

Quantum Chemical Calculations by Parallel Computer from Commodity PC Components

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Abstract. Computational quantum chemistry helps us to determine, calculate, and study new concepts, compounds, reactions and mechanisms. Such way is very useful with compounds that require exceptionally care in their handling, such as explosives, decreasing risk to persons testing and maintenance costs in service. Computational quantum chemistry is the ground of molecular modeling, on prediction the behavior of individual molecules within a chemical system. The molecular modeling let us to obtain the molecular characteristics comparable with experimental date. In this way the molecular structures of for positional isomers of 2,4,6-trinitrotoluene (TNT) were calculated by an *ab initio* HF/6-31G* method using self made local area personal computer (PC) cluster TAURAS. The cluster was made from heterogeneous commodity hardware of teaching class and for high performance computing (HPC) was used the SCore cluster system software developed in Japan. The structure and the features of the cluster are described and the performance is evaluated during solving of linear algebra testing tasks. During the determination of the structures of the positional isomers of TNT, the deformation of the phenyl ring and the distortions of the nitro and methyl groups were concern. The calculations confirmed that both of these were affected by the positions of nitro groups. A comparison of the calculated energies of all the isomers revealed the tendency to form the stable isomers when the close contact effects of the nitro groups were reduced.

Keywords: cluster, parallel calculations, dinitrotoluene, positioned isomer.

1 Introduction

We use the self-made PC Cluster TAURAS with the SCore cluster system software on top of Linux OS to present the investigations of explosive molecules. Created computational facilities were applied to investigate electronic structure and vibration spectra by means of no empirical quantum mechanical computation methods. During investigations, the

General Atomic and Molecular Electronic Structure System (GAMESS) quantum chemistry computer code was used [1]. From the mathematical point, these investigations are nonlinear mathematical modeling problems. They are usually solved by means of computational linear algebra methods. So the parallel computers cluster was used in order to achieve quantitative results comparable with experimental. Cluster TAURAS parameters are comparable with other ones located in academic areas. Cluster is registered in the top500 cluster list [2].

2,4,6-trinitrotoluene is better known by its initials TNT, has been available as explosive since around 1870. It is most widely used explosive because of its compatibility with other explosives. TNT is an important explosive, since it can very quickly change from a solid into hot expanding gases. TNT manufacturing involves stepwise nitration of toluene in a three-stage batch process or continuous process producing mono-, di- and finally trinitrotoluene, respectively. In this work we continue our previous investigations [3,4].

2 Personal computer cluster TAURAS

In Lithuanian Military Academy was self made local area PC cluster TAURAS for parallel calculations. One of important features of cluster TAURAS is that we used the heterogeneous commodity hardware of teaching class. It was personal computers: 2 of them dual AMD 1.2 GHz processors, 8 – dual 733 MHz Pentium III processors, 5 of them have dual 800 MHz Pentium III processors and the rest 1 node have dual 450 MHz Pentium II Celeron processor; two of them have 1024 MB RAM others 768 MB RAM, all have 20 GB disk drives. Machines have been installed with the standard Red Hat 7.3 – Linux OS. Below, in Fig. 1, is presented the cluster TAURAS communication and in Table 1 is shown the brief specification of hardware.

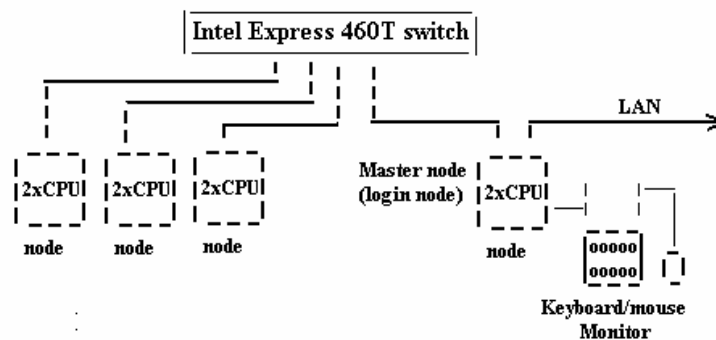


Fig. 1. The communication map of the TAURAS cluster.

The connectivity scheme shows the architecture of the cluster system. All nodes are connected through the fast Ethernet switch, allowing for fast communication network (100 Mb/s) connection to a controlling the cluster network and data exchange between

the connected machines (master node and all nodes). The cluster differs from the network of workstations in security, application software, administration, and booting and files systems. For administering the cluster, we have master node with a keyboard, monitor and mouse. Other nodes can be “headless” (no keyboard, mouse, or monitor) but in our way, there are all workstations like login node, because the cluster TAURAS is based on teaching class.

