Information

PRIRODA-04: a quantum-chemical program suite. New possibilities in the study of molecular systems with the application of parallel computing

D. N. Laikov★ *and Yu. A. Ustynyuk*

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 2677. E-mail: Laikov@physto.se; ustynyuk@nmr.chem.msu.su

Main characteristics are described of the PRIRODA quantum-chemical program suite designed for the study of complex molecular systems by the density functional theory, at the MP2, MP3, and MP4 levels of multiparticle perturbation theory, and by the coupled-cluster single and double excitations method (CCSD) with the application of parallel computing. A number of examples of calculations are presented.

Key words: quantum chemistry; molecular systems; parallel computing; DFT, MP2, MP3, MP4, and CCSD methods.

The year 1998 was marked by the award of the 1998 Nobel prize in chemistry to Walter Kohn "for his development of the density-functional theory" and John Pople "for his development of computational methods in quantum chemistry". Outstanding advances in quantum chemistry made in the last two decades, combined with rapid progress of hardware, have made quantum-chemical calculations an integral part of applied and basic research in chemistry and related fields. Most theoretical studies of the structure and properties of molecular systems involve investigations of the adiabatic potential energy surfaces of the ground and, more rarely, excited electronic states. Often, such investigations are restricted to (i) location of the energy minima corresponding to the equilibrium geometries of stable states and saddle points (transition-state geometries), and (ii) quadratic approximation of the potential energy surface based on the results of calculations of the second derivatives of energy with respect to nuclear coordinates. Besides, some applications require calculations of energy derivatives with respect to the strength of disturbing external uniform electric or magnetic field (polarizability, magnetic susceptibility, NMR shielding tensor, and Raman intensity and polarization calculations). Here, the main difficulty is solving the many-electron problem, which can only be done using simplified approaches that can be divided into three types, namely, the wave-function methods, density functional methods, and semiempirical methods.

Ab initio methods, especially coupled cluster methods, allow, at least in principle, the nonrelativistic many-electron problem to be solved with prescribed accuracy using converging sequences of one-electron basis sets and tak-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 804—810, March, 2005.

ing into account higher-order excited configurations. But at present high computational cost only permits the simplest versions of this type of approximations to be used for quantitative calculations of the properties of relatively small molecular systems.

In density functional methods, solution to the many-electron problem is reduced to solving the effective one-electron self-consistent field (SCF) equations. However, the accuracy of the practically used simple models of the exchange-correlation functional cannot be systematically improved to any desired level. Such models belong to the first-principle models but usually include parametrization. Simplicity of the computational scheme of the density functional methods allows them to be employed in the studies of large molecular systems involving qualitative and semiquantitative estimates of the most important physicochemical characteristics.

Semiempirical quantum-chemical methods employing the SCF parametrization of molecular integrals in a minimum basis set are characterized by a much lower predictive power. Recently, density functional methods have been more widely used, because a small gain in the computing time does not compensate apparent drawbacks of the semiempirical methods.

The demands of most researchers who use quantum-chemical methods are still not met because of the lack of computational resources. Extension of the range of objects accessible to theoretical studies and an increase in accuracy owing to improvement of algorithms and their program implementation with allowance for specific features of modern computer architecture is a topical problem. Parallelization of computations and distributed data storage are the most important tools of enhancement of the performance of quantum-chemical programs. At present, more than ten widely used program systems are available throughout the world, each of them being very specific and having its own field of application. For some years, one of the authors of this work* has been developing a quantum-chemical program suite called PRIPODA. A number of earlier versions of this program suite, which implement the density functional method, has been intensively and successfully used by researchers from the Russian Federation, USA, Switzerland, and Germany for solving a variety of chemical problems.

