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Weak Exchange Interactions in Biradicals: a Pseudopotential for Unpaired Electrons and an Asymptotic Methods for Calculating the Exchange Integral

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Abstract—A theory of weak exchange interactions in biradicals is developed. The basic idea is to describe the motion of two weakly bound electrons on paramagnetic centers by a two-particle Schrödinger equation that takes into account the interaction of these electrons with the closed electron shells of the biradical, described by a model local potential, and their mutual Coulomb repulsion. The model potential can be constructed using the pseudopotential method, based on results of ab initio quantum chemical calculations. The exchange interaction between the unpaired electrons on the paramagnetic centers is calculated by a generalized asymptotic method that takes into account the quasi-classical nature of the subbarrier motion of the electrons in the region between the paramagnetic centers. The developed theory makes it possible to estimate the magnitude of the exchange interaction and to determine how this interaction depends on the distance between the paramagnetic centers and their relative orientation.

Keywords: asymptotic method, biradical, Dirac vector model, semiclassical approximation, rotation matrix, exchange integral, pseudopotential

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1. INTRODUCTION

Biradicals with two spaced-apart paramagnetic centers are convenient objects for modeling intramolecular dynamics [1, 2], the spatial structure of molecules [1, 3], and the specific features of the delocalization of an unpaired electron in a chain of bonds [4–8]. In recent years, these issues have attracted increasing interest in connection with the creation of organic magnetic materials and the development of spin electronics (see, e.g., [9–13]).

The most important characteristic of biradicals in terms of their use as an object for fundamental research and as a technological material is the energy splitting

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

between their lower singlet and triplet electronic states. In the theory of electron paramagnetic resonance, ΔE_{ST} can be conveniently defined as the difference between two eigenvalues of the spin Hamiltonian:

$$\hat{H}_{sp} = -\frac{1}{2} J_{ab} \left(1 + \hat{\mathbf{s}}_a \hat{\mathbf{s}}_b\right). \tag{2}$$

Here, $\hat{\mathbf{s}}_a$, and $\hat{\mathbf{s}}_b$ are the electron spin operators of paramagnetic centers Pc_a and Pc_b, and $J_{ab} = (1/2)\Delta E_{ST}$ is the so-called exchange integral. Such a description of singlet–triplet splitting in two-electron systems goes back to accounting electronic correlations in perturbation theory. In calculating the matrix elements of the Hamiltonian between two-electron wave functions antisymmetric with respect to permutation of electrons, it is convenient to use the Dirac vector model to represent the permutation operator of electron spin coordinates (see, e.g., [14]). Accordingly, hereinafter, along with ΔE_{ST}, the treatment will involve exchange interaction and the exchange integral.

The first attempts of quantum chemical calculations of for biradicals were undertaken more than 50 years ago [15, 16] within the framework of the simplest Hückel approximation. In this method, ΔE_{ST} was calculated in a straightforward manner, as difference between the total electronic energies for the singlet and triplet states. The same straightforward approach continues to be used in modern ab initio methods, such as density functional theory (DFT) and ab initio MCSCF and MCQDPT methods. These methods enable to calculate, with reasonable accuracy, the structural and thermodynamic properties of biradicals and some magnetic resonance parameters (see, e.g., [17–20]).

However, quantum-chemical calculations of a small energy splitting ΔE_{ST} (~1 cm^{-1} or less), which determines the exchange integral, face serious difficulties. The matter is that, in quantum chemistry,

ΔE_{ST} is calculated as the difference between large (10^4–10^5 eV) total negative electron energies E_S and E_T for the singlet and triplet states. The situation is aggravated by the fact that it is necessary to calculate the difference between the total energies of electronic states of different symmetry. In this situation, the calculated value of ΔE_{ST} is strongly dependent on the used quantum-chemical method and basis set (see, e.g., [19]).

This problem was identified a long time ago [21]. The author of [21] tried to calculate ΔE_{ST} in the framework of perturbation theory, in which the problem of difference between large total electronic energies does not arise. In our previous work [22], it was proposed to split the procedure of calculating the ΔE_{ST} into two stages. At the first stage, standard quantum-chemical methods (preferably of a high enough level) are used to calculate the spatial and electronic structure of the biradical. In the case considered here, of small ΔE_{ST}, these structures for the singlet and triplet states are almost identical. In the second stage, the results of these calculations are used to calculate ΔE_{ST} for the biradical by the asymptotic method developed in the theory of atomic collisions [23]. Similarly to [21], in the asymptotic method, ΔE_{ST} is calculated directly, not as the difference between very large quantities in the above-mentioned direct methods of quantum chemistry. However, in [22], the treatment was performed using a rather strong assumption. It consists in the fact that the effective potential energy of the two unpaired electrons in the region of their configuration space, which determines the value of ΔE_{ST}, can be approximated by the Coulomb interaction with the positively charged cores of the biradical's groups containing an unpaired electron (paramagnetic centers) and the mutual Coulomb repulsion. This is evidently valid for short biradicals. However, if the biradical is long enough and the paramagnetic centers are significantly distant from each other, the exchange interaction should be calculated with a more accurate account of the effect of the core on the behavior of the wave functions of the unpaired electrons in the region of their configuration space between these centers. The importance of this point is demonstrated by the available experimental data on the rate of decrease of the absolute value of ΔE_{ST} with increasing distance between the paramagnetic centers (see, e.g., [5]). It is much lower than that obtained in the framework of the simplest model considered in [22].

