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Exchange Interaction between Two Different Atoms at Large Distances

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Different cases of the exchange interaction in the system $(\mathrm{A}+e+\mathrm{C}^+)$ are considered and corresponding expressions for this interaction are obtained. A suitable representation for the electron-atom interaction is also discussed.

Key words: Exchange interaction – Electron-atom interaction – Negative ions

1.

The main purpose of the present paper is to obtain the expressions for the exchange interaction between two atoms (A and C) with considerably different ionization potentials $I_\mathrm{A}=\alpha_0^2/2$ and $I_\mathrm{C}=\gamma_0^2/2$ [1] $(\alpha_0>\gamma_0)$. One-electron approximation will be used for the wave function of the loosely bound valence electron of the atom C. We shall consider the case when the projection of the orbital angular momentum of this electron on the interatomic axis is equal to zero and the effective range ϱ of the interaction $V_\mathrm{A}(r)$ between the electron and perturbing atom A is small compared with the interatomic distance R.

The general expressions for the different cases of the exchange interaction are derived in Sections 2, 3, 4 and 5. In Section 6 the results of other works are discussed and in Section 7 we consider the suitable analytical representation for the potential $V_\mathrm{A}(r)$.

2.

Let $I_\mathrm{C}>1/R$. Then the perturbing atom A is in the classically forbidden region (for the valence electron). We shall determine the energy level shift of the atom C caused by the exchange interaction between two atoms. The corresponding Schrödinger equations are

$$(\tfrac{1}{2}\Delta=V_\mathrm{C}+E_0)\,\psi_0=0\,,\qquad E_0=-I_\mathrm{C}\,;\qquad (\tfrac{1}{2}\Delta-V_\mathrm{C}-V_\mathrm{A}+E)\,\psi=0\,. \tag{1}$$

Multiplying the first equation by ψ (the wave functions are assumed to be real) and the second one by ψ_0 and integrating over the space Ω with the boundary surface S we obtain (Green's theorem is used)

$$E-E_0\left[\tfrac{1}{2}\oint_S(\psi\,\nabla\,\psi_0-\psi_0\,\nabla\,\psi)\,ds+\int_\Omega\psi_0V_\mathrm{A}\psi\,d\boldsymbol{r}\right]\Big/\left(\int_\Omega\psi\cdot\psi_0\,d\boldsymbol{r}\right). \tag{2}$$

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[1] Atomic units are used.

Taking Ω_ϱ (that is the entire space with the exception of the sphere volume $\tilde{\Omega}_\varrho$ of the radius ϱ around the atom A) as Ω we obtain ($\psi \simeq \psi_0$ in Ω_ϱ and $\int\limits_{\Omega} \psi \cdot \psi_0 \, d\boldsymbol{r} \simeq 1$)

$$E - E_0 = \tfrac{1}{2} \oint\limits_{S_\varrho} (\psi \nabla \psi_0 - \psi_0 \nabla \psi) \, ds \,. \tag{3}$$

In $\tilde{\Omega}_\varrho$

$$\psi_0(\boldsymbol{R} + \boldsymbol{r}) \simeq \psi_0(\boldsymbol{R}) \exp(\gamma \cdot r \cdot \cos\theta) = \psi_0(\boldsymbol{R}) \frac{1}{\gamma r} \sum_{l=0} (2l+1) \, P_l(\cos\theta) \, i_l(\gamma r) \tag{4}$$

where $\gamma^2/2 = I_C - 1/R$ (here $1/R$ is the first term of the expansion of V_C); r and θ are the coordinates of the electron with respect to the atom A (the polar axis is directed from A to C); i_l (and further k_l, j_l, n_l) are modified spherical Bessel functions multiplied by their arguments. The general form of the axially symmetrical solution of the Schrödinger equation is [1]

$$\psi(\boldsymbol{R} + \boldsymbol{r}) = \psi_0(\boldsymbol{R}) \frac{1}{\gamma r} \sum_{l=0} (2l+1) \cdot P_l(\cos\theta) \cdot \varphi_l(r) \tag{5}$$

where φ_l is the solution of the corresponding radial equation. If $\varrho \leqq r \ll R$ this function has the following form

$$\varphi_l = a_l i_l(\gamma r) + b_l k_l(\gamma r) \tag{6}$$

At large r ψ must coincide with ψ_0. Then one obtains from (3)

$$E - E_0 = -\psi_0^2(\boldsymbol{R}) \frac{\pi^2}{\gamma} \sum_l (2l+1) \cdot b_l / a_l \,. \tag{7}$$

3.

