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REVIEW ARTICLE

Regarding certain stages of the development of quantum chemistry in Russia: Experience from the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies

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Abstract

Objectives. *To analyze the history of the development of quantum chemistry and software for quantum chemical calculations in Russia at the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies of RTU MIREA.*
Results. *This work presents a historical overview of the development of quantum chemistry at the Ya.K. Syrkin Department of Physical Chemistry from Academician Ya.K. Syrkin to Professor V.R. Flid. It provides a summary of the work with the participation of the author in 1980s–1990s. Quantum-chemical models used to describe some of the intercalation reactions in a bond are considered in comparison with the well-known Woodward–Hoffman and Fukui approaches. The work outlines fundamentals of studies on the design of bifunctional compounds.*
Conclusions. *The physical significance of the exchange interaction constant is given a visual meaning: it establishes the change in spin density on the metals forming complexes of the type in question when passing from isolated cations in the composition of the complexes. The work provides recommendations to synthetic chemists regarding the selection of components in the synthesis of magnetic sublattices of bifunctional materials. It also examines the high level of scientific research carried out at the Ya.K. Syrkin Department of Physical Chemistry and its relevance to the world science level.*

Keywords: *quantum chemical calculations, molecular orbitals, bond embedding reactions, bifunctional materials*

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ОБЗОРНАЯ СТАТЬЯ

О некоторых этапах развития квантовой химии в России и на кафедре физической химии им. Я.К. Сыркина ИТХТ им. М.В. Ломоносова

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Аннотация

Цели. *Проанализировать историю развития квантовой химии и программного обеспечения для квантово-химических расчетов в России и на кафедре физической химии им. Я.К. Сыркина Института тонких химических технологий (ИТХТ) им. М.В. Ломоносова РТУ МИРЭА.*
Результаты. *Представлен исторический очерк развития квантовой химии в ИТХТ на кафедре физической химии им. Я.К. Сыркина от самого академика Я.К. Сыркина до профессора В.Р. Флида. Обобщены данные работ с участием автора, проводимые им на кафедре физической химии им. Я.К. Сыркина в 80-е и в начале 90-х годов XX века. Рассмотрены квантово-химические модели для описания некоторых реакций внедрения в связь в сопоставлении с известными подходами Вудворда–Гоффмана и Фукуи. Изложены основы работ по дизайну бифункциональных соединений.*
Выводы. *Получено наглядное значение физического смысла константы обменного взаимодействия – она определяет изменение спиновой плотности на металлах, образующих комплексы рассмотренного типа, при переходе от изолированных катионов к ним же в составе комплексов. Даны рекомендации химикам-синтетикам по подбору компонент при проведении синтеза магнитных подрешеток бифункциональных материалов. Продемонстрирован высокий уровень научных исследований, выполняемых в ИТХТ на кафедре физической химии им. Я.К. Сыркина и их соответствие мировому уровню науки.*

Ключевые слова: *квантово-химические расчеты, молекулярные орбитали, реакции внедрения в связь, бифункциональные материалы*

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INTRODUCTION

The development of quantum chemistry in Russia as an independent branch of quantum mechanics from its beginnings to the present day is inseparable from the Ya.K. Syrkin Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies (IFCT) of MIREA – Russian Technological University (RTU MIREA). Many researchers rightly believe that the founders of quantum chemistry in the USSR to be Academician Yakov Kivovich Syrkin and Professor Mirra Efimovna Dyatkina. Syrkin and Dyatkina actively promoted and developed the molecular orbital (MO) method at the dawn of quantum chemistry [1], forming the basis of all its modern computational methods [2–7]. This was undoubtedly a gift of scientific foresight, since at that time Roothaan [8] had not yet proposed the MO—linear combination of atomic orbitals (AO) (MO–LCAO) method. This was the practical implementation of the Hartree–Fock method and enabled the resolution of the Schrödinger equation for various multielectronic systems. In contrast to the Heitler–London method [9], which was popular at the time, each electron in the molecule was assumed to move in an averaged field of the remaining electrons and nuclei, i.e., the traditional concept of directed chemical bonds disappeared. It is not surprising, therefore, that at first many researchers were very hostile to this method which Syrkin and Dyatkina called the method of molecular orbits. It was not until many years later when localized orbitals were included in quantum chemical programs. This eliminated the disadvantage of the MO method and it now occupies a leading position in the vast majority of calculations. It is impossible to describe in detail the difficulties experienced by Syrkin and Dyatkina in such a short story, but representatives of the older generation of chemists and physicists are well aware of them. Personally, I regard this struggle for the triumph of truth as a scientific achievement. Since the nature of this review relates to the field of memory, I would say that I studied under the students of our outstanding teachers. These were the loyal followers of Syrkin and Dyatkina: my teachers Oleg Petrovich Charkin and Nina Mikhailovna Klimenko. I would like to cite one encounter with Syrkin, which will forever remain in my memory. In the spring of 1972, Charkin called Syrkin with a request to oversee my entrance exam to the graduate school of the Academy of Sciences of the Soviet Union (USSR). Syrkin asked for as much clarification of the date of the exam as possible. I picked the date at random: 4 October. Six months later, on 5 October, I took the exam with him in the old building of the N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. This showed not only the care of a great scientist for me, then a very young man, but also a great clarity in matters of work. As a result, I was enrolled in the postgraduate course of the Institute of New Chemical Problems of the USSR, at the Academy of Sciences in the Laboratory of Quantum Chemistry of Professor O.P. Charkin. After graduating in 1976, I was appointed to the Department of Physical Chemistry of IFCT, which today bears the name of Academician Ya.K. Syrkin. The work of the founders of quantum chemistry in Russia is now being successfully continued by the Head of the Department, Professor V.R. Flid. I worked here in the group of N.M. Klimenko for fourteen years until 1990. I have to say a few words about the educational process in the department during those years. Although I was not a full-time teacher, but a research associate, the Rector ordered me to deliver a course directly related to quantum chemistry: the theory of symmetry groups in quantum chemistry. At that time, a textbook written by N.M. Klimenko and G.N. Kartsev, "The Theory of Symmetry Groups for Quantum Chemical Calculations," had been published at IFCT. It proved useful in introducing students to the following important concepts: symmetry elements and operations; abstract group theory; point symmetry groups; group representation theory; the relationship of symmetry group theory to quantum mechanics; and linear combinations of functions reduced by symmetry. Later, at the Moscow Institute of Physics and Technology (2001–2003) and the Lomonosov Moscow State University (2011–2021), I saw that these prestigious universities did not have such a course separately. Students had to study, either on their own or in other courses, such concepts as spectroscopy and many others without which it is difficult to imagine fields of physics and chemistry where the properties of individual quantum systems are studied. This was the fundamental approach to the study of quantum chemistry laid down by Syrkin and Dyatkina.

