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TERM SPLITTING IN THE INTERACTION OF TWO IDENTICAL ATOMS IN DIFFERENT STATES

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Splitting of the terms of a quasimolecule composed of two atoms of the same type is calculated for large distances between the nuclei of the atoms. The splitting consists of two parts. One is the exchange splitting corresponding to exchange of valence electrons, and the other is the long-range splitting due to long-range interaction between the atoms. The latter type of splitting vanishes if the spins of the interacting atoms are not the same. The result is employed to determine the cross section for excitation transfer from the metastable 2^3S helium atom to the helium atom in the ground state.

1. In this paper we calculate the splitting of the terms of a quasimolecule made up of two identical atoms in different states, with large distances between their nuclei. This splitting determines the probability of excitation transfer by collision from one atom to the other of the same kind. This splitting consists of two parts—exchange splitting, corresponding to exchange of valence electrons, and long-range splitting, connected with the long-range interaction of the atoms. The long-range splitting vanishes if the spins of the interacting atoms are different. This type of exchange splitting[1)] corresponds to overlap of the wave functions of two valence electrons, so that the problem of finding this quantity is a two-electron problem. In this respect, the problem under consideration is similar to that of finding the splitting of the terms of a quasimolecule made up of two atoms with spin 1/2 at large distances between their nuclei, when this splitting corresponds to a different total spin of the quasimolecule. The latter problem was solved by Gor'kov and Pitaevskiĭ[2] and also by Herring and Flicker[3] for the interaction of two hydrogen atoms, and by Chibisov and the author[4] for the interaction of two alkali-metal atoms. The magnitude of this splitting characterizes the probability of exchange of valence electrons when these atoms collide, and the associated change in the direction of the spin of the atom.

Using the analogy of these two problems, let us determine the exchange splitting of the terms in the case when the excitation is transferred in exactly the same manner as in the case of spin exchange. We shall consider each of the interacting atoms from the point of view of a model in which the valence electron is in a self-consistent field of the atomic core, and the magnitude of this field depends both on the spin state of the electron and of the atomic core. Since the sought exchange splitting of the terms is determined by the large distances between the valence electrons and the atomic core, the use of this model makes it possible to obtain an asymptotically exact value for the exchange splitting in the limit of large distances between atoms.

2. We consider a quasimolecule consisting of two atoms of the same type separated by a large distance. We shall denote by $\Psi(1'a, 2b)S(1a, 2b)$ the wave function of the quasimolecule if, at large distances between the atoms, the first electron is concentrated essentially near the atomic core a, the second near the atomic core b, Ψ denotes the coordinate wave function, and S the spin wave function; the prime denotes the electron that is in a more excited state.

We investigate first the class of eigenfunctions of the electron Hamiltonian, which does not satisfy the Pauli principle. This is possible, since the Pauli principle is an additional condition imposed on the solution of the stationary Schrödinger equation, but does not follow from the equation itself. We move the first (more excited) electron to the atomic core b and the second to the atomic core a (this is possible since the atomic cores are identical). It will be shown later that we can separate from the system of spin functions corresponding to finding the first electron near the core b and the second near the core a such a system of orthogonal spin functions that only one of them T(1b, 2a) is not

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[1)] The energy of exchange interaction of two atoms, calculated in [1], has no bearing on the excitation-transfer process.

orthogonal to S(1a, 2b). Thus, we have separated from the system of eigenfunctions of the Hamiltonian two wave functions of the valence electrons, $\Psi_1 = \Psi(1'a, 2b)S(1a, 2b)$ and $\Psi_2 = \Psi(1'b, 2a)T(1b, 2a)$, which are orthogonal to all the remaining functions. These remaining functions describe the considered state of the quasimolecule made up of atoms whose second electron is in a more excited state than the first.