In deriving (7) we have used the tacit assumption that there was no bound state A^- with the energy $-\gamma^2/2$ (otherwise the corresponding coefficient a_l becomes zero).

Consider now the following process

$$\mathrm{A}^- + \mathrm{C}^+ = \mathrm{A} + \mathrm{C} \,. \tag{8}$$

When $R \to \infty$ we have

$$(-\tfrac{1}{2}\Delta + V_\mathrm{A}) \psi_a = E_a \psi_a; \qquad (-\tfrac{1}{2}\Delta + V_\mathrm{C}) \psi_c = E_c \psi_c \tag{9}$$

where ψ_a and ψ_c describe ionic and covalent states.

The solution of the ordinary secular equation gives the following expression for the splitting between the adiabatic terms at the crossing point R_0 of ionic ($U_a = E_a + V_c^{aa}$) and covalent ($U_c = E_c + V_\mathrm{A}^{cc}$) terms [$U_a(R_0) = U_c(R_0)$, or $I_\mathrm{C} \simeq \beta^2/2 + 1/R_0$; $\beta^2/2$ is the electron affinity of atom A; $V_K^{nm} = \langle n | V_K | m \rangle$; $S_{ac} = \langle a | c \rangle$]

$$\Delta E = 2 \cdot \Delta U / (1 - S_{ac}^2); \qquad \Delta U = | V_\mathrm{C}^{aa} S_{ac} - V_\mathrm{C}^{ac} | \,. \tag{10}$$

By means of some simple transformations one can obtain

$$\Delta U = \tfrac{1}{2} \left| \oint\limits_{S_\varrho} (\psi_c \nabla \psi_a - \psi_a \nabla \psi_c) \, ds \right| . \tag{11}$$

We put (when $r \geqq \varrho$)

$$\psi_a = \frac{\mathrm{A}_L}{r} k_L(\beta r) \, P_L(\cos\theta) \tag{12}$$

and use (4) for ψ_c. Then

$$\Delta U_L = \pi^2 |\mathrm{A}_L \psi_c(\boldsymbol{R}_0)| . \tag{13}$$

For the case $L=0$ we have

$$\psi_a = \sqrt{\frac{\beta}{2\pi}}\,\frac{B}{r}\exp(-\beta r),\, r \geqq \varrho ; \qquad \Delta U = \sqrt{2\pi\beta}\,|B\cdot\psi_c(\boldsymbol{R}_0)| . \tag{14}$$

Note that $B=1$ for the short-range (δ-function) potential.

4.

Consider the case when the perturbing atom A is in the inner region of the atom C ($1/R - I_C = k^2/2 > 0$). In $\tilde{\Omega}_\varrho$ we take the unperturbed wave function in the following form

$$\psi_0(\boldsymbol{R}+\boldsymbol{r}) = \psi_0(\boldsymbol{R})\cdot\cos(kr\cdot\cos\theta) + \psi_1(\boldsymbol{R})\cdot\sin(kr\cdot\cos\theta) . \tag{15}$$

To obtain the perturbed wave function ψ we use the analogy of electron-atom scattering theory. We find a stationary solution which meets the definite demands of symmetry relatively to the substitution $\Theta \to \pi - \Theta$. Then one can obtain the following correspondence between the terms of ψ_0 and ψ (when $\varrho \leqq r \ll R$)

$$\cos(kr\cdot\cos\Theta) \to \cos(kr\cdot\cos\Theta) + \frac{1}{r}\, f_1'(\Theta)\cdot\cos(kr) - f_2'(\Theta)\cdot\sin(kr) , \tag{16}$$

$$\sin(kr\cdot\cos\Theta) \to \sin(kr\cdot\cos\Theta) + \frac{1}{r}\, f_2''(\Theta)\cdot\cos(kr) + f_1''(\Theta)\cdot\sin(kr) , \tag{17}$$

where f_1 and f_2 are real and imaginary parts of the scattering amplitude, f_m' and f_m'' are symmetric and antysymmetric parts of f_m. Expressing f through the scattering phases (δ_l) and using the formulas (16), (17), (15) and (3) we obtain

$$E - E_0 = -\frac{\pi}{k}\left[\psi_0^2(\boldsymbol{R})\sum_l (4l+1)\sin(2\delta_{2l}) + \psi_1^2(\boldsymbol{R})\sum_l (4l+3)\sin(2\delta_{2l+1})\right] . \tag{18}$$

5.