In the present paper, we generalize the approach to calculating ΔE_{ST} developed in [22]. The proposed generalized combined procedure for calculating the weak exchange interaction in biradicals consists of three stages. At the first stage, the equilibrium configuration of the biradical and its electronic wave functions in this configuration are calculated. At the second stage, the results of the quantum-chemical calculation are used to construct a local pseudopotential describing the interaction of the unpaired electron localized on the paramagnetic centers with the core. The literature describes in detail a wide variety of the approaches proposed for constructing pseudopotentials (see, e.g., [24–27] and references therein). In addition, at this stage, the constructed pseudopotential is used to calculate the binding energies and the corresponding one-electron orbitals localized on the paramagnetic centers. In the third stage, the above quantum-chemical information is used to calculate, by the asymptotic method, the exchange interaction between the paramagnetic centers.

The paper is organized as follows. Section 2 discusses the qualitative form of the potential acting on the electrons localized the on paramagnetic centers and their orbitals. Section 3 is devoted to constructing two-electron wave functions in the asymptotic region between the paramagnetic centers with account of the Coulomb repulsion between the electrons. Section 4 describes the derivation of a general formula for the exchange integral for the biradical expressed through the parameters characterizing the molecular orbitals of the unpaired electrons. Unless otherwise indicated, atomic units (a.u.), $e = m_e = \hbar$, are used throughout the paper.

2. PSEUDOPOTENTIAL AND THE LOCALIZED ORBITALS OF PARAMAGNETIC CENTERS

Consider a biradical comprised of two paramagnetic centers Pc_a and Pc_b separated by a number of functional groups Gr_i (Fig. 1). Analysis of the electronic structure of the biradical considered in [22] showed that outer electrons e_1 and e_2 are localized on Pc_a and Pc_b and that their binding energies ε_a and ε_b are smaller than the binding energies of the electrons on functional groups Gr_j ($j = 1, 2, ..., N$) of the framework. It is natural to assume that this situation is typical, so this assumption will be used below. The interaction of each of outer electrons e_1 and e_2 with the framework of the biradical, including the interjacent functional groups Gr_i and positively charged cores C_a and C_b of paramagnetic centers Pc_a and Pc_b, can be described by a pseudopotential. As noted in Section 1, it is assumed that this pseudopotential can be approximated by a local potential $V_{ef}(\mathbf{r}_i)$ ($i = 1, 2$). The vectors $\mathbf{r}_i$ are defined in Fig. 1. The qualitative form of the potential $V_{ef}(\mathbf{r}_i)$ along the z_i axis that passes through the paramagnetic centers is displayed in Fig. 2. Near positively charged cores C_a and C_b, Coulomb attraction takes place, which, as the distance to the core decreases, changes to exchange repulsion. As regards the interaction with functional groups Gr_i, it is assumed (Fig. 2) that they have a certain affinity for the electrons of the paramagnetic centers, which manifests itself as an effective attraction. However, in principle, interaction of another type is possible. To estab-

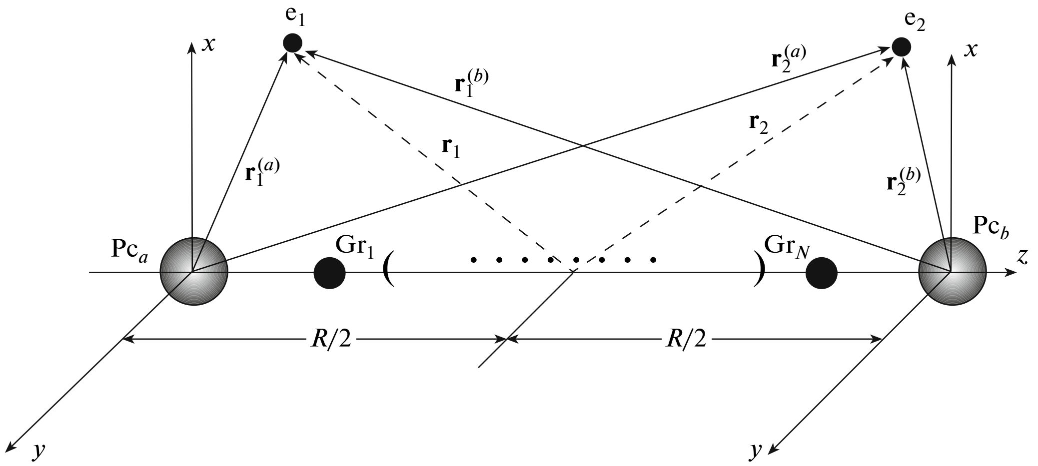

Fig. 1. Coordinate systems of weakly bound electrons e$_a$ and e$_b$. All designations are given in the text.

lish the explicit form of the potential of interaction with Gr$_i$, it is necessary to perform specific quantum-chemical calculations. For further analysis, it convenient to present $V_{ef}(\mathbf{r}_i)$ as

$$V_{ef}(\mathbf{r}_i) = V_{ef,\mathrm{C}_a}(\mathbf{r}_i^{(a)}) + V_{ef,\mathrm{C}_b}(\mathbf{r}_i^{(b)}) + V_{ef,int}(\mathbf{r}_i), \tag{3}$$

where (Fig. 1)

$$\mathbf{r}_i^{(a)} = \mathbf{r}_i + \frac{\mathbf{R}}{2},\quad \mathbf{r}_i^{(b)} = \mathbf{r}_i - \frac{\mathbf{R}}{2},\quad \mathbf{R} = \{0, 0, R\}, \tag{4}$$

