EXCHANGE COUPLING OF TWO DIFFERENT ATOMS AT LARGE DISTANCES

M. Ya. OVCHINNIKOVA

Institute of Chemical Physics, Academy of Sciences, U.S.S.R.

The exchange bond energy of two atoms A and B with very different ionization potentials such that $I_A/I_B \ll 1$ is investigated. In this case the asymptotic exchange bond at large distances R between the atoms is determined by the square of the electron wave function of atom A at the point R: $J \sim \Psi_A^2(R)$.

THE asymptotic value of the exchange coupling of atoms at large distances is needed in many problems dealing with electron transitions occurring in atomic collisions; for example, in the calculation of the spin-exchange cross section for the transition between fine-structure components.[1] It is known[2] that the Heitler-London method gives an incorrect value of the exchange coupling for $R \rightarrow \infty$. The first correct asymptotic value of the difference of the energy of the triplet and singlet states for two hydrogen atoms in 1S states was calculated by Herring and Flicker[3] and by Gor'kov and Pitaevskiĭ.[4] Analogous calculations for any two atoms with equal ionization potentials are given in the paper by Smirnov.[5] Finally, Firsov and Smirnov[6] investigated the behavior of the terms of the system AB^-.

The purpose of the present work was to derive asymptotic values for the exchange coupling in the case of two atoms (A and B) with strongly differing ionization potentials, such that $\alpha = \sqrt{2\mu I_A} \ll \beta = \sqrt{2\mu I_B}$, where I_A and I_B are respectively the ionization potentials of A and B, and μ is the electron mass.

We consider first the splitting between the singlet and triplet states of two single-electron atoms: $\Delta E = E^1 - E^3$. Let $\Psi^1(r_1, r_2)$ and $\Psi^3(r_1, r_2)$ be the exact coordinate wave functions of the corresponding states. The function $\Psi^1(r_1, r_2)$ is symmetrical while $\Psi^3(r_1, r_2)$ is antisymmetrical with respect to the substitution $r_1 \longleftrightarrow r_2$. When the distance between atoms is large ($R \rightarrow \infty$) these functions obviously have the following properties

$$\Psi^1(r_1, r_2) \rightarrow 2^{-1/2}\varphi^1(r_1)\varphi_B(r_2 - R_B),$$

$$\Psi^3(r_1, r_2) \rightarrow 2^{-1/2}\varphi^3(r_1)\varphi_B(r_2 - R_B)$$

$$\text{for} \quad \beta|r_2 - R_B| \sim 1, \quad \beta|r_1 - R_B| \gg 1. \tag{1}$$

Here $\varphi_B(r)$ —atomic wave function of the electron at the atom B, and the functions $\varphi^1(r)$ and $\varphi^3(r)$

tend to the corresponding atomic function $\varphi_A(r_1 - R_A)$ when $|r_1 - R_A| \rightarrow 0$. Near the atom B, at $\alpha|r_1 - R_B| \sim 1$ but at $\beta|r_1 - R_B| \gg 1$, the difference between $\varphi^1(r_1)$ or $\varphi^3(r_1)$ and the atomic functions can, for sufficiently small α, be described by means of a very simple model, as will be done later.

The splitting ΔE is expressed in terms of an integral over the surface S bounding a certain volume Ω[4,5]:

$$\int_\Omega (\Psi^3 H \Psi^1 - \Psi^1 H \Psi^3) dV_1 dV_2 = (E^1 - E^3) \int_\Omega \Psi^1 \Psi^3 dV_1 dV_2$$

$$= -\frac{1}{2\mu} \int_S (\Psi^3 \nabla \Psi^1 - \Psi^1 \nabla \Psi^3) dS. \tag{2}$$

However, the choice of the volume Ω must be made in a different manner than for the case of identical α and β.[4,5]

Let us consider the volume Ω for which $|r_1 - R_B| > a$ ($\beta a \gg 1$, $a \ll R$) and r_2 is arbitrary, i.e., from the total volume (r_1, r_2) of the system for r_2 we exclude the volume of the sphere of radius a with center at the point R_B. The integral over the value Ω in the left side of (2) is equal to $\frac{1}{2}$ accurate to $O(e^{-2\alpha R})$, as can be readily seen from the form of the functions (1). In precisely the same manner, the integral over the hypersurface S reduces to a two-dimensional integral over the sphere $|r_1 - R_B| = a$, so that

$$\frac{1}{2}\Delta E = -\frac{1}{4\mu} \int_{|r_1 - R_B|=a} [\varphi^3(r_1) \nabla \varphi^1(r_1) - \varphi^1(r_1) \nabla \varphi^3(r_1)] dS. \tag{3}$$

