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Conclusions

By using a nongradient minimization method described by *Hooke* and *Jeeves* [7] and a simple scheme for randomly shuffling parameter sequencies, efficient conformation sampling can be achieved. In contrast to conventional conformation-search procedures, we use the same starting geometry in each run and modify the optimizing tool. To search the entire conformation space, defined in terms of flexible dihedral angles, the energy must be high in the beginning of the optimization process and a large rotational increment must be applied. Instead of randomly collecting local minima, each PMPP cycle leads to vastly different areas of dihedral angle space. By gradually reducing parameter increments, a high probability of hitting a chemically significant energy minimum is ensured.

The method can be applied to any kind of flexible molecular system. When optimizing coordination spheres, the number of variables is increased by 6 degrees of freedom for each independent ligand molecule. Since optimization is often connected with tight molecular folding, omitting H-interactions in the first phase helps to avoid ligand conformations unfit for coordination. The sampling results are not very sensitive upon variations of bond lengths and bond angles which remain fixed during optimization. Our program is in part based on a general molecular-mechanics program provided by Prof. *M. Dobler*, ETHZ, which is greatfully acknowledged. It is written in PASCAL and its central part, the energy calculation, in OCCAM. Computations were done on a workstation *Apollo DN 3000*, powered up by a transputer board with 4 parallel *T 800* processors.

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Thomas Bally[a])*, **Pierre-Alain Carrupt**[b]), and **Jacques Weber**[c])

Abstract. Ten different benchmark tests have been performed for different versions of the *Gaussian* as well as for the *Cadpac ab initio* program package on nine different computers ranging from vector supercomputers to workstations. The test jobs form a set representative of the most frequent applications of *ab initio* quantum chemistry, *i.e.* single point and gradient calculations at the SCF and MP2 levels of theory as well as SCF second derivative calculations for both closed-shell and open-shell species (the molecule of bicyclobutane and its radical cation calculated using the 6-31G* basis set). The relative performances of the different programs and machines exhibit considerable variation as a function of the type of calculation and the present results should prove useful for the selection of the most efficient program and computer for a given application. Notably, modern RISC-based workstations were found to be similar or sometimes even superior in performance to most mainframes for calculations of the type represented by the test jobs.

Introduction

Quantum chemical calculations have undoubtedly become a major component of computational chemistry, with a vast number of applications devoted to a broad range of compounds and properties [1]. Together with the impressive recent developments in computer hardware, the growing availability of adequate program packages is certainly to a good extent at the origin of this increasing popularity, although the use of these programs as 'black boxes' is generally not possible.

Among the commonly used quantum chemical models, the *ab initio* techniques occupy an important place, since they attempt to find solutions to the self consistent mean-field (SCF) problem of electronic structure 'from first principles' and subsequently introduce corrections to those by treating the problem of electron correlation by various techniques [2]. In contrast to the so-called semiempirical methods, they are apparently free of parameters although one should of course not underestimate the degree of arbitrariness introduced by the choice of the one-electron basis set in the SCF calculation and the N-electron basis set in post-SCF treatments.

Methodological aspects of the *ab initio* approach to electronic structure theory have recently been outlined in several excellent textbooks [1][3], which also offer guidance as to the best strategy to adopt in calculating different molecular properties with maxi-

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mum accuracy [3][4]. Hence, this will not be the purpose of the present account. Rather, and more prosaically, we would like to present some information to practitioners of *ab initio* calculations about the relative performance of two popular program packages running on a broad range of computers in an attempt to help them to select the most adequate program and/or hardware platform for a given application, provided they have such a choice.

It is well known within the community of computational chemists that the *Gaussian* series of programs [5–8] is beyond any doubt the most popular *ab initio* program package available today. Its user-friendly input makes it straightforward to prepare calculations for a broad range of computers even in cases of molecules with intricate structure such as polycyclic compounds. This process can be facilitated to an even higher degree by the graphical input interfaces for *Gaussian* which are provided by many molecular modelling programs. In addition, very efficient and robust algorithms have been implemented in the latest versions (88 and 90) for routine tasks such as geometry optimizations or frequency calculations while good vectorization rates have been achieved in those parts of the program (especially the post-SCF treatments) amenable to this strategy.

