THREE COULOMB CENTRE PROBLEM AND ITS APPLICATION TO THE THEORY OF ION-MOLECULE COLLISIONS

V.Yu. Lazur[1], M.V. Khoma[1], R.K. Janev[2,3], M.I. Karbovanets[1]

[1] Uzhhorod National University, Uzhhorod, Ukraine
[2] Macedonian Academy of Sciences and Arts, Skopje, Macedonia
[3] Forschungszentrum-Juelich, Institute for Plasma Physics, Juelich, Germany

The asymptotic properties of the solution of quantum-mechanical three Coulomb centers problem eZ_1ZZ are studied. Within the framework of the perturbation theory the asymptotic formulas for energies of eZ_1ZZ system are obtained at large separation L between interacting fragments. As the applications of obtained results the leading term of the asymptotic of exchange interactions between hydrogen-like molecular ion eZZ with nuclei of different elements are calculated. The total cross sections of charge transfer of a hydrogen molecular ion H_2^+ on the nuclei of lithium at not very low impact velocities are calculated.

Introduction

In the present work we study the asymptotic behaviour of discrete spectrum of eZ_1ZZ system (one electron and three fixed nuclear charges: Z_1 and $Z_2 = Z_3 = Z$). This system can serve as a model for collision systems consisting of three ions with closed electronic shells (two of them being identical) and one "active" bound electron. We consider the Schroedinger equation for the problem of electron motion in the field of three Coulomb centres:

$$\hat{H}\Psi \equiv \left(-\frac{1}{2}\Delta_{\vec{r}} - \frac{Z_1}{|\vec{r}-\vec{R}_1|} - \frac{Z}{|\vec{r}-\vec{R}_2|} - \frac{Z}{|\vec{r}-\vec{R}_3|} \right) \times$$

$$\times \Psi(\vec{r};\vec{Q}) = E(\vec{Q})\Psi(\vec{r};\vec{Q}), \qquad (1)$$

where $\vec{r}$ is the radius-vector of the electron, $\vec{R}_i$ is the radius-vector of the i-th nucleus ($i = 1,2,3$), $r_i = |\vec{r} - \vec{R}_i|$ is the distance from the electron to i-th nucleus, $E(\vec{Q})$ and $\Psi(\vec{r};\vec{Q})$ are the electron energy and wave-function, respectively, that depend on three coordinates $Q_1 = L$, $Q_2 = R$, $Q_3 = \beta$, $\vec{Q} = (L, R, \beta)$, the meaning of which is shown in Fig.1.

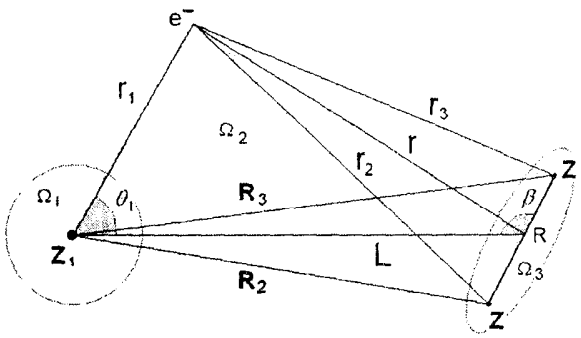

Fig.1. Geometry of quasi-molecule eZ_1ZZ and used notation.

Asymptotic expressions for the potential energy surfaces of eZ_1ZZ system

In the limit $L \to \infty$ the solutions of equation (1) are localized either near the nucleus Z_1 or near the two identical charges (ions), $Z + Z$. Thus, Ψ_i is the wave function that corresponds to the case when system

eZ_1ZZ is separated as a hydrogen-like atomic ion eZ_1 and two identical charges, and Ψ_{II} corresponds to the case of infinitely separated a hydrogen-like molecular ion eZZ and a charge Z_1. The energies $E(\vec{Q})$ of eZ_1ZZ system in the limit $L \to \infty$ can be classified in an analogous manner: $E_I(E_{II})$ energies go over into the energy levels of isolated atomic (molecular) ion eZ_1 (eZZ) for asymptotically large L. We characterize $E_I(\vec{Q})$ and Ψ_I by the set of (parabolic) quantum numbers $I=[n_1n_2m]$ which describe the states of isolated hydrogen-like ion eZ_1; for $E_{II}(\vec{Q})$ and Ψ_{II} will be characterizes by the set of (spheroidal) quantum numbers $II=[k,q,m']$ which describe the states of molecular ion eZZ. The function Ψ_I we expand over the Coulomb parabolic functions [1] $\varphi_{n_1n_2m}(\mu,\nu,\varphi_1)$:

