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The MSRC Ab Initio Methods Benchmark Suite:

A Measurement of Hardware and Software Performance in the Area of Electronic Structure Methods

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Summary

This collection of benchmark timings represents a snapshot of the hardware and software capabilities available for *ab initio* quantum chemical calculations at Pacific Northwest Laboratory's Molecular Science Research Center (MSRC) in late 1992 and early 1993. The "snapshot" nature of these results should not be underestimated, because of the speed with which both hardware and software are changing. Even during the brief period of this study, we were presented with newer, faster versions of several of the codes. However, the deadline for completing this edition of the benchmarks precluded updating all the relevant entries in the tables. As will be discussed below, a similar situation occurred with the hardware.

The timing data included in this report are subject to all the normal failures, omissions, and errors that accompany any human activity. In an attempt to mimic the manner in which calculations are typically performed, we have run the calculations with the maximum number of defaults provided by each program and a near minimum amount of memory. This approach may not produce the fastest performance that a particular code can deliver. It is not known to what extent improved timings could be obtained for each code by varying the run parameters. If sufficient interest exists, it might be possible to compile a second list of timing data corresponding to the fastest observed performance from each application, using an unrestricted set of input parameters. Improvements in I/O might have been possible by fine tuning the Unix kernel, but we resisted the temptation to make changes to the operating system.

Due to the large number of possible variations in levels of operating system, compilers, speed of disks and memory, versions of applications, etc., readers of this report may not be able to exactly reproduce the times indicated. Copies of the output files from individual runs are available if questions arise about a particular set of timings.

Obviously, the results reported here should not be misconstrued as an endorsement by Battelle for any particular software package or computer.

Acknowledgments

Running a large number of diverse calculations with unfamiliar quantum chemistry packages is a sure fire way to get gray hair. A great many things can (and do) go wrong. In order to obtain the timings reported here required the help of many people, both within the MSRC and elsewhere. We wish to acknowledge the assistance and encouragement of all the scientists who had a hand in this project. Specifically, Drs. K. A. Peterson and D. E. Woon helped with the sometimes cryptic MOLPRO input. Dr. R. J. Harrison offered insight into the mysteries of GAMESS-UK and some excellent tips on buying tweed jackets. Dr. M. W. Feyereisen contributed ideas as this project was just getting off the ground. Dr. M. Dupuis is thanked for providing the latest version of HONDO for the RS/6000 workstation.

We also wish to thank Dr. D. Comeau from Prof. R. Bartlett's group at the Quantum Theory Project for providing us with the ACES II benchmark data. And, we wish to thank Drs. R. A. Kendall and R. A. Bair for useful feedback and suggestions throughout the entire course of this project.

Finally, we have to thank the MSRC computer support staff (B. J. Pitre, R. J. Hinds, D. J. Bailey, and D. R. McGee) for their usual professional job of keeping the machines running so that these benchmarks were possible.

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Overview

In the early 1970s, *ab initio* quantum chemistry programs were narrowly focused research instruments of limited capability. Typically, they consisted of less than 20,000 lines of code and were written to satisfy the research needs of a single, small group of people. Today there are more than a dozen *ab initio* packages in worldwide use and that number continues to grow. Hundreds of users may access such software at even a single large supercomputer center. The size of the programs has swelled to hundreds of thousands of lines. A limited number have achieved sufficient popularity to be offered as commercial software, while others are in the public domain or are distributed for little or no cost. Due to the increasing pace of hardware changes, nearly all quantum chemistry packages run on a wide variety of computer hardware, including high-speed, Unix-based desktop workstations; midrange compute servers; traditional mainframes; and supercomputers. As the first generation of massively parallel computer architectures begins to appear, some of these programs will be modified in order to exploit the potential of the new hardware.

The qualities that distinguish one software package from another are much like the qualities that distinguish one new automobile from the next: 1) the number of available options and 2) the relative performance. Both tend to vary widely. The relative performance often varies not only from program to program but, for a given program, from machine to machine. All of these variables confront the scientific staff of Pacific Northwest Laboratory's (PNL) Molecular Science Research Center (MSRC) with a complex set of choices when trying to decide on the best hardware/software combination. A poor choice can result in long, unnecessary delays in obtaining desired results and lost research opportunities.

In unusual cases, where one-of-a-kind capabilities are required, the choice of application may be simplified. In fact, nearly all packages contain one or two unique capabilities, tailored to meet the research needs of the scientific group that spawned it. However, for the overwhelming majority of *ab initio* calculations that fall into the conventional category, any one of many packages might function equally well. There is substantial overlap among the packages in terms of their functionality. In spite of this, there is no publicly available, comprehensive information that would permit a comparison of the relative performance of a significant fraction of these codes. Ideally, the performance data should be based on a common set of molecules and methods and collected on computers that reflect those in popular use. To the best of our knowledge, all presently available benchmarking information on *ab initio* programs is limited to individual programs running on a limited set of hardware. A variety of hardware benchmarks (e.g., LINPACK and SPECmark) are available for measuring the speed of the hardware and operating system, but these are generic tools and lack the specificity desired by the user of *ab initio* packages.

The MSRC *Ab Initio* Methods Benchmark Suite was designed to partially address this need. Specifically, it was intended to:

1. Assist scientists who are performing *ab initio* calculations on a day-to-day basis to make decisions about which hardware/software combinations will run their problem most efficiently. When changes in hardware are not under consideration, these findings should help users determine the best software for a particular type of calculation.

2. Assist anyone trying to track the rapidly changing hardware scene by providing a measure of the relative speed of some of the major hardware platforms in our application-specific area.

3. Assist developers of new codes for advanced architectures by providing a meaningful yardstick by which the performance of the new hardware and software can be measured.

4. Assist developers of graphical user interfaces for *ab initio* applications who wish to provide built-in assistance to the users as they choose programs and/or machines on which to run.

The Choice of Molecules and Methods

Choosing the molecules and methods to be included in the benchmark study involved a balancing act between making the tests as comprehensive as possible and keeping the calculations as short as possible, so that they would be easy to run. Given the speed with which computer hardware is advancing, especially at the workstation level (see Figure 1), we decided to err on the side of including a large number of individual calculations, spanning a considerable range in molecular size and sophistication of methods.

The selected set of molecules, listed in Table 1, contains a typical small molecule with high symmetry (ethylene), intermediate-sized compounds with less symmetry (isobutene and imidazole), and finally, two large molecules with little or no symmetry (caffeine and 18-crown-6). Basis sets include examples of both segmented and generally contracted types. Some use all 6 cartesian d components and others use 5-term d's and 7-term f's. The smallest set includes just 74 functions and, thus, should be able to be run on almost every computer being used for production computational chemistry calculations. The largest basis set includes 630 functions and pushes the limits of the best hardware available at this time. In fact, using the Gaussian 92 code on a Cray C90, we were unable to complete the largest calculation in spite of several restarts of 10 hours each. The geometries used in this study are provided in Appendix A. Most are given in both Z-matrix and cartesian coordinate formats. Energies for the various methods are listed in Appendix B.

The selected *ab initio* methods, shown in Table 2, was intended to be roughly representative of the kinds of calculations being performed daily in the MSRC. It was <u>not</u> intended as an exhaustive list of potentially useful theoretical models. Thus, certain high level methods, such as multireference CI and CCSD(T), are notable by their absence. Likewise, analytical second derivatives at the MP2 and MP4 level are not included. If sufficient interest is expressed by the user community, such methods may be added in subsequent releases of this benchmark. Slightly more than half of the methods include some degree of electron correlation recovery because we felt that the improved efficiency of modern quantum chemistry applications made such methods

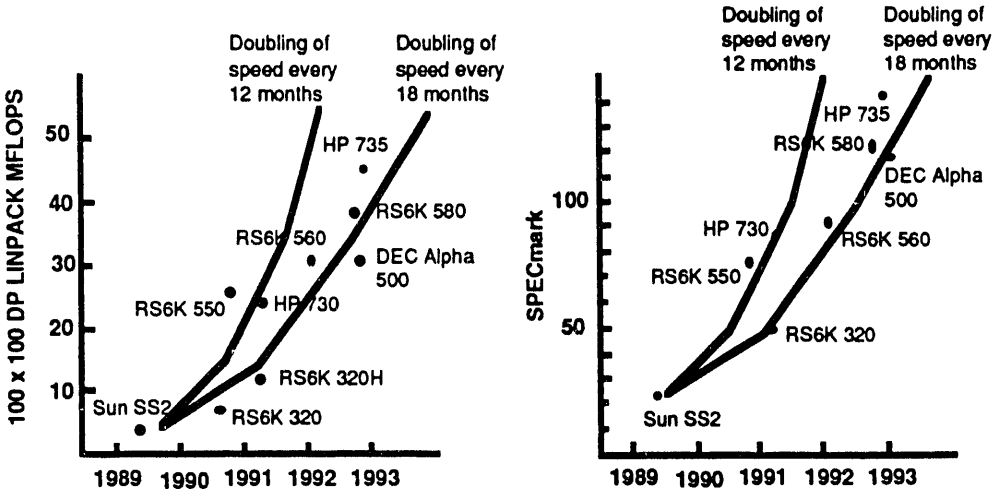

Figure 1. Representative Improvements in Workstation Speed Over the Past Five Years

Table 1. Molecules and Basis Sets

Molecule	# e-	Symmetry	Basis Set	# Functions
Ethylene, C_2H_4	16	^1A_g (D_{2h})	6-311++G** (6d)	74
			cc-pVTZ (5d,7f)	116
			6-311++G(3df,3pd) (5d,7f)	150
Isobutene, C_4H_8	32	$^1A_1$ (C_{2v})	6-311++G** (5d)	144
			cc-pVTZ (5d,7f)	232
Imidazole, $C_3N_2H_4$	36	$^1A'$ (C_s)	6-311++G** (6d)	143
			cc-pVTZ (5d,7f)	206
Caffeine, $C_8H_9O_2N_4$	101	^2A (C_1)	3-21G	144
			6-31G** (6d)	255
18-crown-6, $C_{12}H_{24}O_6$	144	^1A_g (C_i)	3-21G	210
			6-31G** (6d)	390
			aug-cc-pVDZ (5d)	630

Table 2. Theoretical Methods

Methods	Description
Conventional RHF	Restricted Hartree-Fock with the integrals stored on disk
Direct RHF	Restricted Hartree-Fock with the integrals computed as needed
Analytical RHF Gradient	Restricted Hartree-Fock first derivatives of the energy
Analytical RHF Hessian	Restricted Hartree-Fock second derivatives of the energy
Conventional UHF	Unrestricted Hartree-Fock with the integrals stored on disk
Conventional MP2	Second order Møller-Plesset Perturbation theory (disk-based)
Direct MP2	Second order Møller-Plesset Perturbation theory (direct)
MP2 Gradient	Second order Møller-Plesset Perturbation theory first derivatives
MP4(SDTQ)	Fourth order Møller-Plesset Perturbation theory (disk based)
SDCI	Singles and doubles configuration interaction (1 ref. config.)
CCSD	Coupled clusters with singles and doubles
QCISD	Quadratic CI with singles and doubles
CASSCF	Complete Active Space Self Consistent Field energy evaluation

tractable for even fairly large systems. The restricted open shell Hartree-Fock (ROHF) method was initially included in Table 2, but it differed so little from the UHF timings that it was considered redundant and was dropped.

As the detailed tables of results that follow will demonstrate, even with moderately powerful workstations, it possible to perform correlated calculations on molecules containing several dozen atoms, and the speed with which computer hardware improves will likely make even larger systems possible in the 1 to 2 year time frame. Facilitating this trend is the availability of efficient direct methods. Table 2 has a mixture of both conventional (i.e., disk-based) and direct approaches.

The Applications

The eight applications included in this first release of the MSRC Ab Initio Methods Benchmark Suite are listed in Table 3. Most of them were already in use in this laboratory at the time this report was produced or were being considered for use. As mentioned earlier, there are many other excellent

programs available, but due to a lack of accessibility or time, it was not possible to include them in this report. It is hoped that their authors or users would be willing to run at least a representative subset of the benchmark calculations and send us their timings, as discussed below. By so doing they will provide valuable information to the scientific user community.

Near minimal amounts of memory were provided for each application in order to avoid having one program run calculations "in-core" and gain an unfair advantage. Since the emphasis of this study was on larger systems and correlated methods, the possibility of running with enough memory to hold all two-electron integrals in-core was judged to be remote on most systems in common use. The applications were not modified in any way.

