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Abstract

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ON THE BIRADICAL PARADOX

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1. In recent years a number of works have appeared (^{1}-^{3}) devoted to the study, by the electron-paramagnetic-resonance method, of biradical systems consisting of two triphenylmethyl radicals connected by an oxygen, methylene, or phenylenic bridge. These systems can be modeled by two potential wells, each of which contains one electron (Fig. 1). Analysis of the hyperfine structure of the spectrum shows that each of the electrons interacts only with the protons of “its own” well. This means that the hyperfine-interaction frequency $\delta/\hbar = 10^7$ sec^{-1} is much greater than the frequency of electronic transitions between the two wells $\Delta\nu$ (see (^{4})), which is determined by the singlet-triplet splitting in the biradical, $\Delta E = \hbar\Delta\nu$. On the other hand, according to the theoretical estimates of McConnell (^{5}), the magnitude of the singlet-triplet splitting proves to be of the order of 10^{11} sec^{-1}, which is in clear contradiction with the indicated experimental data. This situation was called by McConnell (^{6}) the biradical paradox.

In his calculations McConnell in fact proceeded from the assumption that the magnitude of the singlet-triplet splitting ΔE is determined only by the frequency of electron transfer along the bridge, $b/\hbar$. In reality, however, transitions with such a frequency occur only in one-electron systems, and experiment shows that in the case of short bridges (one or two CH_2 groups) this frequency indeed proves to be greater than $\delta/\hbar$ (^{7}). The essential difference between a biradical and these systems is that the actual frequency of electron transitions between the wells, $\Delta\nu$ (spin exchange), differs from the frequency of electron transfer along the bridge, $b/\hbar$, owing to electrostatic repulsion of the electrons from one another. Taking account of this electron interaction, as done in the present work, shows that the spin-exchange frequency $\Delta\nu$ proves to be much smaller than $b/\hbar$ and even smaller than $\delta/\hbar$. Thus the biradical paradox is resolved in a natural way, and the special hypotheses advanced to explain it (^{6},^{8}) become unnecessary.

2. The Hamiltonian of the system has the form $\hat{H}_A^{(1)} + \hat{H}_B^{(2)} + V_1 + V_2 + \dfrac{e^2}{r_{12}}$, where V_i is a symbolic operator allowing for the possibility of transfer of the i-th electron from one well to the other. If the last term is neglected, then the orbital functions of an individual electron, $\psi_1 = \dfrac{1}{\sqrt{2}}(\varphi_A + \varphi_B)$, $\psi_2 = \dfrac{1}{\sqrt{2}}(\varphi_A - \varphi_B)$, are

Fig. 1

Figure 1: Fig. 1

expressed linearly in terms of the eigenfunctions φ_A and φ_B of the operators $\widehat{H}_A$ and $\widehat{H}_B$, which represent the unperturbed motion of an electron in the left and right wells, respectively. Because of the remoteness of the wells from one another, these functions may be regarded as nonoverlapping. The energy splitting of the states ψ_1 and ψ_2 is equal to $b/2 = |\langle\varphi_A^1|V_1|\varphi_B^1\rangle| = |\langle\varphi_A^2|V_2|\varphi_B^2\rangle|$ (the superscript numbers the electrons).

All possible states of the system under consideration can be represented by six two-electron wave functions

$$\Phi_1 = \psi_2^1\psi_1^2\chi(0,0),$$

$$\Phi_2 = \psi_2^1\psi_2^2\chi(0,0),$$

$$\Phi_{\left\{\begin{smallmatrix}3\\4\\5\end{smallmatrix}\right\}} = \frac{1}{\sqrt{2}}\left(\psi_1^1\psi_2^2 - \psi_1^2\psi_2^1\right)\left\{\begin{array}{c}\chi(1,1)\\ \chi(1,0)\\ \chi(1,-1)\end{array}\right\}, \tag{1}$$

$$\Phi_6 = \frac{1}{\sqrt{2}}\left(\psi_1^1\psi_2^2 + \psi_1^2\psi_2^1\right)\chi(0,0),$$

which exhaust all combinations of ψ_1, ψ_2 and spin functions $\chi(s, s_z)$ of the total spin of the two electrons s allowed by the Pauli principle. If the electrostatic repulsion of the electrons from one another is disregarded, the wave functions (1) are stationary solutions of the Schrödinger equation, and the spectrum of the system consists of three equidistant terms, the middle of which is fourfold degenerate (Fig. 1). The splitting of the terms b here is entirely due to transfer of the electrons through the bridge.

Fig. 1

Taking the Coulomb interaction into account, the energy matrix in the representation (1) takes the form

$$H_{im} = \begin{pmatrix} \dfrac{Q+J}{2} - b & \dfrac{Q-J}{2} & 0 & 0 \\ \dfrac{Q-J}{2} & \dfrac{Q+J}{2} + b & 0 & 0 \\ 0 & 0 & \{J\} & 0 \\ 0 & 0 & 0 & Q \end{pmatrix}.$$