Next, I would like to share my memories of the results of my work at the Department and later at the institutes of the Russian Academy of Sciences (RAS). Almost all of my work (about 270) is done using MO methods. At various times, the Department was headed by such remarkable scientists as Academician V.I. Goldansky and Corresponding Member of the Russian Academy of Sciences A.A. Ovchinnikov and I have fond memories of each of them. Before going into specific scientific results, I would like to mention an important organizational aspect that was discussed at the turn of 1970s–1980s. At that time, scientific collectives were engaged on resolving the fundamental question of whether to write quantum chemical programs themselves or to use foreign software. We actually needed to do this hard work ourselves, in order to keep up with the countries where such programs are written. However, it takes large teams of programmers to write such powerful programs available in countries that developed General Atomic and Molecular Electronic Structure System (GAMESS)[1], GAUSSIAN[2], MOLPRO[3] and other software. This was not the case in the USSR, and the way to acquire such programs within the international division of labor proved to be more effective. This was preferable not only for Soviet scientists, but also for representatives of other developed countries where such programs were not being created. My teacher, Professor O.P. Charkin, played an important role in providing Soviet scientists with modern software systems. This greatly contributed to the development of quantum chemistry in USSR. Charkin also educated a number of well-known quantum chemists, including Professor A.I. Boldyrev and V.G. Zakzhevsky, co-author of the GAUSSIAN program. He is an example of academic prowess and great diligence with regard to his students.

Before moving on to specific scientific results, I would like to note the generally accepted view that quantum chemistry resolves the following main tasks:

- prediction of the possibility of the existence of different molecular systems in the form of a stable combination of atoms;
- prediction of the geometric and electronic structure of such systems;
- prediction of the most probable ways of chemical reactions;
- implementation of computer design of connections with specified properties.

Together with advances in computer technology, the last two tasks, inaccessible at the beginning of the development of quantum chemistry, have become the most urgent. Therefore, in the remainder of this review, the solution to these tasks will be considered with reference to a number of examples.

CERTAIN WORKS OF THE DEPARTMENT AND INSTITUTES OF THE RUSSIAN ACADEMY OF SCIENCES

In the mid-1970s, calculations of the potential energy surfaces (PES) of chemical reactions were just beginning in USSR. Using the model of valence states previously proposed and developed by Professor Charkin to describe the regularities of energies of sequential bond cleavage in iso-bonded variable-valence series, we proposed a model for finding optimal ways of reagent convergence in reactions of type (1) [10–12]:

$$MX_{k-2} + X_2 \rightarrow MX_k. \qquad (1)$$

We were interested not only in the thermodynamic stability of the products of such reactions, but also in the presence of activation barriers along the optimal paths of convergence of the reagents. The model, which enables us to find such paths, is described in sufficient detail in [12]. Here we will only consider its formulation and briefly outline its advantages over other well-known models. The main provisions of the qualitative model for describing the approximate mechanism of reactions of introduction into communication are as follows.

1. If the convergence of the MX_{k-2} and X_2 reagents along the shortest geometrically path is associated with the intersection of terms[4] and the jump-like promotion of the M atom, and effective donor–acceptor interaction is impossible, then the barriers are large at high promotion energies E_v(M), and small if E_v(M) are small. If effective donor–acceptor interaction is allowed without any costs for E_v(M), then there may be no barriers at all.

2. If the shortest path is forbidden, then of all other possible reaction paths, the minimum activation barrier will correspond to those angles of attack and mutual orientations of the reagents where there are the most favorable opportunities for effective donor–acceptor interaction of the reagents throughout the reaction path without significant expenditure of energy E_v(M) for spasmodic promotion.

Thus, it can be assumed that small or zero activation barriers should correspond to the shortest pathways of $M(^1D) + X_2 \rightarrow MX_2$ or $M(^1D) + Y \rightarrow MY$ type reactions, where M are atoms of type O, C, S, Si, and their heavier analogues in the state ^1D, and $XM(^1\Delta) + X_2 \rightarrow MX_3$, where MX are molecules of the type NH and PH in the state $^1\Delta$, X = H, halogen, alkyl, etc., Y is an atom or valence unsaturated molecule with a closed shell of the type $Be(^1S_0)$, $BH(X^1\Sigma)$, $CH_2(^1A_1)$, $CO(X^1\Sigma)$, $NH(^1A_1)$, $HNO(^1A_1)$, etc. Indeed, *ab initio* calculations of the shortest paths of reactions $O(^1D) + H_2 \rightarrow H_2O(^1A_1)$ [13], $C(^1D) + H_2 \rightarrow CH_2(^1A_1)$[14], $Be(^1S) + O(^1D) \rightarrow BeO(^1\Sigma)$ [15],

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[1] https://www.msg.chem.iastate.edu/gamess/. Accessed May 10, 2023.

[2] https://gaussian.com/. Accessed May 10, 2023.

[3] https://www.molpro.net/. Accessed May 10, 2023.

[4] The intersection of terms here refers to the intersection of potential curves corresponding to different spin multiplicities of the reaction system.

and others show the smooth binding nature of their potential curves. According to our ab initio model, calculations of the shortest reaction paths $BH(X_1\Sigma) + H_2 \rightarrow BH_3$ [10], $CH_2(^1A_1)+H_2 \rightarrow CH_4$[16],$CH_2(^1A_1)+CH_2(^1A_1) \rightarrow H_2CCH_2$[17], $CH_2(^1A_1) + CO(X^1\Sigma) \rightarrow CH_2CO$ [18], etc., show the presence of potential barriers with a height of several tens of kcal. The qualitative conclusions of the model should be retained during the transition from symmetric molecules X_2 to asymmetric molecules XX". Indeed, the *ab initio* calculation of the $CO_2 + H_2O \rightarrow OC(OH)_2$ reaction [19] shows the presence of a high barrier (~53 kcal).

For a better understanding of the essence of our model, we will consider the reaction $CH_2(^1A_1) + H_2 \rightarrow CH_4$. Initially, the hydrogen molecule is positioned in such a way that the axis of the unshared electron pair of the carbon atom $^{12}(C)$ is parallel to the axis of the hydrogen molecule. As the reagents approach, when they pass the area with a high barrier, the hydrogen molecule unfolds until its axis is perpendicular to the plane of the $CH_2(^1A_1)$ molecule. It then connects to it without a barrier to form the CH_4 molecule. In the process of convergence of the reagents, a counter smooth flow of electron density occurs from the unsheltered electron pair of the carbon atom $^{12}(C)$ to the vacant $\sigma_u^0(H_2)$ orbital of the hydrogen molecule; then back from the filled orbital $\sigma_g^2(H_2)$ to the vacant $p\pi^0(C)$ orbital of the carbon atom. This confirms the validity of our model, according to which a smooth flow of electron density does not lead to the formation of high barriers.