$V_{ef,\mathrm{C}_a}(\mathbf{r}_i^{(a)})$ and $V_{ef,\mathrm{C}_b}(\mathbf{r}_i^{(b)})$ are the effective potentials of interaction of electron e$_i$ with the cores C$_a$ and C$_b$ of the paramagnetic centers (at large r_i, these potentials are Coulomb potentials), whereas $V_{ef,int}(\mathbf{r}_i)$ is the potential of interaction of electron e$_i$ with the functional groups Gr$_j$ in the framework of the biradical. The potentials $V_{ef,\mathrm{C}_a}(\mathbf{r}_i)$, $V_{ef,\mathrm{C}_b}(\mathbf{r}_i)$, and $V_{ef,int}(\mathbf{r}_i)$ are defined such that

$$\begin{gathered}\left[-\frac{1}{2}\Delta_i + V_{ef,a}(\mathbf{r}_i^{(a)})\right]\psi^{(a)}(\mathbf{r}_i^{(a)}) = \varepsilon^{(a)}\psi^{(a)}(\mathbf{r}_i^{(a)}),\\ \left[-\frac{1}{2}\Delta_i + V_{ef,b}(\mathbf{r}_i^{(b)})\right]\psi^{(b)}(\mathbf{r}_i^{(b)}) = \varepsilon^{(b)}\psi^{(b)}(\mathbf{r}_i^{(b)}).\end{gathered} \tag{5}$$

Here,

$$\begin{gathered}V_{ef,a}(\mathbf{r}_i^{(a)}) = V_{ef,\mathrm{C}_a}(\mathbf{r}_i^{(a)}) + V_{ef,int}\left(\mathbf{r}_i^{(a)} - \frac{\mathbf{R}}{2}\right)\Theta\left(\frac{R}{2} - \mathbf{r}_i^{(a)}\mathbf{n}_z\right),\\ V_{ef,b}(\mathbf{r}_i^{(b)}) = V_{ef,\mathrm{C}_b}(\mathbf{r}_i^{(b)}) + V_{ef,int}\left(\mathbf{r}_i^{(b)} + \frac{\mathbf{R}}{2}\right)\Theta\left(\frac{R}{2} + \mathbf{r}_i^{(b)}\mathbf{n}_z\right),\end{gathered} \tag{6}$$

$\mathbf{n}_z$ is the unit vector in the direction of the z axis, Δ_i is Laplacian in the coordinates of electron e$_i$, and $\varepsilon^{(k)}$ and $\psi_k(\mathbf{r}_i^{(k)})$ are the binding energy and the corresponding wave function of outer electron e$_i$ localized at paramagnetic center Pc$_k$ ($k = a$, b). The available information on the structure of biradicals and binding energies $\varepsilon^{(k)}$ suggests that the distance R between Pc$_a$ and Pc$_b$ is large in the sense that

$$R \gg \frac{1}{\sqrt{2\varepsilon^{(a)}}} + \frac{1}{\sqrt{2\varepsilon^{(b)}}}. \tag{7}$$

As discussed in [22], if inequality (7) holds, ΔE_{ST} is determined by a relatively narrow cylindrical region Ω of spatial coordinates of electrons e$_1$ and e$_2$, positioned midway between Pc$_a$ and Pc$_b$ near the z axis (Fig. 3). This is due to the exponential decay of the orbitals $\psi^{(k)}$ with increasing $r_i^{(k)}$. The orbitals behave in this way because the electrons move far in the classically forbidden region. In this situation, it is natural to assume that, in the region Ω, the potentials $V_{ef,k}(\mathbf{r}_i^{(k)})$ have a local spherical symmetry near the z axis, so that

$$\begin{gathered}V_{ef,a}^{(sph)}(r_i^{(a)}) = V_{ef,a}(r_i^{(a)}, \theta_i = 0, \varphi_i = 0),\\ V_{ef,b}^{(sph)}(r_i^{(b)}) = V_{ef,a}(r_i^{(b)}, \theta_i = \pi, \varphi_i = 0).\end{gathered} \tag{8}$$

For further treatment, it is convenient to represent the orbitals $\psi^{(k)}(\mathbf{r}_i^{(k)})$ in the region Ω as the sum of a finite number of terms in the expansion in spherical harmonics:

$$\begin{gathered}\psi^{(a)}(\mathbf{r}_i^{(a)}) = \sum_{\ell_a=0}^{L^{(a)}}\sum_{m_a=-\ell_a}^{\ell_a} Y_{m_a}^{\ell_a}(\theta_i^{(a)}, \varphi_i)\chi_{\ell_a m_a}^{(a)}(r_i^{(a)}),\\ \psi^{(b)}(\mathbf{r}_i^{(b)}) = \sum_{\ell_b=0}^{L^{(b)}}\sum_{m_b=-\ell_b}^{\ell_b} Y_{m_b}^{\ell_b}(\pi - \theta_i^{(b)}, \varphi_i)\chi_{\ell_b m_b}^{(b)}(r_i^{(b)}),\end{gathered} \tag{9}$$

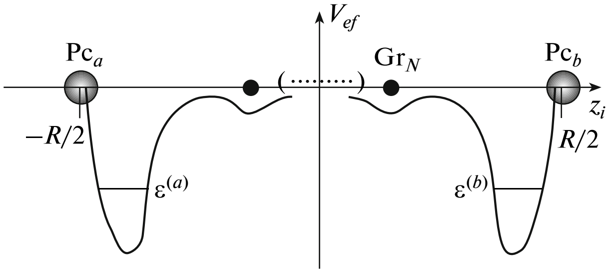

Fig. 2. Qualitative form of the pseudopotential acting on the electron. All designations are given in the text.

