Theoret. chim. Acta (Berl.) 28, 235—239 (1973)

On Asymptotic Calculation of the Exchange Interaction

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Received May 30, 1972

The asymptotic calculation of the exchange interaction between two atoms with the same ionization potentials is carried out. It is established that the second term (of relative order $R^{-1/2}$) of the asymptotic series becomes zero. The dependence of the atom-molecule exchange interaction on vibrational coordinates is also discussed.

Die Austauschwechselwirkung zwischen zwei Atomen mit gleichem Ionisationspotential wird asymptotisch berechnet. Es wird gezeigt, daß der zweite Term (von der relativen Ordnung $R^{-1/2}$) der asymptotischen Reihe verschwindet. Die Abhängigkeit der Atom-Molekül-Austauschwechselwirkung von den Schwingungskoordinaten wird ebenfalls diskutiert.

The total interaction between atoms and molecules at large distances consists of multipole and exchange terms. General expression for multipole interaction are well known (see, for example, Ref. [1]). As for exchange interaction, Gor'kov and Pitaevsky [2] and Herring and Flicker [3] considered the hydrogen molecule and showed that the Heitler-London approximation is inadequate at large interatomic distances R. They introduced the asymptotic method of calculation of the splitting between the lowest singlet and triplet states (due to exchange interaction) of the H_2 molecule. We shall discuss the conditions of validity of this method and also the results of later works.

Consider two one-electron atoms whose nuclei are at the points $+a$ and $-a$ of the z-axis. Let the atoms have the same ionization potentials, equal to $\alpha^2/2$[1]. The asymptotic behaviour of the electron wave functions is given by Ref. [4] as

$$\psi^0_{\pm} = A_{\pm}\, |\vec{r} \mp \vec{a}|^{\frac{1}{\alpha}} \quad \exp(-\alpha\, |\vec{r} \mp \vec{a}|)\,. \tag{1}$$

We shall calculate the first two terms of the asymptotic series for the splitting between the singlet and triplet states, described respectively by the wave functions $\psi_s(\vec{r}_1, \vec{r}_2)$ and $\psi_t(\vec{r}_1, \vec{r}_2)$. We have

$$\boldsymbol{H}\,\psi_{s,t} = E_{s,t}\,\psi_{s,t} \tag{2}$$

where (when $|z_1|$ and $|z_2| \sim a$, and ϱ_1 and $\varrho_2 \sim \sqrt{a}$, z and ϱ-cylindrical coordinates, $a \to \infty$; see also Ref. [2])

$$\boldsymbol{H} \simeq -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{1}{|\vec{r}_1 + \vec{a}|} - \frac{1}{|\vec{r}_2 + \vec{a}|} - \frac{1}{|\vec{r}_1 - \vec{a}|} - \frac{1}{|\vec{r}_2 - \vec{a}|} + \frac{1}{r_{12}} + \frac{1}{2a} \tag{3}$$

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[1] Atomic units are used.

Let

$$\psi_1=\frac{\psi_s+\psi_t}{\sqrt{2}};\qquad \psi_2=\frac{\psi_s-\psi_t}{\sqrt{2}};\qquad \psi_2(\vec{r}_1,\vec{r}_2)=\psi_1(\vec{r}_2,\vec{r}_1)\tag{4}$$

where, for instance, ψ_1 corresponds to the state when the first electron is localized at the atom "$-a$", and the second one – at the atom "$+a$". Then [2]

$$\Delta E=E_t-E_s=-4\oiint_s \psi_2\frac{\partial}{\partial z_1}\psi_1 ds\tag{5}$$

where S is the surface $z_1=z_2$.

Consider firstly the hamiltonian

$$\tilde{H}=H-\frac{1}{r_{12}}.\tag{6}$$

The corresponding localized wave functions $\tilde{\psi}_1$ and $\tilde{\psi}_2$ do not strongly differ from atomic ones and can be determined by analogy with Ref. [5] and [2]

$$\tilde{\psi}_1(\vec{r}_1,\vec{r}_2)=f_1\psi^0(\vec{r}_1+\vec{a})\,\psi^0_+(\vec{r}_2-\vec{a})\equiv f_1\psi^0_1,\tag{7}$$

$$\tilde{\psi}_2(\vec{r}_1,\vec{r}_2)=f_2\psi^0(\vec{r}_2+\vec{a})\,\psi^0_+(\vec{r}_1-\vec{a})\equiv f_2\psi^0_2,\tag{8}$$

$$f_1=\left[\frac{2a(2a-|z_1+z_2|)}{(a-z_1)(a+z_2)}\right]^{1/\alpha}\exp\left(-\frac{2a+z_1-z_2-|z_1+z_2|}{4\alpha a}\right),\tag{9}$$

$$f_2(\vec{r}_1,\vec{r}_2)=f_1(\vec{r}_2,\vec{r}_1).\tag{10}$$

The following terms of asymptotic series for f_1 and f_2 have the relative order $1/R$.

