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High-efficiency parallelization of programs, implementing the Hartree-Fock method, the density functional theory, and the configuration interaction method

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Abstract. It is shown that the modified method of Fock matrix calculation with data compression, using the stored integrals, scales linearly with respect to the number of basis functions for large molecular systems. This method leads to the development of the high-efficient parallel algorithms of the conventional and semi-direct Hartree-Fock and the density functional theory (TDF) methods. The main approaches are formulated for the parallelization of the configuration interaction (CI) method with the configurations selection, in which the matrix elements are calculated by using the Slater rules. The efficiency and the application of the proposed approaches is demonstrated.

Keywords: distributed computations, parallel computations, Hartree-Fock method, Kohn-Sham method, configuration interaction method
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1. Introduction

From the middle of the last decade of XX century, the cluster architecture of computing systems, which were built, in many cases, on the basis of PC computers, gradually became the basic architecture of supercomputers. Nowadays, the cluster architecture has become the overwhelmingly dominant architecture of supercomputers. The development of the multi-core microprocessors and multi-socket motherboards allows for two types of parallel execution of programs on modern supercomputers, both, on the cluster nodes, as well as on the multi-core microprocessors on the multi-socket (up to 32) motherboards on a single node.

The numerical methods for the solution of equations of ab initio electronic structure theory of molecular systems and nanostructures include the use of almost all methods of computational mathematics. These are the computation of multidimensional integrals, the interpolation and extrapolation of functions, the solution of systems of linear equations, the calculation of eigenvalue and eigenvector of the generalized and conventional matrix problems, the minimization of multidimensional functions, series summation, and many other methods. The efficiency of parallelization of these methods differs substantially. Therefore, only those parts of ab initio electronic structure theory programs are parallelized, which are most computationally demanding. In the Hartree-Fock and DFT methods, this is the calculation of two-electron integrals and the Fock matrix from these integrals and the density matrix for the number of contracted basis functions below 15000. In the CI method, this is the calculation of matrix elements between configuration state functions and the solution of the eigenvalue problem with extremely large matrices of dimension of 10^7 and higher. New approaches to the efficient parallelization of these methods are considered in the present paper.

2 Efficient parallelization of the two-electron part of the Fock matrix calculation

The two main methods of the two-electron part of the Fock matrix calculation are now known, which are accompanied by an intermediate method. There are the conventional method, which stores the calculated two-electron integrals on an external peripheral device [1], the direct method, in which the two-electron integrals are recalculated at each step of the iteration procedure [2], and the semi-direct method, in which a part of the integrals are stored on the external device and the others are recalculated at each iterative step [3].

Each of these methods has its own advantages. The conventional method requires smallest number of arithmetic operations, because the two-electron integrals are calculated only once, while the direct method is preferable when the time of reading the integrals from the external device is longer than the time of their calculation, and the intermediate method is the most flexible among these methods, which can have advantages even when the time of reading integrals is greater than the time needed for their recalculation.

The direct method of the two-electron part of the Fock matrix calculation has been seen as advantageous up to now, because it has been shown that this method possesses the super-linear scaling property of the Fock matrix calculation with respect to the number of the basis functions, employed in the calculation of large molecular systems [4, 5, 6].

However, recently we have proven the theorem about the asymptotically linear scaling of the number of non-zero two-electron integrals with respect to the number of basis functions for large molecular systems [7]. It was verified numerically by calculating the dependences of the number of non-zero two-electron integrals from the total number of basis functions and the computation accuracy of the integrals along with similar dependencies for their derivatives in the computations of alanine polymers with the 6-31G basis set, presented in Fig. 1.