It is not the goal of this study to analyze more than one hundred fifty research publications in which the key results were obtained using these versions. We will restrict ourselves to a few representative examples. The authors of this work and their colleagues at the research group have successfully used the PRIPODA program in studies of (i) the structure of organometallic π-complexes and mechanisms of metallotropic rearrangements,[1—4] (ii) mechanisms of alkane activation by electron-deficient compounds of early transition metals,[5—11] (iii) mechanisms of olefin polymerization by π-complexes of Ti, Zr, and Hf,[12—15] (iv) the structure and reactivity of organic compounds of Group 14 elements (Si, Ge, Sn)[16,17] including their subvalent derivatives,[18,19] and (v) the structure of macrocyclic Schiff bases, their complexes with transition metals,[20—22] and their ability to selective binding of anions as artificial anion receptors.[23] Other authors successfully used the PRIPODA system for studying the structure and rearrangements of radical cations in the course of liquid-phase radiolysis,[24—26] the structure of fullerene derivatives,[27—31] the structure and growth mechanism of silsesquioxanes,[32] the structure of novel complexes of the late transition metals and their ability to activate alkanes,[33—45] the structure of new gernatranes and germylenes,[46—48] the structure of crown ether complexes with metal cations,[49] and for solving many other problems concerning the structure and reactivity of rather complex molecular systems. In this work we briefly outline new capabilities of the PRIPODA-04 quantum-chemical program suite implementing a set of high-level methods.

PRIPODA-04 program suite: capabilities. The PRIPODA-04 program suite was developed for parallel computing on multiprocessor systems with shared or distributed memory, driven by the Unix-like operation systems. In most cases these are clusters based on dual-processor nodes connected by a high-speed network. The code was written in C language using a standard message passing interface MPI. The program can easily be adapted for calculations on single-processor workstations and personal computers driven by various operation systems.

The program implementation of all methods permits (i) geometry optimization of stable and transition states of the molecular systems under study using analytically calculated first derivatives of energy and (ii) construction of the intrinsic reaction coordinate (IRC). Vibrational analysis in the harmonic approximation allows one to calculate the IR and Raman frequencies and intensities. It is also possible to calculate the Mulliken and Hirshfeld atomic charges.[50] Using the density functional method, one can calculate the nuclear magnetic shielding tensors with the calibration-invariant AOs (GIAO approach).[51] Program implementations of most methods also provide the means for calculating the HFC constants in the ESR spectra of paramagnetic systems.

In all quantum-chemical methods, the one-electron basis sets used are contracted sets of Gaussian functions with the angular part represented by real spherical harmonics. The largest angular momentum is specified in the compilation stage (by default, it corresponds to the quantum number $L \leq 6$). The program uses original algorithms for calculations of necessary two-, three-, and four-center Coulomb integrals[52] based on recurrent relations.[53] Until very recently, the molecules containing heavy elements

---

* D. N. Laikov.

could be calculated only using pseudopotentials. The PRIPODA program suite permits all-electron computations in the scalar relativistic approximation[54] using both density functional and *ab initio* methods with inclusion of electron correlation. In order to reduce the computational cost, all calculations are performed without symmetry considerations of the molecular system.

Density functional methods. Among different approximate exchange-correlation functionals, generalized gradient approximations are most widely used. Our program suite permits calculations with the PBE functional[55] and its modification, mPBE,[56] and, for the sake of comparison, with the BLYP functional[57,58] and in the local density approximation.[59] Owing to the fact that in these approximations all two-electron contributions to the energy are expressed in explicit form through the electron density, we succeeded[60] in accelerating the calculations of energy and its first derivatives with respect to nuclear coordinates using an approximate electron density expansion over an auxiliary basis set. This approximation provides even greater gain in performance when calculating the second derivatives of energy with respect to nuclear coordinates. We also succeeded in employing larger grids using optimum quadrature formulas for higher-order sphere in three-dimensional numerical integration of exchange-correlation components.[61] This reduced noise in energy and its derivatives down to a level acceptable in all practical applications. To improve the performance, specific basis sets for all elements from H to Xe were constructed,[62] which use the same exponent values for different angular moments; this makes the calculations of three-center Coulomb integrals several times faster. When calculating molecular systems containing a hundred and more atoms, the bottleneck of the algorithm is matrix multiplication, diagonalization, and orthogonalization.

In studies of a series of adamantane ($C_{10}H_{16}$)-based cage hydrocarbons of general formula $C_{\{4+6n+2n(n-1)+(2n3+3n2+13n-18)/6\}}H_{\{4+12n+2n(n-1)\}}$, obtained by layer-by-layer buildup of the diamond-like framework (in the limit, this gives a diamond lattice) we calculated a number of structures with n = 2—8. The structure of the last member of this series (n = 8) is shown in Fig. 1. Characteristics of such systems are of own interest for chemists, but comprehensive treatment of the results of computations goes beyond the scope of this work and will be published elsewhere. Note that until very recently only semiempirical calculations of such large systems were possible. As an example, in Table 1 we list typical computing times taken to perform a geometry optimization cycle in the density functional calculations of these compounds and some other details.