The main contribution to the integral (5) comes from the region $\alpha(|\vec{r}-\vec{a}|+|\vec{r}+\vec{a}|-2a)\sim 1$ – an oblong ellipsoid of revolution in the coordinate space of each electron. In this region

$$\psi^0_-(1)\,\psi^0_+(2)\simeq A_-A_+[(a+z_1)(a-z_2)]^{\frac{1}{\alpha}-1}$$
$$\cdot\exp\left\{-\alpha\left[2a+z_1-z_2+\frac{\varrho_1^2}{2(a+z_1)}+\frac{\varrho_2^2}{2(a-z_2)}\right]\right\}\tag{11}$$

Let $\vec{\varrho}_{12}=\vec{\varrho}_1-\vec{\varrho}_2,\vec{\varrho}=\vec{\varrho}_1+\vec{\varrho}_2,z_{12}=z_1-z_2$ and

$$\psi_1=\chi_1\tilde{\psi}_1;\qquad \psi_2=\chi_2\tilde{\psi}_2;\qquad \chi_2(\vec{r}_1,\vec{r}_2)=\chi_1(\vec{r}_2,\vec{r}_1)\tag{12}$$

We have the following equation for χ_1

$$\left(-\Delta_{12}-2\frac{\nabla_{12}\tilde{\psi}_1}{\tilde{\psi}_1}\nabla_{12}+\frac{1}{r_{12}}\right)\chi_1=0\tag{13}$$

or

$$(H_1+H_2)\chi_1=0\,; \qquad H_2=H'+H''\,, \tag{14}$$

$$H_1=2\alpha\frac{\partial}{\partial z_{12}}+\frac{1}{r_{12}}\,, \tag{15}$$

$$H'=-\Delta_{12}\,, \tag{16}$$

$$H''=2\alpha\left[\frac{\varrho_{12}+\varrho\cos\varphi}{4(a+z_1)}+\frac{\varrho_{12}-\varrho\cos\varphi}{4(a-z_2)}\right]\frac{\partial}{\partial\varrho_{12}}\,, \tag{17}$$

where φ is the angle between $\vec{\varrho}$ and $\vec{\varrho}_{12}$.

The first approximation for χ_1 is obtained by solving the equation $H_1\chi=0$. To obtain the second approximation (whose relative order is $R^{-1/2}$ [3]) we must take into account H_2. Note that we neglected the derivates $\partial/\partial\varrho$, as the first term χ of χ_1 does not depend on ϱ [2].

If we put $\chi_1=\chi+\varkappa$, then we obtain

$$H_1\varkappa=-(H'+H'')\chi \tag{18}$$

– a linear differential equation for $\varkappa$. Therefore

$$\varkappa=\varkappa'+\varkappa'' \tag{19}$$

where

$$H_1\varkappa'=-H'\chi\,; \qquad H_1\varkappa''=-H''\chi \tag{20}$$

Take firstly into account the terms H_1 and H' of the total hamiltonian. Then we find $\varkappa'$ and (at the same time) obtain the correct behaviour of χ_1 when $r_{12}\to 0$.

$$\Delta_{12}\chi'-2\alpha\frac{\partial\chi'}{\partial z_{12}}-\frac{1}{r_{12}}\chi'=0\,; \qquad \chi'=\chi+\varkappa' \tag{21}$$

This equation can be solved by introducing parabolic coordinates (then the variables are separated), but one can use the analogy of the problem of scattering in the Coulomb field [5] with wave number $k=i\alpha$. A solution, satisfying the boundary conditions ($\chi_1\to 1$ when $z_1\to -a$ or $z_2\to a$) has the following form

$$\chi'=\frac{\Gamma(1+1/2\alpha)}{[4\alpha(a-|z|)]^{1/2\alpha}}\,\phi\left(-\frac{1}{2\alpha},1,-\alpha(r_{12}-z_{12})\right); \qquad z=\frac{z_1+z_2}{2} \tag{22}$$

where ϕ is a confluent hypergeometric function. The first term of expansion (22) (when $|z_{1,2}|\sim a$, $\varrho_{1,2}\sim\sqrt{a}$, $a\to\infty$) gives the result obtained in Ref. [2, 3] and the second term gives $\varkappa'$.

Consider now the terms H_1 and H'' together. One can obtain by analogy with Ref. [3]

$$\chi''=\exp\left(-\frac{1}{\alpha}S_1\right); \qquad \chi''=\chi+\varkappa'' \tag{23}$$

The expression for S_1 is very unwieldy (see Ref. [3]). The expansion of S_1 in series gives

$$\chi''=\left[\frac{r_{12}-z_{12}}{4(a-|z|)}\right]^{1/2\alpha}\left[1-\frac{a\varrho_{12}^2-z\varrho_{12}\varrho\cos\varphi}{4\alpha(a^2-z^2)(r_{12}-z_{12})}+\cdots\right]. \tag{24}$$

