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Two-Electron Exchange Interaction Between Atomic Ions and Polar Molecules

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Abstract

The closed analytic expression for matrix element of exchange interaction responsible for direct two-electron capture in slow collisions of ions with polar molecules has been obtained in the framework of asymptotic approach.

Processes of two-electron exchange between ions B^{Z_b+} and polar molecules $A^{(Z_a-2)+}$ of the type

$$A^{(Z_a-2)+} + B^{Z_b+} \longrightarrow A^{Z_a+} + B^{(Z_b-2)+} \tag{1}$$

attract continuous attention both from the theoretical and experimental groups for many decades [1, 2, 3] (here Z_a and Z_b are effective charges of the cores of colliding particles). In order to calculate asymptotically correct exchange matrix elements H_{ab} of the process (1) it is necessary to use correct two-electron wave function of the system $(AB)^{(Z_a+Z_b-2)+}$ in whole configuration space of the electronic coordinates [4]. We shall write electronic Hamiltonian in two-electronic approximation:

$$H_{el} = \sum_{i=1}^{2}\left(-\frac{\Delta_i}{2} + V_a(r_{ia}) + V_b(r_{ib})\right) + r_{12}^{-1}, \tag{2}$$

here $V_{a(b)}$ are the potentials of electronic interaction with ionic core A^{Z_a+} or B^{Z_b+} with the following asymptotics: $V_{a,b} \to -Z_{a,b}/r$, and r_{12} is the distance between two active electrons. Let us define by m_{1a} and m_{2a} orbital momentum projections on dipole axis $\vec{d}_1$ (dipole moment of molecular ion $A^{(Z_a-1)+}$); l_{1b} m_{1b}, l_{2b} m_{2b} are the electronic orbital momentum and its projection on axis $\vec{R}$ (axis between target and projectile) in final state, centered on ion B^{Z_b+}; L_b, S_b are their total orbital and spin momentum and M_L projection of L_b on axis $\vec{R}$. We can represent H_{ab} in the following asymptotic (at $R \to \infty$) form (see [4]):

$$H_{ab} \simeq (-1)^{S_b} \sum_{m_{1b},m_{2b}} C^{L_b M_L}_{l_{1b}m_{1b},l_{2b}m_{2b}} \langle \varphi_b^{(0)}(\vec{r}_{1b})\varphi_{ba}(\vec{r}_{2a})|r_{12}^{-1}|\varphi_{ab}(\vec{r}_{1b})\varphi_a^{(0)}(\vec{r}_{2a})\rangle, \tag{3}$$

where φ_{ab} is the wave function of the "outer" electron of the molecule $A^{(Z_a-2)+}$ in the vicinity of ion B^{Z_b+}, and vice versa; $\varphi_a^{(0)}$ ($\varphi_b^{(0)}$) are the bound state wave functions of the ion $A^{(Z_a-1)+}$ (ion $B^{(Z_b-1)+}$), and C are the Clebsch-Gordan coefficients.

The wave function $\varphi_{ab}(\vec{r}_b)$ satisfy the two-center Schrodinger equation

$$\left(-\frac{\Delta}{2}+U_a(r_a)+V_b(r_b)-E_{1a}\right)\varphi_{ab}(\vec{r}_b)=0, \tag{4}$$

where $U_a(r_a)$ and $V_b(r_b)$ are the interaction potentials of the electron with ions $A^{(Z_a-1)+}$ and B^{Z_b+} respectively. In the following we accept the so-called point-dipole model for description the electronic interaction with permanent dipole moment d_1, hence $U_a(r_a)$ reads:

$$U_a(r_a)=-(Z_a-1)/r_a-\vec{d}_1\cdot\vec{r}_a/r_a^3. \tag{5}$$

In the region between target and projectile $U_a(r_a)$ and $V_b(r_b)$ can be replaced by its Coulomb asymptotics. Solution of equation (4) has been obtained in [3] and reads:

$$\varphi_a(\vec{r}_a)=\frac{n_{1a}^{-1}\pi^{-1/2}}{\sqrt{\Gamma(2n_{1a}(Z_a-1)+1)}}\left(\frac{n_{1a}(Z_a-1)}{e}\right)^{n_{1a}(Z_a-1)}\frac{F(p_a)}{z_a|p_a(z_a)|^{1/2}}\times$$