The Choice of Hardware

Our choice of hardware was heavily influenced by certain practical matters. With few exceptions, the hardware had to be easily accessible and it had to have enough "spare" CPU cycles available so that the benchmarks did not displace on-going calculations. There are obvious gaps in this list. We hope that the availability of the benchmark results and the corresponding input files, via anonymous ftp, will spur users of different hardware platforms to submit their results to us for inclusion in future releases of this report. The nine machines for which timing data was compiled are listed in Table 4.

Table 3. The List of *Ab Initio* Programs

Program Package
Gaussian 90[1]
Gaussian 92[2]
MOLPRO 92.3[3]
DISCO 1.82[4]
GAMESS-US 6/17/92[5]
HONDO 8.3[6]
GAMESS-UK[7]
ACES II[8]

Table 4. List of Computers Included in the Benchmark Study

Hardware
Sun SPARCstation 2
IBM RS/6000 340 (33 MHz)
IBM RS/6000 550 (42 MHz)
IBM RS/6000 580 (62 MHz)
Cray Y-MP
Cray C90
HP 9000 model 730 (66 MHz)
HP 9000 model 735 (100 MHz)
SGI Indigo (50 MHz R4000)

Format of the Timing Data Tables

The detailed tables of results have the following format. Each entry consists of three related numbers:

	Prog. Name
Method Name	*A/B (C)*

A = CPU time in seconds per iteration (for iterative methods) or per step (for noniterative methods). For example, with Hartree-Fock calculations A is just the total run time divided by the number of iterations. This averages the integral evaluation time over the total number of iterations, producing a number which facilitates making a comparison between conventional and direct methods. For a noniterative method like MP2, A is just the difference between the total run time and the time required to do the SCF (assuming that both were done in the same job). This gives a feel for the MP2 part of the calculation separate from the preliminary SCF part.

B = Total CPU time in seconds (User + system).

C = Total wall clock (or elapsed) time in seconds.

A table of iteration counts is provided. Unless otherwise noted, the wall clock times for workstations were obtained on otherwise quiet systems (i.e., there were no competing jobs that might interfere with the benchmark). CPU and wall clock timings were obtained with unmodified versions of the codes as obtained from the original vendors or software distributors, unless otherwise noted.

If an application was unable to perform a certain type of calculation, the corresponding table entry was marked NA. If a run failed to complete due to a lack of disk space, the entry is denoted FTC - ND (Failed to Complete - Not Enough Disk space). If a run failed to complete and the reason was unknown, an FTC - unknown entry was made. Other exceptions and difficulties, such as inability to converge to the desired state or excessive numbers of iterations, are noted in the footnotes at the end of each table corresponding to a particular model of computer.

Wall clock times in a multiuser environment, such as the National Energy Research Supercomputer Center (NERSC) where most of the Y-MP and C90 timings were obtained, are subject to substantial variation depending on the machine load. We have chosen to report this number because the user's perception of the speed of a machine depends mostly on wall clock performance. For otherwise idle workstations, large discrepancies between wall times and CPU times may indicate a weakness in the I/O subsystem. Because many of the algorithms used in *ab initio* quantum chemistry still require substantial amounts of I/O, it is important that users know if a machine is "unbalanced" in the sense that the CPU and I/O subsystems are mismatched in speed. It does little good to have a fast processor sitting largely idle while I/O operations are completing. On the Crays at NERSC, the benchmarks were run at the highest possible priority, so as to minimize unnecessary waits. The wall clock times reported for the multiuser systems does not include time spent waiting in queues prior to the beginning of a run.

Availability of the MSRC Benchmarks

This report is available upon request from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.
Springfield, VA 22161

Output files for all runs performed by PNL personnel are available in the event questions arise concerning the details of a particular calculation. ASCII versions of the tables and input files can be downloaded from an anonymous ftp site (pnlg.pnl.gov) by typing the following commands:

ftp pnlg.pnl.gov
login as ANONYMOUS
provide your e-mail address when asked for a password
cd QCBENCHMARKS
get (whatever files you want to see)
quit

External Contributions to the Benchmark Data

Contributions to this collection of benchmark data from computational chemists outside PNL are encouraged and greatly appreciated. Their inclusion in the official listing of results will be at the discretion of the PNL staff overseeing the database. If the results are for a package that is not already a part of the benchmark program suite, please send input files as well as the timing data. Address any correspondence to:

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Discussion

Missing Entries

A quick glance through the following tables will reveal that they are incomplete. There are several reasons for this. The primary reason is there simply was not enough time to run every possible calculation. Ignoring for the moment the fact that some programs were incapable of running certain methods, the total number of entries in all tables exceeded 10,000. Very large calculations were deliberately used in many of the benchmarks to stretch the capabilities of hardware, which is rapidly increasing in power. Some of the calculations were impossible because of operating system limitations. These are mainly the large conventional Hartree-Fock and MP2 calculations, where the Unix 2 GB file limit was encountered. Nonetheless, it is hoped that the nearly 400 entries that are present will be sufficient to allow users to judge the relative performance of these applications on many of the workstations and supercomputers at their disposal.

A second reason for missing entries in the tables is that some calculations required more scratch disk space than was available on the systems used for benchmarking. Sometimes this appears as a *FTC - ND* (failed to complete - not enough disk) entry, and other times a calculation was not even attempted because we knew the available disk space was insufficient.

The wide range of methods chosen for this study resulted in many *NA* (not available) entries in the table. Only the popular Gaussian 92 package, which includes probably the widest range of computational methods among current *ab initio* packages, was capable of performing all of the

benchmark methods we selected. While significant, this point should not be overemphasized, since it would have been quite easy to have chosen a slightly different set of methods that might have been completely handled by another package, but not Gaussian.

Remarks on Particular Packages

The only programs that were available on every machine tested were Gaussian 90 (G90) and Gaussian 92 (G92) and both turned in respectable numbers in every category. The performance of the latest version in the areas of analytical first and second derivatives was particularly strong, reflecting its popularity for geometry optimization and normal mode analysis. Furthermore, while this is a highly subjective area, G92 struck us as among the easiest of the *ab initio* programs to use across the 14 different methods we examined.

Other packages also had their strong points. For example, HONDO (8.3) turned in very fast Hartree-Fock second derivative times on the RS/6000, and GAMESS-UK did particularly well at conventional RHF. GAMESS-US showed itself to be a consistently good performer across many methods, and the input format seemed well designed. But the clear winner in the area of post-Hartree-Fock energy evaluations was MOLPRO (92). Across a broad range of workstations and supercomputers, it turned in MP2, MP4, SDCI, CCSD, and CASSCF times that were anywhere from 5 to 10 times faster than other packages. Because MOLPRO utilizes symmetry when performing correlated calculations, its advantage over the other codes grew as the amount of symmetry grew. Gaussian, by way of contrast, will exploit symmetry in the preliminary SCF step (unless explicitly told to turn it off) but then requires the same amount of time to compute an MP2 energy regardless of whether symmetry is turned on or off. On the HP 730 workstation, MOLPRO provides special I/O routines that helped it achieve the best combination of low CPU time and low wall-clock-to-CPU ratios of any machine tested.

Representative timings for all program packages and computers are shown in Figures 2 and 3 in order to provide some feel for the spread in CPU times that were observed. Figure 2 displays Hartree-Fock CPU times for ethylene, the smallest of the benchmark molecules, using both the conventional (disk-based) and direct (2-electron integrals are recomputed as needed) approaches. The spread in CPU times might be somewhat surprising given that the Hartree-Fock equations have been programmed for many years, and it is a nearly universal preliminary step for most correlated methods. With this small molecule and the polarized basis sets we have chosen, the direct approach is always slower (in CPU time) than retrieving the integrals from disk. On the two Crays, where suitably written code can exploit fast vector hardware, the direct approach comes closest to matching the speed of the conventional method. For slightly larger systems (e.g., imidazole) the density-based screening algorithms normally employed in direct SCF programs can shift the balance in favor of the direct methods on machines like the Crays. However, even with larger molecules, the details of the basis set can easily cause very large changes in the direct SCF timings. For example, we have seen cases where a change from 6-31G** to 6-31+G* more than triples the direct SCF time because of less effective screening.

CPU times for correlated MP2 and MP4 calculations, shown in Figure 3 for the same seven computer systems, exhibit a much wider range of values than the corresponding Hartree-Fock values, primarily due to the exceptionally fast times obtained with MOLPRO. The overall spread in values from the SPARCstation2 to the Cray C90 is also much larger than for Hartree-Fock calculations because of the increased ability of the codes to exploit the vector capabilities of the supercomputer when performing MP2 and MP4 calculations. From the slowest code running on the slowest computer to the fastest code running on the fastest computer, a difference of nearly three orders of magnitude was observed.

Once again, it should be emphasized that none of these timings is likely to represent the fastest times possible for any of these codes. We have deliberately chosen to use near minimal amounts of memory and not to set any special options, which might improve performance, because, it was feared, that would lead to endless rounds of experimentation. If they were, it is entirely possible that

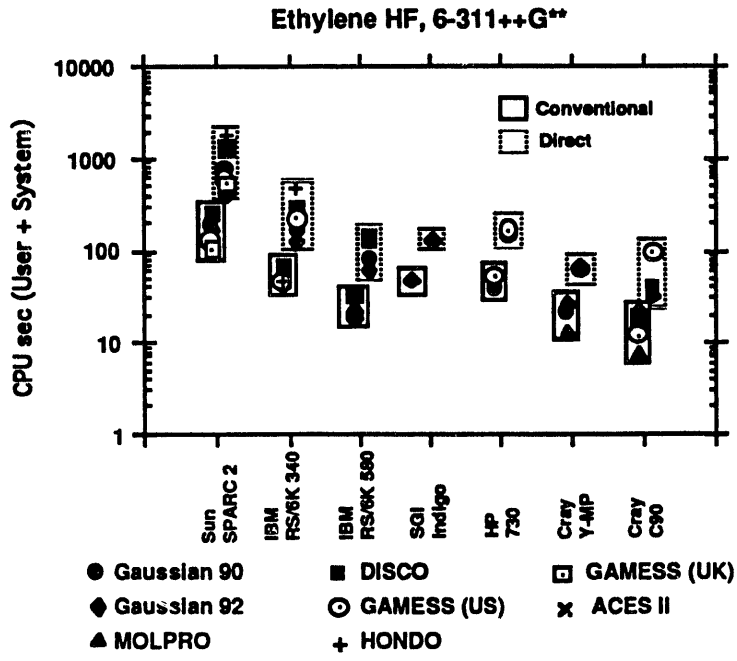

Figure 2. Elapsed CPU Times for Electronic Structure Programs Solving the Hartree Fock Equations for Ethylene. Some symbols may be hidden from view.

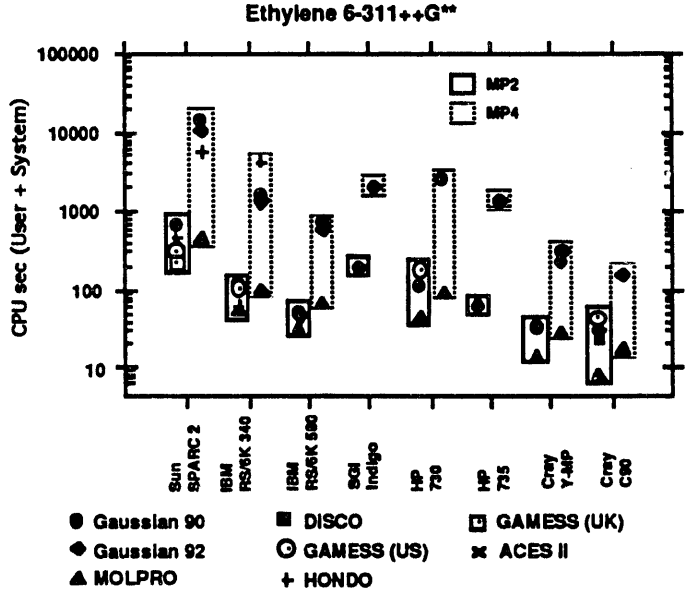

Figure 3. Elapsed CPU Times for Second and Fourth Order Møller-Plesset Perturbation Theory Calculations on Ethylene. Some symbols may be hidden from view.

significant speedups might be observed. For example, with DISCO any extra memory can be used as an integral buffer, thereby significantly improving SCF times can be obtained. Gaussian can exploit extra memory to slash the time needed to perform MP2 calculations. On a Cray C90 it takes over 1600 seconds to perform a direct MP2 calculation (3-21G basis) on 18-crown-6 with 4 million words, but only a little over 800 seconds when the amount of memory is increased to 10 million words.

