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Asymptotic Calculation of Some Exchange Integrals

S. JA. UMANSKI and A. I. VORONIN
Institute of Chemical Physics, Moscow, USSR

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Asymptotic calculations of the exchange integrals with excitation transfer and without excitation transfer are carried out. The atoms are considered in the ground or excited states. The effect of the spin of the atomic core is taken into account.

Es werden asymptotische Ausdrücke für Austauschintegrale berechnet, wobei auch Übergang von Anregung eingeschlossen wird. Ferner wird der Einfluß der Spins der Atomrümpfe behandelt.

Calcul asymptotique des intégrales d'échange avec et sans transfert d'excitation. Les atomes sont envisagés dans l'état fondamental ou les états excités. L'effet du spin sur le coeur atomique est pris en considération.

1. Introduction

Difficulties met by calculations of the interactions between atoms and molecules are well known. To a considerable degree these difficulties are connected with the calculation of exchange integrals. Unfortunately the numerical procedure is not reliable for large internuclear distances. Thus such calculations are almost useless for several analytical investigations.

But there exists a number of problems for which analytical expressions for the exchange integrals can be obtained. The processes in question are those taking place at distances much larger, than the gas kinetic radii of the colliding partners. These will be, processes of charge and excitation transfer, transitions between the fine structure components, the electron-vibrational transitions *etc*. They occur at large distances either because of the slowness of the collisions in the low-temperature plasma or because of the resonance character of the process. In order to calculate the exchange interactions between atoms and molecules involved in such processes asymptotic methods appear to be useful.

The purpose of the present paper is to calculate the exchange interaction between two one-electron atoms. This interaction might be accompanied by the transfer of the excitation. The atoms are considered in ground or excited states and may possess a nonzero orbital angular momentum. An important example for such a situation is presented by atoms of the alkali metals in excited p-states.

The method of calculation is based on the generalization of the procedure, used by Gor'kov and Pitaevski [1], and Herring and Flicker [2], who considered the calculation of the splitting between the lowest singlet and triplet states of the hydrogene molecule. It should be noted, that Ref. [3], [4], which treat the same subject contain either some principle or calculational errors.

2. Outline of the Method

It has been shown in Ref. [1], [2], that the Heitler-London approximation, used initially for the calculations on the chemical bond, is inadequate for the large internuclear distances R. This is connected with the fact, that the treatment of the interelectronic interaction as a perturbation is a valid approximation only for atoms, but not for molecules. The inadequacy of the Heitler-London approximation manifests itself in the logarithmic term in the asymptotic expression for the singlet-triplet splitting in the hydrogene molecule:

$$E_S - E_A = -\left[\frac{56}{45} - \frac{4}{15}(c + \ln R)\right] R^3 \exp(-2R) + O(R^2 \exp(-2R)) \qquad c = 0{,}5772\,. \tag{1}$$

This logarithmic term leads to the incorrect sign of $(E_S - E_A)$ for large R. In reality the electronic repulsion is stronger in the Heitler-London states, than in the correct singlet and triplet states. When this effect is taken into account, the logarithmic term disappears and the correct sign for the splitting is obtained.

Neglecting the spin-orbit interaction the two-electron molecular wave function can be expressed in the form of a simple product:

$$\Psi_\lambda^\gamma(r_1, r_2, a)\, f_{M_S}^S(\sigma_1, \sigma_2) \tag{2}$$

where Ψ depends only on the space variables and f only on the spin variables. Here $\lambda = \pm\Lambda$ is the component of the orbital angular momentum along the molecular axis, Λ is the modulus of this component, S, M_S are the total spin and it's component along the same axis, γ indicates all other quantum numbers, and $2a$ is the distance between the nuclei, which is supposed to be large compared to the characteristic lengths associated with the variables r_1 and r_2. It is suitable to introduce the following linear combinations of the functions:

$$\begin{aligned}\Psi_{\lambda;g,u}^\gamma &= \frac{1}{\sqrt{2}}\left[\sum_i C_i^\gamma \psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i}(r_1, r_2) \pm \sum_i C_i^\gamma \times \psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i}(r_2, r_1)\right] \\ &\equiv \frac{1}{\sqrt{2}}\left[\Psi_{\mathrm{I},\lambda}^\gamma \pm \Psi_{\mathrm{II},\lambda}^\gamma\right].\end{aligned} \tag{3}$$

