Proceedings of Institute of Mathematics of NAS of Ukraine 2004, Vol. 50, Part 3, 1404–1409

Asymptotic Approach to the Quantum Mechanical Problem of the Three Coulomb Centers

Volodymyr LAZUR, Svitlana MYHALYNA and Mykhaylo KHOMA

Uzhgorod National University, 32 Voloshyna Str., 88000 Uzhgorod, Ukraine
E-mail: *lazur@univ.uzhgorod.ua, khoma@uzhgorod.ukrsat.com*

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. Asymptotic for one-electron three-center wave function of the hydrogen-like atomic ion in the vicinity of two Coulomb centers $Z + Z$ are constructed. 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.

1 Introduction

The solutions of a Schrödinger equation with potentials of two and three Coulomb centers represents considerable interest from the point of view of different problems relating few-body systems, considered in adiabatic approximation. In molecular physics these systems play the same fundamental role as atom of hydrogen in atomic physics [1]. The results obtained while solving many-center Coulomb problems have also numerous and relevant applications in physics of slow atomic-molecular collisions, scattering theory, nuclear physics, spectroscopy of complex chemical compounds etc. However till now there is a deep asymmetry in progressing the theory and methods of a two-center eZ_1Z_2 and three-center $eZ_1Z_2Z_3$ Coulomb problems solving. Comparatively with effective asymptotic and numerical methods of eZ_1Z_2 problem solving only a few attempts to solve the three-center problem $eZ_1Z_2Z_3$ using the different approximate methods (see, for example, [2, 3]) are represented now. The reason of such situation is probably that the Schrödinger equations with potential of two Coulomb centers enables variable separation in prolate spheroidal coordinates, so that the problem of finding integrals of motion for system eZ_1Z_2 is reduced to a one-dimensional spectral problem. The possibility of variable separation shows that the system eZ_1Z_2 has higher dynamical symmetry in addition to the geometrical one. This additional dynamical symmetry results in that together with the operator L_z of the electron angular momentum projections to an internuclear axis, the so-called operator Λ of the separation constant [1] commuted with a Hamiltonian of a eZ_1Z_2 system. Naturally the question arises, whether it is possible to find the operator Λ, commuting with a Hamiltonian in many-center Coulomb problems, so that to achieve separation of variables in them also? Coulson and Joseph [4] on an example of a four-center problem showed, that the answer is negative. More general result was obtained by Roy [5], who investigated a dynamical symmetry of multi-center problems. From his work follows, in particular, that the Schrödinger equations of a problem $eZ_1Z_2Z_3$ are not separable in any orthogonal coordinate system and it is necessary to deal with partial differential equations that essentially complicate the problem of calculation electronic wave functions and energy terms. The above mentioned features essentially handicap in-depth analysis of a problem $eZ_1Z_2Z_3$ and require to use some approximate methods. The development of the majority of them is expedient for different limit cases and, in particular, for study of asymptotic properties of the solutions of $eZ_1Z_2Z_3$ problem, both for large and on small intercentre separation.

In the present work we study the asymptotic behavior 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 Schrödinger equation for the problem of electron motion in the field of three Coulomb centers:

$$\hat{H}\Psi \equiv \left(-\frac{\triangle}{2} - \frac{Z_1}{|\vec{r} - \vec{R}_1|} - \frac{Z}{|\vec{r} - \vec{R}_2|} - \frac{Z}{|\vec{r} - \vec{R}_3|} \right) \Psi(\vec{r}; \vec{Q}) = E(\vec{Q})\Psi(\vec{r}; \vec{Q}), \tag{1}$$

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.

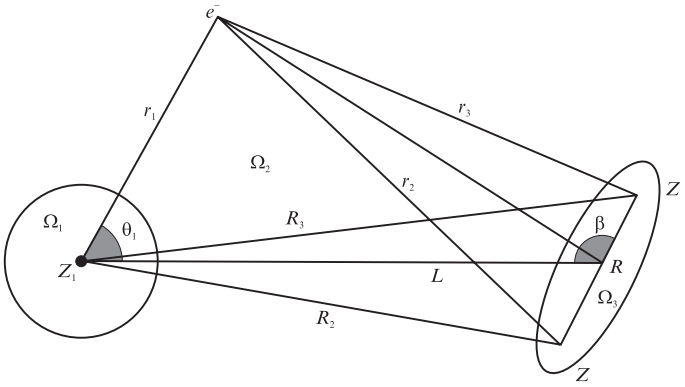

Figure 1. Geometry of quasi-molecule eZ_1ZZ and used notation.