Here Q and J are Coulomb integrals

$$Q = \int \frac{e^2}{r_{12}} (\varphi_A^1 \varphi_A^2)^2 \, d\tau, \qquad J = \int \frac{e^2}{r_{12}} (\varphi_A^1 \varphi_B^2) \, d\tau, \qquad Q > J,$$

and the exchange integrals, because of the absence of direct overlap of the functions φ_A and φ_B, have been set equal to zero. The energy levels obtained by diagonalizing this matrix have energies

$$E_{1,2} = \frac{Q+J}{2} \mp \frac{Q-J}{2} \sqrt{1 + \frac{4b^2}{(Q-J)^2}},$$

$$E_3 = E_4 = E_5 = J,$$

$$E_6 = Q.$$

For a rough estimate one may use the value of the integral Q taken from hydrogenic 1s functions: $Q = 2.7 \cdot 10^{16}$ sec^{-1}. Together with McConnell' s estimates $^{(5)}$ of the magnitude of b ($10^{10} - 10^{12}$ sec^{-1}), this gives

$$\frac{b}{Q-J} \ll 1.$$

Therefore

$$E_1 = J - \frac{b^2}{Q-J}, \qquad E_2 = Q + \frac{b^2}{Q-J},$$

and the regular stationary states corresponding to this limiting case

functions, expressed in terms of the functions of the individual wells, have the form:

$$\Psi_1 = \frac{1}{\sqrt{2}} (\varphi_A^1 \varphi_B^2 + \varphi_B^1 \varphi_A^2) \, \chi(0,0),$$

$$\Psi_2 = \frac{1}{\sqrt{2}} (\varphi_A^1 \varphi_A^2 + \varphi_B^1 \varphi_B^2) \, \chi(0,0).$$

$$\Psi_{\left\{\begin{smallmatrix}3\\4\\5\end{smallmatrix}\right\}} = \frac{1}{\sqrt{2}} (\varphi_B^1 \varphi_A^2 - \varphi_A^1 \varphi_B^2) \left\{ \begin{array}{c} \chi(1,1) \\ \chi(s,0) \\ \chi(1,-1) \end{array} \right\}, \tag{2}$$

$$\Psi_6 = \frac{1}{\sqrt{2}} (\varphi_A^1 \varphi_A^2 - \varphi_B^1 \varphi_B^2) \, \chi(0,0).$$

Fig. 2. Energy levels: E_2, E_6, E_3, E_4, E_5, E_1, $E_0 = 0$; polar states and nonpolar states.

Figure 2: Fig. 2. Energy levels: E_2, E_6, E_3, E_4, E_5, E_1, $E_0 = 0$; polar states and nonpolar states.

Thus, the electrostatic interaction of the electrons substantially changes the character of the energy spectrum of the biradical (Fig. 2).

Fig. 2

The sharp difference in the spectra shown in Figs. 1 and 2, as well as in the structure of the corresponding wave functions, is easily explained. The functions (1) and the corresponding energy spectrum were obtained within the framework of a one-electron approximation which, while taking into account the restrictions following from the Pauli principle, neglects all other interactions of the electrons with one another, including the most important of them, e^2/r_{12}. This approximation, on which the method of molecular orbitals in quantum chemistry and the one-electron model of a solid are based, is justified in those cases where $b \gg Q, J$. Obviously, as the interacting centers are separated by increasing b, this approximation becomes less and less accurate, since the quantity J decreases much more slowly than b, while the quantity Q, corresponding to the energy of electron repulsion within a single well, remains unchanged altogether. For $Q \gg b$ the problem becomes essentially two-electron, and the Coulomb interaction must be taken into account first of all. As is seen from Fig. 2, it determines the principal splitting between the nonpolar and polar states, $Q - J$, whereas the presence of transitions between the wells leads only to a small splitting of the symmetric and antisymmetric states (of order $\frac{b^2}{Q-J}$). As a result, in the biradicals under consideration the singlet-triplet splitting

$$\Delta E = \frac{b^2}{Q - J}$$

turns out to be of order 10^6 sec^{-1} (if $b \simeq 10^{11}$ sec^{-1}), which is not only much smaller than b, but also smaller than the hyperfine-interaction constant δ.

3. Let us now introduce the hyperfine interaction of the electron spins with the nuclear spins I_A and I_B. This will lead to the appearance, in the energy matrix in the representation by the functions (2), of additional terms

$$H_{14} = -\tfrac{1}{2}\delta\,(I_A - I_B), \qquad H_{33} = -H_{55} = \tfrac{1}{2}\delta\,(I_A + I_B).$$

Thus, in the case $I_A \neq I_B$, the hyperfine interaction mixes the ground level Ψ_1 with the triplet level Ψ_4, which has zero spin projection.

The transition probabilities can be determined by the same method as in work (4). Taking into account further that, upon application of a magnetic field H, the levels with nonzero projection of the total spin, E_3 and E_5, respectively rise and fall by the amount $\hbar\gamma H = \hbar\omega$ (γ is the gyromagnetic ratio),

it is easy to obtain the electron-paramagnetic-resonance spectrum:

Line frequency		Intensity
$I_A = I_B$,	$\omega_0 + \frac{1}{2}\delta(I_A + I_B)$	I_0
$I_A \neq I_B$	$\omega_0 \pm \left(\sqrt{B^2+t^2} + B\right) + \frac{\delta}{2}(I_A + I_B)$	$\frac{I_0}{4}\left(1 - \frac{B}{\sqrt{B^2+t^2}}\right)$
	$\omega_0 \pm \left(\sqrt{B^2+t^2} - B\right) - \frac{\delta}{2}(I_A + I_B)$	$\frac{I_0}{4}\left(1 + \frac{B}{\sqrt{B^2+t^2}}\right)$

$$t = \frac{\delta}{2}(I_A - I_B), \qquad B = \frac{1}{2}\frac{b^2}{Q - J}.$$

Let there be one proton in each well. Then, in the case

$$\frac{b^2}{Q - J} \ll \delta,$$

the spectrum consists of two triplets with splitting

$$\frac{b^2}{Q - J},$$

separated from one another by the amount δ. Owing to the smallness of the triplet splitting, the triplet structure will not be manifested experimentally; therefore we shall see the same doublet with splitting δ as is given by one isolated well with one electron. As b increases, the splitting in each of the triplets increases, and in the case

$$\frac{b^2}{Q - J} \gg \delta$$

the spectrum turns into a single triplet with total splitting δ, as presented in work (3).

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