The functions $\psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\cdots)}$ become the products of the atomic functions when $r_1 \to -a$ and $r_2 \to a$, l and m being the orbital angular momentum of the atom and its component along the molecular axis. The summation over i in Eq. (3) is taken over all possible degenerated states of the separated atoms, going over into the given molecular state. If there is not enough symmetry, the coefficients C_i^γ have to be obtained by the variational principle. The functions $\Psi_{\mathrm{I},\lambda}^\gamma$ and $\Psi_{\mathrm{II},\lambda}^\gamma$ introduced above describe the electrons localised close to one of both nuclei (α and β see Eq. (5)).

Following the method of Ref. [1], the triplet-singlet splitting due to the exchange interaction is now expressed by a surface integral:

$$I = \frac{1}{2}\int_\Sigma \left[\left(\Psi_{\mathrm{II},\lambda}^\gamma\ \nabla_6\ \Psi_{\mathrm{I},\lambda}^{\gamma\,*} + \Psi_{\mathrm{II},\lambda}^{\gamma\,*}\ \nabla_6\ \Psi_{\mathrm{I},\lambda}^\gamma\right) - (\Psi_{\mathrm{I}} \to \Psi_{\mathrm{II}})\right] d\Sigma \tag{4}$$

where Σ is a surface separating the regions between which the exchange of the electrons takes place. ∇_6 is the six-dimensional gradient in the configurational space of two electrons. It is convenient to take Σ in the form $z_1 = z_2$ if the ionization potentials of the atoms are approximately equal. In this case we have

$$\begin{aligned} I = {} & \sum_i \sum_j C_i^\gamma C_j^{\gamma *} \cdot \frac{1}{2} \int_{-a}^{a} dz \iiiint_{-\infty}^{\infty} dx_1\, dy_1\, dx_2\, dy_2 \\ & \times \left[\psi_{\mathrm{A}(\alpha l m)_j}^{\mathrm{B}(\beta l',\, \lambda - m)_j *} (r_2, r_1) \cdot \frac{\partial}{\partial z'} \psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i} (r_1, r_2) \right. \\ & \left. - \psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i *} (r_1, r_2) \cdot \frac{\partial}{\partial z'} \psi_{\mathrm{A}(\alpha l m)_j}^{\mathrm{B}(\beta l',\, \lambda - m)_i} (r_2, r_1) \right] \Bigg|_{z' = 0} \\ = {} & \sum_i \sum_j C_i^\gamma C_j^{\gamma *}\, I [(\alpha m)_i\, (\beta, \lambda - m)_i \,|\, (\alpha m)_j\, (\beta, \lambda - m)_j] \end{aligned} \tag{5}$$

where

$$z = (z_1 + z_2)/2\,; \quad z' = z_1 - z_2\,; \quad \alpha = \sqrt{2 I_{\mathrm{A}}}\,; \quad \beta = \sqrt{2 I_{\mathrm{B}}}\,;$$

$$I_{\mathrm{A}}, I_{\mathrm{B}}$$

being the ionisation potentials of the atoms A and B. The quantities $I[\ldots]$ defined by the energy difference [Eq. (4)] correspond to the two-electron exchange integrals in the Heitler-London method. It is possible to limit the variation of z in the first integral in Eq. (5) to the range between the two nuclei, because the neglected part of the integral is of the order of $R^{-1/(\alpha+\beta)}$ in comparison with the main term. In order to calculate the integrals in Eq. (5) we have to find the functions $\psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i}$ which correspond to the product of the atomic functions at $r_1 \to -a$, $r_2 \to a$ and take into account the correlation effects in the intermediate region. To obtain an equation for $\psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\cdots)_i}$ we shall neglect the energy difference between molecular states and states of separated atoms. This difference is of the order of not more than R^{-3}. This assumption leads to a separate equation for each function $\psi_{\mathrm{A}(\cdots)_i}^{\mathrm{B}(\cdots)_i}$. Since the wave function decreases rapidly off the internuclear axis it is only necessary to find it accurately in a narrow cylindrical region with the length R and the radius $R^{1/2}$. We try as a solution