Let us briefly consider how our model compares with other well-known models. Our model introduces a quantitative characteristic of the barrier height estimation: the promotion energy of the atom M E_v(M) which can be estimated from atomic spectra. According to the model, the barrier should be large at high promotion energies E_v(M), and small at low E_v(M). Furthermore, the Woodward–Hoffman rules [20], for example, do not provide recommendations for finding accessible reaction paths when the shortest path is prohibited. Using the approach of Fukui [21] and Pearson [22], it is possible in principle to obtain recommendations for finding ways of reacting with minimal barriers. However, they completely ignore the mechanism of electron density redistribution during the reaction and do not investigate the mechanism of intramolecular interactions, which cause the formation of barriers. The most important advantage of our model is the ability to compare the heights of barriers of the same type of reactions by the value of E_v(M) of isolated atoms, without calculating their PES. This can be done even more precisely by the magnitude of the energies of singlet-triplet or doublet-quartet excitations of MX_n molecules containing the central M atom.

A little later, in collaboration with Professor O.N. Temkin’s group, we studied widespread nucleophilic addition reactions on asymmetric alkynes [23, 24]. The issues were considered in relation to two real problems, which arise in such responses, in addition to the problems of multiple bond activation and regioselectivity of addition in the case of asymmetric alkynes. This is particularly important for directional synthesis. There are nucleophilic addition reactions, which violate the Markovnikov rule. In order to clarify the reasons for non-compliance with the Markovnikov rule, we performed calculations in a number of cases of the reactions of nucleophilic (Nu) addition of hydride ion (H^-), fluoride ion (F^-), lithium hydride molecule (LiH) and Li^+/H^-ion pair to acetylene and methylacetylene molecules.

The study investigated the influence of the Nu type on the course of addition reactions, the validity of the well-known Klopman–Fukui approach and the Hudson “non-intersection” rule, the influence of the substituent, the electrophile and the polarity of the solvent on the reactivity of alkyne. Based on calculations, we interpreted experimental data on the absence of addition reactions with a hard nucleophile F^- in polar media without electrophilic assistance and the ease of reactions with soft nucleophiles H^-, BH_4^-, AlH_4^-, etc. in such media. The study also established the reasons for non-compliance with the Markovnikov rule in reactions with H. The role of the electrophile in controlling the regioselectivity of such reactions was shown.

Other things need to be noted about our work together with the group of Professor E.A. Polenov. Among other works, the angular dependence of the constants of the isotropic hyperfine interaction with the nuclei of atoms in the π-radical β-position was investigated [25]. Based on the assumption that it is possible to isolate two-orbital two-center basis fragments with conformation independent mixing coefficients from a once filled boundary MO, an analytical form of this angular function was obtained.

Using the MO–LCAO method, a method was proposed to theoretically establish the angular dependence of spin populations of AO β-atoms in π-radicals. It was shown that the type of this dependence is determined by the local symmetry of the radical center and the substituent. By isolating conformationally independent blocks in the MO combining AO β-atoms into π-systems, the paper presents an effective technique, which establishes a simple way to consistently describe the angular dependence of the constants of the isotropic hyperfine interaction with β-atoms, taking into account the local symmetry of the substituent. It was also found that for conformational rotation, rather subtle effects of the spin density (SD) distribution can be correctly described by semiempirical methods.

Finally, I would like to focus on the latest stage in the development of quantum chemistry: the computer design of compounds with specific properties. A few years ago, on the initiative of Academician S.M. Aldoshin, we started studying bifunctional compounds with both photochromic and magnetic properties. Bifunctional materials are extremely important in the development of new displays, information and energy storage and conversion devices, sensors, etc. [26].

They consist of anionic layers of a magnetic sublattice between which are photochromic cations, such as spiropyrans. At the same time, the development of new hybrid crystalline materials, in which magnetic and photochromic sublattices are combined and interact with each other, requires the solution of a number of experimental problems. At the present time, hybrids of photochromic diarylethene and ferromagnetic layered compounds Co^{II}, Cu^{II} are known. However, open and closed forms of diarylethene form hybrids with different magnetic properties. When the hybrid compound is irradiated, photochrome isomerization does not occur, and the properties of the magnetic sublattice do not change. Unlike diarylethenes, representatives of another class of photochromes—spiropyrane cations—act as photo switches of magnetic properties of a number of hybrids based on bimetallic oxalate Cr^{III} and Mn^{II}, dithiooxalate Fe^{III} and Fe^{II}, thiophosphate Mn^{II}.

The first photomagnetic hybrid was obtained by S. Benard in 2001, the second, in the laboratory of Academician S.M. Aldoshin in 2007. Research is currently underway there to obtain crystals of photochromic hybrid materials with an oxalate sublattice from other metal pairs (Cr and Ni, Fe and Mn, Cr and Co, and others). It is obtained on the basis of a cationic spiropyran containing a quaternary N^+ atom in a pyridine cycle placed in a side aliphatic chain. Its magnetic sublattice consists of complexes formed by oxalate as an intermetal bridge and a pair of Cr^{III} and Mn^{II}, $[Cr^{III}Mn^{II}(Ox)_3]^-$. This bifunctional compound is a ferromagnet with a Curie temperature of 5.1 K. The value of μ_{eff} at high temperatures (300 K) ~7 μ_B[5] agrees well with the calculated 7.07 μ_B (g = 2) for two paramagnetic ions Mn^{II} and Cr^{III} [26]. Thus, these studies are pioneering. Figure 1 shows a fragment of such a connection.

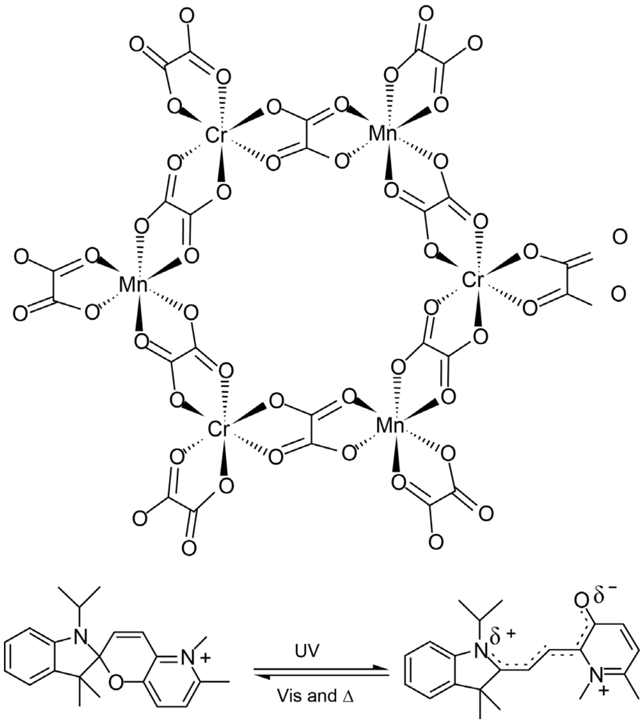

Fig. 1. Fragment of a bifunctional compound is at the top. The opening and closing of the photochromic element under the action of radiation is shown below [26].