$$\Psi_I = \sum_{n_1'n_2'm'} a_{n_1'n_2'm'}(R_2,R_3,\theta_2,\theta_3)\times$$

$$\times\varphi_{n_1'n_2'm'}(\mu,\nu,\varphi_1), \qquad (2)$$

$$\varphi_{n_1n_2m}(\mu,\nu,\varphi_1)=\frac{\sqrt{2}Z_1^{3/2}}{n^2}f_{n_1m}\left(\frac{Z_1\mu}{n}\right)\times$$

$$\times f_{n_2m}\left(\frac{Z_1\nu}{n}\right)\frac{e^{im\varphi_1}}{\sqrt{2\pi}}, \qquad (3)$$

where

$$f_{pm}(\rho)=\frac{1}{|m|!}\left[\frac{(p+|m|)!}{p!}\right]^{\frac{1}{2}}\Phi(-p,|m|+1,\rho)\times$$

$$\times exp(-\rho/2)\,\rho^{|m|/2} \qquad (4)$$

$\Phi(...)$ is the confluent hypergeometric function of the first kind [2], n is the principal quantum number, and $\mu=r_1(1+\cos\theta_1)$ and $\nu=r_1(1-\cos\theta_1)$ are the parabolic coordinates. The wave function $\Psi_{II}(\vec{r};\vec{Q})$ we represent as expansion

$$\Psi_{II}(\vec{r};\vec{Q})=\Psi_i(\xi,\eta,\varphi;\tilde{\xi},\tilde{\eta},R)=$$

$$=\sum_j\sum_{m_j}a_{ijm_j}(\tilde{\xi},\tilde{\eta},R)\varphi_{jm_j}(\xi,\eta,\varphi;R) \qquad (5)$$

over the two-center wave functions φ_{jm_j} of eZZ discrete spectrum

$$\varphi_{jm_j}(\xi,\eta,\varphi;R)=N_{jm_j}\Pi_{jm_j}(\xi;R)\times$$

$$\times S_{jm_j}(\eta;R)\frac{exp(im_j\varphi)}{\sqrt{2\pi}}, \qquad (6)$$

where N_{jm_j} is the normalization factor, m_j is the projection of angular momentum on the axis $\vec{R}$, and j designate all other quantum numbers [3,4]. The coordinates $\tilde{\xi}$ $\tilde{\eta}$, used in Eq.(5), are defined by (see Fig.1)

$$\tilde{\xi}=\left(\sqrt{L^2-RL\cos\beta+R^2/4}+\right.$$

$$\left.+\sqrt{L^2+RL\cos\beta+R^2/4}\right)R^{-1},$$

$$\tilde{\eta}=\left(\sqrt{L^2-RL\cos\beta+R^2/4}-\right.$$

$$\left.-\sqrt{L^2+RL\cos\beta+R^2/4}\right)R^{-1}. \qquad (7)$$

The energies E_I of the system eZ_1+Z+Z (electron is predominantly localized in the Ω_I-region; see Fig.1) in the first order of perturbation theory are given by

$$E_I(\vec{Q})=-\frac{Z_1^2}{2n^2}-\left(\frac{Z}{R_2}+\frac{Z}{R_3}\right)+$$

$$+\frac{3Zn\Delta}{2Z_1}\left(\frac{1}{R_2^4}+\frac{1}{R_3^4}+\frac{2\cos\tilde{\gamma}}{R_2^2R_3^2}\right)^{1/2}, \quad (8)$$