Remarks on Particular Hardware Platforms

In the hotly competitive, rapidly changing workstation market, we failed to obtain access to some of the very latest products from DEC and Sun in time for this report. Neither the SPARC 10/41 nor the DEC Alpha chip workstations were on-site, with the chosen software packages running, as of late 1992. Of the systems which were available for even a limited amount of time, the IBM RS/6000 model 580 and HP 735 yielded the fastest timings. Although the amount of data on the 580 is relatively limited, it appeared to run neck-and-neck with a Cray Y-MP for methods that did not vectorize well and no worse than a third of a Y-MP for methods that did. The reasons for the poor wall clock results with G90 and the (SDCI, QCISD) methods on the 580 are unknown.

Immediately before this benchmark study was completed, a DEC 3000 model 500, containing a 150-MHz Alpha chip, was provided to us on loan from Digital Equipment Corporation. Although none of the eight packages included in this study were available, we ran an older series of *ab initio* benchmarks, based on an ethylene SD-CI calculation with properties using the MELDF-X[10] program suite. The basis set contained 100 basis functions, including up through f-type functions on the two carbons. The workstation was running a beta release version of OSF1 and version 3.3 of the FORTRAN compiler. The codes, which contain approximately 87,000 lines of FORTRAN, compiled without a problem. Overall, the system delivered the fastest CPU times seen, even 20% faster than the IBM 580. For heavily floating point intensive steps, such as integral evaluation, the model 500 ran significantly slower than the IBM 580, but it more than made up for that with excellent integer performance. For reasons probably associated with the newness of the operating system, program steps that included heavy sequential I/O ran more slowly in real time than the corresponding step on the IBM.

All of the high-speed workstations showed some weakness in their file I/O capabilities relative to the CPU. In the detailed tables of timing data there are numerous instances when the wall clock times are nearly twice as long as the CPU times. We have experienced this even on systems with fast SCSI-2 disks.

The fastest overall CPU performance, not surprisingly, went to the Cray C90. However, because of the multiuser nature of the NERSC, it was difficult to obtain meaningful wall clock times. Thus, the occasional poor ratios of wall-clock-to-CPU times are probably more a reflection of competition for machine resources than any inherent weakness in the system. For methods that vectorize well, such as MP4, the raw speed of the C90 still keeps it better than a factor of four faster than the fastest workstation tested.

Gaussian 92 runs significantly faster than Gaussian 90 on the Sun SPARCstation 2. While the Gaussian 92 release shows improvements over the previous version on other machines, the gains in performance are less dramatic. Part of the improvement in this case is due to the use of a much later release of the Sun Fortran compiler for G92. Gaussian 90 would not work correctly when compiled with the newer compiler.

Because they exercise all components of a computer system, including I/O subsystems, memory pathways, compilers, as well as, floating point and integer units, *ab initio* programs provide a severe test of any computer. The detailed timing data is presented in a series of tables later in this report. Relative performance data for a single benchmark series, consisting of 13 individual calculations on ethylene, is presented in Table 5. The CPU and wall clock times are normalized to the total times for the 6-311++G** basis set results obtained on a SPARCstation 2 with Gaussian 92. Gaussian 92 was not available for the HP 730 at the time these numbers were obtained, so an estimate was made using

Table 5. Approximate Relative Performance on Ethylene 6-311++G** Using Gaussian

Hardware	CPU	Wall Clock	Remarks
Sun SPARC 2	1.0	1.0	
IBM RS/6000 340	4.1	3.1	
IBM RS/6000 550	5.9	4.0	
IBM RS/6000 580	9.1	6.1	
HP 730	~ 3	~ 2	Estimate based on G90 timings for 11 tests.
HP 735	4.6	2.9	
SGI Indigo	2.5	2.3	
Cray YMP	14.7	4	Wall times were obtained in multiuser mode
Cray C90	21.0	2	Wall times were obtained in multiuser mode

Gaussian 90 numbers. This probably underestimates the relative performance that one would see with Gaussian 92. Based on the MELDF benchmarks on the 150 MHz DEC Alpha workstation, it is anticipated to fall into the 7-10 range in relative CPU performance.

Miscellaneous Remarks

The detailed tables of results offer a wealth of information for comparing hardware/ software combinations and for judging the relative cost of one method versus another. To give one example, it has long been known that while the time consuming two-electron integral evaluation step in a Hartree-Fock procedure formally scales as N^4, where N is the number of Gaussian primitives in the basis set, in practice the scaling is much less drastic due to clever schemes to avoid calculating small integrals. With direct methods, the importance of integrals can be estimated based on the previous density matrix. The formation of the Fock matrix formally scales as n^4, where n is the number of contracted basis functions. However, the majority of users care very little about such details. All they want to know is how the total run time will grow if they increase the size of the basis set or add a few more atoms to the system. As the present timing data shows, answering that question is more complicated. If the type of basis set is approximately constant and the size of the molecule increases, the scaling is, indeed, much less than N^4, as shown in Figure 4. However, if the size of the molecule does not vary but the size and composition of the basis set increases to include not only more functions, but functions with higher angular momentum quantum numbers (e.g., *d*'s and *f*'s), quite a different behavior is observed.

In Figure 5 the total run times for three Hartree-Fock calculations performed on ethylene with the 6–31G**, 6-311++G**, and the extended 6-311++G(3df,3pd) basis sets are found to display ~N^4 growth over the initial part of the curve, but then to grow even more rapidly than N^4 as the integral generating code is forced to handle the higher one functions.

Yet another wrinkle is introduced if a user's system happens to have a lot of memory. As the amount of memory on local workstations reaches 250-500 MB, the possibility of running many Hartree-Fock calculations "in-core" increases. The same is true, of course, for large mainframes. On Cray supercomputers, in-core Gaussian 92 Hartree-Fock and MP2 calculations ran anywhere from 1.1 to 4 times faster than the corresponding direct calculations. The average speedup seems to be slightly better than 3:1. We are aware of installed computers from Cray which contain a massive 8 GB of memory.

Density Functional Methods

A method that is growing in popularity for both small and extended systems due to its superior scaling characteristics is the density functional method. There are a number of Gaussian function-based implementations that can perform calculations within the local and nonlocal density approximations. Although this set of benchmarks does not include density functional methods, a parallel effort

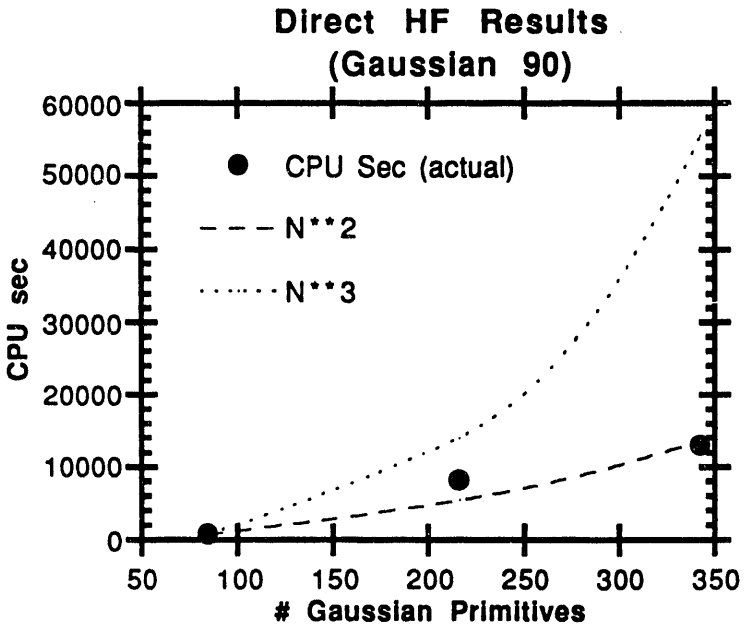

Figure 4. The Growth in Total RHF Times as a Function of the Number of Gaussian Primitives for Ethylene, Imidazole, and 18-Crown-6 on a Sun SPARCstation 2

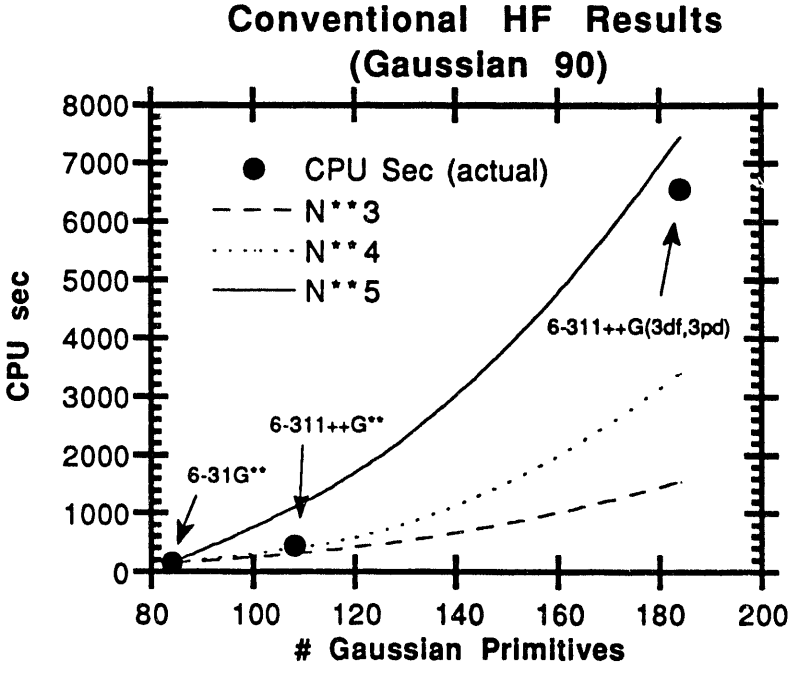

Figure 5. The Growth in Total RHF Times as a Function of the Number Gaussian Primitives for Ethylene on a SPARCstation 2

has been underway at PNL to measure the performance of these codes against each other and against more established ab initio packages. For more information on that report, please contact Dr. Mark Stave or Dr. David Feller of PNL.

Detailed Tables of CPU and Wall Clock Times

Detailed tables of benchmark timings grouped according to computer platform follow. The footnotes at the end of each subsection provide a description of the machine and any additional information pertaining to problems which surfaced during the runs.

Table 6. Sun SPARCstation 2 Timings[a]

Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=6-311++G**
(74 basis functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	18 /196 (269)	12/122 (155)	23 /203 (213)
Direct RHF	69/824 (881)	42/450 (464)	NA
RHF Gradient	193/389 (445)	126/248 (283)	1058/1261 (1292)
RHF Hessian	3123/3319 (3386)	2098/2220 (2313)	NA
UHF	54/697 (640)	36/433 (517)	14/215 (223)
Conv. MP2	526/722 (763)	250/372 (443)	14/217 (226)
Direct MP2	527/1351 (1374)	241/691 (706)	NA
MP2 Gradient	1756/2478 (2685)	816/1188 (1290)	NA
MP4(SDTQ)	14276/14717 (17305)	10684/10806 (11784)	285/488 (497)
SDCI	968/11085 (15885)	457/4698 (5405)	23/362 (379)
CCSD	NA	709/7927 (15694)	31/485 (531)
QCISD	1292/13358 (17406)	527/5396 (5828)	25/427 (441)
CASSCF	434/4101 (6430)[c]	178/1660 (2092)[c]	20/283 (298)

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF	11 /132 (146)	12 /242 (277)	9/106 (124)
Direct RHF	48/626 (631)	62/1882 (1919)[e]	46/554 (566)
RHF Gradient	231/363 (369)	210/474 (491)	89/195 (223)
RHF Hessian	3301/3433 (4091)	2762/3026 (3340)	3649/3755 (3859)
UHF	14/214 (225)	16/429 (439)	
Conv. MP2	183/315 (334)	237/501 (530)	129/235 (255)
Direct MP2	NA	NA	NA
MP2 Gradient	NA	NA	386/621 (742)
MP4(SDTQ)	NA	5596/5860 (6309)	NA
SDCI	250/2380 (2941)[d]	351/3994 (4761)[d]	FTC-unknown
CCSD	NA	NA	NA
QCISD	NA	NA	
CASSCF	843/8569 (10261)[d]	519/5921 (7836)[d]	