We construct from the two separated wave functions Ψ_1 and Ψ_2 combinations which are eigenfunctions of the electron Hamiltonian $\hat{H}$. By virtue of the symmetry of the problem, the eigenfunctions $\Psi_{I,II}$ of the Hamiltonian $H\Psi_{I,II} = E_{I,II}\Psi_{I,II}$ are of the form

$$\Psi_{I,II} = 2^{-1/2}[\Psi(1'a, 2b)S(1a, 2b) \pm \Psi(1'b, 2a)T(1b, 2a)].$$

With this, the splitting of the term of the quasimolecule is

$$E_I - E_{II} \equiv \Delta = 2\langle\Psi(1'a, 2b)S(1a, 2b)$$
$$\times\ |H|\Psi(1'b, 2a)T(1b, 2a)\rangle.$$

The Hamiltonian of the system of electrons is

$$\hat{H} = -{}^1\!/_2\nabla_1^2 - {}^1\!/_2\nabla_2^2 + V(r_1, r_2),$$

where r_1, r_2 is the coordinate of the corresponding electron; we make use of the system of atomic units $\hbar = m = e^2 = 1$. From the equation for Ψ_I and Ψ_{II} it is easy to obtain the relation

$$\Delta\Psi_I\Psi_{II} = \Psi_{II}\hat{H}\Psi_I - \Psi_I\hat{H}\Psi_{II}.$$

Let us integrate this relation over the volume Ω in the space of the electrons, where $z_1 > z_2$ (z_1 and z_2 are the electron coordinates, measured along the axis joining the nuclei, the nucleus a being assumed to be to the right of the nucleus b). Then, at large distances between nuclei we get

$$\int_\Omega \Psi^2(1'a, 2b)\,dr_1\,dr_2 = 1, \qquad \int_\Omega \Psi^2(1'b, 2a)\,dr_1\,dr_2 = 0,$$

and the deviation from these equalities is exponentially small. Using this fact in the right side of the resultant relation, we get

$$\Delta = k_S\int_\Omega (\Psi_1\nabla_1^2\Psi_2 - \Psi_2\nabla_1^2\Psi_1 + \Psi_1\nabla_2^2\Psi_2 - \Psi_2\nabla_2^2\Psi_1)\,dr_1\,dr_2,$$

where

$$k_S = \langle S(1a, 2b)\,|T(1b, 2a)\rangle, \qquad \Psi_1 \equiv \Psi(1'a, 2b),$$
$$\Psi_2 = \Psi(1'b, 2a).$$

We transform the integral in the right side to an integral over the hypersurface $z_1 = z_2$. Since the substitutions $z_1 \to -z_1$ and $z_2 \to -z_2$ yield $\Psi_1 \to \Psi_2$ and $\Psi_2 \to \Psi_1$, which yields

$$\Psi_1\frac{\partial}{\partial z_1}\Psi_2(z_1, z_2) = -\Psi_2\frac{\partial}{\partial z_1}\Psi_1(-z_1, -z_2),$$

we get

$$\int \Psi_1\frac{\partial}{\partial z_1}\Psi_2\Big|_{z_1=z_2} dz = -\int \Psi_2\frac{\partial}{\partial z_1}\Psi_1\Big|_{z_1=z_2} dz.$$

Using this property of the two other terms, we get

$$\Delta = 2k_S\int\Big[\Psi_1\Big(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\Big)\Psi_2\Big]\Big|_{z_1=z_2} dx_1\,dy_1\,dx_2\,dy_2\,dz. \tag{1}$$

3. Let us estimate, on the basis of formula (1), the exponential dependence of the exchange splitting Δ on the distance between the atoms R. It follows from the structure of this formula that Δ is a product of two overlap integrals, so that one of them corresponds to finding the excited electron near the first and second atomic cores, and the second corresponds to finding the unexcited electron near each of the cores. Since at large R we have $\Delta \sim \exp[-(\alpha + \beta)^2]$ ($\alpha^2/2$ and $\beta^2/2$ are the binding energies of the valence electron in the atom). In the case of exchange interaction of the atoms or splitting corresponding to different spin states, this dependence is of the form $\Delta \sim e^{-2\beta R}$ ($\beta < \alpha$).