Let there exist a quasi-stationary state when the electron with the orbital moment L is scattered by the atom A. Then one can establish (modifying the results of Ref. [1]) the following correspondence

$$\sin(2\delta_L) \to \sin(2\delta_L^0) + \Gamma\cos(2\delta_L^0) \Big/ \left[k_n\left(I_C + \varepsilon_0 + \frac{\Gamma}{2}\cdot\frac{\gamma_0}{k_n}\right)\right] \tag{19}$$

where Γ is the width, $E_n = k_n^2/2$ is the resonance energy, δ_L^0 is the "potential" scattering phase, $\varepsilon_0 \simeq E_n - 1/R$. Thus the function $E(R)$ has a pole (as in the case considered in the Sections 2 and 3). This pole corresponds to the pseudo-crossing of the covalent term with the term of the ionic state which becomes stable at $R < R_s (R_s \simeq 1/E_n)$.

For the ionic state we use the wave function (see for example [2]) which is normalized to unity in $\tilde{\Omega}_\varrho$ and has the following form at $r \geqq \varrho$

$$\psi_a = \sqrt{\frac{\Gamma}{k_n}}\,\frac{1}{r}\left[\sin\delta_L^0 \cdot j_L(kr) + \cos\delta_L^0 \cdot n_L(kr)\right] Y_{L0}(\cos\Theta)\,. \tag{20}$$

The splitting of the adiabatic terms at the curve crossing point is given by (10), (11)

$$\Delta U = \sqrt{\pi(2L+1)\Gamma/k_n}\,|\cos\delta_L^0| \begin{cases} |\psi_0(\boldsymbol{R}_0)| & \text{if } L \text{ is even} \\ |\psi_1(\boldsymbol{R}_0)| & \text{if } L \text{ is odd} \end{cases} \tag{21}$$

6.

We have obtained all the results using the assumptions that $\varrho \ll R$ and that the functions γ and k were the slowly varying functions in the interval $(R-\varrho, R+\varrho)$, that is

$$\frac{\varrho^2}{\varkappa R^2} \ll \min(1, \varkappa\varrho) \tag{22}$$

where $\varkappa$ stands for γ or k. Note if $\varkappa\varrho > 1$ then the condition (22) allows to use the quasi-classical description of ψ_0 in $\tilde{\Omega}_\varrho$. If $\varkappa\varrho \ll 1$ (and ψ_0 is slowly varying function in $\tilde{\Omega}_\varrho$) then formulas (7) and (8) give the result of Ovchinnikova [3]

$$E - E_0 = 2\pi L_s \psi_0^2(\boldsymbol{R}) \tag{23}$$

where L_s is the scattering length.

The particular cases of exchange interaction have been previously investigated by other authors. The result analogous to (7) has been obtained by Smirnov [4] who used the more rigid (than $\varrho \ll R$) assumption ($R \gg l/\gamma, \varrho$) which is broken at large l and small γ. Komarov [5] has investigated the splitting of the hydrogen atom terms at large distances ($1/R \ll \beta^2/2, \gamma_0^2/2$) in the δ-potential field. Formulas (14) and (10) give the exact expression (in the case of δ-potential) for ΔU. Smirnov [6] and Janev and Salin [7] have attempted to consider a more general (than in [5]) case. However their approach is incorrect and their results do not turn into the result of Komarov (see the formulas (20) and (21) from [7]).

7.

To determine the coefficients b_l/a_l, B, δ_l in the equations above it is necessary to solve the Schrödinger equation with the concrete potential $V_A(r)$. Following the ideas of Hellman [8, 9] one may suppose that V_A behaves as $-\alpha/2r^4$ at $r > r_A$ (α and r_A are the polarizability and the characteristic size of the atom A) and as $\dfrac{\partial T}{\partial n}$ at $r < r_A$ (T is the electron kinetic energy density and n is the electron density in A). The theory of Thomas-Fermi (TF) gives $\dfrac{\partial T}{\partial n} = \varphi(r)$, where $\varphi(r)$ is the TF potential for A. Thus $V_A(r)$ has a strongly repulsive character at small r.