The aim of our study was to search for such a region in the Periodic table where metal pairs can provide maximum ferromagnetic exchange interaction, in order to facilitate the selection of appropriate components for synthetic chemists during such synthesis. A further aim was to search for such ligands, which, in combination with these metal pairs, lead to maximum ferromagnetic exchange interaction. However, the main objective was to find a complex that correctly simulated the exchange interactions in a magnetic sublattice. We started this search by calculating complexes containing oxalate as a ligand and a pair of Cr^{III}–Ni^{II} metals [27].

Calculations of all complexes were performed using the GAUSSIAN-03 program[6] in the B3LYP/LANL2DZ[7] approximation with full optimization of the geometric structure of each complex in the ground energy state with maximum spin multiplicity. In order to find the optimal complex in terms of structure and size, we calculated several different complexes, of which the complexes shown in Fig. 2.

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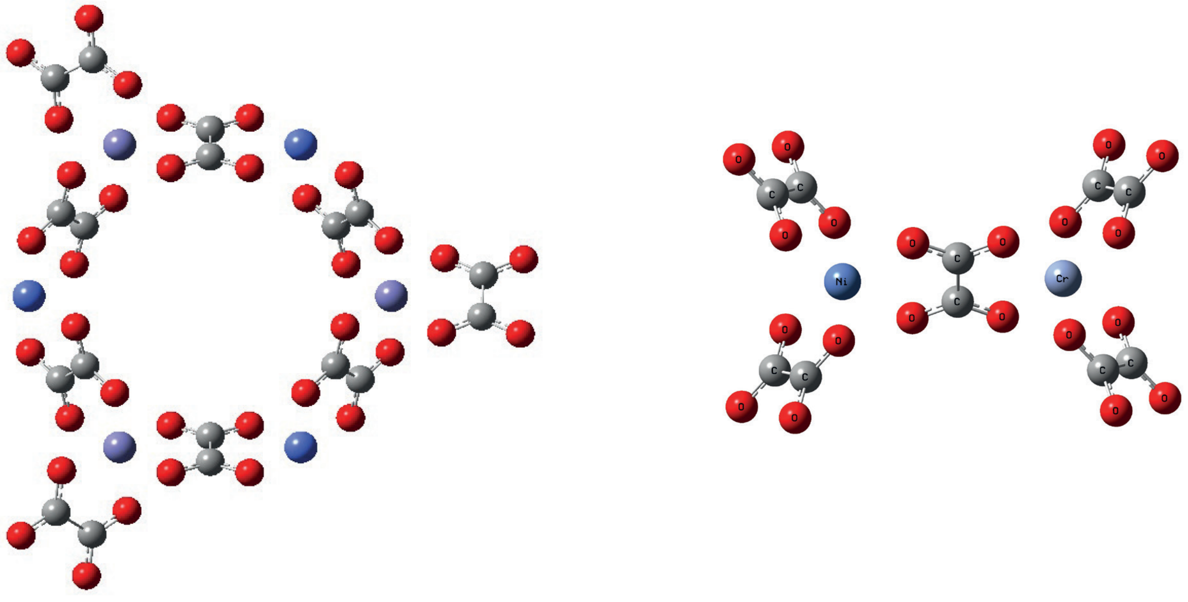
[5] μ_B – Bohr magneton.

[6] License to Use Agreement: Gaussian. Inc. 340 Quinnipiac Street. Building 40. Wallingford. CT 06492.

[7] B3LYP/LANL2DZ is the 3-parametric Becke–Lie–Yang–Parr density functional with a Los Alamos National Laboratory 2 double-ζ (LANL2DZ) basic set.



(a) (b)

Fig. 2. Complex: (a) in the form of a ring, (b) formed by one pair of di- and trivalent transition metal atoms and five anions of oxalate intermetal bridges.

The most effective complex was a pair of metals and five oxalate anions. In less machine time gave almost the same geometric and electronic structure as a much larger complex in the form of a ring. It was chosen by us to calculate complexes with other metal pairs. At the same time, it was shown that optimizing the geometry of such complexes of only nine key structural parameters leads to almost the same results as full geometry optimization. This enables us to preserve the symmetry that these complexes possess in a solid, while at the same time reducing the number of optimized parameters (without such an approach, their number approaches one hundred).

Obviously, this approach makes it possible for a large number of such complexes for different pairs of metals to be calculated with a minimum of human and machine time, necessary to find the most effective ones in terms of ferromagnetic properties. The simplification we propose is optimal for the choice of the structure of the anions of bimetallic complexes and allows us to model the magnetic sublattice quite correctly.

We then carried out calculations to find optimal ligands (intermetallic bridges) which would provide maximum ferromagnetic exchange interaction. To this end, we calculated the exchange interaction constant (*J*) and the SD in such anions for the four most popular ligands L (L is oxalate, oxamide, hydroxamate, or dithiooxamide) and various pairs of tri- and divalent 3d metals [28].

Thus, we calculated anion complexes containing oxalate, oxamide, dithiooxamide anions and hydroxamic acid anion as the intermetallic bridge for various pairs of di- and trivalent transition metal atoms. The types of ligands are shown in Fig. 3 and examples of calculated complex anions are shown in Fig. 4.

All calculations are performed in the above-mentioned approximation with full optimization of the geometry with the maximum spin multiplicity value for each anion. These are complexes of the type $[M_1^{III}M_2^{II}(L)5]$. M_1 and M_2 are transition metal atoms, and $(L)_5$ means five anions of one of the

