Full Articles

Combined calculation method of weak exchange interactions in biradicals*

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A combined calculation method of weak exchange interactions in short biradicals was developed. The combined method includes two stages. The quantum chemical calculations of the high level of the biradical structure and molecular orbitals and binding energies of unpaired electrons are performed at the first stage. Information obtained at the first stage is used further to calculate the exchange interaction between unpaired electrons within the direct exchange model using the asymptotic method. This allows one to estimate the exchange interaction and to determine the dependence of this interaction on the distance between the paramagnetic centers and on their relative orientation. The method developed was used to calculate the exchange interaction in the short nitroxyl biradical containing no conjugate rings between the paramagnetic NO groups. The geometry and electronic structure of the biradical were calculated within the unrestricted DFT method (B3LYP/cc-pvdz) using the ORCA program package.

Key words: exchange interactions, biradicals, quantum chemical calculations.

Biradicals widely used as spin labels and probes[1—3] are convenient objects for modeling diverse intramolecular processes: intramolecular dynamics,[4] spatial organization of molecules,[1,5] and regularities of unpaired electron delocalization along the chain of bonds.[6] Short (with an average distance between groups containing an unpaired electron of 6—12 Å) rigid and flexible biradicals are of special interest.[7—9] Indeed, in this systems one can quantitatively characterize the thermodynamics of conformational transitions, to establish the number of conformations of the

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biradical, and to evaluate the spatial organization of its thermodynamically most favorable conformation from the ESR spectra of its frozen solutions.[10] The change in the sign of the exchange integral was observed for the conformational transition in the biradical molecule.[9]

As for theoretical studies, the current quantum chemical methods (such as DFT and nonempirical multireference MCSCF and MCQD) make it possible to calculate with an appropriate accuracy the structural and thermodynamic properties of biradicals, the spin density distribution, and some magnetic resonance parameters (see, *e.g.*, Refs 11—17). However, the quantum chemical calculations of the small (≤ 1 cm^{-1}) energy splitting

$$\Delta E_{ST} = E_S - E_T \tag{1}$$

between the singlet and triplet states of the biradical, which determines the exchange integral, encounter substantial difficulties. This is due to the fact that in quantum chemistry ΔE_{ST} is calculated as a difference of high ($\sim 10^2$—10^3 eV) total negative electronic energies E_S and E_T in the singlet and triplet states. The situation is aggravated by the necessity to calculate the difference in total electronic energies of the states with different symmetries. In this case, the calculated value of ΔE_{ST} depends very strongly on the used quantum chemical method and basis set (see, *i.e.*, Ref. 16).

We have previously[18] proposed to use the asymptotic method developed in the theory of atomic collisions for the calculation of weak exchange interactions between nitroxyl radicals.[19] An advantage of the asymptotic method is that the exchange integral in this method is calculated directly rather than as a difference between very high values, which takes place in standard quantum chemical methods. The asymptotic method was successfully used[20] for the calculation of the dependence of intermolecular exchange integrals in crystalline oxygen on the mutual orientation of molecules and the distance between them.

A similar approach, in which the exchange interaction between paramagnetic centers is treated as a direct interaction through the space, can be applied to short biradicals as well. These biradicals contain two isolated paramagnetic centers, and electrons localized on these centers have substantially lower binding energies than other electrons of the biradical, which can be considered internal. It can be assumed that these internal electrons screen all Coulomb centers, except for those related to the paramagnetic centers. The corresponding effective field formed by internal electrons and nuclei (pseudo-potential) determines the parameters of orbitals of electrons on the paramagnetic centers.

Quantitative calculations of exchange integrals require reliable information about the unpaired electron density distribution in the paramagnetic centers when the latter is high and about the mutual orientation of these centers and the distance between them. As mentioned above, this information can be provided by the current quantum chemical methods. Therefore, in this work, we propose the combined calculation method of a weak direct exchange interaction in short biradicals, which includes two stages. At the first stage, the high level quantum chemical calculations are performed for the electronic structure of the biradical in the equilibrium configuration. At the second stage, this quantum chemical information is used for the calculation of the exchange interaction between paramagnetic centers by the asymptotic method. If not specially indicated, atomic units (au) are used everywhere: $e = m_e = \hbar = 1$.

Main theses of the asymptotic method for the exchange interaction calculation

Let us consider two isolated paramagnetic centers $\mathrm{Pc_a}$ and $\mathrm{Pc_b}$ with one relatively weakly bound external electron in the sterically nondegenerate states ψ_a and ψ_b and cores C_a and C_b (Fig. 1). At large distances between the cores

$$R >> \frac{1}{\sqrt{2\varepsilon_a}} + \frac{1}{\sqrt{2\varepsilon_b}} \tag{2}$$

(ε_a and ε_b are the binding energies of external electrons e_a and e_b), the interaction energy between the centers can be estimated in the first order of the perturbation theory (Heitler—London approximation). It should be emphasized that inequality (2) takes place for short biradicals, since for them the value $1/\sqrt{2\varepsilon_a} + 1/\sqrt{2\varepsilon_b}$ does not exceed 2 Å. Instead of calculating the matrix elements of the electronic Hamiltonian with antisymmetric products of spin-orbitals localized on paramagnetic centers $\mathrm{Pc_a}$ and $\mathrm{Pc_b}$, one can use the vector Dirac model[21] in which the identity of electrons is described by the addition to the initial electronic Hamiltonian of the exchange interaction operator

$$\hat{V}_{ex} = -\frac{1}{2}(1 + \hat{s}_{e_a}\hat{s}_{e_b})V_{e_a e_b}\hat{P}^{(x)}_{e_a e_b}. \tag{3}$$

