- June, 1990 — AFOSR Non-Linear Optical Polymers Contractors Meeting, Washington, D.C.
- February, 1990 — AFOSR High Energy Density Materials Contractors Meeting, Hotel Queen Mary, Long Beach, CA
- October, 1989 — Meeting on Forty Years of Quantum Chemistry, Athens, GA.
- March, 1989 — High Energy Density Materials Contractors Conference, New Orleans, LA.

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