It is now necessary to determine the functions φ^1 and φ^3 from the exact Schrödinger equation, in which the interaction between electron 1 and atom B is included. In view of the small dimension $1/\beta$ of the atom B, the effective radius of the interaction between the electron and the atom B is small. Therefore, following the known procedure, used for example in [6,7], we can replace

the well by a boundary condition at the point $\mathbf{r}$ = $\mathbf{R}_B$ (for convenience we locate the origin at the point B: $\mathbf{R}_B = 0$):

$$-\frac{1}{r\varphi^i}\frac{\partial}{\partial r}(r\varphi^i)\Big|_{r=0} = -\varkappa_i = -\frac{1}{a_i}, \qquad (4)$$

where $a_{1(3)}$ are the scattering lengths of the electron by the atom B in the singlet and triplet states respectively.

The subsequent analysis is perfectly analogous to that used for negative ions in [6,7]. According to [7] the boundary condition (4) can be replaced by a singularity in the right side of the equation:

$$\left(-\Delta - \frac{2e^2}{|\mathbf{r}_1 - \mathbf{R}|} + \alpha^2\right)\varphi^{1(3)} = -C^{1(3)}\delta(\mathbf{r}_1), \qquad (5)$$

where the constants C^1 and C^3 are obtained from the conditions for joining $\varphi^1(\mathbf{r}_1)$ and $\varphi^3(\mathbf{r}_1)$ with $\varphi_A(\mathbf{r} - \mathbf{R})$ with $\alpha r_1 \gg 1$ and from condition (4). With the aid of Eq. (5) we can easily obtain the integral of (3) over the sphere:

$$\tfrac{1}{2}\Delta E = -\tfrac{1}{2}\int_{|\mathbf{r}_1|=a}[\varphi^1(\mathbf{r}_1)C^3\delta(\mathbf{r}_1) - \varphi^3(\mathbf{r}_1)C^3\delta(\mathbf{r}_1)]dV_1,$$

from which, recognizing that (4) is equivalent to the limit

$$\varphi^i(\mathbf{r}_1) \to C_i(1/r_1 - \varkappa^i)/4\pi$$

at $r_1 \to 0$, we obtain

$$\frac{1}{2}\Delta E = \frac{1}{4\mu}\frac{C^1 C^3}{4\pi}(\varkappa^1 - \varkappa^3). \qquad (6)$$

It remains to find the constants C^1 and C^3, i.e., to solve Eq. (5) with boundary condition (4). It is easy to find such a solution accurate to terms $O(R^{-2})$. Indeed,

$$\varphi^i(\mathbf{r}) = \varphi_A(\mathbf{r} - \mathbf{R}) + \frac{C_i}{4\pi}\frac{e^{-\alpha^1 r}}{r}, \quad \alpha^1 = \left(\alpha^2 + \frac{2e^2}{R}\right)^{1/2}$$

Then the boundary condition is of the form

$$\frac{4\pi}{C^i}\left[\frac{C^i}{4\pi}\alpha^1 + \varphi_A(\mathbf{R})\right] = -\varkappa^i,$$

whence

$$C^i = \frac{4\pi}{\alpha^1 - \varkappa^i}\varphi_A(\mathbf{R})\left(1 + O\left(\frac{1}{R^2}\right)\right). \qquad (7)$$

The same result can be obtained with the same accuracy by taking into account a weak homogeneous field $e^2 z/R$ acting on the electron near the point B. Then the wave function is sought in exactly the same manner as in the problem of the negative ion.[7]

The joining of the obtained function with the atomic function $\varphi_A(\mathbf{r} - \mathbf{R})$, on the one hand, and condition (4), on the other, lead to the same value (7) for the constants C^i. Substituting the obtained constants in (6), we obtain the asymptotic value of the exchange coupling which is of interest to us:

$$\frac{1}{2}\Delta E = \frac{4\pi}{2\mu}\frac{\varkappa^1 - \varkappa^3}{(\alpha^1 - \varkappa^1)(\alpha^1 - \varkappa^3)}\varphi_A^2(R). \qquad (8)$$

It is obvious that this result cannot be used for small $|\alpha - \varkappa^i|$, i.e., when the bound state of the electron with the atom B(B^-) has an energy coinciding with the energy of the electron in the atom A. This is perfectly understandable, for then resonant transfer of an electron is possible, and when $\varkappa^i = \alpha$ the asymptotic value of ΔE turns out to be $e^{-\alpha R}$ (just as for H_2^+), and not $e^{-2\alpha R}$ (as is usual for neutral atoms).