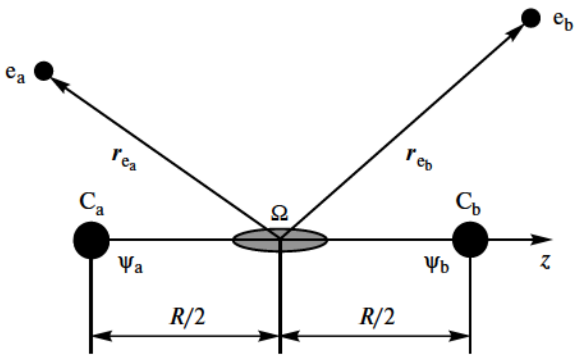

Fig. 1. Model of two paramagnetic centers with one fairly weakly bound external electron used in the asymptotic method. For all designations, see the text.

Here $\hat{s}_{e_a}$ and $\hat{s}_{e_b}$ are the operators of electron spins e_a and e_b, and $\hat{P}_{e_a e_b}{}^{(x)}$ is the permutation operator of their spatial coordinates

$$V_{e_a e_b} = V_{\mathrm{eff,C_b}}(\boldsymbol{r}_{e_a}) + V_{\mathrm{eff,C_a}}(\boldsymbol{r}_{e_b}) + \frac{1}{\left|\boldsymbol{r}_{e_a} - \boldsymbol{r}_{e_b}\right|} + \frac{1}{R}, \qquad (4)$$

where $V_{\mathrm{eff,C_b}}(\boldsymbol{r}_{e_a})$ and $V_{\mathrm{eff,C_a}}(\boldsymbol{r}_{e_b})$ are the interaction potentials of electrons e_a and e_b with cores C_b and C_a and vectors $\boldsymbol{r}_{e_a}$ and $\boldsymbol{r}_{e_b}$ are defined in Fig. 1. At high $\boldsymbol{r}_{e_a}$ and $\boldsymbol{r}_{e_b}$ these potentials are Coulomb. It should be mentioned that the introduction of operator (3) assumes neglecting the overlap integrals normalizing the two-electron wave function.

The singlet—triplet energy splitting ΔE_{ST} is determined as a difference in two eigenvalues of the spin-Hamiltonian

$$\hat{H}_{\mathrm{sp,HL}} = -0.5 J_{\mathrm{ab}}^{(\mathrm{HL})}(1 + \hat{s}_{e_a}\hat{s}_{e_b}), \qquad (5)$$

where the exchange integral assumes the form

$$\begin{aligned} J_{\mathrm{ab}}^{(\mathrm{HL})} &= 0.5\Delta E_{\mathrm{ST}} = \\ &= \int \psi^*{}_{\mathrm{a}}(\boldsymbol{r}_{e_a})\,\psi^*{}_{\mathrm{b}}(\boldsymbol{r}_{e_b}) V_{e_a e_b} \psi_{\mathrm{a}}(\boldsymbol{r}_{e_b})\psi_{\mathrm{b}}(\boldsymbol{r}_{e_a})\mathrm{d}^3\boldsymbol{r}_{e_a}\mathrm{d}^3\boldsymbol{r}_{e_b}. \end{aligned} \qquad (6)$$

As shown by numerous calculations, the Heitler—London approximation gives good estimates for the exchange integral (see, *e.g.*, Ref. 22). However, this method is inconvenient from the practical point of view, because the direct calculation of the six-dimensional integral is difficult and effective potentials $V_{\mathrm{eff,C_b}}(\boldsymbol{r}_{e_a})$ and $V_{\mathrm{eff,C_a}}(\boldsymbol{r}_{e_b})$ are not always determined rather reliably.

It turned out that the Heitler—London approximation has one more basic drawback. At $R \to \infty$, the exchange integral J^{HL} corresponding to the interaction of two same atoms with one external s-electron (hydrogen or alkaline metal atoms) changes the sign. As a result, at very high R, the triplet state corresponding to the spatial wave function antisymmetrical under electron permutation becomes the ground state. This contradicts the theorem about the nonnodal character of the spatial two-electron wave function of the ground state. The study[23—25] of this problem resulted in the formulation of the asymptotic calculation method. The use of this method made it possible to correct the asymptotic behavior of the exchange integral and to obtain further simple expressions for two-electron exchange integrals of different types in the case of interaction of two atoms.[26—28] It is substantial that, unlike the Heitler—London method, these expressions are determined by the Coulomb asymptotic shape of orbitals ψ_a and ψ_b at high $\boldsymbol{r}_{e_a}$ and $\boldsymbol{r}_{e_b}$ (as mentioned above, at high $\boldsymbol{r}_{e_a}$ and $\boldsymbol{r}_{e_b}$ the $V_{\mathrm{eff,C_b}}(\boldsymbol{r}_{e_a})$ and $V_{\mathrm{eff,C_a}}(\boldsymbol{r}_{e_b})$ potentials are Coulomb) and do not require to known the explicit form of these potentials. The asymptotic method for the calculation of the exchange interaction is based on the following conditions fulfilled at high R:

(*1*) the exchange integral is calculated as a half of the difference between the exact electron energies corresponding to even and odd (relatively to the permutation of spatial variables of electrons) spatial wave functions rather than using the perturbation theory;

(*2*) the exchange integral is determined by the area Ω of the spatial coordinates of both electrons e_a and e_b at the middle between the cores C_a and C_b near the z axis (see Fig. 1), which is due to the exponential decrease of the orbitals ψ_a and ψ_b with an increase in $\boldsymbol{r}_{e_a}$ and $\boldsymbol{r}_{e_b}$;

(*3*) the motion of electrons near the z axis in the Ω area is quasi-classical, which makes it possible to obtain explicit expressions for the correlation factor (see further formula (10)).