2 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 $I = [n_1 n_2 m]$ which describe the states of isolated hydrogen-like ion eZ_1; for $E_{II}(\vec{Q})$ and Ψ_{II} will be characterized 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 [6] $\varphi_{n_1 n_2 m}(\mu, \nu, \varphi_1)$:

$$\Psi_I = \sum_{n_1' n_2' m'} a_{n_1' n_2' m'}(R_2, R_3, \theta_2, \theta_3)\varphi_{n_1' n_2' m'}(\mu, \nu, \varphi_1), \tag{2}$$

$$\varphi_{n_1 n_2 m}(\mu, \nu, \varphi_1) = \frac{\sqrt{2} Z_1^{3/2}}{n^2} f_{n_1 m}\left(\frac{Z_1 \mu}{n}\right) f_{n_2 m}\left(\frac{Z_1 \nu}{n}\right) \frac{e^{im\varphi_1}}{\sqrt{2\pi}}, \tag{3}$$

where

$$f_{pm}(\rho)=\frac{1}{|m|!}\sqrt{\frac{(p+|m|)!}{p!}}\Phi(-p,|m|+1,\rho)\exp(-\rho/2)\rho^{|m|/2}, \tag{4}$$

Φ is the confluent hypergeometric function of the first kind [7], 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. We represent the wave function $\Psi_{II}(\vec{r};\vec{Q})$ as expansion

$$\Psi_{II}(\vec{r};\vec{Q})=\Psi_i(\xi,\eta,\varphi;\widetilde{\xi},\widetilde{\eta},R)=\sum_j\sum_{m_j}a_{ijm_j}(\widetilde{\xi},\widetilde{\eta},R)\varphi_{jm_j}(\xi,\eta,\varphi;R) \tag{5}$$

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

$$\varphi_{jm_j}(\xi,\eta,\varphi;R)=N_{jm_j}\Pi_{jm_j}(\xi;R)S_{jm_j}(\eta;R)\frac{\exp(im_j\varphi)}{\sqrt{2\pi}}, \tag{6}$$

where N_{jm_j} is the normalization factor, $\Pi_{jm_j}(\xi;R)$ and $S_{jm_j}(\eta;R)$ are the quasiradial and quasiangular spheroidal wavefunctions [1], m_j is the projection of angular momentum on the axis $\vec{R}$, and j designate all other quantum numbers [1,8]. The coordinates $\widetilde{\xi}$, $\widetilde{\eta}$ used in equation (5), are defined by (see Fig. 1)

$$\begin{aligned}\widetilde{\xi}&=\left(\sqrt{L^2-RL\cos(\beta)+R^2/4}+\sqrt{L^2+RL\cos(\beta)+R^2/4}\right)R^{-1},\\ \widetilde{\eta}&=\left(\sqrt{L^2-RL\cos(\beta)+R^2/4}-\sqrt{L^2+RL\cos(\beta)+R^2/4}\right)R^{-1}.\end{aligned} \tag{7}$$

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

$$E_I(\vec{Q})\equiv E_{n_1n_2m}(R_2,R_3,\widetilde{\gamma})=-\frac{Z_1^2}{2n^2}-\left(\frac{Z}{R_2}+\frac{Z}{R_3}\right)+\frac{3Zn\triangle}{2Z_1}\left(\frac{1}{R_2^4}+\frac{1}{R_3^4}+\frac{2\cos\widetilde{\gamma}}{R_2^2R_3^2}\right)^{1/2}, \tag{8}$$

where $\triangle=n_1-n_2$, and $\widetilde{\gamma}$ 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