$$\sum_{l\geq|m_{1a}|}\sum_{k=-l}^{l}a_{Ll}^{m_{1a}}(d_1)D_{km_{1a}}^{l}(\beta)\frac{1}{2^{|k|}|k|!}\left(\frac{(2l+1)(l+|k|)!}{2(l-|k|)!}\right)^{1/2}\left(\frac{\rho}{z_a}\right)^{|k|}e^{ik\phi_a}, \tag{6}$$

where $p_a^2(z_a)=2(-|E_{1a}|+(Z_a-1)/z_a+Z_b/(R-z_a))$; $p_a(z_{1a})=p_a(z_{2a})=0$; $D_{km_{1a}}^{l}$ are the Wigner functions, and

$$F(p_a)=\exp\left(-\int_{z_{1a}}^{z_a}|p_a(z)|dz\right)\exp\left(-\frac{\rho^2p_a(z_a)}{2z_a}\right).$$

Under condition $r_a\sim 1$ the wave function (6) reduces into the nonperturbed wave function of $A^{(Z_a-2)+}$ [3].

The wave function φ_{ab} in the vicinity of ion B^{Z_b+} can be given in terms of a surface integral

$$\varphi_{ab}(\vec{r}_b)=-\frac{1}{2}\int_S d\mathbf{S}\left(\varphi_{ab}\nabla G_b-G_b\nabla\varphi_{ab}\right), \tag{7}$$

where $G_b(\vec{r}_b,\vec{r}_b\,';E_{1a})$ is the one-electronic two-center Green's function of the quasi-molecular system $A^{(Z_a-2)+}+B^{Z_b+}$, the S-plane divides the electronic location in the initial and final channels of the reactions. The Green's function $G_b(\vec{r}_b,\vec{r}_b\,';E_{1a})$ can be represented as the following expansion over partial waves:

$$G_b(\vec{r}_b,\vec{r}_b\,';E_{1a})=-\frac{2}{r_br_b'}\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}g_l(r_b,r_b';E_{1a})Y_{lm}(\theta_b,\phi_b)Y_{lm}^*(\theta_b',\phi_b'), \tag{8}$$

where the radial Green's function $g_l(r_b, r'_b; E_{1a})$ reads [4]:

$$g_l(r_b, r'_b; E_{1a}) = -\frac{n_{1a}}{2} f_{1l}(r_<) f_{2l}(r_>), \quad r_< = \min(r_b, r'_b), \quad r_> = \max(r_b, r'_b), \tag{9}$$

where $f_{1l,2l}(r)$ are linearly independent solutions of the radial equation

$$\frac{d^2 f_{il}(r)}{dr^2} + 2\left(E_{1a} - U_a(|\vec{R} - \vec{r}|) - V_b(r) - \frac{l(l+1)}{2r^2}\right) f_{il}(r) = 0, \tag{10}$$

$$f_{1l}(r) \underset{r\to\infty}{=} r^{-n_{1a}Z_b} e^{r/n_{1a}}, \quad f_{2l}(r) \underset{r\to\infty}{=} r^{n_{1a}Z_b} e^{-r/n_{1a}}. \tag{11}$$

As one can see from (7), the asymptotic form of the function φ_{ab} over the variable r_a is defined by asymptotic of $G_b(\vec{r}_b, \vec{r}'_b; E_{1a})$ at $r'_b \sim R \gg 1$, $r_b \sim 1$, then $r_< = r_b$ and $r_> = r'_b$. In this region of configuration space one can neglect the potential U_a, therefore, the function $f_{1l}(r_b)$ satisfy the equation

$$\frac{d^2 f^{(0)}_{1l}(r)}{dr^2} + 2\left(E_{1a} - V_b(r) - \frac{l(l+1)}{2r^2}\right) f^{(0)}_{1l}(r) = 0. \tag{12}$$

Using the semiclassical solution of eq. (10) for $f_{2l}(r'_b)$ in asymptotic region $r'_b \gg 1$ we can construct the semiclassical expression for Green's function $G_b(\vec{r}_b, \vec{r}'_b; E_{1a})$ under the condition $r'_b \sim R \gg 1$ and $r_b \sim 1$:

$$G_b(\vec{r}_b, \vec{r}'_b; E_{1a}) \underset{r'_b\sim R}{\approx} \frac{n_{1a}}{4\pi}\left(\frac{n_{1a}^2 Z_b}{2e}\right)^{n_{1a}Z_b} F(p_b) \times \tag{13}$$