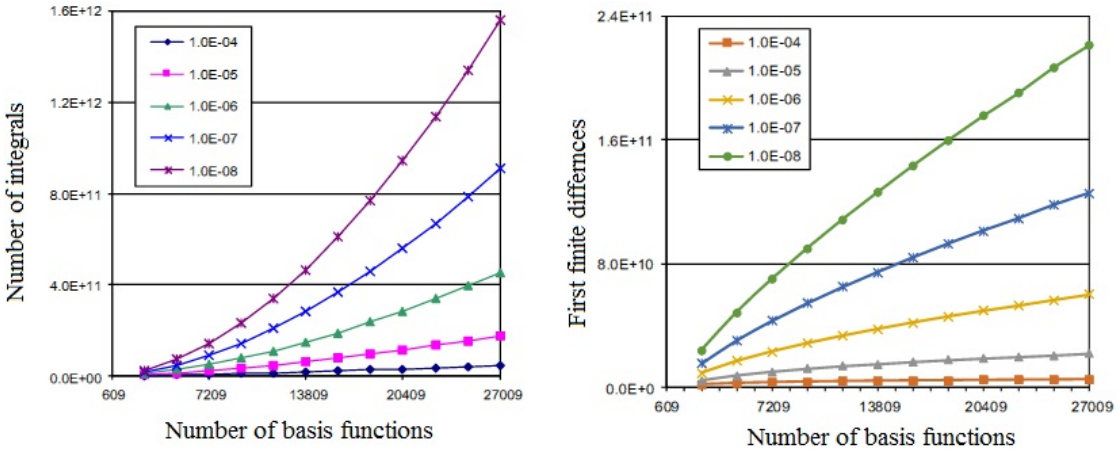

Figure 1: The number of non-zero two-electron integrals (a) and their first finite differences (b) versus the total number of basis functions for different computation accuracies of the integrals in the alanine polymers.

Furthermore, it was shown that the use of data compression methods for storing the two-electron integrals and their indices [8, 9] permits to reformulate the conventional Fock matrix calculation method in a way similar to the direct method, which uses the density difference matrix for preliminary estimation of the contribution of the two-electron integrals to the Fock matrix [10]. The study of thus modified Fock matrix calculation methods has shown that it also possesses the linear scaling property with respect to the total number of basis functions for large molecular systems [7]. This property directly follows from the dependencies of times of the two-electron part of the Fock matrix calculation and their first derivatives from the total number of basis functions in the Hartree-Fock calculations of the alanine polymers with 3-21SP basis for different calculation accuracies of the integrals, presented in Fig. 2. They show that after achieving sufficiently large dimension the Fock matrix calculation becomes linearly dependent with respect to the total number of basis functions.

Thus, the results of the studies briefly mentioned above show that the modified conventional Fock matrix calculation method, similar to the direct one, also possesses the linear scaling property with respect to the dimension of the calculated system. Therefore, the comparison of the two methods of Fock matrix calculation leads to the conclusion that an advantage of one method over the other one is defined exclusively by the relation between the speed of the central processor unit and the speed of reading data from an external device. For this reason, the parallel versions of all methods of Fock matrix calculations (conventional, direct, and semi-direct) have been developed by us.