On the surface $S(z_{12}=0)$

$$\chi_1 \simeq \left[\frac{\varrho_{12}}{4(a-|z|)}\right]^{1/2\alpha}\left[1+\frac{1}{4\alpha^3\varrho_{12}}-\frac{a\varrho_{12}-z\varrho\cos\varphi}{4\alpha(a^2-z^2)}\right]. \tag{25}$$

So we have

$$\Delta E = 8\int_0^a dz \iint d\vec{\varrho}_1 d\vec{\varrho}_2 f_1 f_2 \chi_2 \psi_2^0 \left(\chi_1 \frac{\partial \psi_1^0}{\partial z_1} + \psi_1^0 \frac{\partial \chi_1}{\partial z_1}\right)_{z_1=z_2=z}. \tag{26}$$

By integrating (26) over $\vec{\varrho}_1, \vec{\varrho}_2$, (or $\vec{\varrho}, \vec{\varrho}_{12}$) one finds that contributions from the terms corresponding to $\varkappa$ and $\partial\chi/\partial z_1$ are cancelled (note these terms have the order $(\alpha^3 a)^{-1/2}$ relative to the first term). The final expression for ΔE is

$$\Delta E = A_-^2 A_+^2 R^{\frac{7}{2\alpha}-1}\; e^{-2\alpha R} \frac{4\pi^2 \Gamma\left(\frac{1}{2\alpha}\right)}{2^{1/\alpha}\alpha^{2+1/\alpha}} I(\alpha)[1+0(1/R)] \tag{27}$$

where the function

$$I(\alpha) = \int_0^1 (1+x)^{\frac{1}{2\alpha}} (1-x)^{\frac{3}{2\alpha}} e^{\frac{x-1}{\alpha}}\, dx \tag{28}$$

is given in Table 1.

Table 1.

α	I
0.1	$1.17_{10^{-5}}$
0.2	$2.35_{10^{-3}}$
0.4	$3.78_{10^{-2}}$
0.6	0.101
0.8	0.168
1.0	0.231
1.2	0.287

Equation (27) is valid if the following conditions are satisfied: $R\alpha^2/2 \gg 1$ (then the behaviour of wave functions is determined by the exponential term); $2R\alpha^3 \gg 1$ (then only the first term of the asymptotic expansion of wave function need be retained); as has been shown above, the analogous parameter is used for the asymptotic expansion of the exchange interaction. In particular for the case of two H atoms we have now the condition $R \gg 1$ (instead of the previous one: $\sqrt{R} \gg 1$, which has been obtained in Ref. [3]). Note that the values of the splitting between singlet (E_s) and triplet (E_t) states of H_2 obtained by variational numerical calculations [6] and by the asymptotic method ($E_t - E_s \simeq 1.65 \cdot R^{5/2} \exp(-2 \cdot R)$) are not considerably different from each other even at rather small interatomic distances (25% at $R=3$).

Attempts to obtain the asymptotic expressions for the exchange interaction between two atoms with different ionization potentials have been made by Smirnov and Chibisov [7], and Uwansky and Voronin [8], and the procedure analogous to [2] has been used. But one can show that the results of [7, 8] do not give an exact asymptotic expansion. The point is that the main contribution to the exchange integral (let $\alpha_1 < \alpha_2$) comes from the region $\sim 1/(\alpha_2 - \alpha_1)$ near the second atom (in the case $\alpha_1 = \alpha_2$ it comes from the whole region $\sim R$ between the atoms). So the expansion parameter would not depend on R and not tend to zero when $R \to \infty$.

But if α_1 and α_2 are close to each other then for a variety of practical calculations one can use the formulas from [7] and [8] for $\sigma - \sigma$ exchange integrals. The criterion of their validity is that the quantity $q = (\alpha_2 - \alpha_1) \cdot R < 1$. Then it follows from the results of Ref. [7, 8] that an additional term $ch(q \cdot x)$ appears under the integral (28) (where $\alpha = (\alpha_1 + \alpha_2)/2$). But within the accuracy of the given procedure this term can be neglected thus considerably simplifying the analysis of the exchange interaction.

Consider now the interaction between an atom and a molecule, and let the corresponding α_a and α_m be close to each other. The interaction potential at large distances usually is written in the following form (see e.g. the review [9])

$$U(R,x) = C \exp[-\beta(R - \lambda x)] \tag{29}$$

where x is the vibrational coordinate, C and λ are the parameters of the problem and (in accordance with the given theory) $\beta = \alpha_a + \alpha_m(x)$. Then the perturbation (to first order in x; see Ref. [9]) $V(R, x) = x \cdot \partial U(x=0)/\partial x$ which causes vibration transitions is

$$V = x \cdot C \exp(-\beta R) \left[\beta\lambda - R \frac{\partial \alpha_m(0)}{\partial x} \right]. \tag{30}$$

The usual approach [9] does not take into account the dependence of β on vibrational coordinate x.

I thank Dr. E. E. Nikitin and Dr. M. Ja. Ovchinnikova for the discussion of this work.

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