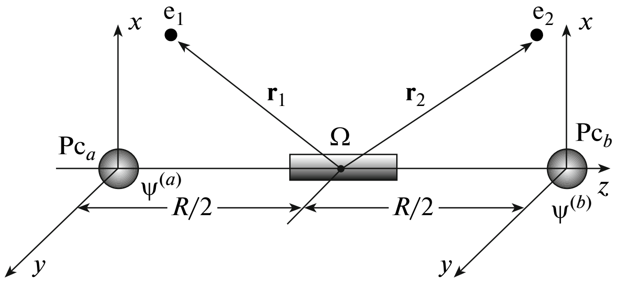

Fig. 3. Illustration of how the wave function with allowance for electron correlation is constructed. All designations are given in the text.

where $r_i^{(k)}$, $\theta_i^{(k)}$, and φ_i are the spherical coordinates of electron e_i in the coordinate system xyz with origin at Pc_k. The lowest singlet and triplet electronic states of biradicals are usually orbitally nondegenerate. Therefore, in what follows, we assumed that the localized one-electron states described by the functions $\psi^{(a)}(\mathbf{r}_i^{(a)})$ and $\psi^{(b)}(\mathbf{r}_i^{(b)})$ are also nondegenerate. Therefore, the functions $\psi^{(a)}(\mathbf{r}_i^{(a)})$ and $\psi^{(b)}(\mathbf{r}_i^{(b)})$ will be considered real. Accordingly, since $Y_m^{\ell}(\theta,\varphi)^* = (-1)^m Y_{-m}^{\ell}(\theta,\varphi)$ the function in (9) must be real and satisfy the relationships

$$\begin{aligned}\chi^{(a)}_{\ell_a - m_a}(r_i^{(a)}) &= (-1)^{m_a}\chi^{(a)}_{\ell_a - m_a}(r_i^{(a)}),\\ \chi^{(b)}_{\ell_b - m_b}(r_i^{(b)}) &= (-1)^{m_b}\chi^{(b)}_{\ell_b - m_b}(r_i^{(b)}).\end{aligned} \tag{10}$$

In this case, in a distant subbarrier region near the z axis, where electron motion is quasiclassical, the function $\chi^{(k)}_{\ell m}(r_i^{(k)})$ in (9) can be approximated by the semiclassical expression

$$\begin{aligned}&\chi^{(k)}_{\ell m, as}(r_i^{(k)})\\ &= \frac{A^{(k)}_{\ell m}}{\left\{2\left[V^{(sph)}_{ef,k}(r_i^{(k)}) - \varepsilon^{(k)}\right]\right\}^{1/2}}\exp\left[-W^{(k)}(r_i^{(k)})\right],\end{aligned} \tag{11}$$

where

$$W^{(k)}(r_i^{(k)}) = \int\limits_{r_0^{(k)}}^{r_i^{(k)}} \left\{2\left[V^{(sph)}_{ef,k}(r) - \varepsilon^{(k)}\right]\right\}^{1/2} dr, \tag{12}$$

and r_0^k is the root of the equation

$$V^{(sph)}_{ef,k}(r) - \varepsilon^{(k)} = 0. \tag{13}$$

The corresponding asymptotic expressions $\psi^{(k)}_{as}(\mathbf{r}_i^{(k)})$ for $\psi^{(k)}(\mathbf{r}_i^{(k)})$ in the region Ω read as

$$\begin{aligned}\psi^{(a)}_{as}(\mathbf{r}_i^{(a)}) &= \sum_{\ell_a=0}^{L^{(a)}}\sum_{m_a=-\ell_a}^{\ell_a} Y^{\ell_a}_{m_a}(\theta_i,\varphi_i)\\ &\times \frac{A^{(a)}_{\ell_a m_a}}{\left\{2\left[V^{(sph)}_{ef,k}(r_i^{(a)}) - \varepsilon^{(a)}\right]\right\}^{1/2}}\exp\left[-W^{(a)}(r_i^{(a)})\right],\\ \psi^{(b)}_{as}(\mathbf{r}_i^{(b)}) &= \sum_{\ell_b=0}^{L^{(b)}}\sum_{m_b=-\ell_b}^{\ell_b} Y^{\ell_b}_{m_b}(\pi-\theta_i,\varphi_i)\\ &\times \frac{A^{(b)}_{\ell_b m_b}}{\left\{2\left[V^{(sph)}_{ef,b}(r_i^{(b)}) - \varepsilon^{(b)}\right]\right\}^{1/2}}\exp\left[-W^{(b)}(r_i^{(b)})\right].\end{aligned} \tag{14}$$

The asymptotic constants $A^{(k)}_{\ell m}$ can be determined in the same way as it was done in [22]: by joining the functions $\psi^{(k)}_{as}(\mathbf{r}_i^{(k)})$ and $\psi^{(k)}(\mathbf{r}_i^{(k)})$ at $r_i^{(k)} \sim 1/\sqrt{2\varepsilon^{(k)}}$ and small θ_i using the least-squares method. A more rigorous approach to determining the asymptotic constants, based on quantum-chemical calculations, was developed in [28, 29].

