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Inhomogeneous spin states as an indicator of the tomographic structure of paramagnetic multielectronic (molecular) structures.

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Abstract

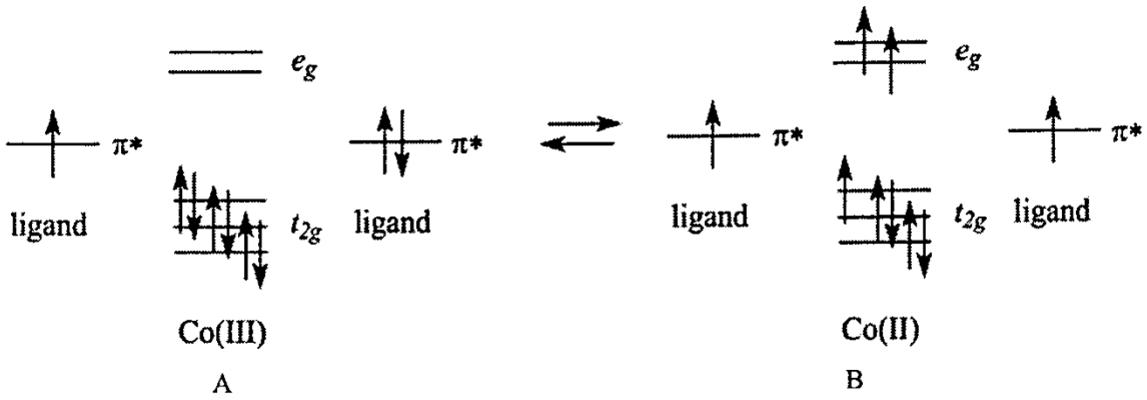
The paper substantiates the existence of inhomogeneous electron spin states in heterospin systems – coordination compounds of paramagnetic ions, including molecules containing unpaired electrons as ligands. It is noted that compounds containing atoms with unfilled $3-d$, $4f-$ and $5f-$ shells are characterized by strong interactions of uncompensated electrons with the electron subsystem of ligands. Due to the interconnection of magnetic and spin moments, it is also possible to assert the existence of inhomogeneous magnetic states within the molecules of these compounds due to the manifestation of interelectron correlations. As an example, the article discusses the nature of the exchange magnetic interaction in a tetranuclear cluster of nickel containing a nitroxide radical as a ligand. The structure of the Heisenberg spin-Hamiltonian of this cluster is discussed using the concept of a magnetic polaron or ferron. Methods of visualization (detection) of inhomogeneous electron spin states in heterospin systems using magnetic resonance methods (EPR and NMR) are discussed. The reality of the existence of such inhomogeneity opens up new opportunities for obtaining detailed information about individual parts of a paramagnetic molecule.

1 Introduction

In recent years, there has been an increased interest of researchers in heterospinic systems synthesized on the basis of coordination compounds of paramagnetic ions of transition metals, in particular, with stable nitroxyl radicals (see, e.g., [1] and the literature cited therein). This is due, first of all, to the possibility of obtaining detailed information about the nature of intramolecular interactions in multielectron systems, the specificity of which is determined by electrons on or $d-$ $f-$ Such information ultimately makes it possible to solve fundamental problems related to the problem of the structure and dynamics of molecules. Among the fundamental problems, the central place is occupied by such intramolecular rearrangements, in the process of which unpaired electrons from ligands are delocalized to a metal ion with a change in the valence of the latter. Such rearrangements are usually called valence tautomerism. As applied to the compounds of the first transition group, these intramolecular processes lead to the colonization of $3d-$ metal orbitals with unpaired electrons. This was illustrated, in particular, by studying spin phase transitions in nanoscale transition metal structures using the example of the $Co(SQ)_2$(2-2′-dipyridine) complex [2,3].