$$\begin{aligned} \psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i} (r_1, r_2) &\equiv \psi_1(r_1, r_2) = \varphi_{\mathrm{A}}(r_1)\, \varphi_{\mathrm{B}}(r_2)\, \chi_1(r_1, r_2) \\ \psi_{\mathrm{A}(\alpha l m)_i}^{\mathrm{B}(\beta l',\, \lambda - m)_i} (r_2, r_1) &\equiv \psi_2(r_2, r_1) = \varphi_{\mathrm{A}}(r_2)\, \varphi_{\mathrm{B}}(r_1)\, \chi_2(r_2, r_1) \end{aligned} \tag{6}$$

where χ is a slowly variing function of r_1, r_2, and $\varphi_{\mathrm{A}}, \varphi_{\mathrm{B}}$ are the wave functions of the electrons, centered on the atoms A and B respectively. We are interested in large internuclear distances so that asymptotic representations for φ_{A} and φ_{B} can be used:

$$\begin{aligned} \varphi_{\mathrm{A}}(r_1) &= A_1 r_1^{1/\alpha - 1} \exp(-\alpha r_1)\, Y_l^{m_1}(\theta_1, \varphi_1) \\ \varphi_{\mathrm{B}}(r_2) &= A_2 r_2^{1/\beta - 1} \exp(-\beta r_2)\, Y_{l'}^{m_2}(\theta_2, \varphi_2)\,. \end{aligned} \tag{7}$$

Introducing the cylindrical coordinates we get the following expression for ψ_1 in the cylindrical region mentioned above:

$$\begin{gathered}\psi_1(r_1,r_2)=A_1A_2(a+z_1)^{1/\alpha-1}(a-z_2)^{1/\beta-1}\exp[-a(\alpha+\beta)-\alpha z_1\\ +\beta z_2-\alpha\varrho_1^2/2(a+z_1)-\beta\varrho_2^2/2(a-z_2)]\,Y_l^{m_1}(\theta_1,\varphi_1)\,Y_{l'}^{m_2}(\theta_2,\varphi_2)\,\chi_1(r_1,r_2)\,;\\ Y_l^m(\theta,\varphi)\simeq\left[\frac{(2l+1)}{4\pi}\,\frac{(l+m)!}{(l-m)!}\right]^{1/2}\frac{\theta^m\exp(im\varphi)}{m!\,2^m}\,.\end{gathered}\tag{8}$$

Approximation (8) is valid under conditions $|z_{1,2}|\leqq a, \varrho_{1,2}\leqq\sqrt{a}$ which allow to use expansions of r_1 and r_2 in terms of $1/a$ and of Y_l^m in terms of $\theta(\theta\sim\varrho/a)$.

Substituting ψ_1 into the wave equation and neglecting the second derivatives of χ_1, we obtain:

$$\begin{gathered}\alpha\frac{\partial\chi_1}{\partial z_1}-\beta\frac{\partial\chi_1}{\partial z_2}-\left[\frac{m_1}{\varrho_1}-\frac{\alpha\varrho_1}{z_1+a}\right]\frac{\partial\chi_1}{\partial\varrho_1}-\left[\frac{m_2}{\varrho_2}-\frac{\beta\varrho_2}{a-z_2}\right]\frac{\partial\chi_1}{\partial\varrho_2}\\ -i\left[\frac{m_1}{\varrho_1^2}\frac{\partial\chi_1}{\partial\varphi_1}+\frac{m_2}{\varrho_2^2}\frac{\partial\chi_1}{\partial\varphi_2}\right]+\left[\frac{1}{r_{12}}-\frac{1}{a-z_1}-\frac{1}{a+z_1}+\frac{1}{2a}\right]\chi_1=0\,.\end{gathered}\tag{9}$$

This equation is still too complicated for practical use, but some simplifications can be made. Brackets before $\frac{\partial\chi_1}{\partial\varrho_1}$ and $\frac{\partial\chi_1}{\partial\varrho_2}$ vanish at the maximum of the functions φ_A and φ_B on Σ and the terms containing $\frac{\partial\chi_1}{\partial\varphi_1}, \frac{\partial\chi_1}{\partial\varphi_2}$ are of less order of magnitude than the main terms in the vicinity of this maximum. Thus we obtain an equation, which has been considered already by Smirnov and Chibisov [5]:

$$\alpha\frac{\partial\chi_1}{\partial z_1}-\beta\frac{\partial\chi_1}{\partial z_2}+\left[\frac{1}{r_{12}}-\frac{1}{a-z_1}-\frac{1}{a+z_2}+\frac{1}{2a}\right]\chi_1=0\,.\tag{10}$$

