Quantum chemistry on the personal computer

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

A possibility of very effective application of advanced quantum chemical calculation on the personal computer is discussed. As an example the potential energy curves of the C_2 molecule calculated by the many-body perturbation theory up to the 4th order and by the linearized coupled clusters method and O_2 molecule calculated by GUGA oriented MCSCF method are presented. The obtained results, in particular, the timing of the implemented correlation energy codes, are very encouraging.

В статье обсуждается возможность очень эффективной реализации современных квантово-химических расчетов на персональных вычислительных машинах. В качестве примера приводятся расчеты кривых потенциальных энергий C_2 молекулы на основе многочастичной теории возмущений до 4-ого порядка и методом сопряженных кластеров, а также O_2 молекулы, которая изучалась методом МК ССП. Полученные результаты указывают на положительный момент, особенно что касается времени расчета на основе использованных программ для расчета корреляционной энергии.

During the last year we have been experimenting with the implementation of relatively large FORTRAN programs for the calculation of interelectronic correlation on the personal computers. The hardware configuration we used was the 32-bit personal computer based on the 20 MHz 80386 Intel processor and 80387 arithmetic coprocessor equipped with 2 MB DRAM memory and 80 MB capacity on hard disk with 28 ms average access time. This configuration seems to be the smallest one for such purposes.

Our activity in this field was to implement an effective program system accounting for:

a) 2-electron integrals program,
b) SCF program,
c) 4-index transformation (TRANSF),
d) many-body perturbation theory calculation program up to the 4th order (MBPT4),

e) distinct-row table and formula tape oriented MCSCF program.

These programs were tested by calculations of large number of small molecules (preferably diatomic). In the present paper we give the results obtained for the C_2 and O_2 molecules as an example. The calculated potential energy curves were expressed in the form of simple polynomial function by two-step optimization procedure [1]. We used the comparison of calculated spectroscopic constants with experiment as the criterion of quality of the resulting potential energy curves.

Software implementation

The speed of our personal computer system was tested by running the *Sparks* benchmark program [2]. This program contains different floating point operations (mainly multiplication and addition). Although the general comparison of computing efficiency and speed of different systems is impossible as a rule, elapsed times listed in Table 1 are very encouraging.

Table 1

Comparison of timings for *Sparks* benchmark [2] for different computer systems

Computer	CRAY-1	IBM-3081	CYBER-205	VAX-11/780	EC-1045	PC-386
t/s	0.022	0.80	4.5	3.1	5.3	1.86

All timings, except the last one are taken from [23].

First of all we have installed the *ab initio* package MICROMOL [3], which is a PC adaptation of the Cambridge Derivative Package (CADPAD) [4]. This program was originally written by Colwell and Amos for personal computer, and will cope with closed and open shell systems, can perform geometry optimization and force constants calculation. Program will also calculate some one-electron properties, namely Mulliken populations, dipole and quadrupole moments, electric field at the nuclei, and rotation constants. We used the smallest version of MICROMOL (developed for microcomputers with 640 kB accessible memory only), although there exists the greater version which can be run in connection with transputer board [5].

Two-electron integrals in the Gaussian basis set and the molecular orbital expansion coefficients are then used as an input to the program TRANSF [6], which performs the two-step four-index transformation. The algorithm adapted by us is very similar to the Elberts method [7]. Table 2 shows the number of floating-point multiplications and some timing statistics *vs.* dimension of basis

Number of floating point multiplication (M) and timings for the two-electron transformation (sort integrals T_1, transformation T_2) program *vs.* dimension of basis (N)

N	9	15	19	25	30	32
M	28 386	219 563	547 534	1 698 194	5 434 072	7 309 746
T_1/s	10	22	39	106	237	291
T_2/s	6	23	59	183	449	619

under consideration. Total transformation times are significantly affected by relatively time-consuming disk operations.

Many-body diagrammatic perturbation theory [8] plays an important role among the techniques for accounting for the correlation effects. Its effectiveness is considerably increased when it is formulated by making use of the coupled-cluster approach [8]. The individual perturbation terms are determined by a chain of coupled nonlinear equations. Solving this chain, we may simultaneously construct and evaluate the perturbation term of arbitrarily high order and prescribe topology. That is, the coupled-cluster approach offers a relatively simple theory to evaluate infinite summations of diagrammatic perturbation terms. Our FORTRAN codes of the many-body perturbation theory up to the fourth order (MBPT4) and the linearized coupled-cluster approach (LCCA) were originally written for personal computer. All four-index integrals in both of these programs are stored on the fast computer memory, except of the integrals having all four indices from the virtual space, which are on the disk storage.