Omitting the details of the phase transition reflected in the above diagram, it should be borne in mind that a substance whose molecules are in **state A** turns out to be diamagnetic, and in state **B**

– paramagnetic [2,3]. These phase transformations can be used, in particular, to describe self-oscillatory processes based on the Prigogine-Lefebvre model [4].



The work mentioned above [3] speaks of "delocalized weakly magnetic electrons on SQ ligands" and "localized strongly magnetic d electrons on the Co ion". As a result of hybridization effects between these electrons, there is a smooth transition from a low-spin to a high-spin state. This refers to the state of the cobalt atom. These effects, as noted in [3], can be taken into account with the help of a hybridization parameter, the variation of which makes it possible to obtain both a jump in the number of magnetic electrons on cobalt and a smooth change in it.

2 Exchange Interactions in Heterospin Complexes.

The studies carried out so far have shown that compounds containing atoms with unfilled $3-d$, $4f-$ and $5f-$ shells are characterized by a variety of physical phenomena. Such atoms in a solid state retain fully or partially localized magnetic moments. Strong interaction of electrons of these groups with each other or with collectivized electrons of the outer shells is a feature that forms the unique properties of a number of compounds containing atoms of transition and rare-earth elements. Systems with strong interaction of electrons are called strongly correlated systems [5].

It is well known that the exchange interaction is usually described by the Heisenberg Hamiltonian of the form

$$\hat{H} = J\hat{S}_1\hat{S}_2, \qquad (1)$$

where $J-$ the exchange integral, determined by the overlap of the electron shells of the interacting ions, $\hat{S}_1, \hat{S}_2 -$ are the operators of the spins. The Hamiltonian of a system of many magnetic ions is written as a sum of paired interactions. To describe intramolecular magnetic interactions in heterospin complexes, a Hamiltonian of a similar type is used. Thus, according to the data obtained by the authors of [6], the spin Hamiltonian, which describes exchange magnetic interactions in a

tetranuclear cluster of nickel $\left[Ni_4(OH)_3(C_5H_9O_2)_5(C_5H_{10}O_2)_4(L)\right]\cdot 1.5C_7H_8$ (I), where $L-$ the nitroxide radical, has the form:

$$H = -2J_0S_1S_2 - 2J_1(S_1S_3 + S_2S_4) - 2J_2(S_1S_4 + S_2S_3), \qquad (2)$$

Compound S $Ni(II)$ $J-$ (I) is a representative of the strongly correlated systems mentioned above. The description of quantum states based on the use of spin Hamiltonians of the form (1) and (2) suggests that we are talking about free (true) quantum particles – spin carriers S Meanwhile, the entry of an unpaired electron on a ligand molecule can lead to the appearance of states caused by the interaction of spin S with electrons of the ligand molecule. The description of such collective behavior in macrosamples is associated with the use of the concept of quasiparticle. For example, the use of the concept of a magnetic polaron or ferron turned out to be fruitful for describing various kinds of inhomogeneous charge and spin states in manganites [7].

We will proceed from the established fact – the localization of unpaired electron spins on ligand molecules and on the coordinating atom, as is the case in paramagnetic heterospin complexes of elements of the first transition group with stable iminoxyl radicals [6]. As for the unpaired electron spins belonging to the central ion to which the ligand molecules are coordinated, the behavior of these spins finds a fairly adequate description, taking into account $3d-$ the orbitals of the metal. Let us therefore turn to the unpaired electron, which turns out to be localized on the ligands. Naturally, this electron will somehow interact with the electronic subsystem of the ligand molecules. Поэтому указанный неспаренный электрон следует рассматривать как некое возмущение. Let us further assume that, due to the peculiarities of the spatial and electronic structure of the complex and under conditions of thermodynamic equilibrium, the ligands are used to realize states similar to those of the ferron. It should be explained here that the total spin of the ferronic state consists of the local spin and the spin of the electron (see [7] and the literature cited therein). As for the local spin, it is determined by the magnetic (in particular, antiferromagnetic) state of the matrix along which the conduction electron moves in the macrosample. The assumption that the states similar to ferronic states are realized must mean that the result of the interaction of the unpaired electron with the electron subsystem of the ligand is a state with an uncompensated electron spin that differs from that of the free electron. Such a state can be modeled by assuming that a state with an average spin is actually formed on the ligand $\langle S \rangle$, the lifetime of which is finite.