The general scheme of calculation of the exchange integral by the asymptotic method has the following form. The singlet and triplet states of the system with energies E_{S} and E_{T} correspond to the symmetrical $\Phi_{\mathrm{S}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and antisymmetrical $\Phi_{\mathrm{T}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ functions, respectively, under permutations of the spatial coordinates of two electrons spatial eigenfunctions of the total Hamiltonian

$$\begin{aligned} \hat{H} = &-0.5\Delta_{e_a} - 0.5\Delta_{e_b} + V_{\mathrm{eff,C_a}}(\boldsymbol{r}_{\mathrm{a}}) + V_{\mathrm{eff,C_b}}(\boldsymbol{r}_{e_a}) + \\ &+ V_{\mathrm{eff,C_b}}(\boldsymbol{r}_{e_b}) + V_{\mathrm{eff,C_a}}(\boldsymbol{r}_{e_b}) + \frac{1}{\left|\boldsymbol{r}_{e_a} - \boldsymbol{r}_{e_b}\right|} + \frac{1}{R}. \end{aligned} \qquad (7)$$

The spatial distributions of electrons e_a and e_b are delocalized in the $\Phi_{\mathrm{S}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\Phi_{\mathrm{T}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ states, and each electron can be found with equal probabilities near the cores C_a and C_b. Based on the $\Phi_{\mathrm{S}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\Phi_{\mathrm{T}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ functions, we can construct the wave functions

$$\begin{aligned} \Psi_{\mathrm{ab}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}) &= \Phi_{\mathrm{S}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}) + \Phi_{\mathrm{T}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}), \\ \Psi_{\mathrm{ba}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}) &= \Phi_{\mathrm{S}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}) - \Phi_{\mathrm{T}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}), \end{aligned} \qquad (8)$$

that describe the state in which electrons e_a and e_b are localized near one of the cores: C_a and C_b in the state $\psi_{\mathrm{ab}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and C_b and C_a in the state $\psi_{\mathrm{ba}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ (Fig. 2). Then, using condition (2) and taking into account the fact that at the considered large distances the functions ψ_a and ψ_b are slightly overlapped, the exchange integral J_{as} can be presented as a surface integral (see Fig. 2)

$$\begin{aligned} J_{\mathrm{ab}}^{(\mathrm{as})} &= 0.5\Delta E_{\mathrm{ST}}^{(\mathrm{as})} = \\ &= \int \left[\Psi_{\mathrm{ba}}\frac{\partial \Psi_{\mathrm{ab}}}{\partial z_{e_a}} - \Psi_{\mathrm{ab}}\frac{\partial \Psi_{\mathrm{ba}}}{\partial z_{e_a}}\right]_{z_{e_a} = z_{e_b}} \mathrm{d}x_{e_a}\mathrm{d}y_{e_a}\mathrm{d}x_{e_b}\mathrm{d}y_{e_b}\mathrm{d}z, \\ z &= z_{e_a} = z_{e_a}. \end{aligned} \qquad (9)$$

A detailed derivation of this equation was described earlier.[29,30]

Then we have to determine the explicit form of the $\psi_{\mathrm{ab}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\psi_{\mathrm{ba}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ functions. For this purpose, they are presented as follows:

$$\begin{aligned} \psi_{\mathrm{ab}}(\boldsymbol{r}_{e_b},\boldsymbol{r}_{e_a}) &= \psi_{\mathrm{a}}(\boldsymbol{r}_{e_a})\psi_{\mathrm{b}}(\boldsymbol{r}_{e_b})\Gamma_{\mathrm{ab}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}), \\ \psi_{\mathrm{ba}}(\boldsymbol{r}_{e_b},\boldsymbol{r}_{e_a}) &= \psi_{\mathrm{a}}(\boldsymbol{r}_{e_b})\psi_{\mathrm{b}}(\boldsymbol{r}_{e_a})\Gamma_{\mathrm{ab}}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b}). \end{aligned} \qquad (10)$$

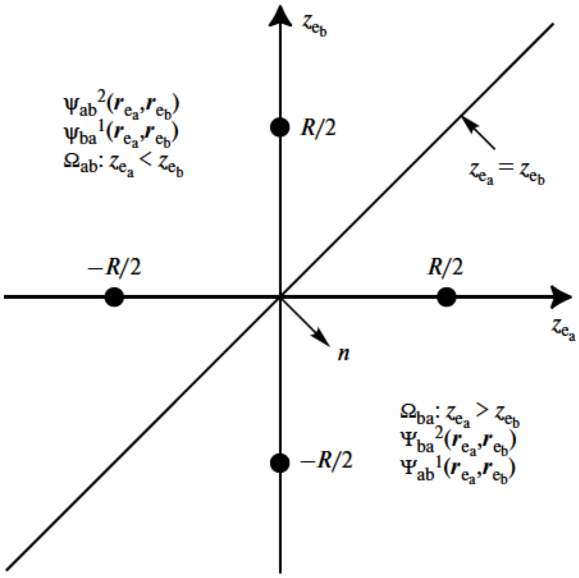

Fig. 2. Illustration of the description of the asymptotic method for the calculation of the exchange integral. All designations are given in text, and indices 1 and 2 at functions $\Psi_{ab}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\Psi_{ba}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ correspond to small and non-small values.