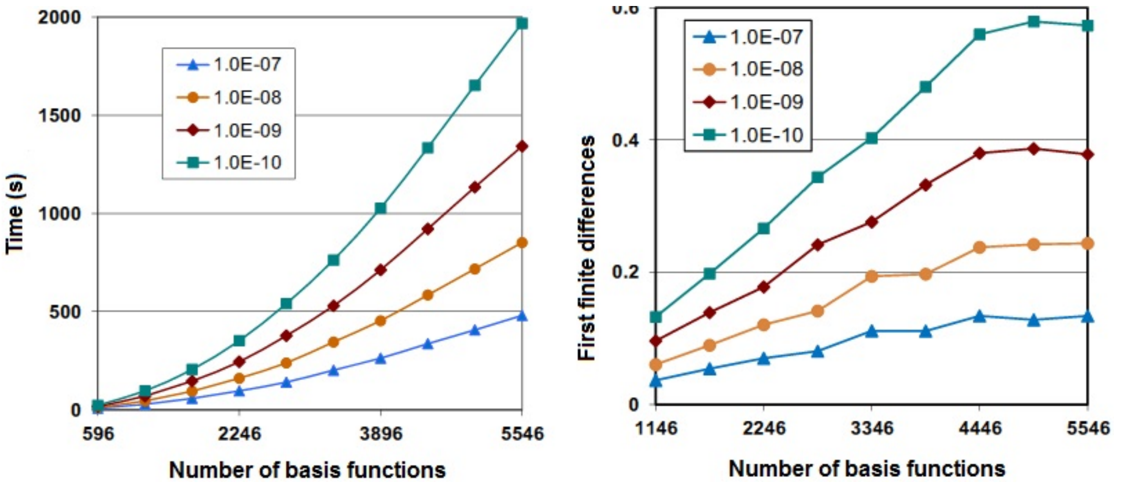

Figure 2: The dependencies of the times of the Fock matrix calculation (a) and its first derivatives (b) from the total number of basis functions in the Hartree-Fock calculations of alanine polymers with 3-21SP basis for different calculation accuracies of the integrals.

Additionally, it should be noted that the recent progress in solid-state hard drive technology substantially improves the modified conventional method of the two-electron part Fock matrix calculation due to having significantly faster data transfer speed compared to conventional hard drives. For example, a data transfer speed of more than 6GB/s is achieved now for RAID arrays of solid state drives, which greatly exceeds that of RAID arrays of usual hard drives. The only problem is how soon the price of solid-state drives will become comparable to the prices of the usual ones.

The efficient parallel algorithm of the Hartree-Fock and DFT methods over the cluster nodes has been developed by us [10] using the Parallel Virtual Machine program system [11].

Most similar parallel methods were developed for supercomputers, in which the node computer had relatively small random-access memory (RAM). Therefore, the Fock and density matrices have been split into blocks in these methods and only a few blocks were stored on each node. Such methods show good scalability for a small number of nodes used. However, the scalability of these methods becomes unsatisfactory for a large number of used nodes due to the fast increase of data flow between them.

In this connection, we have used the parallelization with saving the copies of the Fock and density matrices at each of the nodes. Such an approach significantly simplifies the parallelization and requires the transfer of an insignificant volume of controlling information to each node. For this reason, the developed method has considerable potential for efficient execution on a large number of used nodes. A limitation of this method is defined by the size of RAM required for the allocation of the main matrices at each node.

In the developed parallel Hartree-Fock and DFT methods with data compression, the calculation and the storage of the two-electron integrals and the calculation of parts of the Fock matrix is performed at each of the slave nodes. The control information about the blocks of integrals to be calculated at each of the slave nodes is sent by the main node. The principle of internode communication used in our program is that the first free node is the first to receive the control information for the required task. The summation of the Fock matrix parts is performed at the main node, which also executes other simple operations. Such a parallelization scheme is well suited to both the conventional and the semi-direct methods. In the conventional method, all two-electron integrals are computed and stored on the discs of the slave nodes. In the semi-direct method, at the beginning, the two-electron integrals are calculated and stored on the hard drives of the slave nodes. Then, the contributions to the Fock matrix from the stored integrals are calculated, the remaining integrals are calculated and their contributions to the Fock matrix are determined.

One of the most important problems to be solved for efficient parallelization is the balancing of the slave node operation time. The number of two-electron integrals as an objective function for the slave node balancing was chosen in our case. It permits to balance the operation of slave nodes with respect to both the time of calculations and the time for input-output data. The test calculations show that the time loss due to unbalanced slave nodes was about 2% with the chosen objective function.

The time of molecular calculations using different parallel Hartree-Fock and DFT methods in dependence on the number of nodes in the cluster is presented in Table 1. The obtained results show that the proposed modified conventional and semi-direct parallel methods are considerably faster than the direct method. This advantage is caused mainly by the fact that the conventional and the semi-direct methods require a much smaller number of arithmetic operations.

3. Efficient parallelisation of the CI method

The main problem of the configuration interaction methods, using the unitary group theory for the calculation of matrix elements, consists in the fact that only about 20 electrons can be explicitly correlated by these methods. This is insufficient for the correct theoretical description of large molecular systems.

Table 1: The dependence of molecular calculation time (min.) using the parallel conventional (CL), direct (D) and semi-direct (SD) Hartree-Fock and DFT methods on the number of the used cluster nodes.