Method	DISCO (1.82)	ACES II
Conv. RHF	21/268 (274)	
Direct RHF	106/1381 (1406)	NA
RHF Gradient	1124/1392 (1405)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	1171/2573 (2581)	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=cc-pVTZ
(116 basis functions, 5-term d's, 7-term f's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
RHF	173/1900 (1945)	106/1057 (1170)	142/1415 (1510)
Direct RHF	689/8952 (10790)	327/3274 (3381)	NA
RHF Gradient	4186/6086 (6434)	1183/2240 (2365)	NA[i]
RHF Hessian	28789/30689 (30936)	16101/17158 (17510)	NA
UHF	182/2365 (2735)	119/1424 (2135)	112/1460 (1626)
Conv. MP2	6219/8119 (8274)	3576/4633 (4818)	40/1455 (1583)
Direct MP2	6366/15318 (14500)	3382/6656 (6730)	NA
MP2 Gradient	17284/25403 (27041)	8121/12754 (14189)	NA
MP4(SDTQ)	94140/99935 (218907)	76427/77484 (112614)	1154/2569 (2,808)
SDCI	5489/66171 (103905)	3723/42010 (49485)	82/1989 (2195)
CCSD	NA	53285/54342 (160825)	129/2449 (2613)
QCISD	6380/69592 (115067)	5298/41340 (54032)	103/2339 (2628)
CASSCF	FTC-ND	FTC-ND	33/1548 (1786)

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term d's and 7-term f's.	unable to handle 5-term d's and 7-term f's.	unable to handle 5-term d's and 7-term f's.
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	201/2014 (2047)	
Direct RHF	516/5160 (5765)	NA
RHF Gradient	5988/11148 (11249)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	6766/11944 (12643)	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=6-311++G(3df,3pd)
(150 functions, 5-term d', 7-term f's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (A)	MOLPRO (92.3)
Conv. RHF	205/2259 (2656)	167/1669 (2410)	337/3371 (3966)
Direct RHF	685/8221 (8363)	506/5563 (5726)	NA
RHF Gradient	3787/6046 (6417)	1949/3618 (4361)	
RHF Hessian	45569/47828 (49314)	32070/33739 (36165)	NA
UHF Total	248/3465 (4332)	205/2663 (4081)	
Conv. MP2	9171/11430 (13615)	4133/5802 (8016)	
Direct MP2	9012/17233 (17338)	3791/9354 (9469)	NA
MP2 Gradient	24919/36349 (39236)	12035/17838 (21081)	
MP4(SDTQ)	271564/278221 (363,794)	>18900 FTC-ND	
SDCI	>13300 FTC-ND[f]	FTC-ND	
CCSD	NA	FTC-ND	
QCISD	>14200 FTC-ND[f]	FTC-ND	
CASSCF	FTC-ND[g]	FTC-ND	

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term	unable to handle 5-term	
Direct RHF	d's and 7-term f's.	d's and 7-term f's.	
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	416/5411 (5827)	
Direct RHF	1178/15324 (15425)	NA
RHF Gradient	13798/19209 (19888)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	16420/31744 (31844)	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Imidazole, 36 electrons, $^1A'$ (C_s), Basis Set=6-311++G**
(143 functions, 6-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	764/11466 (13428)	260/3645 (6647)	645/9028 (8988)
Direct RHF	1454/29087 (29273)	917/13761 (13837)	NA
RHF Gradient	9187/11446 (13480)	4222/7867 (10920)	31171/40199 (44249)[h]
RHF Hessian	68176/70435 (75526)	47327/50972 (59925)	NA
UHF	505/12121 (15604)	370/8505 (16126)	
Conv. MP2	6993/18459 (21595)	5209/8854 (13324)	1125/10153 (14127)
Direct MP2	18182/47269 (47497)	8496/22257 (22412)	NA
MP2 Gradient	43303/61762 (71754)	19745/28639 (37539)	
MP4(SDTQ)	>28200 FTC-ND	FTC-ND	
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	1241/11617 (12078)	
Direct RHF	4466/40197 (40428)	NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Isobutene, 32 electrons, $^1A_1$ (C_{2v}), Basis Set=6-311++G**
(144 functions, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	239/3345 (4606)	158/2050 (3575)	
Direct RHF	647/16169 (16353)	408/6543 (6611)	NA
RHF Gradient	2534/5879 (7245)	1793/3843 (5384)	
RHF Hessian	91291/94636 (100117)	46678/48728 (53805)	NA
UHF	326/5541 (7369)	245/3913 (3505)	
Conv. MP2	14195/17540 (20158)	5590/7640 (11212)	
Direct MP2	14930/31100 (31897)	11893/13943 (14121)	NA
MP2 Gradient	FTC - unknown	18159/25799 (32020)	NA
MP4(SDTQ)	FTC-ND	FTC-ND	
SDCI	FTC-ND	FTC-ND	
CCSD	NA	FTC-ND	
QCISD	FTC-ND	FTC-ND	
CASSCF	FTC-ND	FTC-ND	

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term	unable to handle 5-term	unable to handle 5-term
Direct RHF	d's	d's	d's
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	NA
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		NA
SDCI			
CCSD	NA	NA	NA
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Isobutene, 32 electrons, $^1A_1$ (C_{2v}), Basis Set=cc-pVTZ
(232 functions, 5-term d's, 7-term f's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF			
Direct RHF	9384/140756 (142164)	4325/56227 (57012)	NA
RHF Gradient			
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term	unable to handle 5-term	
Direct RHF	d's and 7-term f's	d's and 7-term f's	
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	NA
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		NA
SDCI			
CCSD	NA	NA	NA
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=3-21G,
(144 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
UHF	556/16112 (20580)	427/11950 (22529)	
UHF Gradient	4374/20486 (24869)	3150/15100 (26520)	
UHF Hessian	205561/221673 (240483)	135452/147402 (187180)	NA
Conv. RHF	291/12237 (18489)	216/8867 (33493)	
Direct RHF	837/34306 (34533)	512/27172 (27341)	NA
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
UHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Direct RHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
UHF		
UHF Gradient		
UHF Hessian	NA	
Conv. RHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=6-31G**
(255 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct UHF	7126/242275 (245059)	5922/153966 (155815)	
RHF Gradient			
RHF Hessian			NA
Direct RHF			NA
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Direct UHF			
RHF Gradient			
RHF Hessian			
Direct RHF			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD	NA		
CASSCF			

Method	DISCO (1.82)	ACES II
Direct UHF		NA
RHF Gradient		
RHF Hessian	NA	
Direct RHF		
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=3-21G
(210 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF	905/12670 (12844)	569/7391 (7532)	
RHF Gradient	7724/20394 (20658)	3613/11004 (11222)	
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Direct UHF		NA
RHF Gradient		
RHF Hessian	NA	
Direct RHF		
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=6-31G**
(390 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		5058/65758 (67217)	
RHF Gradient			
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Direct UHF		NA
RHF Gradient		
RHF Hessian	NA	
Direct RHF		
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 6. Sun SPARCstation 2 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD, and CASSCF), each entry consists of a trio of numbers: "CPU-time-per-iteration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the preliminary Hartree-Fock step. Unless otherwise noted all SPARC 2 calculations were performed on a machine with 64 MB of memory, a 900 MB Seagate ST4766 disk and a 600 MB Fujitsu M2266 disk running under SunOS 4.1.1 with Release 1.4 of Sun Fortran. G90 was compiled with version 1.2 of the Fortran compiler because of problems encountered in getting it to run under 1.4. Runs were made on an otherwise quiet system.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 13 digits following the decimal point (7 - 8 digits in the density).

(b) The ethylene UHF calculation treated the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g. MP2, MP4, CISD and QCISD calculations involved all electrons (i.e., there were no "core" electrons). The CAS configuration list contains 8 CSFs in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals ($3a_g$, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two triplet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry. The timing for a UHF $^3B_{1g}$ calculation that did exploit D_{2h} symmetry is 295 CPU (347 Wall).
Gaussian 90 requires that RHF calculations that precede certain correlated methods be run in C_1 symmetry. This results in an increase in the ethylene SCF times from 196 seconds (D_{2h}) to 441 seconds (C_1) for the 6-311G** basis; from 1900 seconds (D_{2h}) to 5795 seconds (C_1) for the cc-pVTZ basis; from 1969 seconds (D_{2h}) to 6657 seconds (C_1) for the 6-311++G(3df,3pd) basis.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed, but the final energy was approximately 20 millihartrees too high. The total times reported have been increased by the amount necessary to perform a SCF calculation.

(d) GAMESS and HONDO could not do a combined RHF + SDCI or RHF + CAS in one job step. In order to make the total time comparable to what is reported for other programs, the time to perform the RHF calculation (exclusive of the 2-el. integral time) was simply added to the SDCI or CAS time.

(e) Failed to converge in 30 iterations. By iteration 11 the energy was within 10^{-7} hartree of the converged result, but the energy subsequently oscillated.

(f) This calculation died due to a lack of disk space in the middle of iteration 2. At that point the size of the "rwf" exceeded 900 MB, the size of the largest scratch partition available.

(g) The number of configurations in the SDCI calculations were 21,037 for 6-311++G** ethylene; 50,741 for cc-pVTZ ethylene.

(h) This MOLPRO calculation failed to produce correct gradients.

(i) The MOLPRO gradient integral package is unable to handle generally contracted basis sets.

Table 7. IBM RS/6000 340 Timings[a]

Ethylene, 16 electrons, ^1A_g, (D_{2h}) Basis Set=6-311++G**
(74 basis functions, 6-term d's)[b]

Method	Gaussian 90 (J)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	4/45 (49)	4/43 (74)	6/55 (91)
Direct RHF	15/175 (179)	12/131 (139)	NA
RHF Gradient	43/88 (94)	37/80 (112)	71/130 (131)
RHF Hessian	487/532 (555)	547/590 (641)	NA
UHF Total	12/152 (156)	10/124 (154)	4/58 (60)
Conv. MP2	72/117 (125)	71/114 (126)	2/57 (62)
Direct MP2	71/245 (254)	76/207 (215)	NA
MP2 Gradient	273/390 (405)	271/385 (426)	NA
MP4(SDTQ)	1497/1613 (1898)	1351/1394 (2099)	54/109 (110)
SDCI	154/1657 (3122)	133/1371 (2005)	5/87 (88)
CCSD	NA	202/2270 (5340)	6/113 (115)
QCISD	180/1913 (3719)	154/1579 (2542)	11/97 (99)
CASSCF	58/520 (1023)[c]	58/586 (1112)[c]	18/71 (73)

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK
Conv. RHF	4/46 (55)	5/47 (52)	
Direct RHF	18/229 (230)	20/268 (270)	
RHF Gradient	61/107 (112)	36/83 (88)	
RHF Hessian	324/370 (802)	243/290 (297)	
UHF	5/71 (86)	5/78 (83)	
Conv. MP2	66/112 (143)	16/63 (108)	
Direct MP2	NA	NA	
MP2 Gradient	NA	162/225 (382)	
MP4(SDTQ)	NA	1593/1640 (2869)	
SDCI	FTC - unknown	106/1113 (2036)	
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF	277/2820 (4622)	80/796 (1334)	

Method	DISCO (1.82)	ACES II
Conv. RHF	5/70 (73)	
Direct RHF	21/298 (301)	NA
RHF Gradient	225/295 (300)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	238/536 (539)	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

Ethylene, 16 electrons, ^1A_g, (D_{2h}), Basis Set=cc-pVTZ
(116 basis functions, 7-term f's, 5-term d's)[b]

Method	Gaussian 90 (J)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	51/557 (620)	32/317 (340)	
Direct RHF	140/1817 (1927)	97/966 (982)	NA
RHF Gradient	695/1252 (1304)	336/653 (678)	
RHF Hessian	7355/7912 (7976)	5046/5363 (5471)	NA
UHF	50/654 (979)	36/432 (726)	
Conv. MP2		1041/1358 (1401)	
Direct MP2		203/2032 (2015)	NA
MP2 Gradient		2389/3747 (4031)	NA
MP4(SDTQ)		10503/10820 (28878)	
SDCI		1104/11365 (14147)	
CCSD	NA	1353/15197 (34939)	
QCISD		1121/11530 (15671)	
CASSCF		FTC - unknown	

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term	35/449 (505)	unable to handle 5-term
Direct RHF	d's and 7-term f's.	244/3181 (3192)	d's and 7-term f's.
RHF Gradient		551/1000 (1042)	
RHF Hessian		2798/3247 (3410)	
UHF			
Conv. MP2			
Direct MP2		NA	
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD		NA	
QCISD		NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	119/1313 (1324)	
Direct RHF	111/1224 (1230)	NA
RHF Gradient	1509/2822 (2840)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