The PRIPODA program suite permits calculations of excited-state energies in the adiabatic approximation to time-dependent density functional theory.[63] An important field of application of this method is calculations of the electronic spectra of delocalized systems (aromatic molecules, dyes, *etc.*). The possibility of analytical calculations of the first derivatives of excited-state energies with respect to atomic coordinates[64] was implemented in the PRIRODA program for the first time; this permits determination of the excited-state equilibrium molecular geometries. As an example, in Table 2 we present the calculated energies of the first seven (out of a total of 299) vertical singlet-singlet electronic transitions of the C_{60} molecule with nonzero dipole moments of transitions. Computations carried out on eight IBM PPC970 (1600 MHz) processors in a basis set including 1,500 functions took a time of 1,000 min.

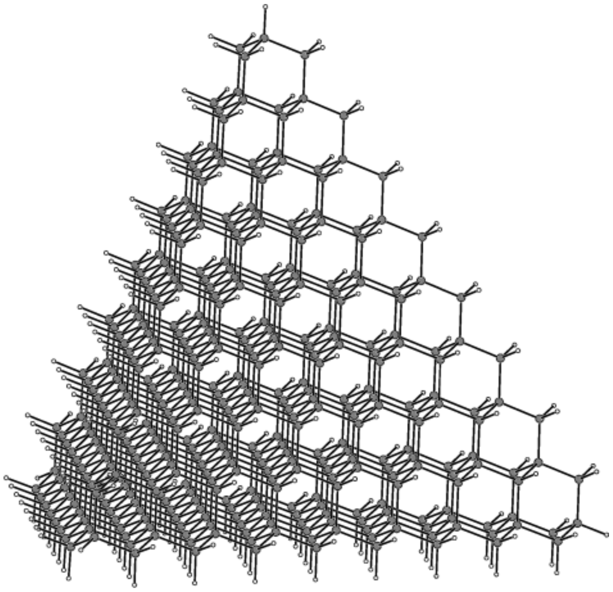

Fig. 1. Structure of symmetrical diamond-like hydrocarbon $C_{381}H_{212}$.

Relativistic effects significant for heavy atoms[5] can most consistently be included using a certain generalization of the Dirac one-electron equation for many-electron systems. Working with four-component spinors requires complex numbers, so the matrix dimensions become at least doubled. Therefore, it is appropriate to use approximate scalar-relativistic approaches which retain a commonly accepted structure of the equations of nonrelativistic theory due to neglect of the spin-orbit coupling. Our program suite permits application of the scalar-relativistic approximation in both density functional[62] and *ab initio* calculations. In this case, the second derivatives of energy with respect to nuclear coordinates in the density functional calculations can be obtained analytically.

Second-order perturbation theory and approximation of the expansion of unity. Among all *ab initio* methods, the Hartree—Fock method[66] is the simplest, although often has an insufficient accuracy. Being "cheaper" than the density functional methods, the Hartree—Fock method

Table 1. Computing time (t) taken to perform a geometry optimization cycle and calculate the second derivatives of energy with respect to nuclear coordinates for diamond-like hydrocarbons by the density functional method with the basis sets of dimension (2s/4s;4s1p) for H and (4s2p1d/8s4p1d;7s2p2d) for C on a cluster of IBM PPC970 (1600 MHz) dual-processor nodes without inclusion of molecular symmetry

Chemical formula	h*	t/min									
		First geometry optimization cycle					Second derivative calculations				
		Number of processors				Memory (disk space)/MB	Number of processors				Memory (disk space)/MB
		2	4	8	16		2	4	8	16	
$C_{26}H_{32}$	454 (822)	2.7	1.4	0.8	0.5	7 (50)	41	24	14	10	14 (258)
$C_{51}H_{52}$	869 (1573)	6.2	3.4	2	1.3	26 (136)		109	69		48 (1152)
$C_{87}H_{76}$	1457(2533)	12.3	6.8	4.1	2.7	63 (326)		405	262		135 (4144)
$C_{136}H_{104}$	2248 (3856)	27	15.4	9.3	6.2	141 (708)				780	319 (12738)
$C_{200}H_{136}$	3272 (5552)	60.2	34.1	21.1	14	289 (1420)					
$C_{281}H_{172}$	4559 (7667)			41.1	26.4	513 (2661)					
$C_{381}H_{212}$	6139 (10247)				56	925 (5300)					

* Number of functions in the main (auxiliary) basis set.