				Number of nodes				
Mol.	Meth.	BF		1	2	3	4	5
$Si_{17}H_{20}$	HF	406	D	81.2	42.4	29.9	22.3	18.5
			Cl	28.3	15.3	11.1	8.8	7.0
			D/Cl	2.9	2.8	2.7	2.5	2.6
Taxol	SVWN	660	D	395.9	202.8	137.3	104.9	85.4
			SD	262.5	145.4	98.0	75.4	60.8
			D/SD	1.5	1.4	1.4	1.4	1.4
Yohimbine	BLYP	494	D	289.8	145.9	99.1	76.6	60.6
			SD	163.9	88.3	59.6	45.6	36.8
			D/SD	1.8	1.7	1.7	1.7	1.6
Porphine	B3LYP	916	D	614.7	319.1	209.6	159.3	130.4
			SD	305.1	182.0	124.8	92.9	77.7
			D/SD	2.0	1.8	1.7	1.7	1.7

However, the modified configuration interaction method with the selection of configurations, in which the matrix elements are calculated by using the Slater rules, allows the explicit correlation of a much larger number of electrons. In the calculation of the adsorption energy of the CH_2 molecule on the metallic nickel surface by such a CI method, presented in Ref. [12], as many as 76 electrons were explicitly correlated. A parallelization of such a CI method is the most interesting, because it will allow to study the molecular systems with a large number of explicitly correlated electrons.

A specific feature of the CI method with the calculation of matrix elements in accordance with the Slater rules consists in the keeping of all two-electron integrals of the molecular orbitals (MO) in RAM. This number is proportional to $1/8N^4$, where N is the number of MO. Therefore, this method has a high requirement for RAM size. For example, for $N = 100$ an allocation of only the two-electron integrals requires nearly 933 GB of RAM. However, for the modern microprocessors this is an insignificant problem. In particular, the memory controller of the latest xeon microprocessors E7-4800 v4 and xeon E7-8800 v4 supports up to 3TB of RAM per processor.

From a general point of view, the CI method is a method for the determination of extreme eigenvalues and their eigenvectors of the an extremely large Hamiltonian matrix of a molecular system of a dimension of about 10^7 and higher (see the author's review [13] of new iteration methods). The mathematical methods for a calculation of extreme eigenvalues are known to be well parallelized both with respect to the number of nodes and with respect to the number of microprocessor cores operating over the shared RAM. Therefore, the parallelization of the CI method, although technically complicated, has no principal problems. The main requirement is to have a sufficient size of RAM for allocating the two-electron integrals of MOs and the wave function.

4. A few examples of test calculations

The first example, demonstrating the efficiency of the described approaches, is the theoretical investigation of the small tetra heme cytochrome *c* (STC) reaction centers in the electron transfer reaction, related with the biological activity of the *Shewanella oneidensis* bacterium, which leads to the biological conversion of heavy-element compounds [14]. The atomic structure of the upper occupied orbitals of STC, formed by more than 1500 atoms, was studied and its active centers in the electron transfer reaction were determined [15]. The electron distribution in STC can be understood by considering its electrostatic potential, an example of which is presented in Fig. 3.