Table 1. Specifications of personal computer cluster TAURAS

Integrator	Self-made
Number of nodes	16
Processors total	32
Total peak performance (GFlops)	30,18
Total memory (GB)	12
Total disk (GB)	320
Interconnect Technology	Fast Ethernet
Operating System	Linux
OS Extension used	SCore
Communication software	SCore
Main application area	Ballistics, Materials Science, Quantum Mechanics of Molecules, Chemistry

All PCs are assumed to boot from their own hard drive. Total peak performance of the cluster is 30.96 Gflops; total memory – 12 GB; total disk space – 320 GB. Our cluster’s TAURAS parameters was comparable with other ones located in academic areas. TAURAS was registered in the top500 clusters list [2]. Parallel computers can be efficiently used if the software exploits the hardware architecture. So, the other important feature of this cluster is the software we used.

System software was developed in Japan by the Real World Computing Partnership, and now is released by a PC Cluster consortium [6]. Score system software can be built on top of a Linux commodity operating system without kernel modifications but with the addition of a driver to the kernel. Such type cluster uses the PM II high performance communication library, which dedicated for cluster computing and realized high bandwidth and low latency for communication. Score system software allows using many types of networks.

SCore cluster system software supports small systems like cluster TAURAS, but it also supports large systems such as a SCore-III PC cluster that consists of 1024 processors. This feature let us to build cluster that corresponds to the application demands. The important feature of the cluster TAURAS that it may be upgrade or expanded without any essential rebuilds, but with the addition necessary resources.

The local area PC cluster TAURAS was made for parallel calculations with the SCore cluster software for high performance computing (HPC). This means that cluster provides several features: high scalability, high-performance network, job management, and checkpoint for long time jobs.

The performance of cluster TAURAS compared with other supercomputers was investigated in high performance Linpack benchmark calculations by solving the system of linear equations of order 25 000 (Fig. 2). Total CPU time necessary for solving of the task were 2080.77 s and real performance of the cluster achieved – 5,007 Gflops. From this figure we can see that performance of cluster TAURAS is higher than IBM SP2 performance, but the price of the cluster is tenths times lower than the price of supercomputer IBM SP2.

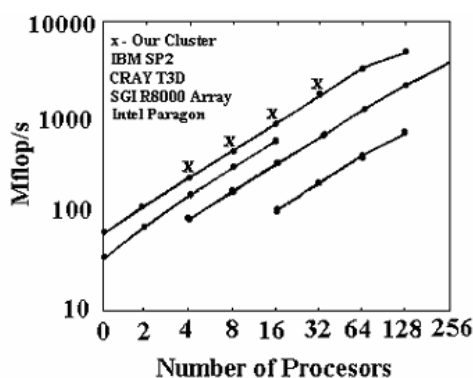


Fig. 2. High performance Linpack benchmark calculations. Solving of linear equation system ($n = 25000$). Results for other supercomputers are from [5].

The cluster was made for scientific investigations of explosive molecules. For this work we choose the GAMESS computer code [1]. This package was integrated and optimized in cluster TAURAS environment. All calculation results are presented below.

3 Quantum chemical calculations in cluster TAURAS

As was declared in the introduction precise computations of explosive molecules may be of interest for experimental spectroscopy. In this section, we briefly describe the complexity of theoretical investigations, show get results and some of them compare with results, that was get after investigations on supercomputer [6].

Theoretical investigations were performed by means of ab initio quantum mechanical methods using GAMESS computer code [1]. The basis of all such calculations is solving of multidimensional time independent Schrödinger equation

$$\hat{H}\Psi_i = E_i\Psi_i, \quad (1)$$

here \hat{H} – Hamilton operator of investigated quantum particle system; Ψ_i – wave function of the system; E_i – allowable energy value. Hamiltonian operator and wave function of the system depend on the coordinates of all particles (electrons and nucleus). The term ab initio means from first principles. It does not mean that we are solving the Schrödinger

equation exactly. It means that we are selecting a method that in principle can lead to a reasonable approximation to the solution of the Schrödinger equation and then selecting a basis set that will implement that method in a reasonable way. By reasonable, we mean that the results are adequate for the application in hand. A method and basis set that is quite adequate for one application may be inadequate for another application. We also have to take recon in the cost of doing calculations and the total amount of computer time required. The most popular ab initio methods are: Hartree-Fock (HF), Moller-Plesset (MP) perturbation, couple-cluster (CC) and density functional theory (DFT).

In the case of Hartree-Fock method the Hamiltonian operator of systems takes the form:

$$H = T_e + T_b + V_{ee} + V_{eb} + V_{bb}, \quad (2)$$

where

$$T_e = - \sum_i^N \frac{\hbar^2}{2m} \nabla_i^2$$

is the kinetic energy operator of electrons,

$$T_b = - \sum_{\alpha}^n \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2$$

is the kinetic energy operator of nuclei,

$$V_{ee} = \sum_{i < k}^N \frac{e^2}{r_{ik}}$$

is the potentials of inter electron interaction,

$$V_{bb} = \sum_{\alpha < \beta}^n \frac{Z_{\alpha} Z_{\beta} e^2}{R_{\alpha\beta}}$$

is the potentials of inter nuclear interaction,

$$V_{eb} = - \sum_i^N \sum_{\alpha}^n \frac{Z e^2}{r_{i\alpha}}$$

is the potential of nuclear-electron interaction.