where $\Delta = n_1 - n_2$, and $\tilde{\gamma}$ is the angle between $\vec{R}_2$ and $\vec{R}_3$. At sufficiently large distances L between Z_1 and eZZ, the potential energy surfaces of $eZZ + Z_1$ quasi-molecular system in the second order approximation of perturbation theory are given by the expression

$$E_{II}(\vec{Q}) = \varepsilon_i(R) - \frac{Z_1R^2}{4\tilde{\xi}} \times$$

$$\times\left[1+\left(\frac{1}{3}+\frac{3\tilde{\eta}^2-1}{2}A_{ii}^{(2)}(R)\right)\frac{1}{\tilde{\xi}^2}\right]+$$

$$+\frac{Z_1^2R^4}{16\tilde{\xi}^4}\left[\left(1-\tilde{\eta}^2\right)\alpha_i^{(+)}(R)+\tilde{\eta}^2\alpha_i^{(-)}(R)\right],$$

$$\alpha_i^{(\pm)}(R) = \sum_j{}' \frac{\left[A_{ij}^{(1)}(R)\right]^2}{\varepsilon_i(R)-\varepsilon_j(R)}, \quad (9)$$

where coefficients $A_{ij}^{(n)}(R)$ are given as

$$A_{ij}^{(n)}(R) = \frac{2^n n!\left[(n-\aleph)!\right]^2}{(2n)!(n+\aleph)!}N_{ij}(R)\times$$

$$\times\left\{\int_{-1}^{1}S_i(\eta;R)P_n^{\aleph}(\eta)S_j(\eta;R)d\eta\times\right.$$

$$\times\int_1^{\infty}\Pi_i(\xi;R)P_n^{\aleph}(\xi)\Pi_j(\xi;R)\xi^2d\xi -$$

$$-\int_{-1}^{1}S_i(\eta;R)P_n^{\aleph}(\eta)S_j(\eta;R)\eta^2d\eta\times$$

$$\left.\times\int_1^{\infty}\Pi_i(\xi;R)P_n^{\aleph}(\xi)\Pi_j(\xi;R)d\xi\right\}, \quad (10)$$

$\aleph = |m_i - m_j|$, $N_{ij}(R) = N_i(R)N_j(R)$, and $\varepsilon_i(R)$ are the energies of hydrogen-like molecular ion eZZ. (The subscript m_j in the notations for $\Pi_{jm_j}(\xi;R)$, $S_{jm_j}(\eta;R)$ and N_{jm_j} has been omitted.) Formulae similar to (8) and (9) for the specific case of $Z_1 + H_2^+$ system have been derived in [5,6].

Exchange interaction of hydrogen-like molecular ion with a nucleus, and charge-exchange cross-sections

We consider the following charge-exchange reaction:

$$eZZ + Z_1 \rightarrow eZ_1 + Z + Z \quad (11)$$

at low collision velocities. The exchange interaction $\Delta(\vec{Q})$ between adiabatic electronic states of quasi-molecules $eZZ + Z_1$ and $eZ_1 + Z + Z$ is given by the expression

$$\Delta(\vec{Q}) = \int_S d\vec{S}\left(\Psi_I^*\vec{\nabla}\Psi_{II} - \Psi_{II}^*\vec{\nabla}\Psi_I\right). \quad (12)$$

Using for Ψ_I and Ψ_{II} the expansions (2) and (5), we obtain (to the leading order of $1/L$)

$$\Delta(L,\beta) = \frac{Z_1^{3/2}2^{Z_1/\alpha_2+1/2}}{n^2(n-1)!}\overline{A}(\beta)\times$$

$$\times\left(\frac{Z_1}{n}\right)^{n-1}L^{n+\frac{2Z}{\alpha_2}-1}\times$$

$$\times exp\left\{-\frac{L}{2}\left(\alpha_2+\frac{Z_1}{n}\right)-\frac{1}{2}\left(\frac{Z_1}{\alpha_2}+\frac{2nZ}{Z_1}\right)\right\}. \quad (13)$$

The coefficient $\overline{A}(\beta)$ is related to the normalisation constant of asymptotic wave function of eZZ system; $\alpha_2 = \sqrt{-2E_{II}^{(0)}(R)}$,

$E_{II}^{(0)}(R)$ is the energy of molecular ion eZZ, and n is a principal quantum number of the state described by Ψ_I wave function. The potential energy surfaces of $Z_1 + H_2^+$ quasi-molecular system, with $Z_1 = 3$ and at a distance between the protons $R = 2$, for the first three σ-states that correlate with the $1s\sigma$, $2s\sigma$, $2p\sigma$ states of H_2^+ molecular ion at infinite distances L, are shown in Fig.2. Using Eq. (9) has performed the calculations.