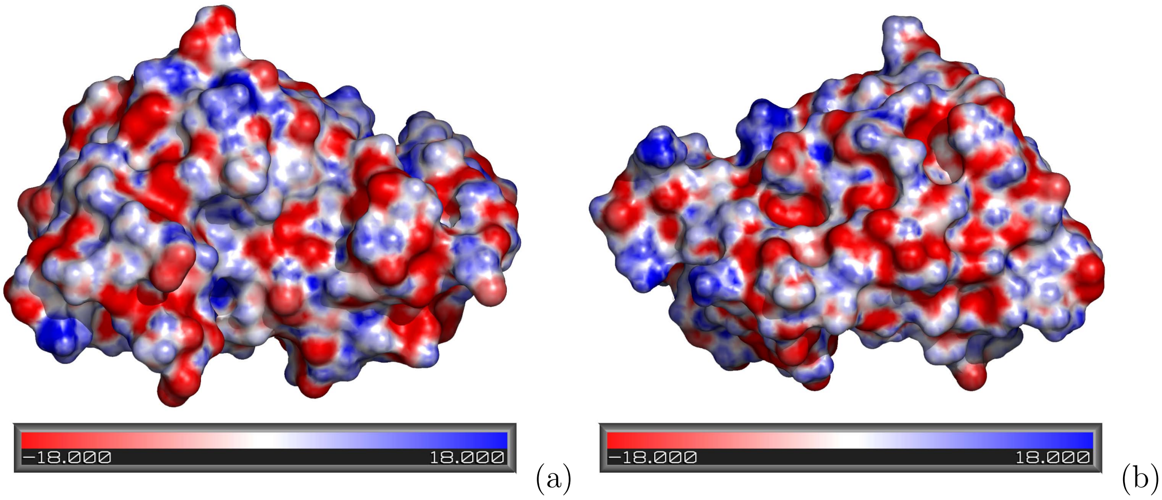

Figure 3: The electrostatic potential ((a) - front view, (b) - back view) of the neutral oxidized STC form calculated with Malliken partial charges on atoms [18].

The second example is related to the efficient implementation of the relativistic two-component DFT method, using the relativistic effective core pseudo-potential, as well as the calculation of ionisation potentials and electron affinity energies of the halogen atoms from Br to At and their diatomic molecules, including the first calculations of the atom and the diatomic molecule of the superheavy 117-th element [16], recently synthesized in LNR JINR (Dubna) [17]).

The third example is connected with high-precision ab initio calculations of small molecules, showing expanded opportunities of ab initio methods developed by the author, in which:

- the new high-precision estimations of the dissociation energy of the diatomic barium molecule was given, which are based on the comparative analysis of the calculated potential curves of ground states of Sr_2 and Ba_2 molecules and other theoretical and available experimental data;

- the new high-precision IR and Raman's spectra of Al_2O_2 and Al_2O_3 molecules were calculated;

- the numerical solution of the Hartree-Fock equations for the hydrogen molecule was obtained with the highest known accuracy by employing the modified linear combinations of atomic orbitals approximation, proposed by the author, and which correctly describes the asymptotic properties of the MOs.

In the last example, the $X^1\Sigma_g^+$ potential curves of the helium and beryllium dimers were calculated by the CI method using the high-precision ab initio methodology. The calculated dissociation energy of the beryllium dimer differs from the experimental one [19] of about $1.5\mathrm{cm}^{-1}$, while all vibration energy levels were calculated with mean square deviation about $4\mathrm{cm}^{-1}$ [20]. Our investigation of the $X^1\Sigma_g^+$ state of Be_2 agrees with the calculation [21] and points out that the ground state of the beryllium dimer has twelve vibrational energy levels and the twelfth vibration level has two rotational states [20, 22].

In conclusion, it should be noted, that the existence of the twelfth vibrational level in the $X^1\Sigma_g^+$ state of the beryllium dimer with $\nu = 11$ and the energy, only slightly below the dissociation limit, allows one to propose new experiments on detecting the Efimov states [23, 24, 25, 26] in the scattering beryllium atoms on beryllium dimers by checking the resonant metastable states of the beryllium trimmer at ultra low energies. The calculated high-precision of the potential curve of the ground state of the beryllium dimer allows one to formulate an appropriate mathematical model and to perform the required theoretical study and numerical modeling of this problem, as well as a more detailed investigation of the quantum transparency effect of barriers and the quantum near surface diffusion of beryllium molecules [27, 28, 29].

5. Conclusions

The developed modified conventional and semi-direct parallel Hartree-Fock and DFT methods are significantly faster than the corresponding parallel direct methods. The main approaches to the parallelization of the CI method with the calculation of matrix elements in accordance of the Slater rules are formulated. The approach allows the explicit correlation of much more than 20 electrons, which is the limit for CI methods, in which the matrix elements are calculated by using group theory methods.

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