Owing to condition (2), correction functions $\Gamma_{ab}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\Gamma_{ba}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ are determined by the first-order equations that assume an exact solution. The detailed derivation of the explicit expressions for correction functions $\Gamma_{ab}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\Gamma_{ba}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ is given in Ref. 30.

The explicit expressions for the exchange integrals were obtained for the interaction of two one-electron atoms. These are hydrogen atoms, alkaline metal atoms (one electron above strongly compressed cores with an noble gas configuration), and atoms with one electron on the excited (with respect to the ground state) orbital (in this case, the effect of the core can be taken into account using the pseudo-potential). These expressions can conveniently be presented in terms of matrix elements of the two-electron exchange operator $\hat{\boldsymbol{J}}_{as}$ between the products of atomic orbitals

$$\left\langle \psi^{(a)}_{\eta_a l_a m_a}; \psi^{(b)}_{\eta_b l_b m_b} \middle| \hat{\boldsymbol{J}}_{as} \middle| \psi^{(a)}_{\eta_a' l_a' m_a'}; \psi^{(b)}_{\eta_b' l_b' m_b'} \right\rangle = \\ = \left\langle \eta_a l_a m_a; \eta_b l_b m_b \middle| \hat{\boldsymbol{J}}_{as} \middle| \eta_a' l_a' m_a'; \eta_b' l_b' m_b' \right\rangle. \quad (11)$$

Here

$$\psi^{(i)}_{\eta_i l_i m_i} = Y^{l_i}_{m_i}(\theta_i, \varphi_i)\chi_{\eta_i l_i}(r_i), \quad (12)$$

i = a, b; r_i, θ_i, and φ_i are the spherical coordinates of electron e_i in the coordinate system with the origin on the core C_i, whose z axis is directed along the internuclear axis from the core C_a to C_b; $Y_{m_i}{}^{l_i}(\theta_i, \varphi_i)$ is the spherical function; l_i is the orbital quantum number; m_i is the quantum number of the projection of the orbital angular moment of an electron e_i on the z axis; $\chi_{\eta_i l_i}(r_i)$ is the radial atomic orbital and

$$\eta_i = \sqrt{2\varepsilon_i}, \quad (13)$$

where ε_i is the binding energy of the electron on the orbital $\psi^{(i)}{}_{\eta_i l_i m_i}$. Due to the axial symmetry of the diatomic system,

$$\left\langle \eta_a l_a m_a; \eta_b l_b m_b \middle| \hat{\boldsymbol{J}}_{as} \middle| \eta_a' l_a' m_a'; \eta_b' l_b' m_b' \right\rangle = 0 \quad (14)$$

at $m_a + m_b \neq m_a' + m_b'$.

Matrix elements (11) depend on the internuclear distance R, quantum numbers n, l, and m, and constants $A_{\eta_i l_i}$ in the asymptotic expressions for radial orbitals at large r_i

$$\chi_{\eta_i l_i}(r_i)_{r_i \to \infty} \approx A_{\eta_i l_i} r^{1/\eta_i - 1} \exp(-\eta_i r_i). \quad (15)$$

This asymptotic is determined by the fact that the interaction potential of an electron e_i with the core is Coulomb at high r_i. Note that the possibility of introducing the formal operator of exchange interaction $\hat{\boldsymbol{J}}_{as}$ depends substantially on the fact that, owing to condition *1*, the correction functions $\Gamma_{ab}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ and $\Gamma_{ba}(\boldsymbol{r}_{e_a},\boldsymbol{r}_{e_b})$ are independent of the quantum numbers $l_a m_a$ and $l_b m_b$.

The expressions for exchange integrals (11) for the case $0 \le l_a$, l_b, l_a', $l_b' \le 3$ are presented in Ref. 28. It should be emphasized that these expressions are very simple and include only the one-dimensional integral in the range from 0 to 1 of the smooth function. An important property of the indicated expressions is that they give exchange integrals with both positive and negative signs for various combinations of magnetic quantum numbers m_i and m_i'. These signs coincide with those obtained by the calculation of similar integrals in the Heitler—London approximation and correspond to the physical concepts based on an analysis of contributions from the positive repulsion potential between electrons and the negative attraction potential of electrons to nuclei. The expression for the exchange integral determining the splitting between the singlet and triplet terms of the system of two same alkaline metal atoms in the ground ^{2}S states is presented below as an example:

$$\left\langle \eta 00; \eta 00 \middle| \hat{\boldsymbol{J}}_{ax} \middle| \eta 00; \eta 00 \right\rangle = -BR^{7/(2\eta)-1},$$

$$B = \frac{A^4_{\eta 0}\Gamma\left(\frac{1}{2\eta}\right)}{2^{1/\eta+2}} \int_0^1 \exp\left(\frac{x-1}{\eta}\right)(1-x)^{3/(2\eta)}(1+x)^{1/(2\eta)}\,dx, \quad (16)$$

where $\Gamma(1/(2\eta))$ is the gamma function.