Ethylene, 16 electrons, ^1A_g, (D_{2h}) Basis Set=6-311++G(3df,3pd)
(150 functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (J)	Gaussian 92 (A)	MOLPRO (92.3)
Conv. RHF		50/496 (1313)	
Direct RHF			NA
RHF Gradient			
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term		unable to handle 5-term
Direct RHF	d's and 7-term f's.		d's and 7-term f's.
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

Imidazole, 36 electrons, $^1A'$, Cs, Basis Set=6-311++G**
(143 functions, 6-term d's)

Method	Gaussian 90 (J)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	104/1559 (3286)	87/1215 (2860)	157/2202 (4699)
Direct RHF	282/5637 (5674)	270/4044 (4078)	NA
RHF Gradient	1137/2969 (4434)	1147/2362 (4010)	3154/5357 (7848)
RHF Hessian	10570/12129 (16973)	11774/12989 (17755)	NA
UHF	121/2902 (7204)	118/2718 (6870)	FTC-unknown
Conv. MP2	1349/2907 (4933)	1333/2548 (4470)	322/2524 (5364)
Direct MP2	2627/8264 (8307)	2364/6408 (6447)	NA
MP2 Gradient	2456/8093 (13027)		NA
MP4(SDTQ)			3516/5718 (8874)
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=3-21G,
(144 functions)

Method	Gaussian 90 (J)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. UHF		128/3590 (9984)	
UHF Gradient		890/4480 (10886)	NA
UHF Hessian			
Conv. RHF		69/2821 (8126)	179/3552 (7921)
Direct RHF			
Conv. MP2		2775/5596 (11468)	FTC - unknown
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. UHF			
UHF Gradient			
UHF Hessian			
Conv. RHF			
Direct RHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. UHF		
UHF Gradient		NA
UHF Hessian		
Conv. RHF	NA	
Direct RHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

Isobutene, 32 electrons, $^1A_1$ (C_{2v}), Basis Set=6-311++G**
(144 functions, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		54/707 (1426)	
Direct RHF		123/1971 (1993)	NA
RHF Gradient		490/1197 (1925)	
RHF Hessian		11474/12181 (14366)	NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term	unable to handle 5-term	unable to handle 5-term
Direct RHF	d's	d's	d's
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	NA
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		NA
SDCI			
CCSD	NA	NA	NA
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

Isobutene, 32 electrons, $^1A_1$ (C_{2v}), Basis Set=cc-pVTZ
(232 functions, 5-term d's, 7-term f's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		548/6574 (10655)	
Direct RHF		1301/16921 (16997)	NA
RHF Gradient			
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term		unable to handle 5-term
Direct RHF	d's and 7-term f's		d's and 7-term f's
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	NA
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		NA
SDCI			
CCSD	NA	NA	NA
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.83)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=3-21G
(210 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		184/2389 (2419)	
RHF Gradient		1034/3424 (3451)	
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Direct UHF		NA
RHF Gradient		
RHF Hessian	NA	
Direct RHF		
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 7. IBM RS/6000 340 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD, and CASSCF), each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the Hartree-Fock.
Calculations were performed on a machine with 64 MB of memory and two 2GB Cambex 6200-90 disks running under AIX 3.2 with Release 2.0 of XLF Fortran. Runs were made on an otherwise quiet system.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 15 digits after the decimal point (8 digits in the density).

(b) The ethylene UHF calculation treated the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g. MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals ($3a_g$, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry.
Gaussian 90 requires that RHF calculations which precede certain correlated methods be run in C_1 symmetry. This results in an increase in the ethylene SCF times from 196 seconds (D_{2h}) to 441 seconds (C_1) for the 6-311G** basis; from 1900 seconds (D_{2h}) to 5795 seconds (C_1) for the cc-pVTZ basis; from 1969 seconds (D_{2h}) to 6657 seconds (C_1) for the 6-311++G(3df,3pd) basis.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed but the final energy was approximately 20 millihartrees too high.

Table 8. IBM RS/6000 550 Timings[a]

Ethylene, 16 electrons, D_{2h}, Basis Set=6-311++G**
(74 functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	3/33 (45)	3/32 (65)	5/41 (115)
Direct RHF	11/125 (154)	8/93 (105)	NA
RHF Gradient	29/62 (74)	25/56 (80)	
RHF Hessian	340/373 (404)	347/378 (415)	NA
UHF	8/107 (115)	8/91 (104)	
Conv. MP2	48/81 (89)	47/78 (92)	
Direct MP2	48/173 (182)	47/140 (154)	NA
MP2 Gradient	180/261 (277)	174/252 (283)	NA
MP4(SDTQ)	1044/1128 (1596)	915/947 (1137)	
SDCI	92/1095 (1991)	86/891 (1442)	
CCSD	NA	141/1580 (4970)	
QCISD	112/1262 (2384)	107/1098 (2122)	
CASSCF	34/343 (652)[c]	54/489 (784)[c]	

Method	GAMESS-US 17/6/92	HONDO (8.3)	GAMESS-UK
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 8. IBM RS/6000 550 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the preliminary Hartree-Fock step. Calculations were performed on a machine with 256 MB of memory and 2 GB of SCSI 1 disk running under AIX 3.2 with Release 2.0 of XLF Fortran. Runs were performed at interactive priority but the system had other jobs running.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 15 digits after the decimal point (8 digits in the density).

(b) The ethylene UHF calculation treated the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g. MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals (3_{ag}, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry. The timing for a UHF $^3B_{1g}$ calculation which did exploit D_{2h} symmetry is 295 CPU (347 Wall).
Gaussian 90 requires that RHF calculations which precede certain correlated methods be run in C_1 symmetry. This results in an increase in the ethylene SCF times from 196 seconds (D_{2h}) to 441 seconds (C_1) for the 6-311G** basis; from 1900 seconds (D_{2h}) to 5795 seconds (C_1) for the cc-pVTZ basis; from 1969 seconds (D_{2h}) to 6657 seconds (C_1) for the 6-311++G(3df,3pd) basis.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed but the final energy was approximately 20 millihartrees too high.

Table 9. IBM RS/6000 580 Timings[a]

Ethylene, 16 electrons, $^1A_1$ (D_{2h}), Basis Set=6-311++G**
(74 functions, 6-term d's)[b]

Method	Gaussian 90 (J)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	2 /21 (27)	2/20 (41)	3/25 (41)
Direct RHF	7/84 (90)	4/66 (69)	NA
RHF Gradient	19/40 (49)	16/39 (52)	
RHF Hessian	217/238 (260)	221/241 (257)	NA
UHF	5/63 (77)	5/58 (66)	
Conv. MP2	32/53 (60)	30/50 (59)	1/26 (42)
Direct MP2	32/116 (123)	31/123 (126)	NA
MP2 Gradient	125/178 (190)	116/166 (177)	NA
MP4(SDTQ)	690/741 (1108)	620/640 (963)	26/51 (77)
SDCI	67/738 (2681)	55/569 (897)	
CCSD	NA	101/1008 (3101)	
QCISD	89/886 (3357)	70/702 (1358)	
CASSCF	19/266 (537)[c]	34/310 (543)	

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	3/33 (36)	
Direct RHF	11/140 (143)	NA
RHF Gradient	105/138 (146)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 9. IBM RS/6000 580 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the Hartree-Fock step.
Calculations were performed on a machine with 128 MB of memory and one 1 GB IBM SCSI 2 disk running under AIX 3.2 with Release 2.0 of XLF Fortran. Runs were made on an otherwise quiet system.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 15 digits after the decimal point (8 digits in the density).

(b) The ethylene UHF calculation treated the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g. MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals ($3a_g$, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry. The timing for a UHF $^3B_{1g}$ calculation which did exploit D_{2h} symmetry is 295 CPU (347 Wall).
Gaussian 90 requires that RHF calculations which precede certain correlated methods be run in C_1 symmetry. This results in an increase in the ethylene SCF times from 196 seconds (D_{2h}) to 441 seconds (C_1) for the 6-311G** basis; from 1900 seconds (D_{2h}) to 5795 seconds (C_1) for the cc-pVTZ basis; from 1969 seconds (D_{2h}) to 6657 seconds (C_1) for the 6-311++G(3df,3pd) basis.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed but the final energy was approximately 20 millihartrees too high.

Table 10. HP 730 Timings[a]

Ethylene, 16 electrons, $^1A_1$ (D_{2h}), Basis Set=6-311++G**,
(74 basis functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	4/43 (93)		5/45 (60)
Direct RHF	12/172 (183)		NA
RHF Gradient	37/80 (138)		35/80 (94)
RHF Hessian	529/572 (716)		NA
UHF Total	10/136 (373)		3/47 (62)
Conv. MP2	75/118 (169)		2/47 (60)
Direct MP2	75/247 (256)		NA
MP2 Gradient	296/414 (541)		NA
MP4(SDTQ)	2500/2593 (4419)		54/99 (115)
SDCI	223/2320 (6470)		4/72 (85)
CCSD	NA		6/97 (115)
QCISD	252/2612 (7203)		4/83 (98)
CASSCF	FTC - unknown		3/58 (70)

Method	GAMESS-US 17/6/92	HONDO (8.3)	GAMESS-UK
Conv. RHF	5/55 (78)		
Direct RHF	13/176 (177)		
RHF Gradient	47/102 (120)		
RHF Hessian	936/991 (1206)		
UHF	6/92 (139)		
Conv. MP2	127/182 (217)		
Direct MP2	NA	NA	
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI	102/970 (1190)		
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF	366/3350 (4694)		

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 10. HP 730 Timings (contd)

Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=cc-pVTZ,
(116 basis functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
RHF	31/342 (541)		
Direct RHF			NA
RHF Gradient			
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 17/6/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term		unable to handle 5-term
Direct RHF	d's and 7-term f's.		d's and 7-term f's.
RHF Gradient			
RHF Hessian			
UHF			
ROHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 10. HP 730 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the preliminary Hartree-Fock step. Calculations were performed on a machine with 64 MB of memory and two 1.3 GB fast differential SCSI 2 disks running under HP Fortran 9000, Release 8.05. Runs were made on an otherwise quiet system.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 15 digits after the decimal point (8 digits in the density).

Table 11. HP 735 Timings[a]

Ethylene, 16 electrons, $^1A_1$ (D_{2h}), Basis Set=6-311++G**,
(74 basis functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		3/26 (34)	
Direct RHF		5/82 (89)	NA
RHF Gradient		28/54 (61)	
RHF Hessian		433/459 (482)	NA
UHF Total		8/101 (237)	
Conv. MP2		51/77 (87)	
Direct MP2		51/133 (139)	NA
MP2 Gradient		193/270 (306)	NA
MP4(SDTQ)		1808/1834 (3921)	
SDCI		128/1305 (1648)	
CCSD	NA	238/2642 (6002)	
QCISD		184/1838 (2252)	
CASSCF		36/369 (1661)	

Method	GAMESS-US 17/6/92	HONDO (8.3)	GAMESS-UK
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 11. HP 735 Timings (contd)

Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=cc-pVTZ,
(116 basis functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
RHF		21/210 (322)	
Direct RHF		66/661 (671)	NA
RHF Gradient		281/491 (603)	
RHF Hessian		2811/3021 (3048)	NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 17/6/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle 5-term		unable to handle 5-term
Direct RHF	d's and 7-term f's.		d's and 7-term f's.
RHF Gradient			
RHF Hessian			
UHF			
ROHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 11. HP 735 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the preliminary Hartree-Fock step. Calculations were performed on a machine with 64 MB of memory and fast-wide SCSI 2 disks running under HP Fortran 9000, Release 8.05. Runs were made on an otherwise quiet system.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 15 digits after the decimal point (8 digits in the density).

Table 12. SGI Indigo 50 MHz R4000 Timings[a]

Ethylene, 16 electrons, ^1A_g, D_{2h} point group, Basis Set=6-311++G**
(74 basis functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		5/49 (64)	Not ported to
Direct RHF		14/152 (166)	an SGI
RHF Gradient		56/105 (115)	
RHF Hessian		918/967 (989)	
UHF		13/159 (328)	
Conv. MP2		113/162 (175)	
Direct MP2		120/272 (284)	
MP2 Gradient		431/593 (658)	
MP4(SDTQ)		2831/2880 (3779)	
SDCI		217/2222 (2654)	
CCSD	NA	338/3771 (6961)	
QCISD		266/2709 (3118)	
CASSCF		58/575 (1359)[c]	

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to	
Direct RHF		an SGI	
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	NA
MP2 Gradient	NA	NA	
MP4(SDTQ)	NA		NA
SDCI			
CCSD	NA	NA	NA
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 12. SGI Indigo 50 MHz R4000 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the preliminary Hartree-Fock step.
Unless otherwise noted all SGI Indigo calculations were performed on a 50 MHz R4000 machine with 112 MB of memory, a 1.2 GB SCSI 2 disk under IRIX version 3 with Release 3.10 of SGI Fortran. Runs were made on an otherwise quiet system.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 13 digits after the decimal point (7 - 8 digits in the density).