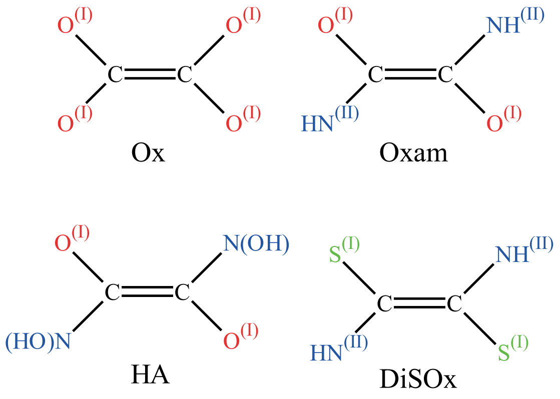
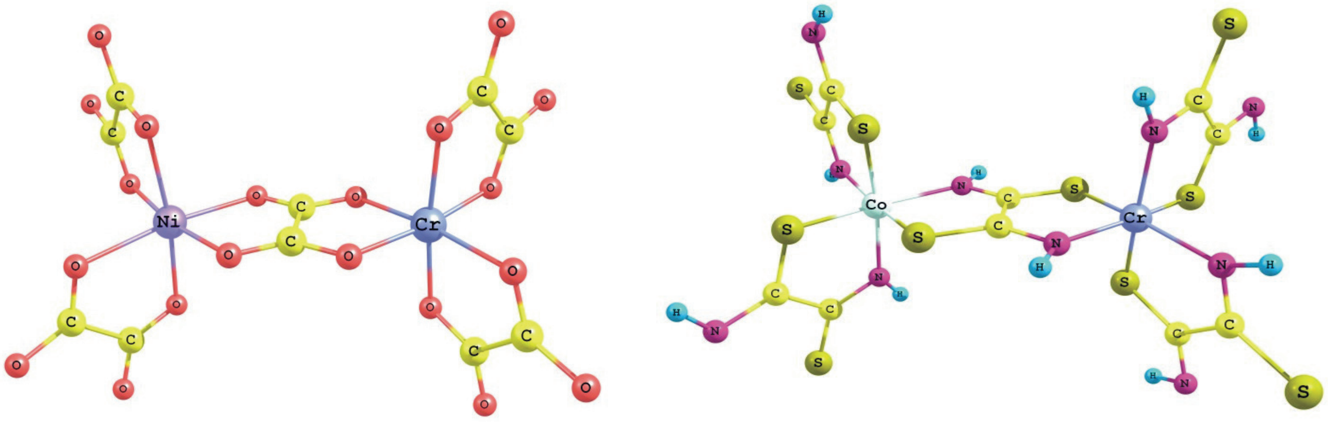


Fig. 3. Types of ligands included in the calculated bimetallic complexes.



(a) (b)

Fig. 4. Anion of a bimetallic complex: (a) with oxalate, (b) with dithiooxamide.

above ligands. Then, using the ORCA program[8], we calculated the values of the exchange interaction constant J. These calculations, as shown by comparison with the literature data, give not only the correct sign of the constant J, but also almost exact quantitative values. In this respect, this program is optimal, since it allows us to obtain the values of the exchange interaction constants with an accuracy of several inverse centimeters. On the other hand, it is only possible to obtain the correct sign of these constants using the GAUSSIAN-03 program. The values of the exchange interaction constants J are estimated in the B3LYP/TZV[9] approximation, in which the broken symmetry (BS) method is implemented [29]. It consists of calculating the total energy of the high-spin (HS) state; subsequent localization of orbitals; and calculation with them of the low spin state with BS. This allows the energy of the low-spin state to be calculated more accurately using a single-determinant Density Functional Theory approach. In the ORCA program, expressions obtained from the analysis of the spin-Hamiltonian of the form $\mathbf{H} = -2J\cdot\mathbf{S}_A\cdot\mathbf{S}_B$ (Heisenberg–Dirac–Van Vleck model) are used to calculate the constants J:

$$J(1) = -(E[\mathrm{HS}]-E[\mathrm{BS}]) / S^2_{\max}) \text{ [31–33]},$$
$$J(2) = -(E[\mathrm{HS}] - E[\mathrm{BS}]) / (S_{\max}(S_{\max} + 1)) \text{ [34]},$$
$$J(3) = -(E[\mathrm{HS}] - E[\mathrm{BS}]) / (<S_2>_{\mathrm{HS}} - <S_2>_{\mathrm{BS}})) \text{ [35]}.$$

With their help, almost identical values of the constant J are obtained, differing by 1–2 cm^{-1}. The values of the exchange interaction constant obtained by the formula $J(3) = -(E[\mathrm{HS}] - E[\mathrm{BS}])/(<S^2>_{\mathrm{HS}} - <S^2>_{\mathrm{BS}}))$ are considered the most theoretically justified, and therefore were taken as its values. The high precision values obtained for the exchange interaction constants allow us to judge not only the nature of the exchange interaction (ferromagnetic or antiferromagnetic), but also where it is strongest. This, in turn, enables us to conclude that it is advisable to use this pair of metals with this ligand (intermetal bridge) for the synthesis of a magnetic sublattice.

Table 1 shows the calculated values for these constants, as well as the charge states of the complexes, the eigenvalues of the operator S^2 for the maximum value of the HS $<S^2>_{\mathrm{HS}}$ and BS states. Table 1 also shows the mononuclear complexes formed by trivalent chromium, divalent nickel and trivalent iron, which have negative values of the exchange interaction constants for all four types of ligands, corresponding to the antiferromagnetic exchange interaction in them. For complexes formed by a pair of trivalent chromium and divalent nickel, the maximum value of J occurs for complexes with dithiooxamide as a ligand (~14 cm^{-1}). For complexes formed by a pair of trivalent chromium and divalent cobalt, the maximum value of J also occurs for complexes with dithiooxamide as a ligand (~9 cm^{-1}). Moreover, for both pairs of metals, the exchange interaction is ferromagnetic in nature. Thus, the combinations of $\mathrm{Cr^{III}}$–$\mathrm{Ni^{II}}$ and $\mathrm{Cr^{III}}$–$\mathrm{Co^{II}}$ with dithiooxamide lead to the most pronounced ferromagnetic properties in the complexes studied by us.

Then, an expanded search was carried out for the components of the magnetic sublattice which provide the maximum ferromagnetic exchange interaction in it [38], based on the assumption that

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[8] Neese F. ORCA – An *ab initio*, DFT, and Semiempirical Program Package 2.8-01. Bonn: Universität Bonn; 2010. http://wild.life.nctu.edu.tw/~jsyu/OrcaManual_2_9.pdf. Accessed August 10, 2023.

[9] B3LYP/TVZ is the 3-parametric Becke–Lie–Yang–Parr density functional with a triple zeta valence (TZV) basis set.