$$\begin{aligned}E_I(\vec{Q})\equiv E_i(\widetilde{\xi},\widetilde{\eta},R)&=\varepsilon_i(R)-\frac{Z_1R^2}{4\widetilde{\xi}}\left[1+\left(\frac{1}{3}+\frac{3\widetilde{\eta}^2-1}{2}A_{ii}^{(2)}(R)\right)\frac{1}{\widetilde{\xi}^2}\right]+\\ &+\frac{Z_1^2R^4}{16\widetilde{\xi}^4}\left[(1-\widetilde{\eta}^2)\alpha_i^{(+)}(R)+\widetilde{\eta}^2\alpha_i^{(-)}(R)\right],\qquad \alpha_i^{(\pm)}(R)=\sum_j{}'\frac{\left[A_{ii}^{(2)}(R)\right]^2}{\varepsilon_i(R)-\varepsilon_j(R)},\end{aligned} \tag{9}$$

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

$$\begin{aligned}A_{ij}^{(n)}(R)&=\frac{2^n n!(n-\kappa)!^2}{(2n)!(n+\kappa)!}N_{ij}(R)\\ &\times\left(\int_{-1}^{1}S_i(\eta;R)P_n^\kappa(\eta)S_j(\eta;R)d\eta\int_1^\infty\Pi_i(\xi;R)P_n^\kappa(\xi)Pi_j(\xi;R)\xi^2d\xi\right.\\ &\left.-\int_{-1}^{1}S_i(\eta;R)P_n^\kappa(\eta)S_j(\eta;R)\eta^2d\eta\int_1^\infty\Pi_i(\xi;R)P_n^\kappa(\xi)Pi_j(\xi;R)d\xi\right),\end{aligned} \tag{10}$$

$\kappa=|m_i-m_j|$, $N_{ij}(R)=N_i(R)N_j(R)$, 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 [2,3].

3 Asymptotic expression for the wave function of $A^{(Z_1-1)+}$ ion in the vicinity of two Coulomb centers $Z+Z$

The asymptotic form of three-center wave function $\Psi_I(\vec{r};\vec{Q})$ of ion $A^{(Z_1-1)+}$ in vicinity of two Coulomb centers $Z+Z$ is necessary to calculate the asymptotic of two-electron exchange interaction (the matrix element for two-electron transition) between highly charged ion and diatomic molecule. The wave function $\Psi_I(\vec{r};\vec{Q})$ satisfies the following integral relation

$$\Psi_I(\vec{r};\vec{Q}) = -\frac{1}{2}\int_S d\vec{S}\left[\Psi_I(\vec{r}\,';\vec{Q})\vec{\nabla}G_{E_I}(\vec{r},\vec{r}\,';\vec{Q}) - G_{E_I}(\vec{r},\vec{r}\,';\vec{Q})\vec{\nabla}\Psi_I(\vec{r}\,';\vec{Q})\right], \tag{11}$$

where S is the surface that surrounds the volume containing the nuclei $Z+Z$. The one-electron three-center Green's function $G_{E_I}(\vec{r},\vec{r}\,';\vec{Q})$, appearing in equation (11), satisfies the equation:

$$\left(-\frac{\triangle}{2} + V_1\left(|\vec{r}+\vec{L}|\right) - \frac{Z}{|\vec{r}+\vec{R}/2|} - \frac{Z}{|\vec{r}-\vec{R}/2|} - E_I\right) G_{E_I}(\vec{r},\vec{r}\,';\vec{Q}) = \delta(\vec{r}-\vec{r}\,'). \tag{12}$$

Here E_I is the energy of the system eZ_1+Z+Z when the electron is predominantly localized in the Ω_I-region; see Fig. 1. For $L\to\infty$, E_I goes into the energy levels of isolated atomic ion eZ_1. The potential $V_1(r_1)$ in equation (12) is a spherically symmetric effective potential which characterizes the field of A^{Z_1+} atomic ion and asymptotically behaves as

$$V_1(r_1) \underset{r_1\to\infty}{\to} -\frac{Z_1}{r_1}. \tag{13}$$

At large distances between Z_1 and $Z+Z$, we represent G_{E_I} as product $G_{E_I} = G^{(0)}_{E_I^{(0)}}\chi(L)$, where $\chi(L)$ is a correction function obtained in [9] and $G^{(0)}_{E_I^{(0)}}$ is the Green's function for two identical Coulomb centers $Z+Z$:

$$\left(-\frac{\triangle}{2} - \frac{Z}{|\vec{r}+\vec{R}/2|} - \frac{Z}{|\vec{r}-\vec{R}/2|} - E_I^{(0)}\right) G^{(0)}_{E_I^{(0)}}(\vec{r},\vec{r}\,';\vec{R}) = \delta(\vec{r}-\vec{r}\,'). \tag{14}$$