3. TWO-ELECTRON WAVE FUNCTIONS AT LARGE R IN THE Ω REGION

As discussed above, the singlet–triplet splitting at R satisfying inequality (7) is determined by the area Ω of the spatial coordinates of the two electrons, e_1 and e_2, midway between Pc_a and Pc_b near the z axis (Fig. 3). Making use of this fact, the authors of [30, 31] formulated an asymptotic method for calculating the exchange interaction.

The general scheme for calculating the exchange integral by the asymptotic method is as follows. The singlet and triplet states of the system with energies E_S and E_T are described by the spatial eigenfunctions $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$ and $\Phi_T(\mathbf{r}_1, \mathbf{r}_2)$ of the full two-electron Hamiltonian $\hat{H}$, accordingly symmetric and asymmetric with respect to permutation of the spatial coordinates of the two electrons. Since the singlet and triplet states in biradicals are spatially nondegenerate, the functions $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$ and $\Phi_T(\mathbf{r}_1, \mathbf{r}_2)$ can be assumed to be real without loss of generality. Within the framework of the above model of two outer electrons, this Hamiltonian is given by

$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_1 + V_{ef}(\mathbf{r}_1) + V_{ef}(\mathbf{r}_2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{15}$$

In the states $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$ and $\Phi_T(\mathbf{r}_1, \mathbf{r}_2)$, the spatial distribution of electrons e_1 and e_2 are delocalized: each electron is equally likely to be found near cores of C_a and C_b. For further analysis, it is convenient to combine the functions $\Phi_S(\mathbf{r}_1, \mathbf{r}_2)$ and $\Phi_T(\mathbf{r}_1, \mathbf{r}_2)$ to construct the wave functions

$$\begin{gathered}\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = [\Phi_S(\mathbf{r}_1, \mathbf{r}_2) + \Phi_T(\mathbf{r}_1, \mathbf{r}_2)]/\sqrt{2}, \\ \Psi_{ba}(\mathbf{r}_1, \mathbf{r}_2) = [\Phi_S(\mathbf{r}_1, \mathbf{r}_2) - \Phi_T(\mathbf{r}_1, \mathbf{r}_2)]/\sqrt{2} = \hat{\mathbf{P}}_{12}\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2),\end{gathered} \tag{16}$$

where $\hat{\mathbf{P}}_{12}$ is the operator of permutation of the coordinates of electrons e_1 and e_2. Electrons e_1 and e_2 in the state $\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2)$ are located near cores C_a and C_b, whereas in the state $\Psi_{ba}(\mathbf{r}_1, \mathbf{r}_2)$, near cores C_b and C_a, respectively (Fig. 4). In this case,

$$\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2)\big|_{R\to\infty} \to \psi^{(a)}(\mathbf{r}_1^{(a)})\psi^{(b)}(\mathbf{r}_2^{(2)}) \tag{17}$$

which can be considered normalized at large R.

At R values satisfying (7), when ΔE_{ST} is exponentially small up to terms of order $1/R^2$, the function $\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2)$ satisfies the equation

$$\begin{gathered}\left\{-\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 + V_{ef,a}(\mathbf{r}_1^{(a)}) + V_{ef,a}(\mathbf{r}_2^{(a)})\right. \\ \left. + V_{ef,b}(\mathbf{r}_1^{(b)}) + V_{ef,b}(\mathbf{r}_b^{(b)}) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right\}\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) \\ = \left(\varepsilon^{(a)} + \varepsilon^{(b)} - \frac{1}{R}\right)\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2).\end{gathered} \tag{18}$$

The appearance of the term $-1/R$ on the right side of (18) is due to Coulomb attraction of electrons e_1 and e_2 to the "alien" cores, C_b and C_a.

The next step is to determine the explicit form of the function $\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2)$. To this end, it must appear as

$$\Psi_{ab}(\mathbf{r}_1, \mathbf{r}_2) = \psi^{(a)}(\mathbf{r}_1)\psi^{(b)}(\mathbf{r}_2)\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2), \tag{19}$$

where, in accordance with (17) if inequality (7) holds, the correction function $\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)$, which takes into account electron correlation, satisfies the boundary conditions

$$\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)\big|_{\mathbf{r}_1\to-\mathbf{R}/2} \to 1, \quad \Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)\big|_{\mathbf{r}_2\to\mathbf{R}/2} \to 1. \tag{20}$$

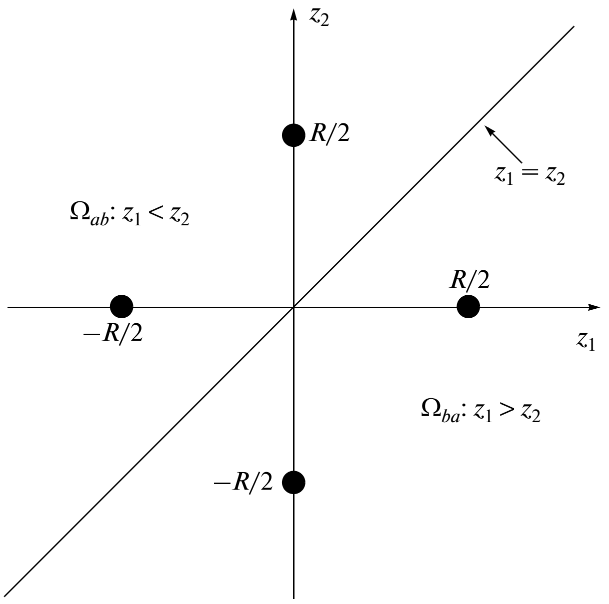

Fig. 4. Illustration to the description of the asymptotic method for calculating the exchange integral. All designations are given in the text.