A solution, satisfying the boundary conditions ($\chi_1\to 1$ when $z_1\to -a$, $z_2\to a$) has the following form in the region $z>0$ of the surface $z_1=z_2$:

$$\begin{gathered}\chi_1=\frac{R^{1/\alpha}\exp[-(a-z)/\alpha R]\,(\alpha+\beta)^{\frac{1}{\beta}-\frac{1}{\alpha+\beta}}\times\varrho_{12}^{\frac{1}{\alpha+\beta}}}{\alpha^{\frac{1}{\beta}-\frac{1}{\alpha+\beta}}\cdot 2^{\frac{1}{\alpha+\beta}}(a-z_1)^{\frac{1}{\alpha+\beta}}\cdot(a+z)^{1/\alpha}}\,;\\ \varrho_{12}=\sqrt{(x_1-x_2)^2+(y_1-y_2)^2}\,.\end{gathered}\tag{11}$$

The function χ_2 is obtained in an analogous way. These functions decrease according to the power law in the region of small ϱ_{12} in contradiction to the Heitler-London behavior. Just this fact yields the correct sign of the exchange integrals at all internuclear distances. To be consistent with all approximations made only the exponentials of the functions ψ_1 and ψ_2 in Eq. (5) are to be differentiated.

3. Exchange Integrals without Excitation Transfer

There are two possible types of exchange integrals according to the assignment of α_i and β_i. The integrals without excitation transfer are defined by requiring $\alpha_i=\alpha_j=\alpha$; $\beta_i=\beta_j=\beta$. The corresponding integrals for atoms in s and p-states will be considered first. The integration over ϱ_1 and ϱ_2 in Eq. (5) is easily carried out if the new variables $\varrho_{12}=\varrho_1-\varrho_2$ and $\varrho=\frac{1}{2}(\varrho_1+\varrho_2)$ are introduced. The integrals $I[m_1\alpha, m_2\beta|\alpha m'_1\beta m'_2]$ corresponding to the exchange $(\alpha m_1)\rightarrow(\beta m'_2)$ and $(\beta m_2)\rightarrow(\alpha m'_1)$ are listed in the Tables 1 and 2, where μ stands for $\alpha+\beta$ and

$$\begin{aligned} I_{kn}(R,\alpha,\beta) = {} & R^{\frac{2}{\alpha}+\frac{2}{\beta}-\frac{1}{\mu}-2}\exp(-\mu R)\frac{9}{2}A_1^2A_2^2\,\Gamma\left(\frac{1}{\mu}\right) \\ & \times\left(\frac{2}{\mu^2}\right)^{\frac{1}{\mu}}\left\{\left(\frac{\mu}{2\beta}\right)^{\frac{2}{\alpha}}\cdot\beta^{\frac{2}{\mu}}\int\limits_0^1\exp\left[-(\alpha-\beta)Rt+\frac{1}{\beta}(t-1)\right]\right. \\ & \times(1+t)^{\frac{2}{\alpha}-\frac{2}{\beta}+\frac{1}{\mu}-n}(1-t)^{\frac{2}{\beta}-\frac{1}{\mu}+n}\,[\mu+(\beta-\alpha)\,t]^{-\left(2+\frac{1}{\mu}+k\right)}dt \quad (12) \\ & +\left(\frac{\mu}{2\alpha}\right)^{\frac{2}{\beta}}\alpha^{\frac{2}{\mu}}\int\limits_0^1\exp\left[(\alpha-\beta)Rt+\frac{1}{\alpha}(t-1)\right](t+1)^{\frac{2}{\beta}-\frac{2}{\alpha}+\frac{1}{\mu}+n} \\ & \left.\times(1-t)^{\frac{2}{\alpha}-\frac{1}{\mu}-n}\,[\mu+(\alpha-\beta)\,t]^{-\left(2+\frac{1}{\mu}+k\right)}dt\right\}. \end{aligned}$$