(b) The ethylene UHF calculation corresponded to the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g.
MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals ($3a_g$, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry. Timings for UHF and ROHF $^3B_{1g}$ wave functions which did exploit D_{2h} symmetry are 295 CPU (347 Wall) and 274 CPU (286 Wall) respectively.
Gaussian 90 requires that RHF calculations which precede certain correlated methods be run in C_1 symmetry. This results in an increase in the ethylene SCF times from 196 seconds (D_{2h}) to 441 seconds (C_1) for the 6-311G** basis; from 1900 seconds (D_{2h}) to 5795 seconds (C_1) for the cc-pVTZ basis; from 1969 seconds (D_{2h}) to 6657 seconds (C_1) for the 6-311++G(3df,3pd) basis.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed but the final energy was approximately 20 millihartrees too high.

Table 13. Cray Y-MP Timings[a]

Ethylene, 16 electrons, ^1A_g, D_{2h} point group, Basis Set=6-311++G**
(74 functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	2/22 (28)	3/27 (85)	2/14 (59)
Direct RHF	5/65 (80)	5/69 (169)	NA
RHF Gradient	15/37 (52)	12/35 (96)	39/53 (154)
RHF Hessian	225/247 (371)	186/213 (354)	NA
UHF	5/61 (67)	7/83 (314)	1/15 (68)
Conv. MP2	12/34 (38)	11/38 (93)	1/15 (62)
Direct MP2	57/79 (136)	37/64 (106)	NA
MP2 Gradient	92/126 (144)	86/124 (221)	NA
MP4(SDTQ)	280/334 (398)	227/254 (1085)	18/32 (151)
SDCI	28/329 (389)	25/281 (741)	1/22 (73)
CCSD	NA	37/435 (1883)	2/28 (105)
QCISD		28/305 (614)	1/26 (115)
CASSCF		56/533 (6313)[c]	1/18 (67)

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a YMP	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA		
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI			
CCSD	NA		
QCISD	NA		
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		/13 (?)
Direct RHF		NA
RHF Gradient		29/42 (?)
RHF Hessian	NA	307/320 (?)
UHF	NA	14 (?)
Conv. MP2	NA	7/20 (?)
Direct MP2		NA
MP2 Gradient	NA	46/66 (?)
MP4(SDTQ)	NA	28/41 (?)
SDCI	NA	1/32 (?)
CCSD	NA	2/31 (?)
QCISD	NA	2/31 (?)
CASSCF	NA	NA

Table 13. Cray Y-MP Timings (contd)

Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=6-311++G(3df,3pd)
(150 functions, 5-term d', 7-term f's)

Method	Gaussian 90 (H)	Gaussian 92 (A)	MOLPRO (92.3)
Conv. RHF			
Direct RHF			NA
RHF Gradient			
RHF Hessian			NA
UHF			
MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a YMP	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA		
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI			
CCSD	NA		
QCISD	NA		
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		10/175 (?)
Direct RHF		NA
RHF Gradient		342/517 (?)
RHF Hessian	NA	6460/6635 (?)
UHF	NA	9/180 (?)
Conv. MP2	NA	91/266 (?)
Direct MP2		NA
MP2 Gradient	NA	697/963 (?)
MP4(SDTQ)	NA	283/458 (?)
SDCI	NA	16/398 (?)
CCSD	NA	23/425 (?)
QCISD	NA	20/390 (?)
CASSCF	NA	NA

Table 13. Cray Y-MP Timings (contd)

Ethylene, 16 electrons, D_{2h},Basis Set=cc-pVTZ
(102 functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (A)	MOLPRO (92.3)
Conv. RHF		12/116 (630)	18/122 (635)
Direct RHF		21/252 (1099)	NA
RHF Gradient		54/170 (771)	
RHF Hessian		1620/1736 (2832)	NA
UHF			
MP2			4/126 (359)
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			3/142 (588)
CCSD	NA		
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a YMP	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA		
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI			
CCSD	NA		
QCISD	NA		
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		8/123 (?)
Direct RHF		NA
RHF Gradient		225/348 (?)
RHF Hessian	NA	2696/2819 (?)
UHF	NA	7/125 (?)
Conv. MP2	NA	32/155 (?)
Direct MP2		NA
MP2 Gradient	NA	455/610 (?)
MP4(SDTQ)	NA	106/229 (?)
SDCI	NA	6/208 (?)
CCSD	NA	8/207 (?)
QCISD	NA	7/196 (?)
CASSCF	NA	NA

Table 13. Cray Y-MP Timings (contd)

Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=3-21G,
(144 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
UHF		80/2234 (4647)	
RHF Gradient			
RHF Hessian			NA
Conv. RHF		63/2589 (5392)	
Direct RHF		18/942 (1040)	
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 13. Cray Y-MP Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-teration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the SCF step.
Unless otherwise noted all Cray Y-MP calculations were performed on a Y-MP/864 running Unicos 6.1 at the National Energy Research Supercomputer Center. Runs were made during off hours at interactive priorities. G90 and ACES II timings were obtained on the Florida State University Supercomputer Center Y-MP/832 running Unicos 7.0.2. All FSU runs were made from a batch queue. Wall clock times for the FSU runs do not include queue wait time.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 13 digits after the decimal point (7 - 8 digits in the density).

(b) The ethylene UHF calculation corresponded to the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g. MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals (3_{ag}, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry. Timings for a UHF $^3B_{1g}$ calculation which did exploit D_{2h} symmetry are 295 CPU (347 Wall) and 274 CPU (286 Wall) respectively.
Gaussian 90 requires that RHF calculations which precede certain correlated methods be run in C_1 symmetry. This results in an increase in the ethylene SCF times from 196 seconds (D_{2h}) to 441 seconds (C_1) for the 6-311G** basis; from 1900 seconds (D_{2h}) to 5795 seconds (C_1) for the cc-pVTZ basis; from 1969 seconds (D_{2h}) to 6657 seconds (C_1) for the 6-311++G(3df,3pd) basis.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed but the final energy was approximately 20 millihartrees too high. The total times reported have been increased by the amount necessary to perform a SCF calculation.

Table 14. Cray C90 Timings[a]

Ethylene, 16 electrons, ^1A_g, D_{2h} point group, Basis Set=6-311++G**
(74 functions, 6-term d's)[b]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)[g]
Conv. RHF		2/21 (263)	1/8 (26)
Direct RHF		3/33 (64)	NA
RHF Gradient		19/40 (207)	26/34 (54)
RHF Hessian		117/138 (278)	NA
UHF		4/53 (301)	1/9 (100)
Conv. MP2		13/34 (127)	1/9 (57)
Direct MP2		12/45 (145)	NA
MP2 Gradient		51/85 (371)	NA
MP4(SDTQ)		150/171 (953)	11/19 (170)
SDCI		18/203 (2329)	1/14 (173)
CCSD		26/310 (3593)	1/20 (56)
QCISD		18/197 (893)	1/16 (128)
CASSCF		44/393 (12387)[c]	1/12 (36)

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	1/13 (73)	Not ported to a C90	
Direct RHF	8/98 (130)		
RHF Gradient	20/33 (185)		
RHF Hessian	171/184 (1,198)		
UHF	1/20 (242)		
Conv. MP2	26/47 (417)		
Direct MP2	NA		
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI	26/257 (1883)[d]		
CCSD	NA		
QCISD	NA		
CASSCF	278/279 (14763)[d]		

Method	DISCO (1.82)	ACES II
Conv. RHF	1/19 (101)	
Direct RHF	3/37 (60)	NA
RHF Gradient	31/50 (77)	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	15/52 (76)	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

Ethylene, 16 electrons, D_{2h}, Basis Set=cc-pVTZ
(116 functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (A)	MOLPRO (92.3)[g]
Conv. RHF		6/63 (138)	8/80 (176)
Direct RHF		13/132 (152)	NA
RHF Gradient		27/90 (169)	NA
RHF Hessian		1019/1157 (1419)	NA
UHF		7/89 (297)	6/82 (283)
Conv. MP2		54/117 (336)	1/81 (156)
Direct MP2		54/186 (351)	NA
MP2 Gradient		291/408 (739)	NA
MP4(SDTQ)		774/837 (8334)	42/122 (368)
SDCI		104/1203 (2491)	2/93 (630)
CCSD		145/1655 (10101)	4/108 (479)
QCISD		118/1242 (3749)	4/120 (517)
CASSCF		FTC-ND	3/93 (501)

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a C90	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA		
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI			
CCSD	NA		
QCISD	NA		
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	3/263 (352)	
Direct RHF	34/339 (394)	NA
RHF Gradient	482/745 (1176)	
RHF Hessian		
UHF		
Conv. MP2		
Direct MP2		NA
MP2 Gradient		
MP4(SDTQ)		
SDCI		
CCSD		
QCISD		
CASSCF		NA

Table 14. Cray C90 Timings (contd)

Ethylene, 16 electrons, D_{2h}, Basis Set=6-311++G(3df,3pd)
(150 functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		14/135 (341)	
Direct RHF		14/173 (269)	NA
RHF Gradient			
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a C90	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA		
MP2 Gradient	NA		
MP4(SDTQ)	NA		
SDCI			
CCSD	NA		
QCISD	NA		
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian		
UHF		
Conv. MP2		
Direct MP2		NA
MP2 Gradient		
MP4(SDTQ)		
SDCI		
CCSD		
QCISD		
CASSCF		NA

Table 14. Cray C90 Timings (contd)

Imidazole, 36 electrons, $^1A'$, Cs, Basis Set=6-311++G**
(143 functions, 6-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		39/542 (1505)	
Direct RHF		17/256 (945)	NA
RHF Gradient		24/564 (2115)	
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)		14046 (60358)	
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a C90	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

Isobutene, 32 electrons, C_{2v}, Basis Set=6-311++G**,
(143 functions, 6-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
UHF		23/303 (627)	
RHF Gradient			
RHF Hessian			NA
Conv. RHF			
Direct RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF		Not ported to a C90	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=3-21G,
(144 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
UHF			
RHF Gradient			
RHF Hessian			NA
Conv. RHF		57/2325 (17212)	
Direct RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF		Not ported to a C90	
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=3-21G
(210 functions)[e]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		16/209 (638)	
RHF Gradient		60/269 (677)	
RHF Hessian		13103/13312 (20935)	NA
Conv. RHF			
Conv. MP2			
Direct MP2		1428/1637 (1740)[f]	NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=6-31G**
(390 functions)[e]

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		85/1111 (1248)	
RHF Gradient		317/1428 (1629)	
RHF Hessian		68140/69251 (107603)	NA
Direct MP2		17804/18915 (48001)[f]	NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=aug-cc-pVDZ
(630 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		6341/82430 (NA)	
RHF Gradient			
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Direct MP2			
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD			
QCISD			
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table 14. Cray C90 Timings (contd)

(a) All times are in seconds. CPU times are the sum of the "user + system" contributions. Wall clock times are given in parentheses. For the iterative methods (RHF, UHF, SD-CI, QCISD and CASSCF) each entry consists of a trio of numbers: "CPU-time-per-iteration/total-CPU (total-wall-clock)". The "CPU-time-per-iteration" for the conventional SCF methods was defined as the total run time (integrals + SCF) divided by the number of iterations. These values are intended to facilitate comparison with direct Hartree-Fock methods. For other methods the leftmost entry corresponds to the incremental time for the method. For example, the MP2 entry preceding the slash is the total run time minus the time needed for the preliminary Hartree-Fock step. All Cray C90 calculations were performed on a C90/16256 (16 processor, 256 Mwords) running Unicos 7.C at the National Energy Research Supercomputer Center.
NA: not available with this program.
FTC-ND: Failed to complete - not enough disk space.
FTC-unknown: Failed to complete for unknown reasons.
SCF calculations were converged to approximately 13 digits after the decimal point (7 - 8 digits in the density).