Table 1. Charge states of complexes (Charge), maximum value of spin (S_{max}), eigenvalues of the operator S^2 for the maximum value of high-spin ($<S^2>_{HS}$) and broken-symmetry ($<S^2>_{BS}$) states, exchange interaction constants calculated by us (J_1, J_2, J_3) and found experimentally (J_{exp}), (cm^{-1})

$[L_2M_1^{III}LM_2^{II}L2]^{n-}$	Charge	S_{max}	$<S^2>_{HS}$	$<S^2>_{BS}$	J_1	J_2	J_3	J_{exp}
Ox$_2$Cr^{III}(Ox)Cr^{III}Ox$_2$	−4	3	12.0411	3.0405	−4.01	−3.01	−4.01	−3.1[34]
Ha$_2$Cr^{III}(Ha)Cr^{III}Ha$_2$	−4	3	12.0888	3.0852	−3.40	−2.55	−3.40	–
DiSOx$_2$Cr^{III}(DiSOx)Cr^{III} DiSOx$_2$	−4	3	12.1188	3.1226	−10.16	−7.62	−10.17	–
Oxam$_2$Cr^{III}(Oxam)Cr^{III}Oxam$_2$	−4	3	12.0483	3.0479	−8.98	−6.73	−8.98	–
Ox$_2$Cr^{III}(Ox)Ni^{II}Ox$_2$	−5	5/2	8.7765	2.7752	7.99	5.7	8.32	3.5 [35]
DiSOx$_2$Cr^{III}(DiSOx)Ni^{II} DiSOx$_2$	−5	5/2	8.8201	2.8149	13.85	9.90	14.42	–
Oxam$_2$Cr^{III}(Oxam)Ni^{II}Oxam$_2$	−5	5/2	8.7771	2.7762	1.33	0.95	1.39	–
HA$_2$Cr^{III}(HA)Ni^{II}HA$_2$	−5	5/2	8.7783	2.7768	5.32	3.80	5.54	–
Ox$_2$Ni^{II}(Ox)Ni^{II}Ox$_2$	−6	2	6.0056	2.0028	−14.66	−9.77	−14.65	−22.8 [36]
Ha$_2$Ni^{II}(Ha)Ni^{II}Ha$_2$	−6	2	6.0092	2.0080	−8.06	−5.37	−8.05	–
DiSOx$_2$Ni^{II}(DiSOx)Ni^{II} DiSOx$_2$	−6	2	6.0084	2.0029	−24.64	−16.4	−24.6	–
Oxam$_2$Ni^{II}(Oxam)Ni^{II}Oxam$_2$	−6	2	6.0081	2.0079	−1.1	−0.73	−1.1	–
Ox$_2$Fe^{III}(Ox)Fe^{III}Ox$_2$	−4	5	30.0135	5.0067	−4.05	−3.37	−4.04	−3.4 [37]
Ha$_2$Fe^{III}(Ha)Fe^{III}Ha$_2$	−4	5	30.0208	5.0163	−1.66	−1.38	−1.66	–
DiSOx$_2$Fe^{III}(DiSOx)Fe^{III} DiSOx$_2$	−4	5	30.0268	5.0136	−6.35	−5.29	−6.35	–
Oxam$_2$Fe^{III}(Oxam)Fe^{III}Oxam$_2$	−4	5	30.0144	5.0058	−5.51	−4.59	−5.51	–
DiSOx$_2$Cr^{III}(DiSOx)Co^{II}DiSOx$_2$	−5	3	12.0726	3.0668	8.93	6.70	8.92	–
Oxam$_2$Cr^{III}(Oxam)Co^{II}Oxam$_2$(I)	−5	3	12.0328	3.0301	7.01	5.26	7.01	–
Oxam$_2$Cr^{III}(Oxam)Co^{II}Oxam$_2$(II)	−5	3	12.0290	3.0284	0.82	0.62	0.82	–
HA$_2$Cr^{III}(HA)Co^{II}HA$_2$	−5	3	12.0295	3.0278	3.13	2.35	3.13	–
Ox$_2$Cr^{III}(Ox)Co^{II}Ox$_2$	−5	3	12.0284	3.0269	5.09	3.82	5.09	1.8 [35]

the exchange interaction constant J between metals forming such complexes increases during the transition from 3d to 4d transition metals.

This assumption is based on an example with a complex containing a pair of metals Mo^{III}–Mo^{III}, for which the value of $J < 0$ is greater in absolute magnitude than in a complex containing a pair of Cr^{III}–Cr^{III} [39]. This can be explained by the greater diffusivity of the 4d Mo shell, compared to the 3d Cr shell. It is natural to assume that even at $J > 0$, the values of J would increase for atoms of other metals during the transition from 3d to 4d metals, and possibly to 5d metals. This is especially interesting in relation to complexes I, optimal for modeling a magnetic lattice, as mentioned earlier. In this regard, we performed calculations of complexes I for metal pairs, including M_1 = Cr, Mo; M_2 = Ni, Co, Tc, Ru, Rh, Pd, with dithiooxamide and oxalate [38].

We will briefly describe the methodology of our calculations in this and subsequent papers. The geometric structure of the complex anions I was calculated using the GAUSSIAN-03 program in the B3LYP/LANL2DZ approximation with optimization of the geometric parameters of the complex for the maximum value of the spin multiplicity corresponding to its ground state. Then, with the geometry obtained in the B3LYP/TZV approximation, the constant *J* and the SD in these complex anions were calculated according to the ORCA program.

Complexes with Pd are designed for its HS state. It is believed [40] that Pd is usually in a low spin state and is diamagnetic. It was interesting to model its magnetic properties for an HS state by analogy with the spin states of other metals of this series. Our calculation of the [DiSOx$_2$ Cr^{III}DiSOxPd^{II}DiSOx$_2$]$^{5-}$complex for the low-spin Pd state in the same approximation as for the HS state showed that its total energy is less advantageous by 6.53 kcal/mol compared to the total energy of the same HS complex.

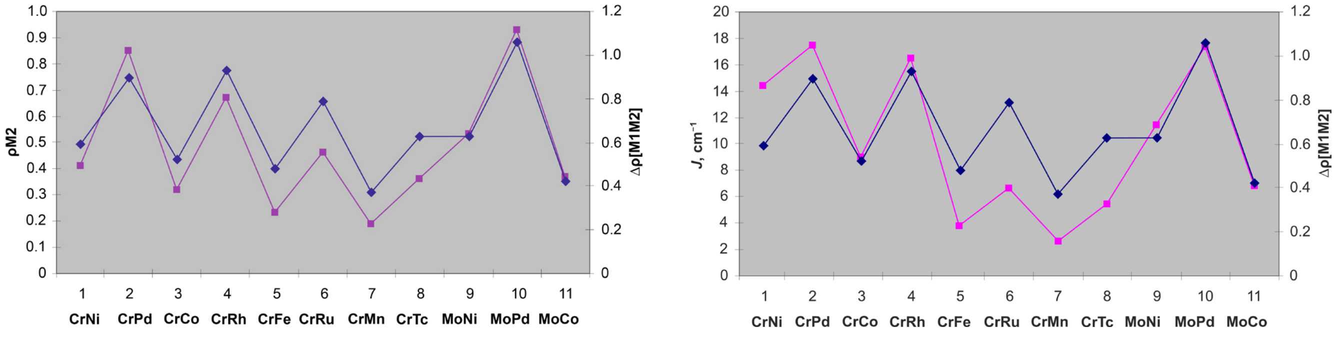
Table 2. Values of the exchange interaction constant *J* (cm^{-1}), energies of the complex in the high-spin (S_{max}) state (E_{HS}) and broken-symmetry state (E_{BS}) (a.u.), calculated using the ORCA program in the approximation B3LYP/TZV, Ox is oxalate, DiSOx is dithiooxamide [38]