It is assumed that if inequality (7) holds, $\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)$ varies slowly as compared with $\psi^{(a)}(\mathbf{r}_1)\psi^{(b)}(\mathbf{r}_2)$, the product of the wave functions localized on the paramagnetic centers. In [30–33], this assumption was confirmed for the exchange interaction between one-electron atoms. Substituting (19) into (18), using (5), and neglecting the second derivatives of $\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)$, we obtain the first-order partial differential equation

$$\begin{gathered}-\psi^{(b)}(\mathbf{r}_2)[\nabla_1\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)]\left[\nabla_1\psi^{(a)}(\mathbf{r}_1)\right] \\ - \psi^{(a)}(\mathbf{r}_1)[\nabla_2\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)]\left[\nabla_2\psi^{(b)}(\mathbf{r}_2)\right] \\ + \left[V_{ef,a}(\mathbf{r}_2^{(a)}) + V_{ef,b}(\mathbf{r}_1^{(b)}) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{R}\right] \\ \times \psi^{(a)}(\mathbf{r}_1)\psi^{(b)}(\mathbf{r}_2)\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2) = 0,\end{gathered} \tag{21}$$

which must be solved with boundary conditions (20).

Equation (21) can be simplified still further if the following points are taken into account:

(1) the motion of electrons near the z axis in the region Ω is quasi-classical, enabling to use the asymptotic expressions $\psi_{as}^{(a)}(\mathbf{r}_1^{(a)})$ and $\psi_{as}^{(b)}(\mathbf{r}_2^{(b)})$ (Eq. (14)) as the wave functions localized at the paramagnetic centers;

(2) the derivatives of the functions $\psi_{as}^{(a)}(\mathbf{r}_1^{(a)})$ and $\psi_{as}^{(b)}(\mathbf{r}_2^{(b)})$ are determined mainly by the exponential function;

(3) in a narrow cylindrical region Ω, at large R, the product $\psi_{as}^{(a)}(\mathbf{r}_1^{(a)})\psi_{as}^{(b)}(\mathbf{r}_2^{(b)})$ decreases very quickly with increasing distance between the electrons and the internuclear axis.

To simplify Eq. (21), it is convenient to introduce the cylindrical coordinates ρ_1, z_1, φ_1 and ρ_2, z_2, φ_2. In these coordinates, in the vicinity of the axis, the above points make it possible to consider the terms with derivatives with respect to ρ_1, φ_1, ρ_2, and φ_2 negligibly small compared with the terms with derivatives with respect to z_1 and z_2. As a result, in the vicinity of the z axis, $\Gamma_{ab}(\mathbf{r}_1, \mathbf{r}_2)$ depends on ρ_1, φ_1, ρ_2, φ_2 as on the parameters and satisfies the equation

$$\begin{gathered}\alpha_a(z_1,\rho_1)\frac{\partial\Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2)}{\partial z_1}\\ -\alpha_b(z_2,\rho_2)\frac{\partial\Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2)}{\partial z_2}\\ +\left[\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+V_{ef,a}\left(\frac{R}{2}-z_2\right)+V_{ef,b}\left(\frac{R}{2}+z_1\right)+\frac{1}{R}\right]\\ \times\Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2)=0\end{gathered}\tag{22}$$

with the boundary conditions (see (20))

$$\begin{gathered}\Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2)\big|_{z_1\to -R/2}\to 1,\quad z_1+z_2<0,\\ \Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2)\big|_{z_2\to R/2}\to 1,\quad z_1+z_2>0.\end{gathered}\tag{23}$$

Here,

$$\begin{gathered}\alpha_a(z_1,\rho_1)=\left\{2\left[V_{ef,a}^{(sph)}\left(\frac{R}{2}+z_1\right)-\varepsilon^{(a)}\right]\right\}^{1/2},\\ \alpha_b(z_2,\rho_2)=\left\{2\left[V_{ef,b}^{(sph)}\left(\frac{R}{2}-z_2\right)-\varepsilon^{(b)}\right]\right\}^{1/2},\\ |\mathbf{r}_1-\mathbf{r}_2|=[z_1^2+\rho_1^2+z_2^2+\rho_2^2\\ -2z_1z_2-2\rho_1\rho_2\cos(\varphi_1-\varphi_2)]^{1/2}.\end{gathered}\tag{24}$$

Equation (22) can be solved numerically using quantum-chemical information.