Note that considering the elastic electron-inert atom scattering Holtsmark [10] and a number of other authors (see the book [11]) took $V_A = -\varphi(r)$ at small r

(the approximation of static field). This potential is strongly attractive. Although the theory-experiment agreement was quite satisfactory at high energies (when Born approximation is valid and the scattering parameters do not depend on sign of the interaction) there was considerable discrepancy at low energies. Besides there are bound states A^- in this attractive potential. This fact is in contradiction with the experimental results (see for example Ref. [12]) that there do not exist negative ions of inert gas atoms in their ground states.

Let the potential $V_A(r)$ have the following form

$$V_A = -\alpha/2r^4, \quad r > r_0; \quad V_A = \infty, \quad r \leqq r_0 \tag{24}$$

which reproduces the main properties of the electron-atom interaction. (Solving the Schrödinger equation with the potential (24) numerically one can obtain the Ramsauer effect.) The Schrödinger equation with the potential $\sim r^{-4}$ has been considered in Ref. [13]. Supposing $E = 0$ and demanding $\psi(r_0) = 0$ we can obtain an exact expression for the scattering length L_s and express L_s through r_0

$$L_s = \sqrt{\alpha}\,\mathrm{ctg}(\sqrt{\alpha}/r_0); \quad r_0 = \sqrt{\alpha}/[N\pi + \mathrm{arcctg}(L_s/\sqrt{\alpha})] \tag{25}$$

where N is a number of bound states in the potential (24) and the condition of the existence of the bound state is $\sqrt{\alpha}/r_0 > \pi$.

To obtain suitable analytical results we shall use (instead of V_A from (24)) a modified potential W_A which equals to zero if $|V_A| < |E|$ and to $V_A + E$ if $|V_A| > |E|$. Then $\varrho = (\alpha/2|E|)^{1/4}$. If there is only one bound state A^- with $L = 0$ than using W_A we obtain the following relations between α, L_s, r_0 and β:

$$r_0 = \frac{\sqrt{\alpha}}{\lambda + \pi - \mathrm{arctg}[\lambda/(1+\lambda)]}; \quad L_s = \sqrt{\alpha}\,\mathrm{ctg}\left(\lambda - \mathrm{arctg}\frac{\lambda}{1+\lambda}\right); \quad \lambda = \beta^{1/2}\cdot\alpha^{1/4}. \tag{26}$$

For the systeme $e - H$ ($\alpha = 4.5$; $\beta = 0.236$ [12]) one can obtain $L_s = 6.55$. Variational calculation with 1156 parameters [14] gives $L_s = 5.96$.

For the coefficient B (14) we obtain

$$B = e^{\lambda}\cdot f(\lambda) = \left\{2\sqrt{(1+\lambda)^2 + \lambda^2}\int_{x_0}^{1} x^2 \sin^2\left[\frac{\lambda(x_0 - x)}{x_0\cdot x}\right] dx + 1\right\}^{-1/2} \tag{27}$$

$x_0 = r_0\beta^{1/2}\alpha^{-1/4}$; $f(\lambda)$ is given in Table 1. Note that f^2 gives the part of the electron density in the region $r > \varrho$. For the ion H^- we obtain $B = 1.66$; variational calculations give 1.63 and 1.68 [12].

Then the splitting between the ionic term $(H^+ + H^-)$ and different covalent ones $(H(1s) + H(nl)$; $n = 2$, $R_0 = 11.1$; $n = 3$, $R_0 = 35.6$ [15]) was calculated and compared with the variational calculation [15] (see Table 2 where ΔE_{nl} are given in eV).

Note that by averaging (18) over different places of the perturbing atom A one can obtain the shift of the spectral line of the perturbed atom C (compare with the result of Alekseev and Sobelman [16]).

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Table 1

λ	f
0	1
0.25	0.956
0.5	0.881
0.75	0.815
1	0.763
1.25	0.722
1.5	0.690
1.75	0.665
2	0.644
2.25	0.627
2.5	0.612
3	0.589
3.5	0.571
4	0.558

Table 2

(n, l)	(2, 0)	(2, 1)	(3, 0)	(3, 1)	(3, 2)
Work [15]	0.333	0.407	$4{\cdot}91_{10}-3$	$6{\cdot}40_{10}-3$	$4{\cdot}58_{10}-3$
Present work	0.381	0.461	$5{\cdot}83_{10}-3$	$7{\cdot}43_{10}-3$	$5{\cdot}43_{10}-3$

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