Here it should be recalled once again that the ferronic state is different from the state of a free electron. In fact, it is well known that a distinguishing feature of objects called quasiparticles is the difference between their mass and the mass of the corresponding free particle. For example, the mass of a polaron is several hundred times greater than the mass of a free electron. This difference is also inherent in ferrons. The total spin of the ferronic state also differs from the value of

the spin of a free electron [7]. Thus, in a paramagnetic molecule (of course, of the appropriate size), the existence of various spin states is possible. Since the magnetic and spin moments are interrelated, it can be said that inhomogeneous magnetic states also exist inside such a molecule. Continuing the analogy with macrosamples, we can talk about phase stratification inside paramagnetic molecules due to the manifestation of interelectron correlations.

3 *Visualization of spin states*

The question, of course, is how to detect (visualize) the above states in a paramagnetic molecule, if they exist. Given that a certain magnetic moment is associated with such states, their manifestation should be expected in the magnetic resonance spectra (EPR and NMR). In the EPR spectra of the paramagnetic systems discussed here, the natural manifestation of the realization of the new states described above should be the appearance of two resonance signals. $\langle S \rangle$ The appearance of two EPR signals must be a consequence of the fact that $g-$ the factors of electrons localized in these two states are likely to differ so much that relaxation processes will not average these values. It is possible, however, that this difference will not be large enough to be resolved in the experimental spectrum, i.e., the difference in $g-$ factors will at best affect only the shape and/or width of the resonant EPR signal.

For a qualitative assessment of the position of the second possible signal in the EPR spectrum, let us assume that the electron in the state $\langle S \rangle$ has an effective mass M^* two orders of magnitude greater than that of the free electron. According to the theory, the EPR phenomenon (see, for example, [8]) occurs when the condition is met:

$$h\nu = g\beta H , \qquad (3)$$

where $\nu-$ the frequency of the electromagnetic field causing the resonance transition, $H-$ the external magnetic field in which the paramagnetic particle is located, $h-$ Planck's constant, $\beta-$ Bohr's electron magneton, is equal to $e\hbar/2mc$; here is e the $m-$ charge and mass of the electron, respectively, $c-$ the speed of light.

For an electron in the $\langle S \rangle$ state , expression (3) is rewritten as:

$$h\langle \nu \rangle = \langle g \rangle \langle \beta \rangle H .$$

It is not difficult to see that for the case considered here, the resonance frequency $\langle \nu \rangle$ turns out to be less than the value ν by $100\frac{g}{\langle g \rangle}$ a factor of one, i.e. shifted to the long-wave region of the electromagnetic spectrum (towards the meter range, which is known, as is known to be characteristic of the NMR phenomenon). Thus, the second resonance, if, of course, the model discussed

here is adequate to the real state of the paramagnetic particle, turns out to be significantly shifted relative to the standard scale of the position of EPR signals.

As for the NMR spectrum, predicting the nature of the manifestation of the ferronal state of the heterospin complex in it is more problematic than for EPR. Electron-nuclear or ultrafine interaction between the spins of unpaired electrons and resonating nuclei leads to specific signal shifts and their broadening. The nature of such a transformation of spectra requires a separate consideration in each specific case (see [9] and the literature cited therein). However, focusing on the features of the NMR phenomenon in compounds whose specificity is determined by electrons in d - or f -orbitals, it is possible to try to predict a characteristic trend for the NMR spectra of paramagnetic molecules, in which the existence of inhomogeneous spin states is possible.