The exchange splitting (1) is calculated in the Appendix. The dependence of this type of exchange splitting on the distance R between the atoms is of the form

$$\Delta \sim R^p e^{-(\alpha+\beta)R}, \qquad p = \frac{2}{\alpha} + \frac{2}{\beta} - 1 - m_1 - m_2 - \frac{1}{\alpha+\beta},$$

where m_1 and m_2 is the projection of the moment of the valence electrons on the axis joining the nuclei. In the case of interaction of a helium atom in the ground and metastable 2^3S state, this quantity is equal to

$$\Delta = 0{,}35R^{3{,}15}e^{-1{,}94R}. \tag{2}$$

4. Let us calculate the spin coefficient $k_S = \langle S(1a, 2b)|T(1b, 2a)\rangle$ which enters in formula (1). This coefficient characterizes the overlap of the spin functions of the quasimolecule for two states under consideration, which differ in positions of the numbered electrons. In the initial state, described by the spin function S(1a, 2b), there are two atoms with total spins J_1 and J_2, with projections M_1 and M_2 on the selected direction, and with atomic-core spins equal to j. The sought spin coefficient k_S depends on these parameters.

The spin wave function of the first atom in the initial state is[5]

$$\Psi^{(1)}_{J_1M_1} = \sqrt{\frac{j - M_1 + {}^1\!/_2}{2j+1}}\,X_{j,\,M_1\pm 1/2}\chi_{\mp}$$
$$\pm\sqrt{\frac{j + M_1 + {}^1\!/_2}{2j+1}}\,X_{j,\,M_1\mp 1/2}\chi_{\pm}, \tag{3a}$$

where the upper sign corresponds to the case $J_1 = j + 1/2$, and the lower to the case $J_1 = j - 1/2$. A similar form is possessed by the spin-wave function of the second atom in the initial state:

$$\Psi^{(2)}_{J_2M_2} = \sqrt{\frac{i - M_2 + {}^1/_2}{2j+1}}\, Z_{j,\, M_2 \pm {}^1/_2}\, \zeta_{\mp} \pm \sqrt{\frac{j + M_2 + {}^1/_2}{2j+1}}\, Z_{j,\, M_2 \mp {}^1/_2}\, \zeta_{\pm}. \tag{3b}$$

Here χ_+, χ_-, ζ_+, and ζ_- are the spin functions of the first and second valence electrons, corresponding respectively to the spin projection +1/2 and −1/2 on the selected direction; X_{jm_1} and Z_{jm_2} are spin functions of the atomic cores a and b with given value of the spin of the atomic core and its projection on the selected direction.

Thus, the spin-wave function of the initial state is $S(1a, 2b) = \Psi^{(1)}_{J_1M_1}\Psi^{(2)}_{J_2M_2}$, where the spin functions $\Psi^{(1)}$ and $\Psi^{(2)}$ of the atoms are given by formulas (3). The spin function of the final state will be represented in the form of the combination of the functions $\Phi^{(1)}_{J_2,M_1-1}\Phi^{(2)}_{J_1,M_2-1}$, $\Phi^{(1)}_{J_2,M_1}\Phi^{(2)}_{J_1,M_2}$, and $\Phi^{(1)}_{J_2,M_1+1}\Phi^{(2)}_{J_1,M_2-1}$. Here $\Phi^{(1)}$ is the spin wave function of the atom made up of the atomic core a and the second electron, and $\Phi^{(2)}$ is the spin wave function of the atom made up of the atomic core b and the first electron. Out of the combination of the given wave functions, we make up three orthogonal wave functions in such a way that two of them are orthogonal to S(1a, 2b). Then the coefficient k_S corresponds to overlap of the spin function of the initial state and of the third wave function, and is equal to