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} (-1)^{|m|} \frac{(2l+1)}{2^{|m|}|m|} \frac{f^{(0)}_{1l}(r_b)}{r_b} P_l^{|m|}(\theta_b) \left(\frac{\rho}{z'_b}\right)^{|m|} \exp(im(\phi_b - \phi'_b)),$$

where

$$F(p_b) = \exp\left(-\int_{z'_a}^{z_{2a}} |p_a(z)| dz\right) \exp\left(-\frac{\rho^2 p(z'_b)}{2z'_b}\right) \frac{1}{z'_b}.$$

Substituting obtained results into the (7) we come to the following expression for φ_{ab} in the vicinity of ion B^{Z_b+}

$$\varphi_{ab}(\vec{r}_{1b}) \approx D_a(R) \sum_{l\geq|m_{1a}|} (2l+1)^{1/2} a_{Ll}^{m_{1a}}(d_1) \sum_{k=-l}^{+l} \frac{(-1)^{|k|}}{|k|!} D^l_{km_{1a}}(\beta) \times$$

$$\left(\frac{(l+|k|)!}{(l-|k|)!}\right)^{1/2} \left(\frac{n_{1a}}{2}\right)^{|k|+1/2} R^{-|k|-1} \sum_{l'\geq|k|} (2l'+1) \frac{f^{(0)}_{1l'}(r_{1b})}{r_{1b}} P_{l'}^{|k|}(\theta_{1b}) e^{ik\phi_{1b}}, \tag{14}$$

where

$$D_a(R) = \frac{-\pi^{-1/2}}{2\sqrt{\Gamma(2n_{1a}(Z_a-1)+1)}} \left(\frac{n_{1a}^2 Z_b}{2e}\right)^{n_{1a}Z_b} \left(\frac{n_{1a}(Z_a-1)}{e}\right)^{n_{1a}(Z_a-1)} e^{-I_a(R)}.$$

Expression for $I_a(R)$ represented through the elliptic integrals

$$I_a(R) = \int_{z_{1a}}^{z_{2a}} |p_a(z)|dz = \frac{n_{1a}^{-1}}{\sqrt{(R - z_{1a})z_{2a}}} \left\{ \left(-R^2 + (z_{1a} + z_{2a})R - z_{1a}z_{2a}\right) K(k_a) \right.$$

$$\left. +(R - z_{1a})z_{2a}E(k_a) + \left(R^2 - (z_{1a} + 2z_{2a})R + z_{1a}z_{2a} + z_{2a}^2\right) \Pi(\eta_a, k_a) \right\}, \quad (15)$$

$$\eta_a = (z_{2a} - z_{1a})/(R - z_{1a}), \quad k_a = \sqrt{\eta_a R/z_{2a}},$$

where $K(k)$, $E(k)$, and $\Pi(\eta, k)$ are the full elliptic integrals of the first, second and third kinds. In the same manner one can construct the wave function φ_{ba} of the ion $B^{(Z_b-2)+}$ in the vicinity of polar molecular core A^{Z_a+} with the permanent dipole moment d_2. The derivation in very lengthy and hence we present here only the final result:

$$\varphi_{ba} \approx D_b(R) \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \sum_{\lambda \geq |m|} \sum_{\mu \geq |m|} (-1)^{\lambda+|m|} a_{l\lambda}^m(d_2) a_{l\mu}^m(d_2) D_{m_{1b}m}^{\mu}(\beta) \times$$

$$\sqrt{\frac{(2\mu+1)(\mu+|m_{1b}|)!}{(\mu-|m_{1b}|)!}} \sqrt{\frac{(2\lambda+1)(\lambda-|m|)!}{(\lambda+|m|)!}} \frac{f_{1lm}^{(0)}(r_{2a})}{r_{2a}} P_\lambda^{|m|}(\theta_{2a}) e^{im\phi_{2a}}, \quad (16)$$

where

$$D_b(R) = \frac{(-1)^{l_{1b}} B_1}{2\sqrt{\pi}|m_{1b}|!} \left(\frac{n_{1b}}{2}\right)^{|m_{1b}|+1} \left(\frac{n_{1b}^2}{2e}\right)^{n_{1b}(Z_a+Z_b-1)} \times$$