On the other hand, the Cadpac (Cambridge Analytical Derivatives Package) program system is also a useful tool in *ab initio* quantum chemistry, especially by virtue of its excellent perfomance in calculations of analytical first and second derivatives for closed-shell systems and for *Møller-Plesset* (MP) calculations of correlation corrections [9]. We assumed, therefore, that benchmark calculations comparing the performances of the *Gaussian* (versions 82 through 90) and *Cadpac* packages would be of interest to quantum chemists by providing quantitative information on *i*) the improvement in performance achieved in successive versions of *Gaussian*, *ii*) the relative performances of the *Gaussian* and *Cadpac* in standard computational chemistry applications, and *iii*) the relative performance of various presently available and/or accessible computers in different applications when running the same code.

We present and discuss, therefore, the timings of ten different jobs which we consider representative of standard applications of *ab initio* methods on nine different machines ranging from supercomputers (CRAY) to UNIX workstations (*Iris*, *IBM/6000*). We wish to emphasize already at this point that the numbers presented below cannot be readily extrapolated to other cases (larger basis sets, different symmetry, higher-order MP2 calculations *etc.*) because the two program packages and the various computers respond differently to such changes. Finally, our study focusses only on a single aspect of interest to users of *ab initio* programs, *i.e.* the raw number crunching power. A consideration of other factors may prove to be important before taking any decision regarding the use of existing and/or the acquisition of new equipment.

Two similar studies have been reported previously [10][11] but they did not include an evaluation of the powerful modern workstations which have recently become available. In addition our investigation extends to new mainframes and supercomputers accessible to Swiss computational chemists.

Technical Details

Standard versions of the following *ab initio* programs have been used: *Gaussian 82* (G82) [5], *Gaussian 86* (G86) [6], *Gaussian 88* (G88) [7], *Gaussian 90* (G90) [8] and *Cadpac 4.0* (CDP) [9]. For evident reasons, no attempt has been made to modify or optimize these codes on any of the machines we had access to. Furthermore, the input decks were identical for each test run except that analytical derivative calculations were specified in cases where both this and the numerical mode are available. No use was made of direct SCF or in-core MP2 options (these will be at the focus of future studies of this kind) and the amount of memory dedicated to each job was not changed from that offered in the respective standard user configurations, *i.e.* it was similar in all cases.

As to the hardware, *Table 1* summarizes some characterstics of the different computers on which the calculations were perfomed. The peak performances of the various machines (Mflops) are as reported by the manufacturers, *i.e.* the highest possible speeds reachable by using all available features for vector and parallel processing to an optimal degree. Since none of the programs used in the present study takes advantage of multitasking (*i.e.* running on multiple processors), and since the presently available *ab initio* codes have a comparatively minor vector content, the impressive peak performances quoted in *Table 1* have little chance to be approached by our tests.

Our series of test jobs is based on calculations for the molecule of bicyclobutane (BCB, C_4H_6) and its radical cation in C_{2v} symmetry using the 6-31G* basis set [12] (72 contracted basis functions, 136 primitives) which is known to provide results of good accuracy and is frequently used for organic compounds [3]. The example of BCB (which came out of a true application [13]) was chosen, because it is small enough for carrying out calculations on different levels of sophistication within reasonable amounts of time, but large enough so that the calculation times are not dominated by system overhead. Furthermore, it incorporates a moderate degree of symmetry not untypical of common applications and presents no special problems of convergence. The characteristics of the individual tests are as follows:

1. SCF single point calculation for BCB at the SCF-optimized geometry.
2. Same as 1 plus calculation of gradients

Table 1. *Technical Specifications of the Computers Used in the Present Study*

Machine[a]) (abbreviation	Word length [bits]	No. of processors	Cycle time [ns]	'Speed'[b]) [Mflops]	Location
Cray 2/2 (CRAY-2/2)	64	2	4.1	1000	EPF Lausanne
Cray 2/4 (CRAY-2/4)	64	4	4.1	2000	EPF Lausanne
Cray Y/MP (CRAY Y)	64	2	6	667	ETH Zürich
IMB 3090/150 (IBM-150)	32	1	17.8	(unavailable)	University of Fribourg
IBM 3090/180 VF (IBM-180V)	32	1	18.5	8 (scalar) 20 (vector)	University of Geneva
HDS AS/XL V60 (HDS)	32	1	18	25 (scalar) 82 (vector)	University of Zürich
Convex C120 (CONVEX)	32	1	100	20 (vector)	University of Fribourg
VAX 9000 (VAX)	32	1	16	80 (vector)	University of Lausanne
IBM/6000-550 (IBM-RS)	32	1	24	25	University of Basel
SGI Iris 4D/35 (IRIS)	32	1	28	6	University of Geneva