(b) The ethylene UHF calculation corresponded to the $\pi \rightarrow \pi^*$ ($^3B_{1u}$) state. The ethylene ground state is ^1A_g. MP2, MP4, CISD and QCISD calculations involved all electrons, i.e., there were no "core" electrons. The CAS configuration list contains 8 CSF's in D_{2h} symmetry and was generated with 4 electrons in 4 orbitals ($3a_g$, $1b_{3u}$, $1b_{2g}$, $2b_{1u}$). This configuration list is sufficient to allow ethylene to dissociate into two singlet methylenes. The time reported includes the time required to compute the integrals and solve the CAS equations using the canonical RHF orbitals as the starting guess.
The default INDO initial guess for ethylene's open shell calculations did not pick up the $\pi \rightarrow \pi^*$ $^3B_{1u}$ state. If the ordering of the initial guess orbitals was corrected using an ALTER command the calculation died with a complaint that symmetry was being broken. Thus, it was necessary to run these calculations with the NOSYMM option, which ignored the available D_{2h} symmetry.
Gaussian 90 requires that RHF calculations which precede certain correlated methods be run in C_1 symmetry.

(c) The Gaussian CAS calculation using RHF canonical orbitals aborted with an error message saying that the initial guess was too poor. After massaging the initial guess, the calculation could be made to proceed but the final energy was approximately 20 millihartrees too high. The total times reported have been increased by the amount necessary to perform a SCF calculation.

(d) GAMESS and HONDO could not do a combined RHF + SDCI or RHF + CAS in one job step. In order to make the total time comparable to what is reported for other programs, the time to perform the RHF calculation (exclusive of the 2-el. integral time) was simply added to the SDCI or CAS time.

(e) The 18-crown-6 MP2 calculations did not treat the carbon and oxygen core electrons.

(f) By increasing the amount of memory for Gaussian 92 MP2 calculations on 18-crown-6 it was possible to reduce the CPU time to 836 sec. for the 3-21G basis (4 MW to 10 MW) and 7782 sec. for the 6-31G** basis (10 MW to 30 MW).

(g) MOLPRO ran in YMP mode.

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HONDO 8.3: Contributors to this version include: M. Dupuis, A. Marquez, S. Chin and E. Hollauer, IBM Corporation, Department MLM/428, Neighborhood Road, Kingston, NY 12401. Contributors to previous versions include: S. A. Maluendes, A. Farazdel, S. P. Karna, P. Mougenot, C. Daniel, R. Lindh, K. Dyall, B. Liu, J. D. Watts, H. O. Villar, G.J.B. Hurst, M. Schmidt, M. S. Gordon, S. Elbert, W. Stevens, H. Basch, T. Takada, D. Spangler, J. J.Wendoloski, B. Brooks, W. Laidig, P. Saxe, M. Dupuis, J. Rys, and H. F. King.

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Appendix A

Molecular Coordinates

Appendix A

Molecular Coordinates

Table A.1. Ethylene, 6-311++G** Basis (Nuclear Rep. = 33.663966)

Z-matrix Coordinates (Å and °)

Atom	Center A	Distance	Center B	Angle	Center C	Dihedral
C						
C	1	RCC				
H	2	RCH	1	ANG1		
H	2	RCH	1	ANG1	3	180.0
H	1	RCH	2	ANG1	3	0.0
H	1	RCH	2	ANG1	3	180.0

Variable	Value
RCC	1.3185
RCH	1.0766
ANG1	121.6612

Cartesian Coordinates in Å

Atom	At. No.	X	Y	Z
C	6	0.0	0.0	0.659250
C	6	0.0	0.0	-0.659250
H	1	0.0	0.916366	-1.224352
H	1	0.0	-0.916366	-1.224352
H	1	0.0	0.916366	1.224352
H	1	0.0	-0.916366	1.224352

Table A.2. Ethylene, cc-pVTZ Basis (Nuclear Rep. = 33.756981)

Z-matrix Coordinates (Å and °)

Atom	Center A	Distance	Center B	Angle	Center C	Dihedral
C						
C	1	RCC				
H	2	RCH	1	ANG1		
H	2	RCH	1	ANG1	3	180.0
H	1	RCH	2	ANG1	3	0.0
H	1	RCH	2	ANG1	3	180.0

Variable	Value
RCC	1.3144
RCH	1.0741
ANG1	121.6537

Cartesian Coordinates in Å

Atom	At. No.	X	Y	Z
C	6	0.0	0.0	0.657200
C	6	0.0	0.0	-0.657200
H	1	0.0	0.914312	-1.220870
H	1	0.0	-0.914312	-1.220870
H	1	0.0	0.914312	1.220870
H	1	0.0	-0.914312	1.220870

Table A.3. Ethylene, 6-311++G(3df,3pd) Basis (Nuclear Rep. = 33.756981)

Z-matrix Coordinates (Å and °)

Atom	Center A	Distance	Center B	Angle	Center C	Dihedral
C						
C	1	RCC				
H	2	RCH	1	ANG1		
H	2	RCH	1	ANG1	3	180.0
H	1	RCH	2	ANG1	3	0.0
H	1	RCH	2	ANG1	3	180.0

Variable	Value
RCC	1.3144
RCH	1.0741
ANG1	121.6537

Cartesian Coordinates in Å

Atom	At. No.	X	Y	Z
C	6	0.0	0.0	0.657200
C	6	0.0	0.0	-0.657200
H	1	0.0	0.914312	-1.220870
H	1	0.0	-0.914312	-1.220870
H	1	0.0	0.914312	1.220870
H	1	0.0	-0.914312	1.220870

Table A.4. Isobutene, 6-311++G** and cc-pVTZ Basis Sets (Nuclear Rep. = 120.116981)

Z-matrix Coordinates (Å and °)

Atom	Center A	Distance	Center B	Angle	Center C	Dihedral
C						
C	1	RCC1				
C	1	RCC2	2	CCC		
C	1	RCC2	2	CCC	3	180.0
H	2	RCH1	1	CCH1	3	0.0
H	2	RCH1	1	CCH1	4	0.0
H	3	RCH2	1	CCH2	2	-DIHE3
H	3	RCH2	1	CCH2	2	DIHE3
H	3	RCH3	1	CCH3	2	0.0
H	4	RCH2	1	CCH2	2	DIHE3
H	4	RCH2	1	CCH2	2	-DIHE3
H	4	RCH3	1	CCH3	2	0.0

Variable	Value
RCC1	1.3224
RCC2	1.5073
CCC	122.2419
RCH1	1.0766
CCH1	121.6245
RCH2	1.0878
CCH2	110.5765
DIHE3	120.8021
RCH3	1.0836
CCH3	111.7128

Cartesian Coordinates in Å

Atom	At. No.	X	Y	Z
C	6	0.0	0.0	0.127225
C	6	0.0	0.0	1.449625
C	6	0.0	1.274879	-0.676912
C	6	0.0	-1.274879	-0.676912
H	1	0.0	0.914312	2.014140
H	1	0.0	-0.914312	2.014140
H	1	-0.874748	1.320027	-1.321960
H	1	0.874748	1.320027	-1.321960
H	1	0.0	2.151026	-0.039295
H	1	-0.874748	-1.320027	-1.321960
H	1	0.874748	-1.320027	-1.321960
H	1	0.0	-2.151026	-0.039295

Table A.5. Imidazole, 6-311++G** and cc-pVTZ Basis Sets (Nuclear Rep. = 164.969257)

Z-matrix Coordinates (Å and °)

Atom	Center A	Distance	Center B	Angle	Center C	Dihedral
N						
C	1	RN1C1				
N	2	RC1N2	1	ANG1		
C	3	RN2C2	2	ANG2	1	0.0
C	4	RC2C3	3	ANG3	2	0.0
H	2	RC1H1	1	ANG4	5	180.0
H	3	RN2H2	2	ANG5	6	0.0
H	4	RC2H3	3	ANG6	7	0.0
H	5	RC3H4	4	ANG7	8	0.0

Variable	Value
RN1C1	1.2878
RC1N2	1.3499
ANG1	112.128
RN2C2	1.3725
ANG2	106.7994
RC2C3	1.3507
ANG3	105.2405
RC1H1	1.0713
ANG4	125.5984
RN2H2	0.9919
ANG5	126.3916
RC2H3	1.0684
ANG6	122.5807
RC3H4	1.0697
ANG7	128.0903

Cartesian Coordinates in Å

Atom	At. No.	X	Y	Z
N	7	-0.741162	-0.964252	0.0
C	6	-1.075551	0.279377	0.0
N	7	0.0	1.095109	0.0
C	6	1.110055	0.287933	0.0
C	6	0.630803	-0.974885	0.0
H	1	-2.078690	0.655404	0.0
H	1	-0.013611	2.086916	0.0
H	1	2.104819	0.677707	0.0
H	1	1.183777	-1.890569	0.0

Table A.6. Caffeine, 3-21G and 6-31G** Basis Sets (Nuclear Rep. = 916.319741)

Z-matrix Coordinates (Å and °)

Atom	Center A	Distance	Center B	Angle	Center C	Dihedral
N						
C	1	RN1C1				
N	2	RC1N2	1	ANG1		
C	3	RN2C2	2	ANG2	1	0.
C	4	RC2C3	3	ANG3	2	0.
C	3	RN3C6	2	ANG5	1	180.
H	6	RC6H7	3	ANG6	2	DIHE1
H	6	RC6H8	3	ANG7	2	DIHE2
H	6	RC6H9	3	ANG8	2	DIHE3
C	4	RC4C10	5	ANG9	2	180.
O	10	RC10O11	4	ANG10	3	0.
N	10	RC10N12	4	ANG11	3	180.
C	12	RN12C13	10	ANG12	4	180.
H	13	RC13H14	12	ANG13	10	DIHE4
H	13	RC13H15	12	ANG14	10	DIHE5
H	13	RC13H16	12	ANG15	10	DIHE6
C	12	RN12C17	10	ANG16	4	0.
O	17	RC17O18	12	ANG17	10	180.
N	17	RC17N19	12	ANG18	10	0.
C	19	RN19C20	17	ANG19	12	180.
H	20	RC20H21	19	ANG20	10	DIHE11
H	20	RC20H22	19	ANG21	10	DIHE12
H	20	RC20H23	19	ANG22	10	DIHE13

Variable	Value
RN1C1	1.3087
RC1N2	1.3489
ANG1	114.5714
RN2C2	1.3945
ANG2	104.4811
RC2C3	1.3626
ANG3	106.2146
RN3C6	1.47
ANG5	128.9068
RC6H7	1.0807
ANG6	109.9109
DIHE1	299.5553
RC6H8	1.0807
ANG7	109.904
DIHE2	60.552
RC6H9	1.0765
ANG8	107.0593
DIHE3	180.044
RC4C10	1.424
ANG9	122.4338
RC10O11	1.2228
ANG10	126.254
RC10N12	1.3956
ANG11	111.7592
RN12C13	1.4778

Table A.6. Caffeine, 3-21G and 6-31G** (contd)

Variable	Value
ANG12	118.0931
RC13H14	1.0746
ANG13	107.4187
DIHE4	360.1356
RC13H15	1.0792
ANG14	109.572
DIHE5	120.4648
RC13H16	1.0793
ANG15	109.5885
DIHE6	239.811
RN12C17	1.3935
ANG16	126.8636
RC17O18	1.2147
ANG17	121.2827
RC17N19	1.3766
ANG18	117.0862
RN19C20	1.4719
ANG19	118.5543
RC20H21	1.0797
ANG20	109.7104
DIHE11	300.1115
RC20H22	1.0797
ANG21	109.7318
DIHE12	59.782
RC20H23	1.0768
ANG22	107.5607
DIHE13	179.9684

		Cartesian Coordinates in Å		
Atom	At. No.	X	Y	Z
N	7	1.228476	-2.127881	-0.000008
C	6	2.386568	-1.518357	-0.000001
N	7	2.311572	-0.171544	0.000005
C	6	0.944076	0.101558	0.000001
C	6	0.314717	-1.106990	-0.000007
C	6	3.402380	0.813869	0.000013
H	1	4.011462	0.688664	0.883900
H	1	4.010282	0.689803	-0.884845
H	1	2.946841	1.789233	0.000806
C	6	0.230834	1.334060	0.000003
O	8	0.722107	2.453833	0.000010
N	7	-1.150153	1.132633	-0.000003
C	6	-2.026933	2.322234	-0.000001
H	1	-1.392426	3.189506	-0.002421
H	1	-2.656429	2.307381	-0.876464
H	1	-2.653224	2.310145	0.878920
C	6	-1.816465	-0.091242	-0.000011
O	8	-3.029799	-0.148835	-0.000016
N	7	-1.039749	-1.227789	-0.000013
C	6	-1.710197	-2.538129	-0.000022
H	1	-2.330029	-2.630036	0.879247
H	1	-2.331588	-2.629653	-0.878229
H	1	-0.944250	-3.294979	-0.000588