$$Z_a^{n_{1b}Z_a} (Z_b - 1)^{n_{1b}(Z_b-1)} \sqrt{\frac{(2l_{1b}+1)(l_{1b}+|m_{1b}|)!}{(l_{1b}-|m_{1b}|)!}} \frac{\exp(-I_b(R))}{R^{|m_{1b}|}+1},$$

$$I_b(R) = \int_{z_{1b}}^{z_{2b}} |p_b(z)|dz = \frac{n_{1b}^{-1}}{\sqrt{(R - z_{1b})z_{2b}}} \left\{ \left(-R^2(z_{1b} + z_{2b})R - z_{1b}z_{2b}\right) K(k_b) + \right.$$

$$\left. (R - z_{1b})z_{2b}E(k_b) + \left(R^2 - (z_{1b} + 2z_{2b})R + z_{1b}z_{2b} + z_{2b}^2\right) \Pi(\nu_b, k_b) \right\},$$

$$\nu_b = (z_{2b} - z_{1b})/(R - z_{1b}), \quad k_b = \sqrt{\nu_b R/z_{2b}}.$$

In order to calculate the exchange matrix element H_{ab} it is necessary also to know the functions $f_{1l}^{(0)}(r_{1b})$ and $f_{1lm}^{(0)}(r_{2a})$. The function $f_{1l}^{(0)}(r_{1b})$ satisfy the equation (12) and the function $f_{1lm}^{(0)}(r_{2a})$ satisfy the equation:

$$\frac{d^2 f_{1lm}^{(0)}(r)}{dr^2} + 2\left(E_{1b} + \frac{Z_a}{r} - \frac{s_{lm}(s_{lm}+1)}{2r^2}\right) f_{1lm}^{(0)}(r) = 0. \quad (17)$$

$$V_b(r_b) = -Z_b/r_b + C/r_b^2, \quad (18)$$

and $s_l = \sqrt{(l+1/2)^2 + 2C} - 1/2$. In this case the function $f_{1l}^{(0)}(r_{1b})$ reads:

$$f_{1l}^{(0)}(r_{1b}) = \left(\frac{2}{n_{1a}}\right)^{n_{1a}Z_b} \frac{\Gamma(1 + s_l - n_{1a}Z_b)}{\Gamma(2s_l+2)} M_{n_{1a}Z_b, s_l+1/2}(2r_{1b}/n_{1a}). \quad (19)$$

The normalized wave function $\varphi_b^{(0)}$ in the model potential (18) has the form [4]

$$\varphi_b^{(0)}(\vec{r}_{1b}) = B_2 r_{1b}^{s_{l_{2b}}} e^{-r_{1b}/n_{2b}} Y_{l_{2b},m_{2b}}(\theta_{1b},\phi_{1b}), \tag{20}$$

$$B_2 = \left(\frac{2}{n_{2b}}\right)^{s_{l_{2b}}+3/2} \Gamma^{-1/2}\left(2s_{l_{2b}}+3\right).$$

By the same method we can write

$$f_{1lm}^{(0)}(r_{2a}) = \left(\frac{2}{n_{1b}}\right)^{n_{1b}Z_a} \frac{\Gamma(1+s_{lm}-n_{1b}Z_a)}{\Gamma(2s_{lm}+2)} M_{n_{1b}Z_a,s_{lm}+1/2}\left(2r_{2a}/n_{1b}\right), \tag{21}$$

and the wave function is [3]

$$\varphi_a^{(0)}(\vec{r}_{2a})\varphi = A_2 r_{2a}^{n_{2a}Z_a-1} e^{-r_{2a}/n_{2a}} \sum_{n\geq|m_{2a}|} b_{Ln}^{m_{2a}}(d_2) Y_{nm_{2a}}(\theta_{2a},\phi_{2a}), \tag{22}$$

$$A_2 = \frac{1}{2\sqrt{Z_a\Gamma(2n_{2a}Z_a)}}\left(\frac{2}{n_{2b}}\right)^{n_{2a}Z_a+1}.$$