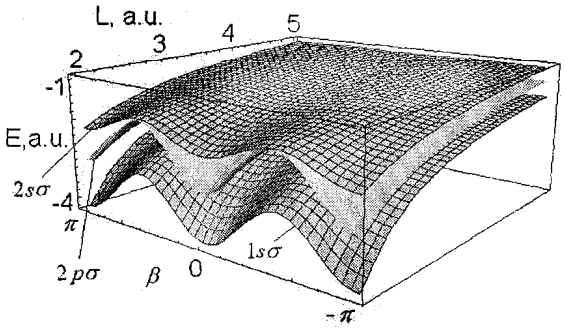

Fig. 2. Adiabatic energy surfaces of $Z_1 + H_2^+$ ($Z_1 = 3$, $R = 2$), calculated by using Eq. (9), for the first three σ-states that asymptotically correlate with the $1s\sigma$, $2s\sigma$, $2p\sigma$ states of H_2^+.

Figure 3 shows the potential energy surfaces $E_{000}(L,R,\beta)$ and $E_{010}(L,R,\beta)$ of the system $p + p + Li^{++}$ calculated for R=2 by using Eq. (8).

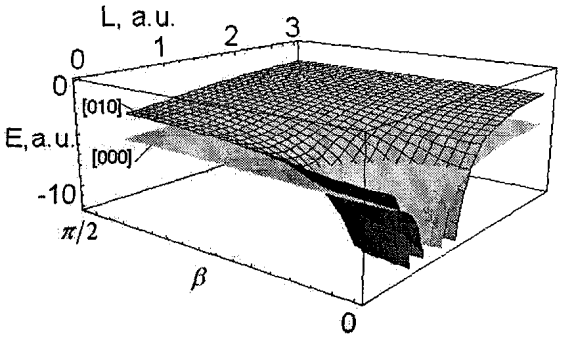

Fig. 3. Adiabatic potential energy surfaces $E_{000}(L,R,\beta)$ and $E_{010}(L,R,\beta)$ of the $p + p + Li^{++}$ quasi-molecule.

As an application of above described asymptotic method for determination of eigenfunctions and eigenenergies of a three-centre Coulomb system, as well as the pertinent radial couplings (Eq.(13)), we have calculated the cross section of charge exchange reaction

$$H_2^+ + Li^{3+} \rightarrow 2p + Li^{2+} \qquad (14)$$

by using the standard MO close coupling method, with radial coupling matrix elements in the form of Eq. (13). In the semi-classical version of this method, the electron capture probability $p_n(\rho)$ (transition from the initial state "1" to a particular final state "n") is given by

$$p_n(\rho) = |a_n(+\infty)|^2, \qquad (15)$$

where ρ is the impact parameter. The coefficients a_n satisfy the standard time-dependent system of differential equations (with the effects of electron translation factors and rotational transitions omitted):

$$\begin{aligned} i\frac{da_1}{dt} &= H_{11}a_1 + H_{12}a_2 + \ldots + H_{1n}a_n, \\ i\frac{da_2}{dt} &= H_{12}a_1 + H_{22}a_2 + \ldots + H_{2n}a_n, \\ &\bullet\bullet\bullet \\ i\frac{da_n}{dt} &= H_{1n}a_1 + H_{2n}a_2 + \ldots + H_{nn}a_n, \end{aligned} \qquad (16)$$

with the initial condition $a_j(-\infty) = \delta_{j1}$. The diagonal matrix elements H_{jj}, which correspond to adiabatic energy levels of eZ_1ZZ system, are calculated by using Eqs. (8), (9), whereas the non-diagonal matrix

elements H_{ij}, which correspond to the exchange interaction between initial and final adiabatic electronic states, are calculated by using Eq. (13). The cross section for the specific $1 \to n$ transition,

$$\sigma_n = 2\pi \int_0^\infty p_n(\rho)\rho d\rho \qquad (17)$$

has been calculated within the straight-line trajectory approximation, $L(t) = \sqrt{\rho^2 + v^2 t^2}$, for nuclear motion ($v$ being the collision velocity).