In these expression, m and M are the masses of electrons and nuclei, respectively, $R_{\alpha\beta}$ is the distance between nuclei, r_{ik} is the distance between electrons, $r_{i\alpha}$ is the distance between a nuclei and an electron, e is the electron charge, Z is the nuclear charge. Equation (2) may be solved explicitly only for a two-particle system.

To check the possibilities specific of the cluster TAURAS we performed quantum mechanical investigation of the explosive molecules. As was explain above was used

the specific environment for calculations, so it is important to confirm that molecular modeling calculations can be doing correct on the cluster TAURAS and get results can be comparable with calculations on known supercomputers.

The calculations were performed at the HF level using a 6-31 G* basis set (with polarization d functions on second period elements). These studies can provide valuable information in the field of aromatic nitro compounds. The obtained performances were compared with other published results [6].

Dinitrotoluenes, namely 2,4-dinitrotoluene, 2,6-dinitrotoluene, 4,5-dinitrotoluene, 4,6-dinitrotoluene, were chosen in this study.

The most stable molecule has the lowest HF energy. Energies of the dinitrotoluene isomers calculated by HF/6-31G* method coincides with results presented in [6]. According to our results of the investigation, the 2,4-dinitrotoluene is more stable than 4,5-dinitrotoluene. Their geometries are presented in Fig. 3. and calculated bond lengths of dinitrotoluenes are presented in Table 2. The geometrical structure (bond length, angles, and dihedral angles) had been compared and good coincidences were found also. Both P. C. Chen and we obtain that the isomers deformations of the phenyl ring were affected by the methyl and nitro groups [6].

The most important results of these investigations indicate that more stable molecules are if the nitro and methyl groups of 2,4-dinitrotoluene, 2,6-dinitrotoluene are separated

Table 2. Calculated bond lengths of dinitrotoluenes on cluster TAURAS and by P. C. Chen [6]

Bond	2,4-dinitrotoluene	2,4-dinitrotoluene [6]	2,6-dinitrotoluene	2,6-dinitrotoluene [6]
C1-C2	1.3899	1.3982	1.3970	1.3964
C2-C3	1.3843	1.3831	1.3841	1.3838
C3-C4	1.3758	1.3758	1.3790	1.3793
C4-C5	1.3833	1.3827	1.3790	1.3793
C5-C6	1.3789	1.3793	1.3840	1.3839
C1-C6	1.3937	1.3948	1.3960	1.3963
C1-C7	1.5133	1.5135	1.5191	1.5189
C7-H8	1.0800	1.0810	1.0816	1.0815
C7-H9	1.0801	1.0811	1.0768	1.0770
C7-H10	1.0802	1.0812	1.0769	1.0770
C2-N10	1.4600	1.4611	1.4621	1.4624
N10-O11	1.1899	1.1932	1.2920	1.2921
N10-O12	1.1930	1.1926	1.1940	1.1937
C3-H7	1.0689	1.0691	1.0719	1.0716
C4-N13	1.4601	1.4556	1.0728	1.0730
N13-O14	1.1933	1.1921	–	–
N13-O15	1.1918	1.1933	–	–
C5-H8	1.0701	1.0712	1.0715	1.0716
C6-H9	1.0733	1.0735	1.4622	1.4624
N20-O21	–	–	1.1939	1.1937
N20-O22	–	–	1.1920	1.1921

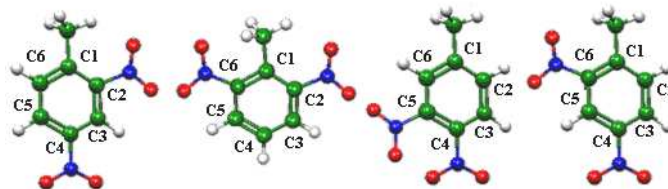


Fig. 3. The geometrical structures of studied dinitrotoluene molecules.

from each other. These results confirm also predictions of P. C. Chen [6].

To extend our research and confirm the above mentioned observation, we performed investigation of the 4,5-dinitrotoluene molecule where nitro groups are as close as possible. Investigation results indicate that stability of the 4,5-dinitrotoluene is the lowest.

So, the calculations confirm the above theoretical prediction. The results allow us foresee that cluster TAURAS allows solving of modern quantum chemical problems at necessary level.

4 Conclusions

The General Atomic and Molecular Electronic Structure System (GAMESS) quantum chemistry computer code was implemented and improved correctly under the specific environment of cluster TAURAS.

Created computational facilities were applied to investigate electronic structure and vibration spectra by means of no empirical quantum mechanical computation methods.

Calculations of positional isomers of 2,4,6-trinitrotoluene molecule at Hartree-Fock level show the influence of NO_2 groups to electronic structure of TNT compounds.

Comparison of the performances obtained by different environments, self-made PC cluster from commodity hardware and supercomputer from National centre for High-Performance Computing, confirms that created PCs cluster allows solving of modern quantum chemical problems at necessary level.

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