4. ASYMPTOTIC EXPRESSION FOR ΔE_{ST}

To derive an asymptotic expression for ΔE_{ST} if inequality (7) holds, we introduce regions Ω_{ab} (at $z_1 < z_2$) and Ω_{ba} (at $z_1 > z_2$) in the configuration space of electrons e_1 and e_2, separated by the hypersurface $z_1 = z_2$ (Fig. 4). Recall that, in accordance with (16),

$$\begin{gathered}\hat{H}[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)+\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)]\\ =E_S[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)+\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)],\end{gathered}\tag{25a}$$

$$\begin{gathered}\hat{H}[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)-\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)]\\ =E_T[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)-\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)].\end{gathered}\tag{25b}$$

We now multiply Eqs. (25a) and (25b) by $[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2) - \Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)]$ and $[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2) + \Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)]$, respectively, subtract from the first resulting equation the second resulting equation, and integrate the difference over Ω_{ab} to obtain

$$\begin{gathered}(E_S-E_T)\int\limits_{\Omega_{ab}}\left[\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)^2-\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)^2\right]d^3\mathbf{r}_1d^3\mathbf{r}_2\\ =\int\limits_{\Omega_{ab}}[\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)(\Delta_1+\Delta_2)\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)\\ -\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)(\Delta_1+\Delta_2)\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)]d^3\mathbf{r}_1d^3\mathbf{r}_2.\end{gathered}\tag{26}$$

In the region Ω_{ab}, the function $\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)$ is non-small, whereas $\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)$ is exponentially small. Conversely, in the region Ω_{ba}, the function $\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)$ is non-small, whereas $\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)$ is exponentially small. Therefore, at large R, the integral on the right-hand side of (26) equals unity with exponential accuracy. Rearranging the right-hand side by means of the Gauss theorem and taking into account the symmetry properties of $\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)$ with respect to permutations of the coordinates of the electrons (see (16)) and the fact that these functions tend exponentially to zero at $r_1 \to \infty$ and $r_2 \to \infty$, we arrive at the following expression in the form of an integral over the hypersurface $z_1 = z_2$ (Fig. 4) for the exchange integral $J_{ab} = 1/2\,\Delta E_{ST}$:

$$\begin{gathered}J_{ab}=\int\limits_{-\infty}^{\infty}dx_1\int\limits_{-\infty}^{\infty}dy_1\int\limits_{-\infty}^{\infty}dx_2\int\limits_{-\infty}^{\infty}dy_2\\ \times\int\limits_{-\infty}^{\infty}dz\left(\Psi_{ba}\frac{\partial\Psi_{ab}}{\partial z_1}-\Psi_{ab}\frac{\partial\Psi_{ba}}{\partial z_1}\right)_{z_1=z_2},\quad z=z_1=z_2.\end{gathered}\tag{27}$$

Substituting the asymptotic forms of the functions $\Psi_{ab}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Psi_{ba}(\mathbf{r}_1,\mathbf{r}_2)$: into (27) yields

$$\begin{gathered}\Psi_{ab}^{(as)}(\mathbf{r}_1,\mathbf{r}_2)=\psi_{as}^{(a)}(\mathbf{r}_1^{(a)})\psi_{as}^{(b)}(\mathbf{r}_2^{(b)})\Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2),\\ \Psi_{ba}^{(as)}(\mathbf{r}_1,\mathbf{r}_2)=\Psi_{ab}^{(as)}(\mathbf{r}_2,\mathbf{r}_1),\end{gathered}\tag{28}$$

where $\psi_{as}^{(a)}(\mathbf{r}_1^{(a)})$ and $\psi_{as}^{(b)}(\mathbf{r}_2^{(b)})$ are given by (14), whereas the correction function $\Gamma_{ab}(z_1\rho_1, z_2\rho_2, \varphi_1-\varphi_2)$, describing electron correlation, is obtained by solving Eq. (22). Thus, we obtain the following expression for J_{ab}:

$$J_{ab}=\sum_{\ell_a=0}^{L_a}\sum_{\ell_b=0}^{L_b}\sum_{\ell'_a=0}^{L_a}\sum_{\ell'_a=0}^{L_b}\sum_{m_a=-\ell_a}^{\ell_a}\sum_{m_b=-\ell_b}^{\ell_b}\sum_{m'_a=\ell'_a}^{\ell'_a}\sum_{m'_b=-\ell'_b}^{\ell'_b}\left\langle\ell_a m_a;\ell_b m_b\middle|\hat{\mathbf{J}}\middle|\ell'_a m'_a;\ell'_b m'_b\right\rangle,\tag{29}$$

where

$$\begin{aligned}&\left\langle \ell_a m_a;\ell_b m_b\left|\hat{\mathbf{J}}\right|\ell'_a m'_a;\ell'_b m'_b\right\rangle\\&= \int\limits_0^{\infty}\rho_1 d\rho_1\int\limits_0^{2\pi}d\varphi_1\int\limits_0^{\infty}\rho_2 d\rho_2\int\limits_0^{2\pi}d\varphi_2\int\limits_{-\infty}^{\infty}dz\\&\times\Bigg[\exp\left[i\left(m_a\varphi_2+m_b\varphi_1+m'_a\varphi_1+m'_b\varphi_2\right)\right]\\&\times\Theta^{(ba)}_{\ell_a m_a;\ell_b m_b}\frac{\partial\Theta^{(ab)}_{\ell'_a m'_a;\ell'_b m'_b}}{\partial z_1}-\exp\left[i\left(m_a\varphi_1+m_b\varphi_2\right.\right.\\&\left.\left.+\,m'_a\varphi_2+m'_b\varphi_1\right)\right]\Theta^{(ab)}_{\ell_a m_a;\ell_b m_b}\frac{\partial\Theta^{(ba)}_{\ell'_a m'_a;\ell'_b m'_b}}{\partial z_1}\Bigg]_{z_1=z_2},\\&z=z_1=z_2,\end{aligned}\tag{30}$$