$$\begin{aligned} k_S = [&\langle \Psi^{(1)}_{J_1M_1}\Psi^{(2)}_{J_2M_2} | \Phi^{(1)}_{J_2,\, M_1-1}\Phi^{(2)}_{J_1,\, M_2+1}\rangle^2 \\ &+ \langle \Psi^{(1)}_{J_1M_1}\Psi^{(2)}_{J_2M_2} | \Phi^{(1)}_{J_2M_1}\Phi^{(2)}_{J_1M_2}\rangle^2 \\ &+ \langle \Psi^{(1)}_{J_1M_1}\Psi^{(2)}_{J_2M_2} | \Phi^{(1)}_{J_2,\, M_1+1}\Phi^{(2)}_{J_1;\, M_2-1}\rangle^2]^{1/2}. \end{aligned} \tag{4}$$

Using the explicit form of the spin wave functions, we obtain for the spin coefficient

$$\begin{aligned} k_S = (2j+1)^{-2}\{[[&(j - M_1 + {}^1/_2)(j - M_2 + {}^1/_2)(j \mp M_1 + {}^1/_2) \\ &\times (j \mp M_2 + {}^1/_2)]^{1/2} + [(j + M_1 + {}^1/_2) \\ &\times (j + M_2 + {}^1/_2)(j \pm M_1 + {}^1/_2)(j \pm M_2 + {}^1/_2)]^{1/2}]^2 \\ &+ (J_1 \pm M_2)(J_1 - M_2 + 1)(J_2 - M_1)(J_2 \pm M_1 + 1) \\ &+ (J_1 \mp M_2)(J_1 + M_2 + 1)(J_2 + M_1)(J_2 \mp M_1 + 1)\}^{1/2}. \end{aligned} \tag{5}$$

The upper sign corresponds to the case $J_1 = J_2$ and the lower to $-|J_1 - J_2| = 1$. In particular, in the case j = 0 (interaction of two atoms of alkali metals), formula (5) yields $k_S = 1$, and in the case $J_1 = 1$, $j = 1/2$, $J_2 = 0$ (interaction of metastable 2^3S helium atom and helium atom in the ground state) we have $k_S = 1/2$.

5. If we take the Pauli principle into consideration, then the two wave functions of the quasimolecule, from which we make up the eigenfunctions of the Hamiltonian, take the form

$$\begin{aligned} \Psi_1 &= 2^{-1/2}[\Psi(1'a, 2b)S(1a, 2b) - \Psi(1b, 2'a)S(2a, 1b)], \\ \Psi_2 &= 2^{-1/2}[\Psi(1'b, 2a)T(1b, 2a) - \Psi(1a, 2'b)T(1a, 2b)]. \end{aligned}$$

The term splitting Δ_t corresponding to excitation transfer, is as before equal to the matrix element of the Hamiltonian, taken over the two wave functions under consideration. It is equal to

$$\begin{aligned} \Delta_{\text{п}} &= \Delta - 2\langle \Psi(1'a, 2b) | \hat{H} | \Psi(1a, 2'b)\rangle\langle S(1a, 2b) | T(1a, 2b)\rangle \\ &= \Delta - 2\delta_S \langle \Psi(1'a, 2b) | \hat{H} | \Psi(1a, 2'b)\rangle, \\ \delta_S &= \langle S(1a, 2b) | T(1a, 2b)\rangle. \end{aligned} \tag{6}$$

The first term corresponds to exchange splitting and is determined by formula (1). The second term corresponds to long-range interaction and was not obtained earlier, since the long-range interaction was neglected in the method employed in the calculation.

Let us calculate the long-range part of the splitting under consideration. We have $\hat{H} = \hat{H}_0 + V$, where $\hat{H}_0$ is the Hamiltonian of the non-interacting atoms, and V is the perturbation operator. In calculating the splitting connected with the long-range interaction, we assume that the first electron is at the atom a, the second at the atom b, and there is no exchange of electrons. The wave function of the electrons is

$$\Psi(1a, 2'b) = \varphi_1\chi_2 + \sum_{i,k} \frac{V_{1i,\,2k}\varphi_i\chi_k}{E_{12} - E_{ik}} - \frac{\varphi_2\chi_1}{2}\sum_{i,k}\frac{V_{1i,\,2k}V_{2i,\,1k}}{(E_{12} - E_{ik})^2},$$