In the dipole approximation for electronic interaction r_{12}^{-1} we get the following result for exchange matrix element H_{ab}:

$$H_{ab} = \frac{8\pi(-1)^{S+1}}{3R^3} \sum_{m_{1b},m_{2b}} C_{l_{1b}m_{1b},l_{2b}m_{2b}}^{L_bM_{L_b}} \sum_{q=-1}^{+1}\sum_{j=-1}^{+1} \frac{D_{qj}^1(\beta)}{(1+q)!(1-q)!} H_{1b}H_{2a}, \tag{23}$$

$$H_{1b} = \int \varphi_{ab}(\vec{r}_{1b})\varphi_b^{(0)*}(\vec{r}_{1b}) r_{1b} Y_{1,-q}(\theta_{1b},\phi_{1b}) d\vec{r}_{1b},$$

$$H_{2a} = \int \varphi_{ba}^*(\vec{r}_{2a})\varphi_a^{(0)}(\vec{r}_{2a}) r_{2a} Y_{1,j}(\theta_{2a},\phi_{2a}) d\vec{r}_{2a}.$$

After calculation of all integrals we come to the following expression for H_{1b}:

$$H_{1b} = \sqrt{3}B_2D_a(R)(2l_{2b}+1)^{1/2} \sum_{l\geq|m_{1a}|}\sum_{k=-l}^{+l} \frac{a_{Ll}^{m_{1a}}(d_1)}{|k|!}\left(\frac{n_{1a}}{2}\right)^{|k|+1/2} D_{km_{1a}}^l(\beta)\times$$

$$\sqrt{\frac{(2l+1)(l+|k|)!}{(l-|k|)!}} \sum_{l'\geq|k|} (-1)^{l'}(2l'+1)\sqrt{\frac{(l'+|k|)!}{(l'-|k|)!}} T_{000}^{l'l_{2b}1} T_{km_{2b}-q}^{l'l_{2b}1} \frac{J_b(n_{2b})}{R^{|k|+1}}, \tag{24}$$

$$J_b(n_{2b}) = \left(\frac{2}{n_{1a}}\right)^{n_{1a}Z_b+s_{l'}+1} \frac{\Gamma(1+s_{l'}-n_{1a}Z_b)\Gamma(s_{l_{2b}}+s_{l'}+4)}{\Gamma(2s_{l'}+2)}\times$$

$$\left(\frac{n_{1a}n_{2b}}{n_{1a}+n_{2b}}\right)^{s_{l_{2b}}+s_{l'}+4} {}_2F_1(-n_{1a}Z_b+s_{l'}+1, s_{l_{2b}}+s_{l'}+4; 2s_{l'}+2; \frac{2n_{2b}}{n_{1a}+n_{2b}}),$$

where ${}_2F_1$ is the hypergeometric function, and T is the 3-j Wigner's symbols. Analogously, one can calculate the expression for H_{2a}:

$$H_{2a} = \sqrt{3}A_2D_b(R)\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\sum_{\lambda\geq|m|}\sum_{\mu\geq|m|} a_{l\lambda}^m(d_2)a_{l\mu}^m(d_2)\sqrt{\frac{(2\mu+1)(\mu+|m_{1b}|)!}{(\mu-|m_{1b}|)!}}\times$$

$$D_{m_{1b}m}^{\mu}(\beta)\sum_{n\geq|m_{2a}|} b_{L'n}^{m_{2a}}(d)\sqrt{(2n+1)(2\lambda+1)}T_{000}^{\lambda n1}T_{mm_{2a}j}^{\lambda n1}J_a(n_{2a}), \qquad (25)$$

$$J_a(n_{2a}) = \left(\frac{2}{n_{1b}}\right)^{n_{1b}Z_a+s_{lm}+1}\frac{\Gamma(1+s_{lm}-n_{1b}Z_a)\Gamma(n_{2a}Z_a+s_{lm}+3)}{\Gamma(2s_{lm}+2)}\times$$

$$\left(\frac{n_{2a}n_{1b}}{n_{2a}+n_{1b}}\right)^{n_{2a}Z_a+s_{lm}+3} {}_2F_1(-n_{1b}Z_a+s_{lm}+1, n_{2a}Z_a+s_{lm}+3; 2s_{lm}+2; \frac{2n_{2a}}{n_{2a}+n_{1b}}).$$

We have obtained a closed analytical form (in terms of full elliptic integrals) of the leading asymptotic term of exponentially small two-electron exchange interaction between polar molecule and atomic ion. Calculation has been done in the framework of semiclassical version of the asymptotic theory.

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