Table 1. *Exchange integrals $I[\alpha m_1\,\beta m_2|\alpha m'_1\,\beta m'_2]$ without excitation transfer for atoms in P-states*

	m'_1	1	1	0	1	-1	0
m_1	m'_2 m_2	1	0	1	-1	1	0
1	1	$-\left[2+\left(2+\frac{1}{\mu}\right)\times\left(1+\frac{1}{\mu}\right)\right]R^{-1}I_{20}$					
1	0		$\frac{1}{\mu}I_{11}$	$\left(2+\frac{1}{\mu}\right)I_{10}$			
0	1		$\left(2+\frac{1}{\mu}\right)I_{10}$	$\frac{1}{\mu}I_{1-1}$			
1	-1				$\frac{R^{-1}}{\mu}\left(1-\frac{1}{\mu}\right)I_{20}$	$-\left[2+\left(2+\frac{1}{\mu}\right)\times\left(1+\frac{1}{\mu}\right)\right]R^{-1}I_{20}$	$\frac{1}{\mu}I_{10}$
-1	1				$-\left[2+\left(2+\frac{1}{\mu}\right)\times\left(1+\frac{1}{\mu}\right)\right]R^{-1}I_{20}$	$\frac{R^{-1}}{\mu}\left(1-\frac{1}{\mu}\right)I_{20}$	$\frac{1}{\mu}I_{10}$
0	0				$\frac{1}{\mu}I_{10}$	$\frac{1}{\mu}I_{10}$	$-RI_{00}$

It is seen from Eq. (12) that in the case of $\alpha \neq \beta$ it is impossible to find an explicit dependence on R (in contrast to the integrals with excitation transfer, see below). But the integrals in Eq. (12) can easily be estimated or calculated numerically. For the case of almost equal α and β the integrand can be expanded in powers of $(\alpha - \beta) R$.

Table 2. *Exchange integrals without excitation transfer for atoms in S or P-states*

$I(S\alpha, 0\beta \mid S\alpha 0\beta) = -\frac{R}{3} I_{00}(R, \alpha, \beta)$
$I(S\alpha 1\beta \mid S\alpha 1\beta) = \frac{1}{3\mu} I_{1-1}(R, \alpha, \beta)$
$I(S\alpha S\beta \mid S\alpha S\beta) = -\frac{R}{9} I_{00}(R, \alpha, \beta)$

4. Exchange Integrals with the Excitation Transfer

There exists another type of the exchange integrals which corresponds to the case $\alpha_i = \beta_j = \alpha$; $\alpha_j = \beta_i = \beta$. These integrals appear, when interactions between identical atoms in the ground and excited states are considered. Let the exchange take place in the following way: $(\alpha m_1) \to (\alpha m_2')$, $(\beta m_2) \to (\beta m_1')$. The integrals are listed in the Tables 3 and 4 for the case of atoms in S or P-states, using the notations: $\mu = \alpha + \beta$,

$$\begin{aligned} I_k'(R, \alpha, \beta) = {} & R^{\frac{2}{\alpha} + \frac{2}{\beta} - \frac{1}{\mu} - 2} \exp(-\mu R) A_1^2 A_2^2 \Gamma\left(\frac{1}{\mu}\right) \\ & \times \frac{9}{\alpha\beta[2\mu]^2} \left[\frac{\mu}{2}\right]^{\frac{1}{\alpha} + \frac{1}{\beta}} (\alpha)^{-\frac{1}{\beta}} (\beta)^{-\frac{1}{\alpha}} \int_0^1 dt \exp\left\{\left(\frac{1}{2\alpha} + \frac{1}{2\beta}\right)\right. \\ & \times \left.(t-1)\right\} (1+t)^{\frac{1}{\mu} + k} \cdot (1-t)^{\frac{1}{\alpha} + \frac{1}{\beta} - \frac{1}{\mu} - k} \cdot (1+t^2)^k . \end{aligned} \tag{13}$$

The calculation is carried out according to Eq. (5) with the help of the substitution $\varrho_{12} = \varrho_1 - \varrho_2$; $\varrho = \alpha\varrho_1 + \beta\varrho_2$. It is possible to find an explicit dependence of $I[m_1 \alpha\, m_2 \beta \mid m_1' \beta\, m_2' \alpha]$ on R.

