MP2 calculations on EC 1040 and EC 1045 computers

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UMP2 calculations were performed for eight small radicals and biradicals to show typical timings on EC 1040 and EC 1045 computers for basis sets of about 60 basis set functions. Two programs were used: GAUSSIAN 80 and a newly developed program HONDO 5/UMP2, which can make use of molecular symmetry in the MP2 step. Time saving in MP2 runs is discussed and a few hints for users of EC 1040 and EC 1045 computers are given.

Проведены расчеты методом UMP2 для восьми малых радикалов и бирадикалов с целью определения необходимой затраты времени на компьютерах ЕС 1040 и ЕС 1045 с базисными наборами, состоящими из около 60 базисных функций. Использовались две программы: GAUSSIAN 80 и недавно разработанная программа HONDO 5/UMP2, учитывающая молекулярную симметрию на стадии MP2. Обсуждается экономия машинного времени в операциях MP2, и предлагается несколько полезных советов для использователей компьютеров ЕС 1040 и ЕС 1045.

Recently we have developed a computer program [1] for second-order Møller —Plesset (MP2) calculations which, in contrast to existing MP2 programs, can make use of molecular symmetry [2]. Since the program is compatible with the program HONDO 5 [3], we called it HONDO 5/MP2. A later version [4] of the program has been called HONDO 5/UMP2 and, as its name indicates, it can now be applied to both closed and open shell systems. The program was developed primarily for large symmetrical systems for which MP2 treatments by other existing programs would be difficult. To test the performance of our program, seven open shell systems were selected as a benchmark and UMP2 calculations [4] performed for them by means of the programs HONDO 5/ /UMP2 and GAUSSIAN 80 [5]. We considered it expedient to repeat these calculations on EC 1040 and EC 1045 computers with the aim of showing the feasibility of such calculations.

Calculations

The systems selected and the geometries assumed for them are listed in Table 1. All the calculations were performed with the 6-31G* basis set, except for the cyclopropenyl

Table 1

Geometries assumed

Molecule	Origin and specification
Planar allene	Optimum D_{2h} configuration for the ^3A_u state given by STO-3G calculations [6]
Twisted ethylene	$R_{CC} = 1.47 \times 10^{-10}$ m (optimum by CI calculations [7]); $R_{CH} = 1.084 \times 10^{-10}$ m and $\angle$ HCH $= 118°$ (assumed)
Ethyl radical	Optimum C_s structure given by the SCF calculations [8] with the $[4s3p/3s]$ basis set. The geometry parameters are given in [9].
Isopropyl radical	Structure *I* in [10] (4-31G optimization)
Allyl radical	Idealized planar structure with $R_{CC} = 1.40 \times 10^{-10}$ m, $R_{CH} = 1.08 \times 10^{-10}$ m and valence angles of 120°
Cyclopropenyl anion	Idealized D_{3h} structure with $R_{CC} = 1.40 \times 10^{-10}$ m and $R_{CH} = 1.08 \times 10^{-10}$ m
CF$_3$	$R_{CF} = 1.341 \times 10^{-10}$ m and $\angle$ FCF $= 111.8°$ (optimum for the DZ + dif. basis set [11])
NO$_3$	Optimum D_{3h} structure with $R_{NO} = 1.20 \times 10^{-10}$ m given by 4-31(N*) calculations [12]

anion, for which the 6-31G* basis set was augmented by a single set of diffuse carbon p-type functions with the exponent of 0.034 [13]. A frozen core was assumed in all UMP2 runs. SCF and UMP2 energies obtained are presented in Table 2 and the respective timings are given in Table 3.

With the exception of the twisted ethylene and the ethyl radical, convergence problems were encountered in all 6-31G* HONDO runs if the "extended basis set" MO guess [3] was used. We found it necessary first to run 4-31G calculations in order to have a suitable guess for 6-31G* MO's. In these cases the HONDO SCF times in Table 3 are the sums of 4-31G and 6-31G* CPU times. With the cyclopropenyl anion it was even necessary to run calculations in the sequence STO-3G, 4-31G, and 6-31G* with diffuse p-functions.

Results and discussion

Second-order Møller—Plesset theory (MP2) has become a widely used approach in beyond-Hartree—Fock calculations because of its favourable ratio of reliability/cost, and also because of the availability and popularity of the GAUSSIAN 80 program. First MP2 results by GAUSSIAN 80 obtained on an

SCF and valence shell UMP2 energies[a]

System	State	SCF	UMP2
Allene planar	^3A_u	− 115.802753	− 0.32867
Ethylene twisted	$^3A_2$	− 77.964098	− 0.21253
Ethyl radical	$^2A'$	− 78.597034	− 0.23828
Isopropyl radical	$^2A'$	− 117.635624	− 0.36888
Allyl radical	$^2A_2$	− 116.466588	− 0.34165
Cyclopropenyl anion	$^3A_2'$	− 115.101158	− 0.38082
CF_3	$^2A_1$	− 336.125700	− 0.61777
NO_3	$^2A_2'$	− 278.765731	− 0.74508

a) All entries are in E/E_h, $E_h = 2625.5 \ kJ \ mol^{-1}$.
6-31G* basis set was used throughout, except for the cyclopropenyl anion, in which case the basis set for carbon atoms was augmented by a set of diffuse *p*-type functions (see the text).