[a]) Abbreviation in brackets corresponds to *Table 2*. [b]) Peak performance in million floating-point operations per second derived from the *Linpack* benchmark.

(*i.e.* one cycle of geometry optimization).

3. Same as 1 plus calculation of second derivatives (*Hessian* matrix, force constants).
4. UHF single point calculation for $BCB^{+\cdot}$ at the UHF optimized geometry.
5. Same as 4 plus calculation of gradients (*i.e.* one cycle of geometry optimization).
6. Same as 4 plus calculation of second derivatives (*Hessian* matrix, force constants).
7. MP2(full) single point calculation for $BCB^{+\cdot}$ at MP2-optimized geometry.
8. Same as 7 plus calculation of gradients (*i.e.* one cycle of geometry optimization).
9. UMP2(full) single point calculation for $BCB^{+\cdot}$ at UMP2-optimized geometry.
10. Same as 9 plus calculation of gradients (*i.e.* one cycle of geometry optimization).

MP2 calculations were included, because nowadays correlations effects are routinely taken into account wherever quantitative information (especially of thermochemical properties) is desired [1–3]. Secondly, we designed parallel tests for closed- and open-shell electronic configurations in view of the increasing importance of free radical intermediates and single-electron transfer processes in organic chemistry. Thirdly, to test the preformance of the programs in geometry optimizations, we added runs where one set of energy gradients (first derivatives with respect to internal coordinate displacements) is calculated after SCF convergence. For the purpose of benchmarking, a single such calculation was found to be preferable to a full geometry optimization, because the different algorithms implemented in these packages may result in a different number of optimization steps before reaching a potential energy minimum. Finally, the full *Hessian* matrix (second derivatives of the energy with respect to cartesian coordinate displacements of all atoms) was computed at the SCF level [14], because such calculations are required to characterize the nature of stationary points (minima, transition states, maxima) on potential energy surfaces [1][3].

A check of the accuracy of the results has been performed in all cases, the total SCF and MP2 energies being the same for each comparable test within 10^{-6} hartrees. All data files used for these tests are available form the authors on request.

Results and Discussion

The results of the above described benchmark calculations are collected in *Table 2*. The values reported there correspond to CPU times (with the exception of the VAX) and normalization to the performance of *Gaussian 90* on the *Cray 2* is presented for the purpose of facilitating their comparison. Before discussing them in some detail, let us remember that they should be taken '*cum grano salis*' as they reflect the performances of different computers in their standard user configuration (memory, disk space *etc.*) for a limited number of cases and for a compound of moderate size. The results of similar calculations for larger or smaller compounds or for molecules of higher or lower symmetry could well lead to different conclusions. In addition, some of the present calculations could be executed in a different manner (*i.e.* by direct SCF, in-core MP2 *etc.*) which could lead to considerable time savings provided the necessary amount of central memory is available.

Note that the different rows in *Table 2* should only be the subject of *direct* comparison on identical or similar machines (*e.g.* the group of computers running under some variant of the UNIX operating system which allows to assess user + system CPU time in a reasonably consistent way). Also, the ratio of CPU to job turnaround times varies considerably, being close to one for the two workstations and the CONVEX, if the benchmark job is running 'alone', and can be orders of magnitude lower for the mainframes, depending on their occupation by other tasks [15]. Nevertheless, we are confident that the main trends exhibited by the results in *Table 2* are reasonably good indicators of the average performance of the different programs and computers selected for this study.