Table 2. Energies of seven (out of 295) first vertical singlet-singlet electronic transitions of C_{60} molecule with nonzero dipole moments obtained in the adiabatic approximation of time-dependent density functional theory[63] with the basis set including a total of 1500 functions on a cluster of IBM PPC970 (1600 MHz) dual-processor nodes without inclusion of molecular symmetry

Transition number	E_{tr}/eV	λ/nm	μ_{tr}/a.u.
28	2.790	444.4	0.145
55	3.408	363.8	1.116
122	4.302	288.2	1.669
170	4.826	256.9	0.128
176	4.880	254.1	0.160
250	5.301	233.9	2.504
289	5.604	221.2	0.218

Note. Degeneracy order N = 3; E_{tr} is the transition energy; and μ_{tr} is the dipole moment of the transition.

ranks much below the best of them in accuracy. The simplest way of inclusion of electron correlation effects is to use the second-order multiparticle perturbation theory (MP2),[67] which offers some advantages in the field of its application. For instance, characteristics of typical organic compounds including the energies of reactions are most often reproduced by this method with a higher accuracy compared to the existing density functional methods provided the use of high-quality one-electron basis set. Besides, this is the simplest method for the description of the Van der Waals interactions (in some cases, they can play the key role) with an acceptable accuracy. Unfortunately, the approach is inapplicable to calculations of systems with strong electron correlation including most compounds formed by transition metals in low oxidation states. In our program suite, two versions of the MP2 method are implemented. A standard version for closed-shell systems[68] can be used for calculations of small molecular systems; here, the memory required is a cubic function of the size of the system under study. It permits analytical calculations of the first derivatives of energy with respect to nuclear coordinates. A spin-restricted version of the MP2 method for open-shell systems[69] involving analytical calculations of the first derivatives of energy is also available. An original feature is the use of an approximation to the expansion of unity[70] in solving both Hartree—Fock SCF equations and in further inclusion of electron correlation effects in the MP2 method, which allows significant improvement of performance of the method owing to reduced memory requirements. This approach also permits a more efficient parallelization of computations. As an example, Table 3 lists the computing times and memory requirements per a geometry optimization cycle in the RI-MP2 calculations of diamond-like hydrocarbons with the basis set (2s1p)/(6s2p), (2s1p)/(5s2p) for H and (3s2p1d)/(10s6s2d), (5s4p3d1f)/(10s6p5d2f) for C on a cluster of IBM PPC970 (1600 MHz) dual-processor nodes without inclusion of molecular symmetry.

Fourth-order perturbation theory and coupled-cluster methods. In those cases where the properties of a system under study can be quite correctly described at the MP2 level of theory, even better accuracy can be achieved using the third-order (MP3) and fourth-order (MP4) perturbation theory. At the MP4 level, it is possible to restrict oneself to the inclusion of the contributions of the singly, doubly, and quadruply excited configurations and renormalization (MP4(SDQ)) or one can also include the contribution of triply excited configurations (MP4(SDTQ)). Our program suite permits MP3,

Table 3. Computing time and memory requirements for a geometry optimization cycle in RI-MP2 calculations of diamond-like hydrocarbons with the basis set of dimensions (2s1p)/(6s2p), (2s1p)/(5s2p) for H and (3s2p1d)/(10s6s2d), (5s4p3d1f)/(10s6p5d2f) for C on a cluster of IBM PPC970 (1600 MHz) dual-processor nodes without inclusion of molecular symmetry

Parameter	Value			
Chemical formula	$C_{26}H_{32}$		$C_{51}H_{52}$	
Number of electrons	188		358	
Number of functions in the main (auxiliary) basis set[a]	524 (1174)		974 (2249)	
Hartree—Fick energy, E_1/a.u.	−1003.481		−1962.122	
MP2 correlation energy, E_2/a.u.	−3.739		−7.270	
Number of processors	8	16	32	64
Computational procedures:	Computing time/min			
integrals	7	4	9	5
HF equations	14	11	122	77
MP2 energy	13	7	73	44
HF response	8	5	59	33
derivatives of integrals	8	4	10	6
total computing time	51	33	305	186
Memory[b]/MBytes	128	128	256	256
Disk space[c]/MBytes	590 (540)	325 (280)	1100 (900)	783 (500)

[a] Listed are the numbers of contracted/elementary Gaussian functions for the main/auxiliary basis set.