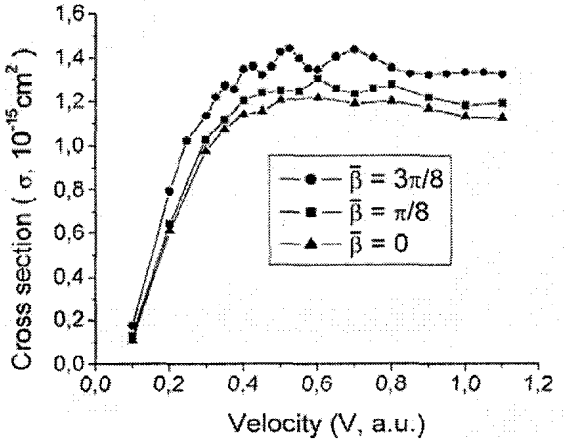

Fig. 4. Cross sections of reaction (14) for different orientation angles of molecular axis $\vec{R}$ relative to the projectile velocity vector $\vec{V}$: $\bar{\beta}$ =0, $\pi/8$, $3\pi/8$.

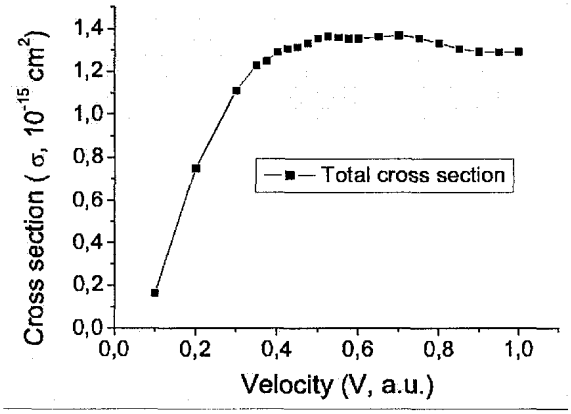

Fig. 5. Total cross sections of reaction (14) averaged over the orientation angles of molecular axis $\vec{R}$ relative to the projectile velocity vector $\vec{V}$.

The cross sections of reaction (14) for different orientations of molecular axis with respect to the vector of projectile velocity are shown in Fig. 4, as function of collision velocity. These cross sections exhibit weak oscillations for collision velocities above 0,4 a.u. The total cross section, summed over the orientation angles of axis R, is shown in Fig. 5. Remnants of the oscillations in the collision velocity region above 0,4 a.u. are still present in the structure of the cross section.

References

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ЗАДАЧА ТРЬОХ КУЛОНІВСЬКИХ ЦЕНТРІВ ТА ЇЇ ЗАСТОСУВАННЯ В ТЕОРІЇ ІОН-МОЛЕКУЛЯРНИХ ЗІТКНЕНЬ

В.Ю. Лазур[1], М.В. Хома[1], Р.К. Янев[2,3], М.І. Карбованець[1]

[1]Ужгородський національний університет, Ужгород, Україна
[2] Macedonian Academy of Sciences and Arts, Skopje, Macedonia
[3] Forschungszentrum-Juelich, Institute for Plasma Physics, Juelich, Germany

Вивчаються асимптотичні властивості розв'язків квантовомеханічної задачі трьох кулонівських центрів eZ_1ZZ. В рамках теорії збурень отримано асимптотичні формули для енергій системи eZ_1ZZ при великих відстанях L між взаємодіючими фрагментами. В якості застосування отриманих результатів розраховано головний член асимптотичного розкладу обмінної взаємодії водневоподібного молекулярного іона eZZ з ядрами різних хімічних елементів. Обчислено повні перерізи перезарядки іона молекулярного водню H_2^+ на ядрах атома літію при не дуже малих швидкостях зіткнення.