After this preliminary remark, a first general statement which emerges from our study is, that the timings vary considerably with the type of application such that a single test to evaluate the relative performance of the programs or computers could be thor-

Table 2. *Timings* (in s) *of the Different Benchmark Jobs* (rows) *on Different Computers* (columns), *with Relative Performances* (*rel*) *with Respect to G90 on the Cray 2/4*

Job	program:	G88	G88	G86	G82	G90	CDP	CDP	G88	G90	G90	G90	G90
No.	machine:	IBM-150 a)	IBM-180V a)	HDS b)	CRAY 2/2c)	CRAY 2/4c)	CRAY Y c)	CONVEX c)	CONVEX c)	CONVEX c)	VAX b)	IBM-RS c)	IRIS c)
1	RHF single pt.	103	98	67	87	67	34	401	481	478	20+93	49	160
	(*rel*)	*1.54*	*1.46*	*1.00*	*1.29*	***1.00***	*0.51*	*5.98*	*7.18*	*7.13*	*3.20*	*0.73*	*2.38*
2	RHF+gradients	187	158	149	191	97	76	921	681	695	140+182	87	310
	(*rel*)	*1.92*	*1.63*	*1.54*	*1.97*	***1.00***	*0.78*	*9.49*	*7.02*	*7.17*	*3.32*	*0.89*	*3.10*
3	RHF force	1 534	1 678	1 557	2 054	760	233	2 860	7 578	5 780	1 862+360	690	3 169
	(*rel*)	*2.02*	*2.21*	*2.05*	*2.70*	***1.00***	*0.31*	*3.76*	*9.97*	*7.61*	*2.92*	*0.91*	*4.17*
4	UHF single pt.	162	142	94	127	78	44	590	792	660	283+196	63	234
	(*rel*)	*2.07*	*1.82*	*1.21*	*1.63*	***1.00***	*0.56*	*7.56*	*10.15*	*8.46*	*6.14*	*0.81*	*3.00*
5	UHF+gradients	264	202	176	234	112	90	1 140	935	869	302+218	102	380
	(*rel*)	*2.36*	*1.80*	*1.57*	*2.09*	***1.00***	*0.80*	*10.18*	*8.51*	*7.77*	*4.64*	*0.91*	*3.39*
6	UHF force	2 641	2 462	2 784	2 601	1 389	3 544	53 828	10 944	8 184	2 952+664	1 033	4 970
	(*rel*)	*1.90*	*1.77*	*2.00*	*1.87*	***1.00***	*2.55*	*38.75*	*7.88*	*5.89*	*2.60*	*0.74*	*3.58*
7	MP2 single pt.	804	634	494	613	107	41	845	3 903	946	156+331	142	560
	(*rel*)	*7.51*	*5.93*	*4.62*	*5.73*	***1.00***	*0.38*	*7.90*	*36.48*	*8.84*	*4.55*	*1.32*	*5.23*
8	MP2+gradients	1 970	1 402	1 108	1 327	287	109	1 917	8 361	2 516	e	444	2 070
	(*rel*)	*6.87*	*4.89*	*3.86*	*4.62*	***1.00***	*0.38*	*6.68*	*29.13*	*8.77*	–	*1.55*	*7.21*
9	UMP2 single pt.	1 111	967	829	1 079	172	85	1 899	5 214	1 445	277+623	249	1 072
	(*rel*)	*6.46*	*5.62*	*4.82*	*6.27*	***1.00***	*0.49*	*11.04*	*30.31*	*8.40*	*5.23*	*1.45*	*6.23*
10	UMP2+gradients	3 528	2 414	2 244	2278	926	231	6 017	13 559	5 279	e	865	3 449
	(*rel*)	*3.81*	*2.61*	*2.42*	*2.46*	***1.00***	*0.25*	*6.50*	*14.64*	*5.70*	–	*0.93*	*4.80*

a) CPU time (SRB+TCB), no I/O. b) CPU time. c) User + system CPU time. d) CPU+IO time, sum relative to standard. e) Jobs did not execute due to technical problems.

oughly misleading. Actually, the ten tests can be classified into the two categories of SCF (1–6) and MP2 (7–10) calculations, the gross features of which are quite different, because the former class is dominated by purely scalar operations while the latter lends itself more readily to vectorization.