where φ_i is the wave function of the first electron, χ_k that of the second electron, E_{ik} is the electron energy of the atoms, so that $\hat{H}_0\varphi_i\chi_k = E_{ik}\varphi_i\chi_k$, and the indices 1 and 2 correspond to the two considered states of the atoms. Similarly

$$\Psi(1'a, 2b) = \varphi_2\chi_1 + \sum_{j,l} \frac{V_{2l,\,1j}\varphi_l\chi_j}{E_{12} - E_{jl}} - \frac{\varphi_1\chi_2}{2}\sum_{j,l}\frac{V_{1j;\,2l}V_{2j,\,1l}}{(E_{12} - E_{jl})^2}$$

On the basis of this we obtain for the long-range part of the splitting, accurate to terms of second order in V,

$$\langle \Psi(1'a, 2b) | \hat{H} | \Psi(1a, 2'b)\rangle = V_{12,21} + \sum_{i,k}\frac{V_{1i,\,2k}V_{2i,\,1k}}{E_{12} - E_{ik}}.$$

In particular, if we choose for V the dipole interaction of the atoms $V = R^{-3}[\mathbf{D}_a\mathbf{D}_b - 3(\mathbf{D}_a\mathbf{n})(\mathbf{D}_b\mathbf{n})]$, where $\mathbf{D}_a$ and $\mathbf{D}_b$ are the operators of the dipole moment of the corresponding atom, the long-range part of the splitting takes the form

$$\langle \Psi(1'a, 2b) | \hat{H} | \Psi(1a, 2'b)\rangle = R^{-3}[\mathbf{D}_{12}^2 - 3(\mathbf{D}_{12}\mathbf{n})^2] - C/R^6.$$

Here $\mathbf{D}_{12}$ is the matrix element of the operator of the dipole moment of the atom, taken between the atoms under consideration, C is the Van der Waals constant, and **n** is a unit vector directed along **R**.

Let us calculate the spin factor in (6). It turns out to be equal to

$$\delta_S = k_S^{-1} \langle \Psi^{(1)}_{J_1M_1} \Psi^{(2)}_{J_2M_2} | \Phi^{(1)}_{J_2M_1} \Phi^{(2)}_{J_1M_2} \rangle \delta_{J_1J_2}, \qquad (7)$$

where the spin wave functions $\Psi^{(i)}$ and $\Phi^{(i)}$ are determined in the same manner as in (4), and k_S is given by (5). As follows from (7), $\delta_S = 0$ if $J_1 \neq J_2$. Therefore long-range splitting takes place only if atoms of the same kind having the same spin interact. Then

$$\delta_S = k_S^{-1} \{ (j - M_1 + {}^1/_2)(j - M_2 + {}^1/_2) + (j + M_1 + {}^1/_2) \times (j + M_2 + {}^1/_2) \} \delta_{J_1J_2}. \qquad (8)$$

Accordingly, the splitting of the terms of the quasimolecule, corresponding to the transfer of excitation from one atom to another, at large distances between them, is in the case of dipole-dipole interaction of the atoms

$$\Delta_t = \Delta + 2\delta_S \left\{ \frac{1}{R^3} [3(\mathbf{D}_{12}\mathbf{n})^2 - D_{12}^2] + \frac{C}{R^6} \right\}, \qquad (9)$$

where the first term corresponds to exchange splitting (1), and the second corresponds to long-range splitting.