Here $E_I^{(0)}$ is the electron energy of isolated ion eZ_1. Our work is dedicated to investigation of the two-center Coulomb Green's function $G^{(0)}_{E_I^{(0)}}$ has been studied in [10] in detail. Using the results of [10], one obtains the following expression for $\Psi_I\left(\vec{r};\vec{Q}\right)$:

$$\Psi_I\left(\vec{r};\vec{Q}\right) = D_I(\alpha_1,L)\sum_{\ell=0}^{\infty}\sum_{m\geq m_1}^{+\ell}\widetilde{B}^{\ell}_{mm_1}(p_I;\alpha,\beta)\,\Pi^{(1)}_{m\ell}(p_I,\xi)\,\bar{S}_{m\ell}(p_I,\eta)\,\frac{e^{im\varphi}}{\sqrt{2\pi}}, \tag{15}$$

$$D_I(\alpha_1,L) = 2\widetilde{A}_{\alpha_1\ell_1}\left(\frac{2}{\alpha_1}\right)^{m_1}(2\alpha_1)^{2Z/\alpha_1}\,m_1!B_{\ell_1m_1}e^{-2Z/\alpha_1}L^{\frac{Z_1+2Z}{\alpha_1}-m_1-1}e^{-\alpha_1 L}, \tag{16}$$

$$\widetilde{B}^{\ell}_{mm_1}(p_I;\alpha,\beta) = (-1)^{m_1+m}N^{-1}_{m\ell}(p_I)\sum_{s=0,1}^{\infty}(-1)^s C_{m_1,m+s}d^{m\ell}_s(p_I)\,D^{m+s\,*}_{m_1m}(\alpha,\beta,0), \tag{17}$$

$$B_{\ell_1m_1} = \frac{1}{2^{m_1}m_1!}\left(\frac{2\ell_1+1}{2}\frac{(\ell_1+m_1)!}{(\ell_1-m_1)!}\right)^{1/2}, \qquad C_{m_1,m+s} = \frac{(m+m_1+s)!}{2^{m_1}m_1!(m+s-m_1)!}. \tag{18}$$

The coefficient $\widetilde{A}_{\alpha_1\ell_1}$ is related to the normalization constant of asymptotic wave function of eZ_I system, $D^{m+s\,*}_{m_1m}(\alpha,\beta,0)$ is the Wigner rotation matrix [6], $\alpha_1=\sqrt{-2E_I}$ and $p_I = R\sqrt{-2E_I}/2$.

The regular solution $\Pi^{(1)}_{m\ell}(p_I,\xi)$ is given as expansion over the Coulomb radial wave function

$$\Pi^{(1)}_{m\ell}(p_I,\xi)=\left(\frac{\xi-1}{\xi+1}\right)^{m/2}\sum_{s=-\infty}^{\infty}h_s\left(\alpha_1,\lambda_{m\ell},\nu\,|p_I\right)R^{(1)}_{\nu+s}(x),\qquad x=p_I\left(\xi+1\right), \tag{19}$$

$$R^{(1)}_{\nu+s}(x)=x^{\nu+s}e^{-x}\Phi\left(-\alpha_1+\nu+s+1,2\nu+2s+2;2x\right), \tag{20}$$

where $\Phi(a,b,x)$ is the confluent hypergeometric function and $\lambda_{m\ell}$ is the value of separation constant [1] for the two-center system $Z+Z$ with given electron energy E_I and internuclear distance R. Asymptotic behavior at large ξ of the $\Pi^{(1)}_{m\ell}(p_I,\xi)$ solutions leads to the normalization condition for coefficients h_s:

$$\sum_{s=-\infty}^{\infty}h_s\frac{\Gamma\left(2s+2\nu+2\right)}{2^{s+\nu}\Gamma\left(s+\nu+1-\tilde{\alpha}\right)}=1. \tag{21}$$

The procedure for calculation of the acceptable values $\nu=\nu_{m\ell}(p_I)$ (which ensure convergence of the expansion (19)) is described in [11, 12].