[b] Memory on each node.

[c] Disk space on the master node and average disk space on other nodes.

MP4(SDQ), and MP4(SDTQ) calculations of the energy and its first derivatives with respect to nuclear coordinates for closed-shell systems. Similarly to the coupled cluster methods (see below), this involves extensive calculations and requires a large amount of disk space for data storage. All four-index supermatrices (excitation amplitudes, two-electron integrals and density matrices, and intermediate products) are distributed over cluster nodes with respect to the last index. Thus, in the case of parallel computations the number of processors used can be as high as half the number of electrons (for closed-shell systems) for which electron correlation is included. Table 4 lists the computing time for a typical example of MP4 calculations.

The coupled cluster method with inclusion of single and double excitations (CCSD)[71] is implemented in the PRIRODA program for both closed-shell systems and open-shell systems (spin-unrestricted version). The method is highly time-consuming (the computing time increases in proportion to the sixth power of the size of the system), which makes it of limited use. Nevertheless, at present our parallel implementation of the approach allows systems of real interest for chemists to be calculated. One geometry optimization cycle for dibenzene-chromium molecule in a basis set including a total of 271 contracted Gaussian functions using 37 IBM PPC (1.6 GHz) processors takes about 24 h.

Table 4. Computing time (*t*) taken to perform MP4 calculations of the energy and analytical calculations of the first derivatives of energy with respect to nuclear coordinates for C_6H_6 molecule (one geometry optimization cycle) in the basis set including a total of 114 contracted Gaussian functions of dimensions (3s2p1d)/(10s6p2d) for C and (2s1p)/(6s2p) for H on a cluster of IBM PPC970 (1600 MHz) dual-processor nodes without inclusion of molecular symmetry

Computational operations	*t*/min		
	Number of processors		
	4	8	15
Two-electron integrals	0.46	0.25	0.17
Transformation of integrals	1.1	0.85	0.78
MP3 and MP4(SDQ) energies and density matrices	2.37	1.55	1.23
MP4(T) energies and density matrices	36.83	17.37	9.38
Density matrix transformation	1.6	1.1	0.88
Derivatives of integrals	5.4	2.9	1.73
Total computing time/min	49	24.93	15

Coupled cluster methods also permit calculations of the properties of excited electronic states. The simplest approximation is the method with inclusion of single and double excitations (so-called eom-CCSD method),[72] which is available in our program suite for the ground state of closed-shell systems. The energy of the *n*th singlet excited state can be determined and its first derivatives with respect to nuclear coordiantes can be calculated analytically. These computations are about two or three times more "expensive" than ground-state CCSD calculations. Table 5 lists the computing times taken to perform geom-

Table 5. Computing time (t) taken to perform eom-CCSD calculations of the excited-state energy and first derivatives of energy for azulene molecule ($C_{10}H_8$) in the basis set including a total of 180 functions (general contraction patterns were (3s2p1d)/(12s7p2d) for C and (2s1p)/(8s2p) for H) on 24 IBM PPC970 (1600 MHz) processors without inclusion of molecular symmetry

Computational operations	t/min
Two-electron integrals	0.63
Transformation of integrals	6.58
CCSD equations for ground-state energy (17 iterations)	53.74
CCSD equations for the first excited-state energy (17 iterations) and conjugated equations (16 iterations)	213.9
Ground-state response conjugated equations	94.3
Two-electron density matrix transformation	6.57
Derivatives of two-electron integrals	7.38
Total computing time/min	383.1

etry optimization of the first singlet excited state of azulene molecule by the eom-CCSD method.

Prospects for further development and improvement. The main direction of improvement of the PRIPODA program suite in the nearest future will be construction of atomic basis sets including Gaussian functions with a common contraction pattern for both nonrelativistic and relativistic computational methods for all elements of the periodic system based on a unified approach. This will allow one to avoid uncertainties due to the well-known effect of the basis set type and size on the characteristics to be computed.