Table A.7. 18-crown-6, 3-21G Basis (Nuclear Rep. = 1485.9218009)

Atom	Cartesian Coordinates in Å X	Y	Z
O	-2.852953	-2.134361	-0.141930
O	2.852953	2.134361	0.141930
C	-1.614812	-1.627784	0.360229
C	1.614812	1.627784	-0.360229
C	-0.525733	-2.438177	-0.335927
C	0.525733	2.438177	0.335927
O	0.698049	-2.066187	0.295152
O	-0.698049	2.066187	-0.295152
C	1.828020	-2.675136	-0.324822
C	-1.828020	2.675136	0.324822
C	3.061549	-2.086443	0.352453
C	-3.061549	2.086443	-0.352453
O	3.396054	-0.900601	-0.361791
O	-3.396054	0.900601	0.361791
C	4.101957	0.057978	0.421232
C	-4.101957	-0.057978	-0.421232
C	3.979847	1.395299	-0.304190
C	-3.979847	-1.395299	0.304190
H	-1.515266	-0.533904	0.126301
H	1.515266	0.533904	-0.126301
H	-1.572378	-1.776284	1.470718
H	1.572378	1.776284	-1.470718
H	-0.700807	-3.538236	-0.205824
H	0.700807	3.538236	0.205824
H	-0.489048	-2.195589	-1.429810
H	0.489048	2.195589	1.429810
H	1.790377	-3.784455	-0.161639
H	-1.790377	3.784455	0.161639
H	1.834505	-2.451386	-1.4240991
H	-1.834505	2.451386	1.424099
H	3.922018	-2.801991	0.272858
H	-3.922018	2.801991	-0.272858
H	2.845607	-1.867358	1.430933
H	-2.845607	1.867358	-1.430933
H	3.666580	0.133909	1.452229
H	-3.666580	-0.133909	-1.452229
H	5.177195	-0.255057	0.488254
H	-5.177195	0.255057	-0.488254
H	4.851875	2.050672	-0.036884
H	-4.851875	-2.050672	0.036884
H	3.936261	1.235602	-1.413295
H	-3.936261	-1.235602	1.413295

Appendix B

Iteration Count

Appendix B

Iteration Count

Table B.1. Ethylene, 16 electrons, ^1A_g, $D_{2h\ point\ group}$, Basis Set=6-311++G** (74 functions, 6-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	11	10	9
Direct RHF	12	15	NA
RHF Gradient	11	10	9
RHF Hessian	11	10	NA
UHF	13	12	15
Conv. MP2	11	11	9
Direct MP2	12	11	NA
MP2 Gradient	11	11	NA
MP4(SDTQ)	11	11	9
SDCI	11-SCF, 11-CI	10-SCF,10-CI	9-SCF,7-CI
CCSD	NA	10-SCF,11-CC	9-SCF, 9-CC
QCISD	11-SCF,10-CI	10-SCF,10-CI	9-SCF,9-CI
CASSCF	9-CAS	10-SCF,9-MC	9-SCF,4-CAS

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	12	13	12
Direct RHF	13	13	
RHF Gradient	12	13	12
RHF Hessian	12	13	
UHF	15	15	
Conv. MP2	12	13	
Direct MP2	NA	NA	
MP2 Gradient	12	13	
MP4(SDTQ)	NA	13	
SDCI	12-SCF, 9-CI	13-SCF, 10-CI	
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF	12-SCF, 10-CAS	13-SCF, 10-MC	

Method	DISCO (1.82)	ACES II
Conv. RHF	13	
Direct RHF	13	NA
RHF Gradient	13	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	13	NA
MP2 Gradient	13	
MP4(SDTQ)	NA	
SDCI	NA	14-CI
CCSD	NA	11-CC
QCISD	NA	11-CI
CASSCF	NA	NA

Table B.2. Ethylene, 16 electrons, ^1A_g, $D_{2h\ point\ group}$, Basis Set=cc-pVTZ (102 functions, 7-term f's, 5-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
RHF	11	10	10
Direct RHF	13	10	NA
RHF Gradient	11	10	NA
RHF Hessian	11	10	NA
UHF	13	12	13
MP2	11	10	10
Direct MP2	13	10	NA
MP2 Gradient	11	10	NA
MP4(SDTQ)	11	10	10
SDCI	11-SCF, 11-CI	11-SCF, 11-CI	10-SCF, 7-CI
CCSD	NA	10-SCF, 11-CC	10-SCF, 8-CC
QCISD	11-SCF, 10-CI	11-SCF, 10-QCI	10-SCF, 9-QCI
CASSCF			10-SCF, 4 MC

Method	GAMESS-US 6/17/92	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle	13	unable to handle
Direct RHF	5-term d's, 7-term f's	13	5-term d's, 7-term f's
RHF Gradient		13	
RHF Hessian		13	
UHF			
Conv. MP2			
Direct MP2		NA	
MP2 Gradient			
MP4(SDTQ)			
SDCI			
CCSD		NA	
QCISD		NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	11	16
Direct RHF	11	NA
RHF Gradient	11	16
RHF Hessian	NA	16
UHF	NA	19
Conv. MP2	NA	
Direct MP2	11	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	11
QCISD	NA	11
CASSCF	NA	NA

Table B.3. Ethylene, 16 electrons, ^1A_g (D_{2h}), Basis Set=6-311++G(3df,3pd) (150 functions, 7-term f's)

Method	Gaussian 90 (H)	Gaussian 92 (A)	MOLPRO (92.3)
RHF	11	10	
Direct RHF	12	11	NA
RHF Gradient	11	10	
RHF Hessian	11	10	NA
UHF Total	14	13	
MP2	11	10	
Direct MP2	12	11	NA
MP2 Gradient	11	10	
MP4(SDTQ)	11	10	
SDCI	FTC-ND	FTC-ND	
CCSD	NA	FTC-ND	
QCISD	FTC-ND	FTC-ND	
CASSCF	FTC-ND	FTC-ND	

Method	GAMESS-US	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF	unable to handle		
Direct RHF	5-term d's		
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	13	
Direct RHF	13	NA
RHF Gradient	13	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	13	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table B.4. Imidazole, 36 electrons, $^1A'$, Cs, Basis Set=6-311++G** (143 functions, 6-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	15	14	14
Direct RHF	20	15	
RHF Gradient	15	14	
RHF Hessian	15	14	NA
UHF	24	23	
MP2	15	14	
Direct MP2	20	15	NA
MP2 Gradient	15	14	
MP4(SDTQ)	15	15	
SDCI	15-SCF	14-SCF	
CCSD	NA	14-SCF	
QCISD	15-SCF	14-SCF	
CASSCF	15-SCF	14-SCF	

Method	GAMESS-US	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF	9	
Direct RHF	9	NA
RHF Gradient	9	
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2	9	NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table B.5. Imidazole, 36 electrons, $^1A'$, Cs, Basis Set=cc-pVTZ (206 functions, 6-term d's, 7-term f's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			NA
UHF			
MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.3)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table B.6. Isobutene, 32 electrons, C_{2v}, Basis Set=6-311++G** (148 functions, 6-term d's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF	14	13	
Direct RHF	25	16	NA
RHF Gradient	14	13	
RHF Hessian	14	13	NA
UHF	17		
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table B.7. Isobutene, 32 electrons, C_{2v}, Basis Set=cc-pVTZ (232 functions, 5-term d's, 7-term f's)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Conv. RHF		12	
Direct RHF	15	13	NA
RHF Gradient			
RHF Hessian			NA
UHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
Conv. RHF			
Direct RHF			
RHF Gradient			
RHF Hessian			
UHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Conv. RHF		
Direct RHF		NA
RHF Gradient		
RHF Hessian	NA	
UHF	NA	
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF	NA	NA

Table B.8. Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=3-21G (144 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
UHF	42	41	
UHF Gradient	42	41	
UHF Hessian	42	41	NA
Conv. RHF	41	53	18
Direct RHF			NA
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US 6/17/92	HONDO (8.1)	GAMESS-UK (2)
UHF			
UHF Gradient			
UHF Hessian			
Conv. RHF			
Direct RHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
UHF		
UHF Gradient		
UHF Hessian		
Conv. RHF		
Direct RHF		
Conv. MP2		
Direct MP2	NA	NA
MP2 Gradient		
MP4(SDTQ)	NA	
SDCI		
CCSD	NA	NA
QCISD	NA	NA
CASSCF		

Table B.9. Caffeine, $C_8H_9O_2N_4$, 101 electrons, C1, Basis Set=6-31G** (255 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct UHF	34	26	NA
RHF Gradient			
RHF Hessian			NA
ROHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.1)	GAMESS-UK (2)
Direct UHF			
RHF Gradient			
RHF Hessian			
ROHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Direct UHF		
RHF Gradient		
RHF Hessian		
ROHF		
Conv. MP2		
Direct MP2	NA	NA
MP2 Gradient		
MP4(SDTQ)	NA	
SDCI		
CCSD	NA	NA
QCISD	NA	NA
CASSCF		

Table B.10. 18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=3-21G (210 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		13	NA
RHF Gradient		13	
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Direct RHF		
RHF Gradient		
RHF Hessian		
Conv. RHF		
Conv. MP2		
Direct MP2	NA	NA
MP2 Gradient		
MP4(SDTQ)	NA	
SDCI		
CCSD	NA	NA
QCISD	NA	NA
CASSCF		

Table B.11. 18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=6-31G**(390 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		13	NA
RHF Gradient		13	
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Direct RHF		NA
RHF Gradient		
RHF Hessian		
Conv. RHF		
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF		

Table B.12. 18-crown-6, $C_{12}H_{24}O_6$, 144 electrons, C_i, Basis Set=aug-cc-pVDZ (630 functions)

Method	Gaussian 90 (H)	Gaussian 92 (C)	MOLPRO (92.3)
Direct RHF		>13	NA
RHF Gradient			
RHF Hessian			NA
Conv. RHF			
Conv. MP2			
Direct MP2			NA
MP2 Gradient			NA
MP4(SDTQ)			
SDCI			
CCSD	NA		
QCISD			
CASSCF			

Method	GAMESS-US	HONDO (8.1)	GAMESS-UK (2)
Direct RHF			
RHF Gradient			
RHF Hessian			
Conv. RHF			
Conv. MP2			
Direct MP2	NA	NA	
MP2 Gradient			
MP4(SDTQ)	NA		
SDCI			
CCSD	NA	NA	
QCISD	NA	NA	
CASSCF			

Method	DISCO (1.82)	ACES II
Direct RHF		NA
RHF Gradient		
RHF Hessian		
Conv. RHF		
Conv. MP2	NA	
Direct MP2		NA
MP2 Gradient	NA	
MP4(SDTQ)	NA	
SDCI	NA	
CCSD	NA	
QCISD	NA	
CASSCF		

Appendix C

Molecular Energies (Hartrees)

Appendix C

Molecular Energies (Hartrees)

Ethylene

Method	6-311++G**	cc-pVTZ	6-311++G(3df,3pd)
RHF	-78.056131	-78.064420	-78.063304
UHF	-77.927107	-77.751241	-77.752705
MP2	-78.387513	-78.429760	-78.444065
MP4	-78.427097	-78.469627	
SDCI	-78.386763	-78.422819	
CCSD	-78.416244	-78.455169	
CASSCF	-78.108478	-78.116214	

Isobutene

Method	6-311++G**	cc-pVTZ
RHF	-156.153387	-156.169067
UHF	-156.021366	
MP2	-156.830902	
MP4		
SDCI		
CCSD		
CASSCF		

Imidazole

Method	6-311++G**	cc-pVTZ
RHF	-224.874971	
UHF	-224.714239	
MP2	-225.745074	
MP4		
SDCI		
CCSD		
CASSCF		

Caffeine

Method	3-21G	6-31G**
UHF	-671.906322	
RHF	-671.498350	
MP2	-672.902242	
MP4		
SDCI		
CCSD		
CASSCF		

18-crown-6

Method	3-21G	6-31G**	aug-cc-pVDZ
RHF	-912.371076	-917.520266	Failed to Conv.
UHF			
MP2		-920.281140	
MP4			
SDCI			
CCSD			
CASSCF			

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