6. We use the result to find the cross section for the transfer of excitation in the case of collision of a metastable helium atom 2^3S and a helium atom in the ground state. If we neglect the elastic scattering, the excitation transfer cross section σ_t is determined in a manner similar to the cross section for resonance charge exchange[6], and is found to be

$$\sigma = \pi R_0^2 / 2, \qquad (10a)$$

where R_0 is given by the relation

$$[\pi R_0 / 2(\alpha + \beta)]^{1/2} \Delta(R_0) = 0.28v \qquad (10b)$$

(v is the collision velocity). The exchange splitting in the case of interaction between a metastable helium atom and helium atom in the ground state is given by formula (2). The cross sections obtained on the basis of formulas (2) and (10) for the transfer of excitation from the metastable atom He (2^3S) to the atom He (1^1S), in the absence of elastic scattering of the atoms, assumes the following values:

Energy of incoming atom, eV:	100	10	1	0.1
Excitation-transfer cross section, 10^{-16} cm^2:	11	15	20	25

The experimentally measured cross section for the transfer of excitation from the metastable helium atom[7] at a temperature of 500°K turns out to be 5×10^{-16} cm^2 and decreases with decreasing temperature to a value of $\sim 10^{-17}$ cm^2 at 4°K. The reason for such a behavior is that the excitation-transfer cross section is connected in essential fashion with elastic scattering at thermal collision energies. Indeed, the energy of exchange interaction between the metastable helium atom and the helium atom in the ground state is[1] $4.2R^{1.34}e^{-1.07}R$, and the energy of the Van der Waals interaction[8] is $58/R^6$, which is much lower in the distance range of interest. Exchange interaction leads to repulsion of the atoms, and at large distances between the atoms the energy of this interaction greatly exceeds the exchange splitting (2) corresponding to excitation transfer. Therefore, at low collision velocities, a situation arises in which, at the collision impact parameters R_0 that determine the cross section (10), the energy of the exchange interaction of the atoms becomes comparable with the kinetic energy of the nuclei. In this case, when atoms collide at impact parameters on the order of R_0, the repulsion does not cause the internuclear distances to reach values at which intense excitation transfer takes place. Thus, elastic scattering of the atoms leads to a decrease in the cross section of excitation transfer.

APPENDIX

CALCULATION OF EXCHANGE SPLITTING CORRESPONDING TO EXCITATION TRANSFER

The exchange splitting of interest to us is given by formula (1)

$$\Delta = 2k_S \int \left[\Psi(1'a, 2b) \left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} \right) \Psi(1'b, 2a) \right] \Bigg|_{z_1 = z_2} \times dx_1\, dy_1\, dx_2\, dy_2\, dz, \qquad (A.1)$$

where $\Psi(1'a, 2b)$ corresponds to a situation wherein the first electron is distributed essentially around the atomic core a, and the second around the atomic core b, and the prime denotes the electron in the higher excited state. If one of the electrons is brought closer to the atomic core near which it is essentially concentrated, and the other is moved sufficiently far from this core, then the coordinate wave functions entering in (A.1) can be represented in the form of a product of atomic wave functions:

$$\Psi(1'a, 2b) = \varphi(1'a)\varphi(2b), \qquad (A.2)$$

where $\varphi(1'a)$ and $\varphi(2b)$ are the wave functions of the electron in the corresponding atom.

However, the integral (A.1), which we calculate for large distances between nuclei, is determined essentially by the region of the coordinates of the electrons located near the axis joining the nuclei in the region between the nuclei. If the distances between the electrons themselves and between the electrons and the atomic cores are of the same order, as is the situation in our case, then the interaction of one electron with the other electron and with the foreign atomic core will greatly distort the form of the wave function, compared with (A.2), in the region of interest to us. We represent the wave functions that enter in (A.1) in the form

$$\Psi(1'a,2b)=\varphi(1'a)\varphi(2b)\chi_{\mathrm{I}},\quad \Psi(1'b,2a)=\varphi(1'b)\varphi(2a)\chi_{\mathrm{II}}. \tag{A.3}$$