* * *

The results presented in this work show that the PRIPODA-04 quantum-chemical program suite designed for the study of complex molecular systems by the density functional theory, at the MP2, MP3, and MP4 levels of multiparticle perturbation theory, and by the coupled cluster method with inclusion of single and double excitations (CCSD) using parallel computers offers significant new capabilities and considerably extends the range of molecular systems accessible to high-level quantum-chemical investigations.

The authors express their gratitude to the Joint Supercomputer Center of the Russian Academy of Sciences for providing computing time on the MVS-1000M and MVS-5000 clusters, to the Research Computing Center of the M. V. Lomonosov Moscow State University, and to the Department of Computational Mathematics and Cybernetics of the M. V. Lomonosov Moscow State University for providing time for debugging and computations on the IBM p690 supercomputer and on the SCI, AQUA, and LEO clusters.

This work was carried out with the financial support from the Russian Foundation for Basic Research (Project No. 04-07-90365) and the M. V. Lomonosov Moscow State University (MSU Interdisciplinary Research Program, Project No. 30).

References

1. O. I. Trifonova, E. A. Ochertyanova, V. A. Roznytovsky, N. G. Akhmedov, D. N. Laikov, N. A. Ustynyuk, and Yu. A. Ustynyuk, *Inorg. Chim. Acta*, 1998, **220**, 328.
2. Yu. F. Oprunenko, D. N. Laikov, S. G. Malugina, V. I. Mstislavsky, V. A. Roznytovsky, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1999, **583**, 136.
3. Yu. F. Oprunenko, I. P. Gloriozov, K. A. Lyssenko, S. Malyugina, D. Mityuk, V. Mstislavsky, H. Guenther, G. von Firfs and M. Ebener, *J. Organomet. Chem.*, 2002, **656**, 27.
4. I. P. Gloriozov, A. Yu. Vasil´kov, Yu. F. Oprunenko, and Yu. A. Ustynyuk, *Zh. Fiz. Khim.*, 2004, **78**, 313 [*Russ. J. Phys. Chem.*, 2004, **78** (Engl. Tramsl.)].
5. L. Yu. Ustynyuk, Yu. A. Ustynyuk, D. N. Laikov, and V. V. Lunin, *Izv. Akad. Nauk. Ser. Khim.*, 1999, 2248 [*Russ. Chem. Bull.*, 1999, **48**, 2222 (Engl. Transl.)].
6. Yu. A. Ustynyuk, L. Yu. Ustynyuk, D. N. Laikov, and V. V. Lunin, *J. Organomet. Chem.*, 2000, **597**, 182.
7. L. Yu. Ustynyuk, Yu. A. Ustynyuk, D. N. Laikov, and V. V. Lunin, *Izv. Akad. Nauk. Ser. Khim.*, 2001, 359 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 376].
8. L. Yu. Ustynyuk, Yu. A. Ustynyuk, D. N. Laikov, and V. V. Lunin, *Izv. Akad. Nauk. Ser. Khim.*, 2001, 1959 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2050].
9. D. V. Besedin, L. Yu. Ustynyuk, Yu. A. Ustynyuk, and V. V. Lunin, *Mendeleev Commun.*, 2002, 173.
10. L. Yu. Ustynyuk, D. V. Besedin, V. V. Lunin, and Yu. A. Ustynyuk, *Zh. Fiz. Khim.*, 2003, **77**, 1269 [*Russ. J. Phys. Chem.*, 2003, **77** (Engl. Transl.)].
11. L. Yu. Ustynyuk, D. V. Besedin, V. V. Lunin, and Yu. A. Ustynyuk, *Zh. Fiz. Khim.*, 2003, **77**, 1478 [*Russ. J. Phys. Chem.*, 2003, **77** (Engl. Transl.)].
12. I. E. Nifant´ev, L. Yu. Ustynyuk, and D. N. Laikov, *Izv. Akad. Nauk. Ser. Khim.*, 2000, 1168 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1164].
13. I. E. Nifant´ev, L. Yu. Ustynyuk, and D. N. Laikov, *Izv. Akad. Nauk. Ser. Khim.*, 2000, 1754 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1735].
14. I. E. Nifant´ev, L. Yu. Ustynyuk, and D. N. Laikov, in *Organometallic Cataysts and Olefin Polymerization*, Eds R. Blom, A. Follestad, E. Rytter, M. Tilset, and M. Ystenes, Springer Verlag, Berlin, 2001, 72.
15. I. E. Nifant´ev, L. Yu. Ustynyuk, and D. N. Laikov, *Organometallic*, 2001, **20**, 5375.
16. N. N. Zemlyanskii, I. V. Borisova, M. S. Nechaev, V. N. Khrustalev, and Yu. A. Ustynyuk, *Izv. Akad. Nauk. Ser. Khim.*, 2002, 665 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 721].
17. N. N. Zemlyansky, I. V. Borisova, and Yu. A. Ustynyuk, *Adv. Organomet. Chem.*, 2003, **49**, 36.
18. N. N. Zemlyansky, I. V. Borisova, V. V. Lunin, Yu. A. Ustynyuk, M. Yu. Antipin, and M. S. Nechaev, *Organometallic*, 2003, **22**, 5441.