Exchange integral for a biradical in the framework of the combined method

The following assumptions are used for the generalization of the described above asymptotic calculation method in the case of calculation of the exchange integral in a biradical:

(1) A reliable information about the equilibrium geometric structure of the biradical and molecular orbitals on

which unpaired electrons are localized is available. For this purpose, the corresponding quantum chemical calculation at a fairly high level should be performed.

(2) The binding energies of unpaired electrons are substantially lower than those of the core electrons. This suggests that the interaction of unpaired electrons with the core is rather weak.

(3) The radial asymptotic behavior of orbitals of unpaired electrons of paramagnetic centers is Coulomb (type (15)) and is determined by their binding energies.

(4) The effective potential energy of two unpaired electrons in the Ω area determining the exchange interaction (see Fig. 1) can be approximated by the Coulomb interaction with positively charged cores of paramagnetic centers and the mutual Coulomb repulsion. Therefore, in the calculation of the exchange integral, the Hamiltonian of two unpaired electrons can be considered as having an axial symmetry relatively to the axis passing through the cores of the paramagnetic centers.

(5) One can choose the coordinate systems related to the paramagnetic centers in which the molecular orbitals of unpaired electrons are satisfactorily approximated by a small number of terms in one-center decompositions over spherical functions.

The calculations of the exchange interaction between the molecules have previously been performed[20,31—33] successfully on the basis of assumptions (3)—(5).

Using assumptions (1)—(5), the explicit expressions for exchange integral $J_{\mathrm{ab}}^{(\mathrm{as})}$ in the biradical are obtained as follows through the known exchange integrals (11).

At the first stage, according to assumption (5), the coordinate systems $x_\mathrm{a}y_\mathrm{a}z_\mathrm{a}$ and $x_\mathrm{b}y_\mathrm{b}z_\mathrm{b}$ with origins on the $\mathrm{C_a}$ and $\mathrm{C_b}$ cores are introduced (Fig. 3). In these coordinate systems, orbitals $\psi_i(\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)})$ are presented as a sum of the finite number of decomposition terms over the spherical functions (i = a, b)

$$\psi_i(\boldsymbol{r}_{\mathrm{e}_i}^{(i)}) = \sum_{l_i=0} \sum_{\mu_i=0}^{\mathrm{e}_i} Y_{\mu_i}^{l_i}(\theta_{\mathrm{e}_i}^{(i)}, \varphi_{\mathrm{e}_i}^{(i)}) \chi_{i,l_i\mu_i}(\boldsymbol{r}_{\mathrm{e}_i}^{(i)}), \tag{17}$$

where $\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)}$, $\theta_{\mathrm{e}_i}{}^{(i)}$, and $\varphi_{\mathrm{e}_i}{}^{(i)}$ are the spherical coordinates of electron e_i in the $x_iy_iz_i$ coordinate system. In this case, the dependence of the asymptotic (at $r_{\mathrm{e}_i}{}^{(i)} \to \infty$) expression for all $\chi_{i,l_im_i}(\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)})$ on $\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)}$ is the same and takes the form

$$\chi_{\eta_il_i\mu_i}(r_{\mathrm{e}_i}^{(i)})_{r_{\mathrm{e}_i}^{(i)} \to \infty} \approx A_{\eta_il_i\mu_i} r^{(i)1/\eta_i - 1} \exp(-\eta_i r_{\mathrm{e}_i}^{(i)}). \tag{18}$$

It should be mentioned that the summation over μ_i for the most part of practically interesting cases is required only to provide the real character of functions $\psi_i(\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)})$ corresponding to the nondegenerate spatial states of unpaired electrons.

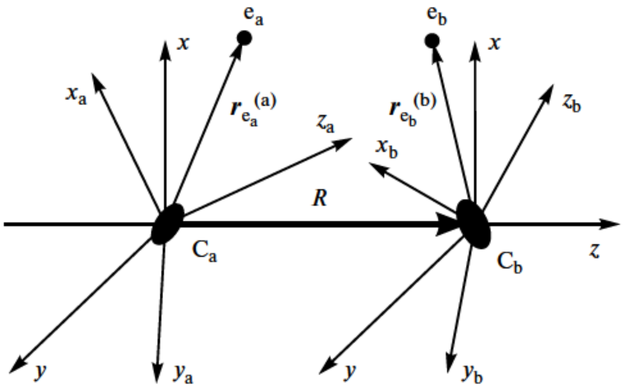

Fig. 3. Coordinate systems of weakly bond electrons $\mathrm{e_a}$ and $\mathrm{e_b}$ on the paramagnetic centers with the $\mathrm{C_a}$ and $\mathrm{C_b}$ cores.

At the second stage, the single coordinate system xyz is introduced, whose axis z is directed along vector $\boldsymbol{R}$ from core $\mathrm{C_a}$ to core $\mathrm{C_b}$ and axes x and y are chosen in such a way that the coordinate system would be right (see Fig. 3). The coordinate systems $x_iy_iz_i$ are obtained from the coordinate system xyz by rotations with sets $\alpha_i,\beta_i,\gamma_i$ of Eyler angles and functions $\psi_i(\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)})$ can be presented as follows:

$$\psi_i(\boldsymbol{r}_{\mathrm{e}_i}^{(i)}) =$$
$$= \sum_{l_i=0} \sum_{\mu_i=-l}^{l_i} \sum_{m_i=-l}^{l_i} \chi_{i,l_i\mu_i}(r_{\mathrm{e}_i}^{(i)}) D_{m_i,\mu_i}^{l_i}(\alpha_i, \beta_i, \gamma_i) Y_{m_i}^{l_i}(\theta_{\mathrm{e}_i}, \varphi_{\mathrm{e}_i}), \tag{19}$$

where $D^{l_i}{}_{m_i,\mu_i}(\alpha_i,\beta_i,\gamma_i)$ are the Wigner rotation matrices (see, *e.g.*, Ref. 34), and $\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)}$, θ_{e_i}, and φ_{e_i} are the spherical coordinates of electron e_i in the coordinate system xyz with the origin on the C_i core. At the third stage, using Eq. (19) for the orbitals of unpaired electrons and the known expressions for exchange integrals (11), exchange integral $J_{\mathrm{ab}}^{(\mathrm{as})}$ is calculated by formula (20).