Finally, we have implemented the relatively large program system COLUMBUS [9, 10]. Numerous versions of this program system are maintained at different sites on different computers (VAX, VAX with FPS, IBM, CDC, Cray, *etc.*). Present adaptation on the personal computer covers: *a*) the Gaussian integral program computing one- and two-electron integrals over symmetry adapted orbitals using a segmented basis set (program ARGOS); *b*) SCF program based on the "one Hamiltonian" approach [11] which allows the optimization of closed- and open-shell restricted Hartree—Fock wave function (program SCF); *c*) MCSCF distinct-row table, formula file, and wave function optimization programs (MDRT, MFT, MCSCF). MR CI part of the COLUMBUS system was not implemented yet, but it will be done in the near future.

Illustrative calculations

The C_2 molecule was studied extensively by experimental as well as theoretical methods. Accurate experimental spectroscopic constants are available for

some lowest electronic state of this molecule [12]. Theoretical studies of C_2 include the MCSCF study by *Dupuis* [13], CEPA calculation of excitation energies by *Staemler* [14], the MCSCF studies by *Werner* [15], the coupled-cluster calculation by *Raghavachari* [16], the MCSCF results by *Nichols* [17], and others.

The O_2 molecule in its ground state ($^3\Sigma_g^-$) was the subject of investigations of many authors. Recently, the detail studies were done by *Langhoff et al.* [18], applying the complete active space SCF MRCI and *Roos et al.* [19], who used MCSCF method to account for dynamic correlation effects.

We report here on SCF, MBPT4, and LCCA calculations of the potential energy curve for $^1\Sigma_g^+$ state of C_2 molecule, and MCSCF results for $^3\Sigma_g^-$ state (ground state) of O_2 molecule. The purpose of these calculations is to illustrate the possibility of the realization of "advanced" *ab initio* calculations with inclusion of the correlation effects on the personal computer. The basis sets in both cases presented here were DZ + P quality $9s5p1d[4s2p1d]$ for C_2 and $9s5p1d[5s3p1d]$ for O_2 molecules with exponents according to Refs. [20, 21]. The MICROMOL program produces approximately 38 000 two-electron integrals (calculations did not use the point group symmetry) consuming roughly 5.5 min. Because of the strict orientation of the actual version of MICROMOL to the use of disk files instead of core memory, elapsed times for SCF iterations are slightly large (roughly 35 s per one iteration).

The calculated potential energy curves for the ground state of C_2 molecule are shown for MBPT4 and LCCA methods in Figs. 1 and 2. It is well known that the bigger time-consuming part of the many-body perturbation calculations is
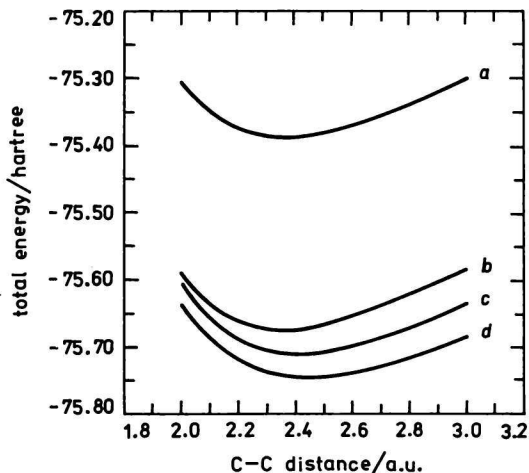

Fig. 1. Potential energy curves of C_2 molecule. *a*) SCF; *b*) MBPT 2nd order; *c*) MBPT 2nd + 3rd order; *d*) MBPT 2nd + 3rd + 4th order. (1 hartree = 4.3598×10^{-18} J.)

the inclusion of the tri-excited states in the fourth order correlation energy. Elapsed time for this part of calculation was approximately 37 min in comparison with 40 min for the complete 4th order. On the other hand, one iteration in the linearized coupled-cluster method consumed approximately 6 min of CPU time.
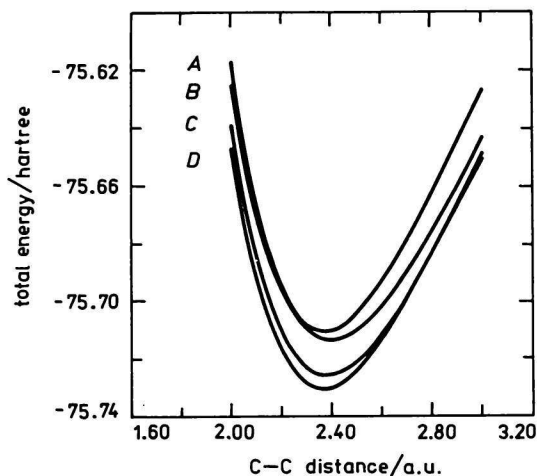

Fig. 2. Potential energy curves of C_2 molecule calculated by the linearized coupled-cluster method. (*A—D* curves represent 3rd—6th iteration.)