Table 3. *Exchange integrals with excitation transfer for atoms in S or P-states:* $I[S\alpha m\beta \mid m'\beta S\alpha]$

$I[S\alpha 0\beta \mid 0\beta S\alpha] = \frac{R}{3} \mu^2 I_0'(R, \alpha, \beta)$
$I[S\alpha 1\beta \mid 1\beta S\alpha] = -\frac{\mu}{3}\left[1 + \frac{\alpha}{\beta}\left(1 + \frac{1}{\mu}\right)\right] I_0'(R, \alpha, \beta)$
$I[S\alpha S\beta \mid S\beta S\alpha] = -\frac{R}{9} \mu^2 I_0'(R, \alpha, \beta)$

Table 4. *Exchange integrals* $I[m_1\alpha\, m_2\beta\,|\,\beta m'_1\,\alpha m'_2]$ *with excitation transfer for atoms in P-states*

	m'_1	1	1	0	1	-1	0
m_1	m'_2 / m_2	1	0	1	-1	1	0
1	1	$-\left[4+\frac{3}{\mu}+\frac{1}{\mu^2}+\frac{(\alpha-\beta)^2}{\alpha\beta}\left(1+\frac{1}{\mu}\right)\right]\times R^{-1}I'_0$					
1	0		I'_1	$\mu\left[1+\frac{\beta}{2}\times\left(1+\frac{1}{\mu}\right)\right]\times I'_0$			
0	1		$\mu\left[1+\frac{\beta}{\alpha}\times\left(1+\frac{1}{\mu}\right)\right]\times I'_0$	I'_1			
1	-1				$\frac{R^{-1}}{\mu}\left[1-\frac{1}{\mu}\right]I'_0$	$-\left[4+\frac{3}{\mu}+\frac{1}{\mu^2}+\frac{(\alpha-\beta)^2}{\alpha\beta}\left(1+\frac{1}{\mu}\right)\right]\times R^{-1}I'_0$	I'_0
-1	1				$-\left[4+\frac{3}{\mu}+\frac{1}{\mu^2}+\frac{(\alpha-\beta)^2}{\alpha\beta}\left(1+\frac{1}{\mu}\right)\right]\times R^{-1}I'_0$	$\frac{R^{-1}}{\mu}\left(1-\frac{1}{\mu}\right)\times I'_0$	I'_0
0	0				I'_0	I'_0	$-\mu^2RI'_0$

5. The Effect of the Spin of the Atomic Core

Till now we have neglected the spin of the atomic core. Let the cores of the atoms A and B possess spins S_A and S_B. The total spins S_1 and S_2 result from the addition of the spins of the cores and the electronic spins s_1 and s_2. If the spin-orbit interaction is neglected, the total spin S and it's z-component M_S are good quantum numbers for the molecule. At large internuclear distances the following coupling scheme of the spin momenta is chosen: $S_A+s_1=S_1$; $S_B+s_2=S_2$. We shall take the wave function of the two atoms as the eigenfunctions of the total spin S and its z-component M_S, antisymmetrized with respect to the permutations of the electrons:

$$\begin{aligned}\Psi^{S_1S_2}_{\lambda\gamma,SM_S} = \tfrac{1}{2}\,[&|S_As_1S_1\,;\,S_Bs_2S_2,SM_S\rangle\,(\Psi^{\gamma}_{\lambda,g}+\Psi^{\gamma}_{\lambda,u})\\ &-|S_As_2S_1\,;\,S_Bs_1S_2,SM_S\rangle\,(\Psi^{\gamma}_{\lambda,g}-\Psi^{\gamma}_{\lambda,u})]\,.\end{aligned} \quad (14)$$

The functions $\Psi^{\gamma}_{\lambda,g,u}$ are defined by Eq. (3). When the atomic cores possess nonzero spins, the splitting between the molecular terms is due not only to the Hamiltonian $H(r_1, r_2)$ of the valence electrons, but also to the total atomic spins S_1 and S_2. The fact that the functions $\Psi^{\gamma}_{\lambda,g,u}$ are substituted into Eq. (4) from Eq. (3) is equivalent to the assumption that the intra-atomic interactions effect negligibly the correction to the atomic functions for the correlation of the valence electrons characterized by the functions χ. Now we have obtained for the energy of the interatomic interactions:

$$\begin{aligned}\langle\Psi^{S_1S_2S_\mathrm{A}S_\mathrm{B}}_{\lambda\gamma SM_S}|\,H(r_1r_2)\,|\Psi^{S_1S_2S_\mathrm{A}S_\mathrm{B}}_{\lambda\gamma S'M_{S'}}\rangle &= \tfrac{1}{2}(E^{\gamma}_{\lambda u}+E^{\gamma}_{\lambda g})\\ &\times \delta_{SS'}\delta_{M_SM_{S'}} - \tfrac{1}{2}(E^{\gamma}_{\lambda g}-E^{\gamma}_{\lambda u})\,\langle S_\mathrm{A}s_1S_1\,;S_\mathrm{B}s_2S_2\,;SM_S|S_\mathrm{A}s_2S_1\,;\\ &\times S_\mathrm{B}s_1S_2\,;S'M_{S'}\rangle = \tfrac{1}{2}\big[(E^{\gamma}_{\lambda u}+E^{\gamma}_{\lambda g})+\tfrac{1}{2}(E^{\gamma}_{\lambda g}-E^{\gamma}_{\lambda u})(-1)^{2S_\mathrm{B}-2S_2}\\ &\times [2S_1+1]\,[2S_2+1]\begin{Bmatrix}S_\mathrm{A} & \frac{1}{2} & S_1\\ \frac{1}{2} & S_\mathrm{B} & S_2\\ S_1 & S_2 & S\end{Bmatrix}\Big]\;\delta_{SS'}\delta_{M_SM_{S'}}\end{aligned} \tag{15}$$

where $\begin{Bmatrix}S_\mathrm{A} & \frac{1}{2} & S_1\\ \frac{1}{2} & S_\mathrm{B} & S_2\\ S_1 & S_2 & S\end{Bmatrix}$ is the 9*j*-symbol, which characterizes the "overlap" of the spin wave functions, corresponding to the different schemes of the coupling of the spin momenta. The algebraic expressions for different 9*j*-symbols are listed in Ref. [6] (see also Ref. [7]).

In the case of identical atoms in different states the exchange of the spin states can take place. An analogous argumentation leads in this case to the following expression for the interatomic interaction energy:

$$\begin{aligned}\langle\Psi^{S_1S_2S_\mathrm{A}S_\mathrm{B}}_{\lambda\gamma SM_S}|\,H(r_1r_2)\,|\Psi^{S_1S_2S_\mathrm{A}S_\mathrm{B}}_{\lambda\gamma SM_S}\rangle &= \tfrac{1}{2}(E^{\gamma}_{\lambda g}+E^{\gamma}_{\lambda u})\\ &+ \tfrac{1}{2}\sum_{ij} C_iC_j^{*}(-1)^{2S_\mathrm{B}-2S_{2i}-2S_{j2}}\,[(2S_{1i}+1)(2S_{1j}+1)(2S_{2i}+1)\\ &\times (2S_{2j}+1)]^{\frac{1}{2}}\begin{Bmatrix}S_\mathrm{A} & \frac{1}{2} & S_{1i}\\ \frac{1}{2} & S_\mathrm{B} & S_{2i}\\ S_{1j} & S_{2j} & S\end{Bmatrix} I[(\alpha m)_i(\beta,\lambda-m)_i|(\alpha m)_j(\beta,\lambda-m)_j]\,.\end{aligned} \tag{16}$$

S_{1j}; S_{2j} may be equal to either S_1 or S_2, thus taking into account the exchange of the spin states.

6. Conclusion

The method of the asymptotic calculation of the exchange integrals provides the easiest way for the estimation of the interatomic interaction at large distances. At these distances the corrected first order (exchange) contribution and the uncorrected second order contribution to the interatomic energy are additive, so that the comparison between both is strait forward. For systems such as alkali atoms the exchange interaction is stronger than the Van-der-Waals interaction up to distances of 10–15 a.u.

The method presented here might be extended to atoms with equivalent electrons, such as oxygen and nitrogen. However, this extension needs some modifications of the coupling scheme, which will be discussed elsewhere.

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Dr. S. Ja. Umanski and A. I. Voronin
Institute of Chemical Physics
Academy of Sciences
Vorobyevskoye chaussée 2-b
Moscow V-334, USSR