$[L_2M1^{III}LM2^{II}L_2]^{5-}$	E_{HS}	E_{HS}	S_{max}	J
L = DiSOx				
Cr^{III}–Ni^{II}	−7469.309739	−7469.309344	5/2	14.42
Cr^{III}–Pd^{II}	−10901.226790	−10901.226312	5/2	17.46
Cr^{III}–Co^{II}	−7343.774151	−7343.773785	3	8.92
Cr^{III}–Rh^{II}	−10649.077525	−10649.076847	3	16.52
Cr^{III}–Fe^{II}	−7224.704428	−7224.704222	7/2	3.78
Cr^{III}–Ru^{II}	−10404.686713	−10404.686350	7/2	6.64
Cr^{III}–Mn^{II}	−7112.017316	−7112.017139	4	2.59
Cr^{III}–Tc^{II}	−10167.887799	−10167.887428	4	5.43
Mo^{III}–Ni^{II}	−10402.537096	−10402.536783	5/2	11.42
Mo^{III}–Pd^{II}	−13834.344788	−13834.344315	5/2	17.29
Mo^{III}–Co^{II}	−10276.884624	−10276.884348	3	6.75
L = Ox				
Cr^{III}–Ni^{II}	−4438.630797	−4438.630570	5/2	8.31
Cr^{III}–Pd^{II}	−7870.426056	−7870.425737	5/2	11.68
Cr^{III}–Co^{II}	−4313.084500	−4313.084500	3	5.09
Cr^{III}–Rh^{II}	−7618.362167	−7618.361861	3	7.47
Cr^{III}–Fe^{II}	−4194.030180	−4194.030027	7/2	2.80
Cr^{III}–Ru^{II}	−7373.977893	−7373.977694	7/2	3.64
Cr^{III}–Mn^{II}	−4081.347112	−4081.346974	4	2.01
Cr^{III}–Tc^{II}	−7137.188425	−7137.188211	4	3.13
Mo^{III}–Ni^{II}	−7371.736998	−7371.736806	5/2	7.04
Mo^{III}–Pd^{II}	−10803.531705	−10803.531433	5/2	9.97
Mo^{III}–Co^{II}	−7246.190992	−7246.190797	3	4.76

It follows from Table 2, obtained in [38], that in complexes with dithiooxamide and oxalate anion, the maximum values of the constant *J* occur in a complex containing a pair of metals Cr^{III}–Pd^{II}. Moreover, for complexes with dithiooxamide and oxalate anions as ligands, the values of the constant *J* decrease in the series $J(\mathrm{Cr^{III}{-}Pd^{II}}) > J(\mathrm{Cr^{III}{-}Rh^{II}}) > J(\mathrm{Cr^{III}{-}Ru^{II}}) > J(\mathrm{Cr^{III}{-}Tc^{II}})$. Thus, for 4d metals, during the sequential transition from Tc^{II} to Pd^{II} with the same trivalent 3d metal atom, the ferromagnetic properties of complexes I, and hence the properties of the magnetic sublattice formed by these complexes, are enhanced. Table 2 shows $J(\mathrm{Cr^{III}{-}Pd^{II}}) \approx J(\mathrm{Mo^{III}{-}Pd^{II}})$ in complexes with dithiooxamide, which indicates a slight change in the constant *J* when replacing a trivalent 3d metal atom with a trivalent 4d metal atom. Approximately the same ratio holds with the oxalate ligand. It was also shown in [38] that the replacement of a divalent 3d metal atom with a divalent 4d metal atom leads to an increase in *J*. Thus, together with the established regularity about an increase in the constant *J* during the transition from Tc^{II} to Pd^{II}, we confirmed and clarified the assumption about an increase in the constant *J* during the transition from 3d metal atoms to 4d metal atoms.

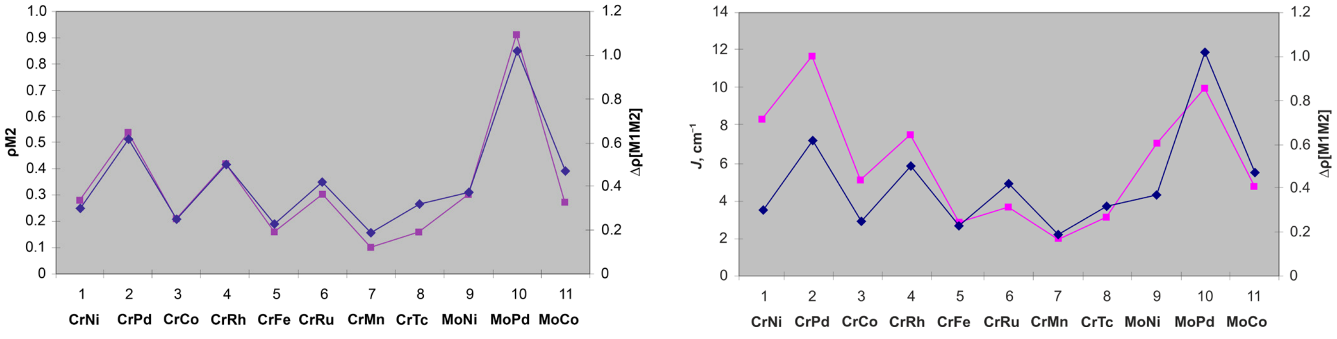
Based on these results, it was concluded in [38] that in the magnetic sublattice of bifunctional materials, an increase in the ferromagnetic exchange interaction should be expected during the transition from divalent 3d metal atoms to divalent 4d metal atoms.

The SD distribution on metal atoms in the complexes under consideration was analyzed in comparison with their isolated M1^{3+} and M2^{2+} cations. We also examined changes in SD depending on the M1 and M2 metals and L ligands included in the complex. Concepts such as ρM1 and ρM2 (the sum of SDs on the atoms of the coordination sphere of tri- and divalent metals, respectively) and Δρ[M1M2] (the total change in SD on the M1 and M2 atoms compared with isolated M1^{3+} and M2^{2+} cations) were also introduced. A clear correlation was shown between ρM2 and Δρ[M1M2], as well as between the constant *J* and Δρ[M1M2] for both ligands. This correlation is shown in Figs. 5 and 6.



(a) (b)

Fig. 5. Correlations in I complexes with dithioxamide L = DiSOx [38]: (a) ρM2 (red line) and Δρ[M1M2] (blue line), (b) constants *J* (red line) and Δρ[M1M2] (blue line).