As a second illustration example we carried out the MCSCF calculation of potential energy curve of the O_2 molecule in the $^3\Sigma_g^-$ state (Fig. 3). Using the $\mathbf{D}_{2h}$ point group symmetry (because of the limitation of the COLUMBUS program), the integral part of the program produced approximately 36 000 integrals in 4.1 min. As the starting orbitals for the MCSCF iterations for the first interatomic distance the SCF orbitals were used, and in all next cases we started with the previously calculated MCSCF orbitals. The active space used for MCSCF was not very large (14 configurations), we used all excited states within the orbital space $1\pi_u^4 3\sigma_g^2 1\pi_g^2 3\sigma_u$ with the correct space and spin symmetry. The same active space was used by *Lischka et al.* [9] in their MCSCF preliminary investigations. The typical timings in the case of O_2 molecule were 10 s/iteration in the SCF step (convergence achieved after 14 iterations) and 90 s/iteration in the MCSCF step (converged after 10 iterations).

The quality of the obtained potential energy curves was tested by calculation of spectroscopic constants. The calculated total energies were approximated by the polynomial fit using the transformed (dimensionless) internuclear displacement $\xi = (R - R_e)/R_e$ (R_e — equilibrium internuclear distance) by the two-step

optimization procedure (in fact of the R_e dependence of ξ). The results of these calculations are shown in Tables 3 and 4 along with the experimental results for comparison. The LCCA results are reported (Fig. 2 and Table 3) for the third to sixth iterations. Obtained LCCA spectroscopic constants agree surprisingly well with the experimental data and follow the expected trend — a higher iteration leads to more accurate results.
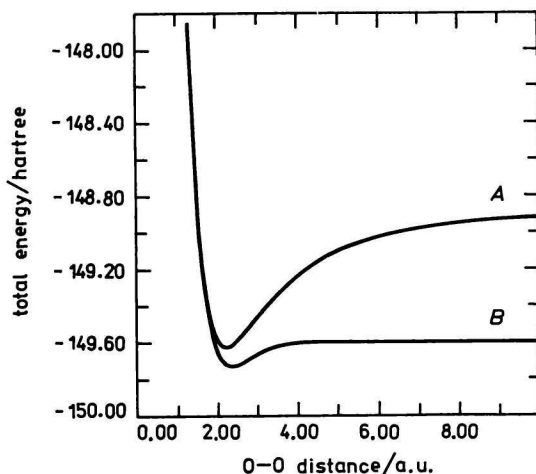

Fig. 3. Potential energy curves of O_2 molecule (A — SCF, B — 14 configurations MCSCF).

Table 3

Calculated spectroscopic constants for the C_2 molecule ($^1\Sigma_g^+$). (All entries in cm^{-1}, except of R_e which is in a.u. (1 a.u. = 5.2918 × 10^{-11} m))

Method	R_e	ω_e	B_e	$\omega_e x_e$	α	$D_e \cdot 10^5$
SCF	2.359	1922	1.802	12.92	0.0168	0.634
MBPT(2)	2.408	1865	1.730	12.17	0.0156	0.596
MBPT(2 + 3)	2.353	1962	1.812	14.25	0.0172	0.618
MBPT(2 + 3 + 4)	2.442	1720	1.683	10.09	0.0158	0.644
LCCA 3. it	2.401	1811	1.739	12.91	0.0173	0.642
LCCA 4. it	2.366	1915	1.792	13.78	0.0171	0.627
LCCA 5. it	2.381	1837	1.769	13.81	0.0180	0.657
LCCA 6. it	2.366	1883	1.791	13.56	0.0174	0.648
Experiment [12]	2.348	1854	1.820	13.39	0.0177	0.639

Table 4

Calculated spectroscopic constants for the O_2 molecule ($^3\Sigma_g^-$) within the MCSCF (14 configurations) method. (All entries in cm^{-1}, except of R_e which is in a.u.)

R_e	ω_e	B_e	$\omega_e x_e$	α	$D_e \cdot 10^5$
2.317	1540	1.402	12.92	0.0132	0.465
(2.282)	(1580)	(1.438)	(11.98)	(0.0159)	(0.484)

(Experimental data [12] in parenthesis.)

Conclusion

We described our experience in adapting code to run on 32-bit personal computer, outlining the implementation of correlation energy calculations (MBPT4, LCCA, and MCSCF) on the microcomputer. We tried to assess the efficiency of quantum chemical applications on the personal computer and reported on some provisional timings. Results presented here show the powerful possibilities in exploitation of microcomputers for not very expensive quantum chemical purposes.

Experience of other theoretical groups shows that the possibilities of personal computers, especially in connection with parallel processors, converge to the big supercomputers (like a CRAY). In the preliminary calculations with 8 transputers *Wedig et al.* [22] achieved the comparable efficiency (in the evaluation of two-electron integrals) with CRAY-X/MP, which is only 3 to 5 times faster (not considering the fact that the elapsed times on the latter computer are of course larger).

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