Several remarks can be made concerning formula (20).

— Since, unlike the interaction of two atoms (see Eq. (15)), the constants in the asymptotic expressions for the radial functions in decompositions $\psi_i(\boldsymbol{r}_{\mathrm{e}_i}{}^{(i)})$ over the spherical functions depend not only on η_il_i but also on μ_i (see Eq. (18)), these values are explicitly indicated in the matrix elements $\langle\eta_\mathrm{a}l_\mathrm{a}\mu_\mathrm{a}m_\mathrm{a};\eta_\mathrm{b}l_\mathrm{b}\mu_\mathrm{b}m_\mathrm{b}|\hat{\mathbf{J}}_{\mathrm{as}}|\eta_\mathrm{a}l_\mathrm{a}{}'\mu_\mathrm{a}{}'m_\mathrm{a}{}';\eta_\mathrm{b}l_\mathrm{b}{}'\mu_\mathrm{b}{}'m_\mathrm{b}{}'\rangle$, which do

$$J_{\mathrm{ab}}^{(\mathrm{as})} = \left\langle \psi_\mathrm{a}\psi_\mathrm{b} \middle| \hat{\boldsymbol{J}}_{\mathrm{as}} \middle| \psi_\mathrm{a}\psi_\mathrm{b} \right\rangle =$$
$$= \sum_{l_\mathrm{a}} \sum_{\mu_\mathrm{a}=-l_\mathrm{a}}^{l_\mathrm{a}} \sum_{l_\mathrm{b}} \sum_{\mu_\mathrm{a}=-l_\mathrm{b}}^{l_\mathrm{b}} \sum_{l_\mathrm{a}'} \sum_{\mu_\mathrm{a}'=-l_\mathrm{a}'}^{l_\mathrm{a}'} \sum_{l_\mathrm{b}'} \sum_{\mu_\mathrm{b}'=-l_\mathrm{b}'}^{l_\mathrm{b}'} \sum_{m_\mathrm{a}=-l_\mathrm{a}}^{l_\mathrm{a}} \sum_{m_\mathrm{b}=-l_\mathrm{b}}^{l_\mathrm{b}} \sum_{m_\mathrm{a}'=-l_\mathrm{a}'}^{l_\mathrm{a}'} \sum_{m_\mathrm{b}'=-l_\mathrm{b}'}^{l_\mathrm{b}'} D_{m_\mathrm{a},\mu_\mathrm{a}}^{l_\mathrm{a}}(\alpha_\mathrm{a}, \beta_\mathrm{a}, \gamma_\mathrm{a})^* \cdot$$
$$\cdot D_{m_\mathrm{b},\mu_\mathrm{b}}^{l_\mathrm{b}}(\alpha_\mathrm{b}, \beta_\mathrm{b}, \gamma_\mathrm{b})^* D_{m_\mathrm{a}',\mu_\mathrm{a}'}^{l_\mathrm{a}'}(\alpha_\mathrm{a}, \beta_\mathrm{a}, \gamma_\mathrm{a}) D_{m_\mathrm{b}',\mu_\mathrm{b}'}^{l_\mathrm{b}'}(\alpha_\mathrm{b}, \beta_\mathrm{b}, \gamma_\mathrm{b}) \cdot$$
$$\cdot \left\langle \eta_\mathrm{a}l_\mathrm{a}\mu_\mathrm{a}m_a; \eta_\mathrm{b}l_\mathrm{b}\mu_\mathrm{b}m_b \middle| \hat{\boldsymbol{J}}_{\mathrm{ax}} \middle| \eta_\mathrm{a}l_\mathrm{a}'\mu_\mathrm{a}'m_a'; \eta_\mathrm{b}l_\mathrm{b}'\mu_\mathrm{b}'m_\mathrm{b}' \right\rangle. \tag{20}$$

not differ from standard diatomic exchange integrals (11) at specified asymptotic constants $A_{\eta_i l_i \mu_i}$.

— In spite of seemingly cumbersome formula (20) for $J_{ab}^{(as)}$, real calculations by this formula are fairly simple for two reasons. First, a small number (two—three) different values of l_i usually contributes to decomposition (17) over spherical functions, and the contributions with different μ_i, as mentioned above, provide reality of $\Psi_i(\mathbf{r}_{e_i}^{(i)})$. Second, the expressions for exchange integrals (11) themselves are fairly simple (see, *i.e.*, Eq. (16)).