EC 1045 computer have been reported recently [14, 15] and one may anticipate an increasing number of such calculations in the near future. The main purpose of this paper is to show that the use of GAUSSIAN 80 is not economic for this purpose, though the program is very efficient for SCF calculations. As the GAUSSIAN 80 results in Table 3 show the computer time needed for the evaluation of the MP2 energy is by no means negligible when compared to the SCF times, and the MP2 treatment becomes quickly formidable as the basis set is somewhat extended. The HONDO 5/UMP2 results in Table 3 show however, that the UMP2 time may be considerably reduced. It may be reduced by as much as a factor of 5 (C_1 runs), if the number of basis set functions is over 60, or even by a factor of 10 if moreover the system treated has some symmetry. HONDO 5/UMP2 is faster than GAUSSIAN 80 for several reasons which have been analyzed in some detail previously [4]. Here we only note some practical suggestions for improving GAUSSIAN 80 for those, who still prefer using this program: 1. Run the first two steps of the integral transformation in single precision. 2. Increase the dimension of the array for storing partially transformed integrals. 3. Make use of molecular symmetry, which is easy for point groups containing no degenerate representations [2].

Finally we comment briefly on technical aspects of MP2 calculations on EC 1040 and EC 1045 computers. GAUSSIAN 80 has no options for restarting a job, which makes MP2 runs for somewhat larger basis sets troublesome. The jobs often fail either because of frequent machine errors or because the space required for scratch files on disks is not available. More success has been met with HONDO 5/UMP2, even on EC 1040 computers, although they are for this type of calculations slower than the EC 1045 by a factor of about 2.5.

Table 3

Timings[a] of UMP2 calculations on EC 1040 and EC 1045 computers

System	Symmetry assumed	Program	Computer	t_{SCF} min	t_{UMP2} min	t_{total} min
Allene	C_1	HONDO 5/UMP2	EC 1040	149	78	227
planar	C_1	HONDO 5/UMP2	EC 1045	72	31	103
	C_1	GAUSSIAN 80	EC 1045	58	82	140
	D_{2h}	HONDO 5/UMP2	EC 1040	90	42	132
	D_{2h}	HONDO 5/UMP2	EC 1045	36	17	53
Ethylene	C_1	HONDO 5/UMP2	EC 1040	87	29	116
twisted	C_1	HONDO 5/UMP2	EC 1045	34	12	46
	C_1	GAUSSIAN 80	EC 1045	18	19	37
	D_{2d}	HONDO 5/UMP2	EC 1040	34	16	50
	D_{2d}	HONDO 5/UMP2	EC 1045	14	7	21
Ethyl	C_1	HONDO 5/UMP2	EC 1040	111	40	151
radical	C_1	HONDO 5/UMP2	EC 1045	47	16	63
	C_1	GAUSSIAN 80	EC 1045	29	36	65
	C_s	HONDO 5/UMP2	EC 1040	82	33	115
	C_s	HONDO 5/UMP2	EC 1045	33	13	46
Isopropyl	C_1	HONDO 5/UMP2	EC 1040	360	311	671
radical	C_1	HONDO 5/UMP2	EC 1045	179	122	301
	C_1	GAUSSIAN 80	EC 1045	100[b]	234[b]	334
	C_s	HONDO 5/UMP2	EC 1040	241	209	450
	C_s	HONDO 5/UMP2	EC 1045	107	86	193
Allyl	C_1	HONDO 5/UMP2	EC 1040	265	122	387
radical	C_1	HONDO 5/UMP2	EC 1045	110	52	162
	C_1	GAUSSIAN 80	EC 1045	78	118	196
	C_{2v}	HONDO 5/UMP2	EC 1040	168	80	248
	C_{2v}	HONDO 5/UMP2	EC 1045	70	32	102
Cyclo-	C_1	HONDO 5/UMP2	EC 1040	325	156	481
propenyl	C_1	HONDO 5/UMP2	EC 1045	132	64	196
anion	C_1	GAUSSIAN 80	EC 1045	90[b]	240[b]	330[b]
	D_{3h}	HONDO 5/UMP2	EC 1040	139	54	192
	D_{3h}	HONDO 5/UMP2	EC 1045	51	23	74
CF_3	C_1	HONDO 5/UMP2	EC 1040	359	391	750
	C_1	HONDO 5/UMP2	EC 1045	134	167	301
	C_1	GAUSSIAN 80	EC 1045	100[b]	400[b]	500[b]
	C_{3v}	HONDO 5/UMP2	EC 1040	124	148	272
	C_{3v}	HONDO 5/UMP2	EC 1045	46	59	105
NO_3	C_1	HONDO 5/UMP2	EC 1040	400	224	624
	C_1	HONDO 5/UMP2	EC 1045	164	90	254
	C_1	GAUSSIAN 80	EC 1045	—	—	—
	D_{3h}	HONDO 5/UMP2	EC 1040	134	74	208
	D_{3h}	HONDO 5/UMP2	EC 1045	50	31	81

a) See a note on convergence problems in the text.
b) Estimates based on the timings on a DEC 1099 computer.

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