The functions χ_{I} and χ_{II} were calculated in the general case in[4]. To determine them we used the fact that in the region between the nuclei they change much less abruptly than the atomic wave functions. We present their values for $z_1 = z_2 = z$:

$$\chi_{\mathrm{I}}=\frac{(2\varkappa)^{1/\beta}\exp[-(\varkappa-z)/2\beta\varkappa](\alpha+\beta)^{1/\alpha-1/(\alpha+\beta)}\rho_{12}^{1/(\alpha+\beta)}}{\beta^{1/\alpha-1/(\alpha+\beta)}2^{1/(\alpha+\beta)}(\varkappa-z)^{1/(\alpha+\beta)}(\varkappa+z)^{1/\beta}},$$

$$z>0,$$

$$\chi_{\mathrm{II}}=\frac{(2\varkappa)^{1/\alpha}\exp[-(\varkappa+z)/2\alpha\varkappa](\alpha+\beta)^{1/\beta-1/(\alpha+\beta)}\rho_{12}^{1/(\alpha+\beta)}}{\alpha^{1/\beta-1/(\alpha+\beta)}2^{1/(\alpha+\beta)}(\varkappa+z)^{1/(\alpha+\beta)}(\varkappa-z)^{1/\alpha}},$$

$$z<0, \tag{A.4}$$

where $\kappa = R/2$; $\alpha^2/2$ and $\beta^2/2$ are the binding energies of the valence electrons, $\rho_{12}^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2$. The function χ_{II} is obtained from χ_{I} by making the substitution $z \to -z$.

For the electron-coordinate region defined by the integral (A.1) we have r_{ia}, $r_{ib} \sim R$, so that the distance from the electrons to their own atomic cores is large compared with the atomic dimensions, and we can use for the atomic wave functions the asymptotic expressions

$$\begin{aligned}\varphi(1'a)&=Ar_{1a}^{1/\alpha-1}e^{-\alpha r_{1a}}Y_{l_1m_1}(\theta_1,\Phi),\\ \varphi(2b)&=Br_{2b}^{1/\beta-1}e^{-\beta r_{2b}}Y_{l_2m_2}(\theta_2,\Phi),\end{aligned} \tag{A.5}$$

where r_{1a}, θ_1, Φ, and r_{2b}, θ_2, Φ are the spherical coordinates of the given electrons, reckoned from the corresponding nucleus, Y_{lm} is a normalized angular function of the electrons, and A and B are asymptotic coefficients. On the basis of (A.5) we find, that for $r_{1a}\alpha^2 \gg 1$ and $r_{2b}\beta^2 \gg 1$ we have

$$\frac{\partial\varphi(1'a)}{\partial z_1}=-\alpha\varphi(1'a),\quad \frac{\partial\varphi(2b)}{\partial z_2}=\beta\varphi(2b)$$

near the axis joining the nuclei (in this region $r_{1a} \approx z_1 + \kappa$ and $r_{2b} \approx \kappa - z_2$). Therefore, differentiating in (A.1) only the most rapidly decreasing factors $\exp\{-r_{1b}\alpha\}$ and $\exp\{-\beta r_{2a}\}$, we obtain, accurate to terms $\sim 1/R$:

$$\Delta=2k_S(\alpha-\beta)\int\varphi(1'a)\varphi(1'b)\varphi(2a)\varphi(2b)\chi_{\mathrm{I}}\chi_{\mathrm{II}}|_{z_1=z_2}\times dx_1\,dy_1\,dx_2\,dy_2\,dz. \tag{A.6}$$

The main contribution to the interval (A.6) is made by the region of the coordinates of the electrons situated near the axis joining the nuclei. In this region of coordinates ($\theta \ll 1$) we have

$$Y_{lm}(\theta,\Phi)=\left[\frac{(2l+1)}{4\pi}\frac{(l+m)!}{(l-m)!}\right]^{1/2}\frac{\theta^m e^{im\Phi}}{m!\,2^m},$$

so that the product of the atomic wave functions near the axis joining the nuclei is, in accordance with (A.5),