— The mutual orientation of the electron density distributions corresponding to orbitals ψ_a and ψ_b and, hence, the degree of overlapping are determined by sets of Eyler angles α_a, β_a, γ_a and α_b, β_b, γ_b. Expression (20) for $J_{ab}^{(as)}$ is a linear combination of exchange integrals (11) with various combinations of magnetic quantum numbers m_i and m_i', which can be either positive, or negative with coefficients depending on α_a, β_a, γ_a and α_b, β_b, γ_b. Therefore, depending on the mutual orientation of electron density distributions corresponding to the ψ_a and ψ_b orbitals, the value of $J_{ab}^{(as)}$ can be both positive (ferromagnetic coupling) and negative (antiferromagnetic coupling).

Example of calculation and discussion

The combined calculation method described above for the exchange interaction in the biradical was used for nitroxyl biradical NBR, whose structure is shown in Fig. 4. This compound is the simplest analog of biradicals: precursors of organic ferromagnets and ferromagnetic polymers.[35] According to the ESR spectroscopic data, the absolute value of the exchange integral for this system exceeds[36] 0.1 cm^{-1}.

The electronic structure and geometry of NBR were calculated within the unrestricted DFT method using the B3LYP hybrid functional[37—39] and the cc-pvdz basis set. All calculations were performed using the ORCA program.[40] The geometry was optimized without symmetry restrains checking stationary points of the potential surface by the calculation of normal vibration frequencies.

The main geometric and electronic characteristics that determine the exchange interaction between the NO groups are the following:

— the axes of the NO$_a$ (N(16)—O(17)) and NO$_b$ (N(42)—O(43)) groups are nearly collinear and lie in the z axis; the N(16)—N(42) distance is 7.219 Å; the N—O distances (N(16)—O(17), N(42)—O(43)) are 1.279 Å; the distance between the centers of the NO$_a$ and NO$_b$ groups (R) is 8.498 Å;

— the ψ_a and ψ_b orbitals in both NO groups on which unpaired electrons are localized have the symmetry π_x;

— the binding energies of unpaired electrons (*i.e.*, ionization potentials) on both NO groups are $\varepsilon_{\pi x} = 0.188$ au = = 5.11 eV and, therefore, $\eta_a = \eta_b = 0.613$; the ionization potentials were estimated by Koopman´s theorem using canonical orbital energies for the open shell.[41]

According to the above described geometric structure of NBR and directions of the ψ_a and ψ_b orbitals, it is natural to choose the coordinate systems xyz, $x_a y_a z_a$, and $x_b y_b z_b$ introduced in the previous section in such a way as it is shown in Fig. 5. The following sets of Eyler angles in Eqs (19) and (20) correspond to this choice of coordinate systems: $\alpha_a = \beta_a = \gamma_a = 0$; $\alpha_b = -\pi/2$, $\beta_b = \pi$, and $\gamma_b = \pi/2$.

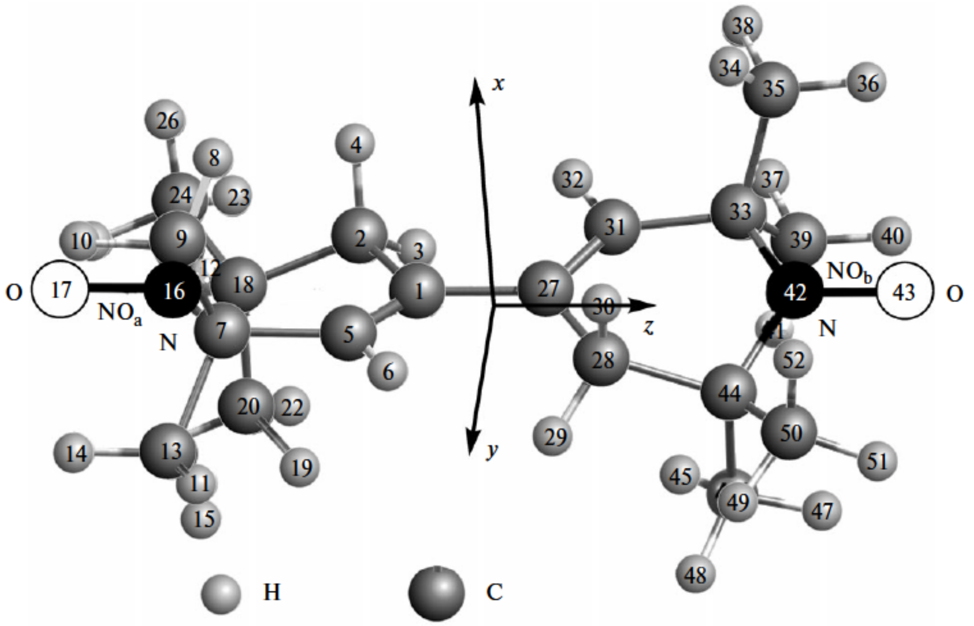

Fig. 4. Structure of nitroxyl radical NBR.

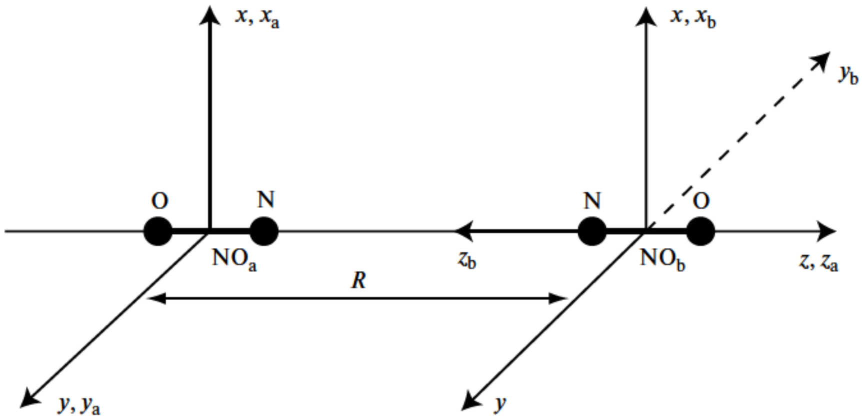

Fig. 5. Coordinate systems of weakly bound electrons e_a and e_b on the paramagnetic centers NO_a and NO_b in which the exchange interaction in NBR was calculated.