4 Exchange interaction of hydrogen-like molecular ion with a nucleus

Results obtained above can be used for study of the many problems of atomic theory and, in particular, of the problems of slow ion-molecules collision. Consider the following charge-exchange reaction:

$$eZZ+Z_1\to eZ_1+Z+Z \tag{22}$$

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

$$\triangle(\vec{Q})=\int_S d\vec{S}\left[\Psi^*_I\vec{\nabla}\Psi_{II}-\Psi^*_{II}\vec{\nabla}\Psi_I\right]. \tag{23}$$

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

$$\begin{aligned}\triangle(L,\beta)=&\frac{Z_1^{3/2}2^{Z_1/\alpha_2+1/2}}{n^2(n-1)!}\bar{A}(\beta)\\&\times\left(\frac{Z_1}{n}\right)^{n-1}L^{n+\frac{2Z}{\alpha_2}-1}\exp\left[-\frac{L}{2}\left(\alpha_2+\frac{Z_1}{n}\right)-\frac{1}{2}\left(\frac{Z_1}{\alpha_2}+\frac{2nZ}{Z_1}\right)\right].\end{aligned} \tag{24}$$

The coefficient $\bar{A}(\beta)$ is related to the normalization constant of asymptotic wave function of eZZ system; $\alpha_2=\sqrt{-2E^{(0)}_{II}(R)}$, $E^{(0)}_{II}(R)$ is the energy of molecular ion eZZ, and n is a principal quantum number of the state described by Ψ_I wave function. Obtained result for matrix element of exchange interaction (24) usually used for calculation of the total cross-sections of the one-electron transition at low energy ion-molecule collision [9].

Acknowledgements

This work was partially supported by INTAS grant No. 99-01326.

[1] Komarov I.V., Ponomarev L.I. and Slavyanov S.Yu., Spheroidal and Coulomb spheroidal functions, Moscow, Nauka, 1976.

[2] Kereselidze T.M., Mourad H.A. and Tzulukidze M.F., Electron in the field of three Coulomb centres: asymptotic solutions, *J. Phys. B: At. Mol. Opt. Phys.*, 1992, V.25, 2957–2968.

[3] Kereselidze T.M., Diabatic molecular orbital correlation for electron in the field of three Coulomb centers, *Zh. Eksp. Teor. Fiz.*, 1989, V.96, N 2, 543–551.

[4] Coulson C.A. and Joseph A., Constant of the motion for the two-centre Kepler problem, *Int. J. Quant. Chem.*, 1967, V.1, 337–347.

[5] Roy S., Suggestive approximate dynamical symmetry of an electron moving in the field of manystationary nuclei, *J. Math. Phys.*, 1970, V.11, N 9, 2931–2935.

[6] Landau L.D. and Lifshitz E.M., Quantum mechanics: non-relativistic theory, Oxford, New York, Pergamon Press, 1977.

[7] Bateman H. and Erdelyi A., Higher transcendental functions, New York, McGraw-Hill, 1953.

[8] Bates D.R. and Reid R.H.G., Electronic eigenenergies of the hydrogen molecular ion, *Adv. At. Mol. Phys.*, 1968, V.4, 13–35.

[9] Chibisov M.I. and Janev R.K., Asymptotic exchange interaction in ion-atom systems, *Physics Reports*, 1988, V.166, N 1, 1–87.

[10] Khoma M.V. and Lazur V.Yu., Green's function of the model two-centre quantum-mechanical problem, *J. Phys. Stud.*, 2002, V.6, N 1, 60–73.

[11] Leaver E.W., Solutions to a generalized spheroidal wave equation: Teukolsky's equations in general relativity, and the two-center problem in molecular quantum mechanics, *J. Math. Phys.*, 1985, V.27, N 5, 1238–1265.

[12] Liu J.W., Analytical solution to the generalized spheroidal wave equation and the Green's function of one-electron diatomic molecules, *J. Math. Phys.*, 1992, V.33, N 12, 4026–4036.