$$\begin{aligned}\varphi(1'a)\varphi(1'b)\varphi(2a)\varphi(2b)&=A^2B^2(\varkappa^2-z^2)^{1/\alpha+1/\beta-2}\\ &\times\exp\left[-2(\alpha+\beta)\varkappa-\frac{(\beta\varkappa\rho_1^2+\alpha\varkappa\rho_2^2)}{2(\varkappa^2-z^2)}\right]\\ &\times\frac{(2l_1+1)(2l_2+1)(l_1+m_1)!\,(l_2+m_2)!}{16\pi^2 2^{2(m_1+m_2)}(m_1!\,m_2!)^2(l_1-m_1)!\,(l_2-m_2)!}\\ &\times\frac{\rho_1^{2m_1}\rho_2^{2m_2}}{(\varkappa^2-z^2)^{m_1+m_2}}.\end{aligned} \tag{A.7a}$$

In addition,

$$\chi_{\mathrm{I}}\chi_{\mathrm{II}}|_{z_1=z_2}=\frac{\exp\left[-\frac{1}{2\beta}-\frac{1}{2\alpha}+\frac{z}{2\varkappa}\left(\frac{1}{\alpha}+\frac{1}{\beta}\right)\right]\rho_{12}^{2/(\alpha+\beta)}(2\varkappa)^{1/\alpha+1/\beta}(\alpha+\beta)^{1/\alpha+1/\beta}}{\beta^{\beta/\alpha(\alpha+\beta)}\alpha^{\alpha/\beta(\alpha+\beta)}[2(\alpha+\beta)(\varkappa-z)]^{2/(\alpha+\beta)}(\varkappa+z)^{1/\alpha+1/\beta}}, \tag{A.7b}$$

The value of $\chi_{\mathrm{I}}\chi_{\mathrm{II}}$ for $z < 0$ is obtained from the latter expression by making the substitution $z \to -z$.

Calculating the integral (A.6) with the aid of (A.7), we get for the exchange splitting

$$\Delta=R^p e^{-R(\alpha+\beta)}k_S\Phi_{\alpha\beta}J_{\alpha\beta}j_{m_1m_2}(\alpha,\beta),$$

$$p=\frac{2}{\alpha}+\frac{2}{\beta}-1-m_1-m_2-\frac{1}{\alpha+\beta}, \tag{A.8}$$

where

$$\Phi_{\alpha\beta}=\frac{A^2B^2}{\pi^2}(\alpha-\beta)\frac{(2l_1+1)(2l_2+1)(l_1+m_1)!\,(l_2+m_2)!}{(l_1-m_1)!\,(l_2-m_2)!\,(m_1!)^2(m_2!)^2}\times\frac{(\alpha+\beta)^{1/\alpha+1/\beta-1/(\alpha+\beta)}}{2^{1/\alpha+1/\beta}\alpha^{1/\beta-1/(\alpha+\beta)}\beta^{1/\alpha-1/(\alpha+\beta)}},$$

$$J_{\alpha\beta}=\int_0^1 dy\exp\left\{-\frac{(1-y)}{2}\left(\frac{1}{\alpha}+\frac{1}{\beta}\right)\right\}$$

$$\times\ (1-y)^{1/\alpha+1/\beta-1/(\alpha+\beta)}(1+y)^{1/(\alpha+\beta)}$$

$$j_{m_1m_2}(\alpha,\beta)=\int d\rho_1\,d\rho_2 e^{-\alpha\rho_1^2-\beta\rho_2^2}|\rho_1-\rho_2|^{2/(\alpha+\beta)}\rho_1^{2m_1}\rho_2^{2m_2}.$$

Here $\rho_1 = ix_1 + jy_1$ and $\rho_2 = ix_2 + jy_2$. In the case $m_1 = m_2 = 0$ we have

$$j_{00}(\alpha,\beta)=\frac{\pi 2^{1/(\alpha+\beta)-1}}{\sqrt{\alpha\beta}}\Gamma\left(1+\frac{1}{\alpha+\beta}\right)$$

$$\times\int_0^{2\pi}\frac{d\varphi}{(\alpha\cos^2\varphi+\beta\sin^2\alpha)^{1+1/(\alpha+\beta)}}$$

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