Coefficients $A_{\eta_i l_i \mu_i}$ in the asymptotic approximations of $\Psi_i^{(as)}$ at large $r_{e_i}^{(i)}$ in decompositions of type (17) for the ψ_i orbitals obtained by the quantum chemical calculation were determined by cross-linking $\Psi_i^{(as)}$ and ψ_i in the region $2 < r_{e_i}^{(i)} < 3$ au using the least-squares method. It turned out that it is enough to take into account only the terms with $l_i = 1, 2$ and $\mu_i = \pm 1$. In this case,

$$A_{\eta_i,l_i=1,\mu_i=\pm1} = 0.0573,\ A_{\eta_i,l_i=2,\mu_i=\pm1} = 0.0344. \qquad (21)$$

A comparison of this constructed asymptotic approximation of $\Psi_i^{(as)}$ for the ψ_a orbital with this orbital itself is shown in Fig. 6. A satisfactory agreement is observed.

The calculation by formula (20) using the above presented parameters gives the following expression for $J_{ab}^{(as)}(R)$:

$$J_{ab}^{(as)}(R) = -6.7 \cdot 10^5 R^{2.71} \exp(-1.226R)\ \mathrm{cm}^{-1},$$

$$J_{ab}^{(as)}(R = 16.059) = -3.5\ \mathrm{cm}^{-1}. \qquad (22)$$

The plot of function $J_{ab}^{(as)}(R)$ is shown in Fig. 7.

The obtained result (22) has a reasonable order of magnitude and a "correct" negative sign, since the electron density distributions corresponding to orbitals ψ_a and ψ_b are "parallel" and well overlapped. Therefore, the main contribution to the exchange integral is made by the Coulomb attraction of electrons to the positively charged cores C_a and C_b.

Thus, the described combined calculation method makes it possible to rather easily estimate the exchange interaction and, in particular, to determine its dependence on the electronic structure of paramagnetic centers. In the described simplest variant of the combined method. it is enough to know the biradical geometry and the binding energy of unpaired electrons and orbitals of unpaired electrons in the area of the configurational space of electrons where these orbitals are high. This is possible when assumptions (*2*)—(*4*) are fulfilled, which seem to be quite reasonable for short biradicals. However, if the biradical is long and the paramagnetic centers are strongly remote from each other, then the possibility of influence of the core on the character of the asymptotic behavior of orbit-

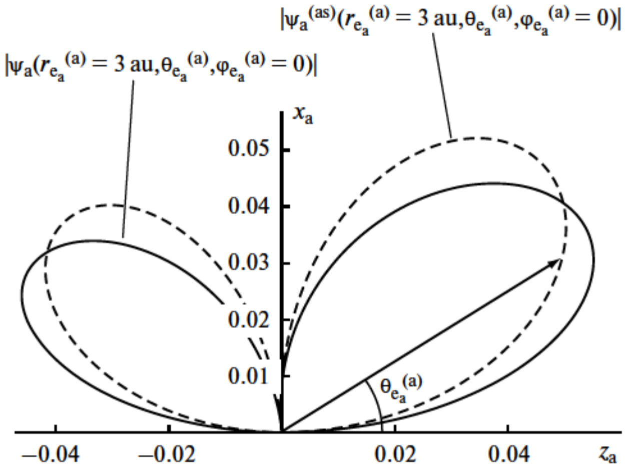

Fig. 6. Polar plots $|\Psi_a(r_{ea}^{(a)} = 3\ \mathrm{au}, \theta_{ea}^{(a)}, \varphi_{ea}^{(a)} = 0)|$ and $|\Psi_a^{(as)}(r_{ea}^{(a)} = 3\ \mathrm{au}, \theta_{ea}^{(a)}, \varphi_{ea}^{(a)} = 0)|$.

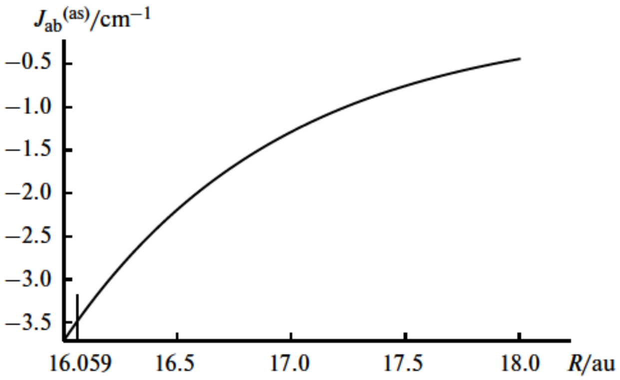

Fig. 7. Exchange integral $J_{ab}^{(as)}(R)$.

als of unpaired electrons localized on these centers should be considered for the calculation of the exchange interaction. These studies need a detailed information on the electronic structure of the biradical for modeling the pseudo-potential describing the interaction of unpaired electrons with the core. We are planning to perform further studies in this direction.

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