(a) (b)

Fig. 6. Correlations in I complexes with oxalate L = Ox [38]: (a) ρM2 (red line) and Δρ[M1M2] (blue line), (b) constants *J* (red line) and Δρ[M1M2] (blue line).

It was concluded that a ligand could be regarded as a SD conductor when it flows from one atom of one metal to another during complex formation. The greater this overflow, the greater the constant of exchange interaction between them, and the more pronounced the magnetic properties. This circumstance clarifies the physical meaning of the constant of exchange interaction.

Our recent study continues the search for metal pairs providing maximum ferromagnetic exchange interaction in complexes modeling the magnetic sublattice of bifunctional materials [41]. The aim of this work was to further expand the range of transition metals, which provide the maximum value of *J*. In order to do this, we performed calculations of type I complexes and metal pairs containing M1 = Mo; M2 = Mn, Fe, Tc, Ru, Rh and Pd with a dithiooxamide ligand. This is most effective in providing the maximum value of *J*, as shown above. We have now considered not Cr, but Mo as a trivalent metal. The calculations were performed in the same approximation as in previous works. The settlement procedure also remained the same: the hexametric structure of complex anions I was calculated using the GAUSSIAN-03 program. This was done in the B3LYP/LANL2DZ approximation with optimization of the geometric parameters of the complex for the maximum value of the spin multiplicity corresponding to their basic energy state. Then, with the geometry obtained in the B3LYP/TZV approximation, the constant *J* and the SD in these complex anions were calculated using the ORCA program.

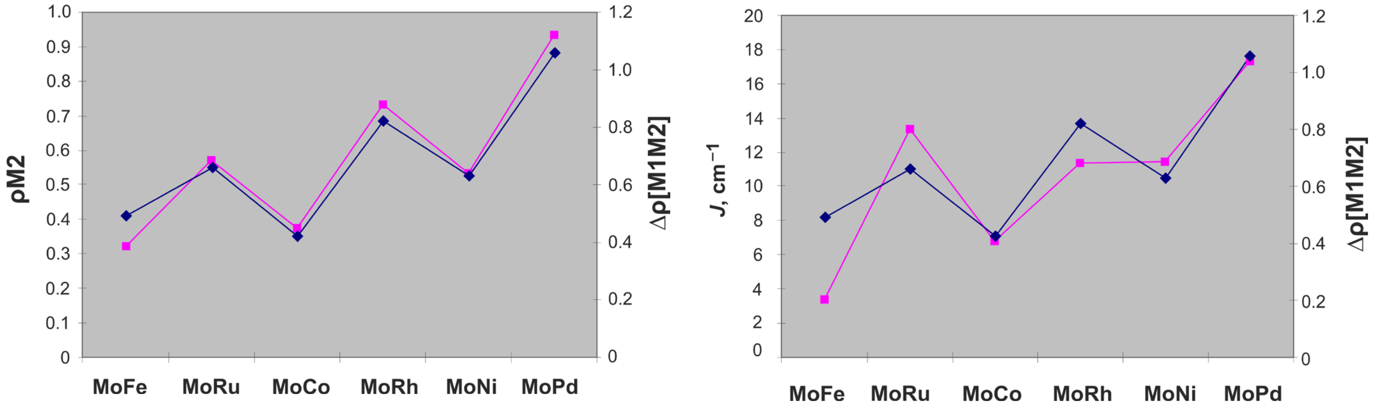
The values of the exchange interaction constant *J* (cm^{-1}) calculated in [41], the energy of complexes in the HS state (E_{HS}) and the BS state (E_{BS}) (a.u.), the HS state (S_{max}) are given in Table 3.

Table 3 shows that the maximum values of *J* take place in complex with MoIII–PdII. In addition, the value of *J* increases during the transition from Fe^{II} to Pd^{II}, i.e., when moving along the period from left to right, similar to the complexes considered in the previous work. Thus, for 4d metals, the ferromagnetic properties of complexes I increase during transition from FeII to PdII without changing the trivalent atom of the 4d metal. At the same time, the values of *J* also increase when moving along the subgroup from top to bottom. It can be said that the values of the exchange interaction constant increase as one moves from left to right and from top to bottom on the Periodic table. Thus, we managed to determine the area of the Periodic table with the maximum values of the constant *J*. This conclusion may be useful to synthetic chemists in selecting components for the synthesis of a magnetic sublattice of bifunctional materials.

Analysis of the Mulliken SD distribution on metal atoms in complexes compared to isolated cations by a trivalent and a divalent cation showed the presence of correlations similar to those obtained in the previous work. There is a correlation between ρM2 and Δρ[M1M2], as well as the correspondence of Δρ[M1M2] to the value of *J* (Fig. 7).

Table 3. Calculated values of the exchange interaction constant *J* (cm^{-1}), the energy of complexes in the HS state (E_{HS}) and the BS state (E_{BS}) (a.u.), and the HS state (S_{max}) [41]

$[L_2M1^{III}LM2^{II}L_2]^{5-}$	E_{HS}	E_{BS}	S_{max}	*J*
Mo^{III}–Fe^{II}	−10157.92816	−10157.92798	7/2	3.27
Mo^{III}–Ru^{II}	−13337.79223	−13337.79150	7/2	13.34
Mo^{III}–Co^{II}	−10276.88462	−10402.53678	3	6.75
Mo^{III}–Rh^{II}	−13582.18732	−13582.18685	3	11.32
Mo^{III}–Ni^{II}	−10402.53710	−10402.53678	5/2	11.42
Mo^{III}–Pd^{II}	−13834.34479	−13834.34432	5/2	17.29



(a) (b)

Fig. 7. Correlation on M1 and M2 atoms in I complexes compared with SD on isolated cations—trivalent M1 and divalent M2 [41]: (a) ρM2 (red line) with total change in SD Δρ[M1M2] (blue line), (b) constant *J* (red line) with total change SD Δρ[M1M2] (blue line).

It can be concluded that here, too, the ligand plays the role of a SD conductor when redistributed from one metal atom to another as a result of complex formation. The greater the redistribution, the greater the exchange constant between the atoms. This fact illustrates another aspect of the physical significance of the exchange constant interaction.

CONCLUSIONS

In this way, our research has given a visual meaning to the physical significance of the exchange interaction constant: it determines the SD change on metals forming complexes of the type under consideration during the transition from isolated cations to them as part of complexes. Recommendations can be given to synthetic chemists for the selection of components in the synthesis of magnetic sublattices of bifunctional materials.

Throughout the development of quantum chemistry, from its emergence as an independent branch of physical chemistry and quantum mechanics to the present day, research by Russian scientists has been in line with the most important areas of science. In terms of their level, they were no inferior to foreign studies and continue to be popular. This is evidenced by publications in leading scientific journals and regular invitations to participate in major international forums.

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