19. N. N. Zemlyanskii, I. V. Borisova, M. S. Nechaev, V. N. Khrustalev, V. V. Lunin, M. Yu. Antipin, and Yu. A. Ustynyuk, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 939 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 901].
20. A. Yu. Chernyad´ev, M. D. Reshetova, Yu. A. Ustynyuk, O. V. Yazev, E. A. Kataev, A. A. Sidorov, G. G. Aleksandrov, V. N. Ikorskii, V. M. Novotortsev, S. E. Nefedov, I. L. Eremenko, and I. I. Moiseev, *Izv. Akad. Nauk. Ser. Khim.*, 2001, 2334 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2445].
21. Yu. A. Ustynyuk, N. E. Borisova, M. D. Reshetova, G. G. Aleksandrov, I. I. Moiseev, I. L. Eremenko, *Mendeleev Commun.*, 2003, 2002.
22. N. E. Borisova, Yu. A. Ustynyuk, and M. D. Reshetova, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 174 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 181].
23. J. L. Sessler, G. D. Pantos, E. A. Katayev, and Yu. A. Ustynyuk, *Chem. Commun.*, 2004, 1276.
24. V. N. Belevskii, S. I. Belopushkin, I. A. Baranova, and D. A. Tyurin, *Khim. Vys. Energ.*, 1999, **33**, 434 [*High Energy Chem.*, 1999, **33** (Engl. Transl.)].
25. D. A. Tyurin, M. Ya. Mel´nikov, and V. N. Belevskii, *Khim. Vys. Energ.*, 2001, **35**, 266 [*High Energy Chem.*, 2001, **35**, 236 (Engl. Transl.)].
26. D. A. Tyurin and V. N. Belevskii, *Khim. Vys. Energ.*, 2001, **35**, 441 [*High Energy Chem.*, 2001, **35**, 404 (Engl. Transl.)].
27. S. I. Troyanov, P. A. Troshin, O. V. Boltalina, I. N. Ioffe, L. N. Sidorov, and E. Kemnitz, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 2285.
28. I. N. Ioffe, A. S. Ievlev, O. V. Boltalina, L. N. Sidorov, H. C. Dorn, S. Stevenson, and G. Rice, *Int. J. of Mass-Spectrometry*, 2002, **213**, 183.
29. O. V. Boltalina, A. A. Goryunkov, V. Y. Markov, I. N. Ioffe, and L. N. Sidorov, *Int. J. of Mass-Spectrometry*, 2003, **228**, 807.
30. S. I. Troyanov, A. A. Popov, N. I. Denisenko, O. V. Boltalina, L. N. Sidorov, and E. Kemnitz, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 2395.
31. V. V. Zverev, V. P. Gubskaya, and I. A. Nuretdinov, *Zh. Obshch. Khim.*, 2003, **73**, 1305 [*Russ. J. Gen. Chem.*, 2003, **73** (Engl. Transl.)].
32. K. Jug and I. P. Gloriozov, *Phys. Chem. Chem. Phys.*, 2002, 1062.
33. A. N. Vedernikov, R. Miftakhov, S. V. Borisoglebski, K. G. Caulton, B. N. Solomonov, *Chem. Heterocycl. Compd.*, 2002, **418**, 471.
34. A. N. Vedernikov, P. Wu, J. C. Huffman, and K. G. Caulton, *Inorg. Chim. Acta*, 2002, **330**, 103.
35. A. A. Sobanov, A. N. Vedernikov, G. Dyker, and B. N. Solomonov, *Mendeleev Commun.*, 2002, 14.
36. A. V. Marchenko, A. N. Vedernikov, D. F. Dye, M. Pink, J. M. Zaleski, and K. G. Caulton, *Inorg. Chem.*, 2002, **41**, 4087.
37. A. N. Vedernikov, J. C. Huffman, and K. G. Caulton, *New J. Chem.*, 2002, **26**, 1267.
38. A. N. Vedernikov, J. C. Huffman, and K. G. Caulton, *Inorg. Chem.*, 2002, **41**, 6244.
39. A. N. Vedernikov, J. C. Huffman, and K. G. Caulton, *Inorg. Chem.*, 2002, **41**, 6867.