We can attempt to use the same model for an estimate of the exchange interaction of the atoms A of alkali metals with sufficiently "compressed" atoms B of inert gases. For these $\alpha/\beta = \tfrac{1}{2}$. If we assume that the multipole interaction of the atoms is small, then we attempt to describe the short-range potential of the interaction of the atom B with the electron by means of the boundary condition (4). Then the wave function of the external electron of the atom A satisfies the equation

$$\left(\Delta - \alpha^2 + \frac{2e^2}{|\mathbf{r} - \mathbf{R}|}\right)\varphi(\mathbf{r}) = C\delta(\mathbf{r} - \mathbf{R}_B).$$

when $C = 0$ the equation describes $\varphi_A(\mathbf{r} - \mathbf{R}_B)$.

In analogy with the derivation of (3), we get

$$J = E_A^0 - E = \int_\Omega (\varphi_A H\varphi - \varphi H\varphi_A)dV = \frac{1}{2\mu}\int C\delta(\mathbf{r})\varphi_A(\mathbf{r})dV$$

$$= \frac{C}{2\mu}\varphi_A(R).$$

Using for C the already calculated value (7), we obtain

$$J = \frac{1}{2\mu}\frac{4\pi}{\alpha^1 - \varkappa}\varphi_A^2(R), \qquad (9)$$

where $\varkappa^{-1}$ is the scattering length of the electron by an atom of an inert gas. The accuracy of the obtained formulas is determined by the value $O(R^{-2})$ of the discarded terms. Consequently, it is necessary to retain in the asymptotic expression for the wave function[8]

$$\varphi_A(R)_{R\to\infty} = e^{-\alpha R}KR^{1/\alpha - 1}(1 + O(1/R))$$

only the first two terms.

We now discuss the conditions for the applicability of formulas (8) and (9). In the model in question, the binding energy I_A of the electron in

the atom A should be so small, that for an electron near the atom B we can use the approximation of the effective potential. But the deductions of the applicability of this approximation in the region of negative energies $E \sim -I_A$ of the electron can be drawn by starting from data on the scattering of the electrons by the atom B. We therefore examine the results on scattering of electrons by atoms of noble gases. It turns out that for Ar, Kr, and Xe the radius of the potential r_0 does not coincide at all with the magnitude $1/\beta$ owing to the presence of a very strong polarization interaction between the electron and the atom: $V = \text{const} \cdot r^{-4}$ (for Ar, for example, const = 10.8 atomic units).[9] As a result, the region of linearity of $\tan \delta_0$ as a function of $k = \sqrt{2\mu E_{el}}$ for Ar and Kr, for example, is of the order of $\Delta k \sim 0.1$ atomic units.[9] This is precisely connected with the Ramsauer effect observed in these gases. Thus, for the atoms Na and K with $|k| = \alpha = 0.5$ atomic units we cannot deduce any information at all on the value of κ from the data on electron scattering. However, for the systems Na–He and K–He formula (9) apparently makes possible an estimate of the exchange coupling, in view of the small value of the polarizability of the He atom, with the scattering length of the electron by the He atom being $a = 1.44$ atomic units.[10] As regards formula (8), it is apparently applicable when $\alpha \sim 0.5 - 0.4$ atomic units only when the hydrogen atom is atom B. In this case[10] $a^1 = 1.9$ atomic units and $a^3 = 6.7$ atomic units.

It must also be noted that in condition (4) we can take into account also the next higher term of the expansion in the energy k^2. It must be remembered here that owing to the presence of the potential $\text{const} \cdot r^{-4}$ this expansion differs[11] from the ordinary expansion

$$k \cot \delta_0 = -a^{-1} + \gamma k + \nu k^2 \ln k + O(k^2).$$

An investigation of the scattering of the electrons of smaller energies by atoms with approximate account of the polarization potential is given in [12]. The condition for the applicability of their approximation is apparently the smallness of the electron energy compared with the depth of the polarization well. The binding energies of the electrons in alkaline metals do not satisfy this condition in systems with Ar and Xe, and therefore, to find the exchange coupling, it is necessary to obtain a more accurate solution of the problem.

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