Advantage has been taken of this in the most recent release of *Gaussian* (G90) and in *Cadpac*, a feature which expresses itself very clearly in a comparison of tests 1 and 7 (the additional CPU time required by test 7 over test 1 is due exclusively to the MP2 calculation). The ratio is 1.6, 1.3 and 2.1 for G90/CRAY 2, CAD/CRAY Y, and CDP/CONVEX, respectively, compared to 7.1, 7.8, 7.4, and 8.2 for G82/CRAY 2 G88/IBM150, C86/HDS, and G88/CONVEX, respectively (the low level of vectorization of G88 expresses itself also in the small advantage gained by the vector processor on the *IBM 3090* mainframes). However, a part of this improvement must be due also to optimization of the scalar parts of the MP2 calculation in G90 because the MP2/SCF ratio for the two workstations which do not profit from vectorization (~3) lies midway between the above two groups.

Due to the different architecture of the two CRAY's, a direct comparison of G90 and CDP is only possible on the CONVEX: with the exception of the force calculation which is perfomed twice as fast with *Cadpac*, the two programs perform comparably in both SCF and MP2 applications for closed-shell systems (*cf.* tests 1,2,7,8: average ratio 1.1) while G90 does slightly better for open-shell cases (tests 4, 5, 9, 10, average ratio 0.88) and much better in the UHF force calculation (*Cadpac* cannot calculate second derivatives analytically for open-shell systems). If we exclude the force calculations, we can use the fact that the *average* performance of *Cadpac* and G90 on the same machine is almost identical to evaluate the relative power of the two *Cray*'s: apparently the CRAY/Y-MP is about twice as efficient as the CRAY/2 for standard quantum chemical applications in spite of its inferior peak performance.

As mentioned above, one should be cautious in comparing different types of machines. It is for example difficult to assess the place of the *IBM* or *VAX* mainframes relative to the *Crays* because their time accounting procedures differ signficantly from that offered under UNIX-type operating systems. Nevertheless, one of the most surprising conclusions emerging from the results in *Table 2* concerns the performance of the two workstations (SGI *Iris* and *IBM/6000*) with G90: For SCF jobs the Iris is only around three times slower than the *Cray 2* while the *IBM Riscstation 550* is actually about *15% faster than the Cray 2* running G90! This trend is reverted for MP2 calculations, where the *Iris* is now 5–7 times and the *IBM/6000* ≈30–50% slower than the *Cray 2*. Given the peak performance of the latter compared to that of the two workstations (1000 *vs.* a few to a few tens of Mflops) this result is indeed astonishing.

When making comparisons between mainframe computers and workstations, additional factors have to be taken into account: in particular, workstations are usually not occupied by interactive users during most of the night and weekend times and can hence yield the equivalent of many hours of 'free' Cray CPU time per day to computational chemists. In addition, no real accounting of the CPU time is generally performed on workstations and the user can, therefore, focus on the production of results. In view of this, our findings seem to suggest that – at least for problems of the size of the present benchmark jobs – modern workstations are the hardware platform of choice for doing routine *ab initio* quantum chemical calculations. Of course, such workstations must be adequatly equipped with scratch disk space (>1 GByte) and central memory (>32 MB) but even then their prices are comparatively moderate (≈50–150 kSFr).

However, it must be kept in mind that this picture is expected to change drastically when one deals with more demanding problems such as CAS-SCF, higher order *Møller-Plesset* or large CI calculations. Either such jobs cannot be executed at all on workstations, or they take an inordinately long time. Therefore, vector supercomputers are still very useful tools in *ab initio* computational chemistry, albeit more in the domain of specialized applications. On the other hand, computational chemists may be interested in performing SCF calculations on larger molecules where the novel direct SCF schemes come into play. It will be the aim of future benchmark studies to evaluate the performance of various computers and programs in this area which will surely become very important in the future.

Conclusions

The *ab initio* benchmark tests performed in this study suggest that, for calculations on closed shell molecules characterized by small to medium size one-electron basis sets (≈100 contracted basis functions), the *Cadpac* package running on *Cray Y/MP* is the most efficient solution, especially for MP2 applications where its high vectorization rate is clearly an advantage. For SCF calculations (including gradients) and for open shell systems, the performance of *Gaussian 90* is similar and this program has the advantage to run on a much wider variety of computers. The tests have also shown that the powerful modern workstations, which are increasingly used to run molecular graphics applications, are surprisingly efficient for performing *ab initio* calculations on medium sized molecules during off-hours. They provide a very interesting alternative to supercomputers for such calculations, especially when the performance/cost ratio is taken into account.