40. A. N. Vedernikov and K. G. Caulton, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 4102.
41. A. N. Vedernikov, J. C. Huffman, and K. G. Caulton, *Chem. Commun.*, 2003, 358.
42. A. N. Vedernikov, J. C. Huffman, and K. G. Caulton, *New J. Chem.*, 2003, **27**, 665.
43. A. V. Marchenko, A. N. Vedernikov, J. C. Huffman, and K. G. Caulton, *New J. Chem.*, 2003, **27**, 680.
44. A. N. Vedernikov, M. Pink, and K. G. Caulton, *J. Org. Chem.*, 2003, **68**, 4806.
45. A. N. Vedernikov, J. C. Huffman, M. Pink, and K. G. Caulton, *Org. Lett.*, 2003, **5**, 2591.
46. J. Lorberth and G. S. Zaitseva, *Inorg. Chem.*, 2002, **41**, 6147.
47. A. A. Selina, S. S. Karlov, K. Harms, D. A. Tyurin, Yu. F. Oprunenko, J. Lorberth, and G. S. Zaitseva, *Naturforsch.*, 2003, **58b**, 613.
48. A. V. Churakov, L. G. Kuz´mina, S. S. Karlov, E. V. Gauchenova, D. A. Tyurin, and G. S. Zaitseva, *Zh. Neorg. Khim.*, 2003, 1008 [*Russ. J. Inorg. Chem.*, 2003 (Engl. Transl.)].
49. V. G. Avakyan, S. P. Gromov, A. I. Vedernikov, S. N. Dmitrieva, and M. V. Alfimov, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 1 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 1].
50. F. L. Hirshfeld, *Theoret. Chim. Acta. (Berl.)*, 1977, **44**, 129.
51. S. K. Wolf and T. Ziegler, *J. Chem. Phys.*, 1998, **109**, 895.
52. D. N. Laikov, Ph.D. (phys.-math.) Thesis, M. V. Lomonosov Moscow State University, 2000 (in Russian).
53. L. E. McMurchie and E. R. Davidson, *J. Comput. Phys.*, 1978, **26**, 218.
54. K. G. Dyall, *J. Chem. Phys.*, 1994, **100**, 2118.
55. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
56. C. Adamo and V. Barone, *J. Chem. Phys.*, 2002, **116**, 5933.
57. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
58. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
59. J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.
60. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
61. V. I. Lebedev and D. N. Laikov, *Dokl. Akad Nauk*, 1999, **366**, 741 [*Dokl. Math.*, 1999 (Engl. Transl.)].
62. D. N. Laikov, Abstracts *DFT2000 Satellite Symposium of the 10th Int. Congress of Quantum Chemistry*, France, June 2000, P43.
63. M. A. L. Marques and E. K. U. Gross, *Annu. Rev. Phys. Chem.*, 2004, **55**, 427.
64. A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer, *J. Chem. Phys.*, 1987, **87**, 5361.
65. P. Pyykkö, *Chem. Rev.*, 1988, **88**, 563.
66. V. Fock, *Z. Phys.*, 1930, **61**, 126.
67. C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.
68. M. J. Frisch, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.*, 1990, **166**, 275.
69. T. J. Lee and D. Jayatilaka, *Chem. Phys. Lett.*, 1993, **201**, 1.
70. R. A. Kendall and H. A. Früchtl, *Theor. Chem. Acc.*, 1997, **97**, 158.
71. A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer, *J. Chem. Phys.*, 1987, **87**, 5361.
72. J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.*, 1993, **98**, 7029.

Received March 1, 2005