In accordance with the theory of the NMR phenomenon in paramagnetic systems, uncompensated electron spins induce contact and pseudocontact paramagnetic shifts in NMR spectra [9]. To specify the problem, we will proceed from the assumption that in the spectrum of a paramagnetic molecule for which the existence of inhomogeneous spin states is possible, only a contact paramagnetic shift is induced. This shift is directly proportional to the constant of the ultrafine interaction between the resonating nucleus and the unpaired electron spin localized on it, the value of which is given by the Fermi formula:ωA

$$A = \frac{8\pi}{3} g\beta g_N \beta_N \rho(N). \qquad (4)$$

Here $g_N -$ g is the nucleus factor N , $\beta_N -$ the nuclear magneton, $\rho(N) -$ and the value of the unpaired electron spin fee localized on the nucleus; N the other notations have the same meaning as in expression (3).

For an electron in the state $\langle S \rangle$, expression (4) will be rewritten as:

$$A^{\bullet} = \frac{8\pi}{3} g^{\bullet}\beta^{\bullet} g_N \beta_N \rho^{\bullet}(N).$$

From the comparison of expressions (1) and (2), taking into account the following $M^{\bullet} = 100m$:

$$A^{\bullet} = A\frac{g^{\bullet}\rho^{\bullet}(N)}{100g\rho(N)} .$$

Typical values of experimental paramagnetic shifts in the NMR spectra of paramagnetic complexes of elements of the first transition group from hydrogen nuclei are ones and tens of millionths [9]. From this follows the conclusion that with the same values of the value of the uncompensated electron spin density, i.e. when $\omega\rho(N) \cong \rho^{\bullet}(N)$, in the NMR spectra, the signals determined by the state $\langle S \rangle$ of , should be significantly shifted to the strong-field region.

Here it is appropriate to refer to the work [10], in which a method for obtaining a "tomographic" image of multielectronic (molecular) systems is proposed and theoretically substantiated. The meaning of the mentioned method can be explained as follows. Usually, in all studies related to the molecular level, we are talking about problems the solution of which is sought in the laboratory (in relation to molecular systems) coordinate system. It is in these conditions that experiments are carried out. In the above-mentioned work, the problem is to find the tomographic structure of molecules without relation to the problem that the researcher is solving. In other words, we are talking about the structure (which one is a separate question) in the coordinate system associated with the molecule, i.e. in the coordinate system fixed in relation to the molecule. This is a system in which a molecule, if it makes any movements, is only a consequence of intramolecular processes. In accordance with existing ideas, the spin-spin interaction (SWS) is carried out by means of electrons moving in the space occupied by the molecule. Thus, it can be considered that the space in which the SWR is realized is adequate to its (the molecule's) dimensions. Hence the possibility of obtaining a spatially continuous image at the molecular level. We obtain information about the spin-spin interaction in a molecule while being in a laboratory (in relation to this molecule) coordinate system. Therefore, its use (meaning information) can be effective only when solving the corresponding inverse problem.

The reality of the existence of such inhomogeneity opens up new opportunities for obtaining detailed information about individual parts of a paramagnetic molecule. In particular, it is possible to obtain a tomographic image of such a molecule. The appearance of inhomogeneous spin states also means the ability to distinguish electrons in such states. Thus, another way of obtaining information at the level of the macrocosm about the state of matter in nanoscale regions of space is opened.

4 Conclusion

The following remark can be used as a summary of this work. In heterospin systems, i.e. coordination compounds of paramagnetic ions that include molecules containing unpaired electrons as ligands, inhomogeneous spin states can exist. Since the magnetic and spin moments are interrelated, it can be said that inhomogeneous magnetic states also exist within the molecules of these compounds due to the manifestation of interelectron correlations. The inhomogeneity of electron spin states should be manifested in the EPR and NMR spectra. The reality of the existence of such inhomogeneity opens up new opportunities for obtaining detailed information about individual parts of a paramagnetic molecule. In particular, it is possible to obtain a tomographic image of such a molecule. The appearance of inhomogeneous spin states also means the ability to distinguish electrons that find themselves in such states.

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