Benchmarks such as those reported there are necessarily incomplete as new versions of the program packages, and new computers of all varieties appear on the market at an ever increasing pace. It could, therefore, well happen that the present conclusions will eventually be invalidated by future tests using these new products, some of which are actually being planned by the present team of authors. In spite of their transitory validity, the results presented in this report should, however, be useful as they provide raw information about the most efficient tools to perform routine *ab initio* computational chemistry at the present time.

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[14] Our original benchmark suite contained also the input for force calculations at the (U)MP2 level. However, these jobs took too long to run on all tested machines and thus we left them out of the comparison.

[15] Interestingly, on the IBM mainframes, the job turnaround times regularly exceeded the CPU times by factors of 10-30 even during periods when the machines were otherwise idle. We have not been able to obtain an explanation for this strange observation.

[16] Actually these improvemens are underestimated in the above results because the change from the CRAY 2/2 (on which G82 was tested) to the CRAY 2/4 (used for the G90 tests) resulted in a ≈10% increase in single-processor CPU times due to increasing system overhead (*J. Chenais*, EPFL, private communication to *J.W.*).

Buchbesprechung

Freimut Marschner, 'Quantenchemie mit Personal Computern. Eine Einführung mit interaktiven Programmen für IBM-PC und Kompatible', Walter de Gruyter, Berlin, 1991, 409 Seiten. Das Buch enthält 2 Disketten. Preis *ca.* Fr. 90.–, ISBN 3-11-011944-7

Leistungsfähige Personal Computer wecken zunehmend das Interesse am Thema dieses Buches. Was habe ich als Leser von diesem Buchtitel erwartet? Natürlich tauchen sofort einige grundlegende Systeme vor meinem geistigen Auge auf: Das Elektron im Kasten, der Harmonische Oszillator, das H-Atom usw. Doch Quantenchemie verspricht noch mehr: HMO, EHT, PPP, CNDO, MNDO, *ab initio* u.a., alles Verfahren, für die heute Programme auf Personal Computern erhältlich sind. Viele dieser Programme erlauben ein interaktives Arbeiten mit benützerfreundlichen Graphikoberflächen.

Ich möchte gleich vorwegnehmen, dass meine Erwartungen arg enttäuscht wurden. Die 400 Seiten bestehen ziemlich genau zur Hälfte aus Listen von BASIC-Programmen (viel Papier hätte gespart werden können, wenn diese Source-Codes auf Diskette beigefügt worden wären, was dem Leser erst noch erlaubt hätte, diese zu variieren). Die Hälfte des Rests sind technische Beschreibungen zu den Programmen, Input-Beispiele, quantenchemisch wenig relevante Output-Beispiele und ähnliches. Bleiben *ca.* 100 Seiten für eine Einführung in die Quantenchemie, die allerdings weitgehend aus Formelsammlungen besteht und für den Anfänger kaum verständlich ist. Ob sich fortgeschrittene Leser für ein Buch interessieren, das besser den Titel 'Eine Einführung in BASIC anhand quantenchemischer Beispiele' tragen würde, sei dahingestellt.

Die Gewichtung des quantenchemischen Gehalts kann auch nicht überzeugen. Während von den oben erwähnten Stichworten nur das HMO-, das EHT- und das PPP-Verfahren auf *ca.* 80 Seiten behandelt werden, sind nicht weniger als 100 Seiten der graphischen Darstellung von Orbitalen durch verschiedene kleine Programme gewidmet. Weitere Kapitel bzw. Programme behandeln die *Schrödinger*-Gleichung, numerische Integrationsverfahren, Lineare Regressions- und Varianzanalyse und Symmetriegruppen.

Die graphische Aufmachung des Buches ist derart, dass der Text-Teil kaum von den vielen Computerlisten zu unterscheiden ist, dagegen hebt sich der Buchdeckel angenehm blau ab.

H. Huber