$$\begin{aligned}&\Theta^{(ab)}_{\ell_a m_a;\ell_b m_b}\left(z_1\rho_1;z_2\rho_2;\varphi_1-\varphi_2\right)\\&=\chi^{(a)}_{\ell_a m_a,as}\left[r_1^{(a)}(z_1\rho_1)\right]\left[\frac{2\ell_a+1}{4\pi}\frac{(\ell_a-m_a)!}{(\ell_a+m_a)!}\right]^{1/2}\\&\times P^{\ell_a}_{m_a}\left\{\cos\left[\theta_1^{(a)}(z_1\rho_1)\right]\right\}\chi^{(b)}_{\ell_a m_a,as}\left[r_2^{(b)}(z_2\rho_2)\right]\\&\times\left[\frac{2\ell_b+1}{4\pi}\frac{(\ell_b-m_b)!}{(\ell_b+m_b)!}\right]^{1/2}(-1)^{\ell_b+m_b}P^{\ell_b}_{m_b}\\&\times\left\{\cos\left[\theta_2^{(b)}(z_2\rho_2)\right]\right\}\Gamma_{ab}(z_1\rho_1,z_2\rho_2,\varphi_1-\varphi_2),\\&r_1^{(a)}(z_1\rho_1)=\left[\left(z_1+\frac{R}{2}\right)^2+\rho_1^2\right]^{1/2},\\&r_2^{(b)}(z_2\rho_2)=\left[\left(z_2-\frac{R}{2}\right)^2+\rho_2^2\right]^{1/2},\\&\cos\left[\theta_1^{(a)}(z_1\rho_1)\right]=\frac{z_1+R/2}{\left[(z_1+R/2)^2+\rho_1^2\right]^{1/2}},\\&\cos\left[\theta_2^{(b)}(z_2\rho_2)\right]=\frac{z_2-R/2}{\left[(z_2+R/2)^2+\rho_2^2\right]^{1/2}},\\&\Theta^{(ba)}_{\ell_a m_a;\ell_b m_b}\left(z_1\rho_1\varphi_1;z_2\rho_2\varphi_2\right)\\&=\Theta^{(ab)}_{\ell_a m_a;\ell_b m_b}\left(z_2\rho_2\varphi_2;z_1\rho_1\varphi_1\right).\end{aligned}\tag{31}$$

Here, $P^{\ell}_{m}(\cos\theta)$ are the associated Legendre polynomials.

CONCLUSIONS

In conclusion, we would like to make a few comments regarding formulas (29) and (30).

(1) The functions $\Theta^{(ab)}_{\ell_a m_a;\ell_b m_b}\left(z_1\rho_1;z_2\rho_2;\varphi_1-\varphi_2\right)$ have axial symmetry with respect to rotations about the z axis. Therefore, the quantities $\left\langle \ell_a m_a;\ell_b m_b\left|\hat{\mathbf{J}}\right|\ell'_a m'_a;\ell'_b m'_b\right\rangle$ have the following properties:

$$\begin{aligned}&\left\langle \ell_a m_a;\ell_b m_b\left|\hat{\mathbf{J}}\right|\ell'_a m'_a;\ell'_b m'_b\right\rangle=0\text{ at}\\&m_a+m_b+m'_a+m'_b\neq 0,\\&\left\langle \ell_a-m_a;\ell_b-m_b\left|\hat{\mathbf{J}}\right|\ell'_a-m'_a;\ell'_b-m'_b\right\rangle\\&=\left\langle \ell_a m_a;\ell_b m_b\left|\hat{\mathbf{J}}\right|\ell'_a m'_a;\ell'_b m'_b\right\rangle.\end{aligned}\tag{32}$$

(2) If $V_{ef,int}(\mathbf{r}_i)$ can be neglected (Eq. (3)), $\left\langle \ell_a m_a;\ell_b m_b\left|\hat{\mathbf{J}}\right|\ell'_a m'_a;\ell'_b m'_b\right\rangle$ is identical to the standard two-electron diatomic exchange integrals, explicit expressions for which were derived in [32–34]. One can expect that, if $V_{ef,int}(\mathbf{r}_i)$ is taken into account, the signs of $\left\langle \ell_a m_a;\ell_b m_b\left|\hat{\mathbf{J}}\right|\ell'_a m'_a;\ell'_b m'_b\right\rangle$, which are mainly determined by the competition between their Coulomb repulsion and attraction to the cores of paramagnetic centers C_a and C_b, will be the same as the signs of the corresponding standard diatomic exchange integrals.

(3) Exchange integral (29) depends on the relative orientation of paramagnetic centers Pc_a and Pc_b through sets of asymptotic coefficients $A^{(a)}_{\ell_a m_a}$ and $A^{(b)}_{\ell_b m_b}$ in expansions (14) of the asymptotic expressions for the orbital $\psi^{(k)}_{as}(\mathbf{r}^{(k)}_i)$ of the outer electrons localized on these centers.

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