INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **35** (2002) 1–17 PII: S0953-4075(02)23271-X

The quantum mechanical two-Coulomb-centre problem in the Dirac equation framework

O K Reity, V Yu Lazur and A V Katernoha

Department of Theoretical Physics, Uzhgorod National University, Voloshina Street 32, Uzhgorod 88000, Ukraine

E-mail: lazur@univ.uzhgorod.ua

Received 19 March 2001, in final form 12 September 2001
Published 19 December 2001
Online at stacks.iop.org/JPhysB/35/1

Abstract

The asymptotic expansions (at small and large internuclear distances R) of the eigenvalues (potential curves) $E(R)$ of the two-Coulomb-centre problem are obtained. The Dirac equation with an axially symmetrical potential, not allowing complete separation of variables, is solved analytically by the Wentzel–Kramers–Brillouin approach and boundary-layer method. In the framework of this scheme, the relativistic two-Coulomb-centre wavefunction is constructed. The first two terms of the asymptotic (at large internuclear distance) behaviour of the exchange interaction potential for an ion with an atom are calculated.

1. Introduction

At the present time a severe asymmetry exists in the developments of the theories of nonrelativistic and relativistic quantum mechanical problems of two Coulomb centres (the so-called Z_1eZ_2 problems). Numerous effective asymptotic and numerical methods of solving the two-Coulomb-centre problem in Schrödinger equation theory (see, for instance, [1] and references therein) can be compared against only few examples of the consideration of the same problem in Dirac equation theory within various approximations [2–10] (the Galerkin method, diagonalization, the variational method, perturbation theory, Furry–Sommerfeld–Maue approximation). This situation is a surprising example of inertia in a theoretical field in the face of the deficiency of experimental data for heavy and superheavy quasi-molecular systems due to the difficulties in construction of sources of multiply charged ions and formation of beams of rather slow particles.

Also, with the recent construction of powerful accelerators of highly charged ions in many laboratories [11–13], the need for a consistent Dirac theory of the quantum mechanical Z_1eZ_2 problem has become more and more urgent in different fields of physics. Previously, this problem was addressed, basically, in the theory of supercritical atoms for the description of

effects of spontaneous and enforced creation of positrons in a supercritical field of a quasi-atom formed at slow collisions of heavy ions with a total atomic number $Z_1 + Z_2 > 173$. This problem was first considered by Gershtein and Zel'dovich [14] and was studied in [15–18] (for later work see, for instance, [12, 19, 20] and references therein), though this (retrospective) list may be incomplete. Note that the intensive experimental investigation of the processes of positron generation at slow collisions of heavy ions carried out in recent years can highly effectively complement our knowledge about the vacuum shell of the supercritical atom and also verifies the status of quantum electrodynamics in the range of strong external fields [3–14, 17], provided that the theory of these processes is developed correspondingly. In view of the expected applications of Z_1eZ_2 problem formalism, the main interest was focused on the lower-potential curves of the Z_1eZ_2 system with total charge of the two nuclei, $Z = Z_1 + Z_2$, exceeding the critical value, $Z_{cr} \cong 173$, at intercentre distances of the order of the critical value R_{cr} [17] (the model of a united atom). Recently [21], this problem was used in a model approximation in investigations of elementary processes of collisions (excitation, charge exchange, ionization) of multiply charged ions. Thus the relativistic problem was considered in an asymptotic limit, when the internuclear distance is larger than the Compton wavelength of an electron. The prospects of application of the relativistic model in the theory of collisions became especially significant in connection with the recent communications [11] appearing from a group of physicists working at the ion accelerator at the Lawrence Laboratory (Berkeley, USA), who had obtained and detected H-like and He-like uranium ions (U^{91+} and U^{90+}) with energies below 100 eV per unit charge. At such values of the electric charge, relativistic and radiative effects are not small corrections, and fundamentally determine the orders of spectral characteristics. Here the approach based on the Breit–Pauli Hamiltonian clearly becomes inapplicable, and employing modern methods of relativistic quantum mechanics and quantum electrodynamics becomes necessary. This problem can be solved only by comparison of the results of energy structure calculations with experimental data.

Another application of the relativistic problem approach in the theory of collisions is more traditional, and is reduced to using the model functions of a continuous spectrum for the analysis of the scattering of relativistic electrons on heavy diatomic molecules [9, 10, 21, 22].

The difficulty in considering the problem consists in the fact that the Dirac equation with the potential of two Coulomb centres does not permit complete separation of variables in any orthogonal system of coordinates and, thus, one has to deal with first-order partial differential equations. This greatly complicates the whole problem of finding the electron wavefunction and potential curves. Unfortunately, solving this system of differential equations numerically is a rather complicated and onerous task [6, 8, 23], requiring rather complicated calculations for each specific Z_1eZ_2 system. This renders it necessary to create and investigate approximative methods of solving this problem, which are based on clear physical ideas and well-elaborated mathematical devices, and have a clear area of application. It is expedient to begin the development of such methods from the limiting cases of small and large internuclear distances R.

In the present paper we determine the energy and the wavefunctions of an electron for two asymptotic cases: when the distance R between the Coulomb centres is rather small or rather large. To determine asymptotic solutions of the Z_1eZ_2 problem in these cases, one can use different types of expansion and various methods for their calculation (WKB method, perturbation theory, etc).

The main aim of this article is the elaboration of a new approach to mathematical problems that arise in solving the relativistic Z_1eZ_2 problem at large internuclear distances. The asymptotic expansions for the energy of the Z_1eZ_2 system at $R \gg 1$ are divided into two classes. The first class is that of the clear power series determined by the region

of electron localization near the atom eZ_1 or eZ_2. This part of the interaction can be calculated using perturbation theory (see section 2). We concentrate our attention on the second class that represents the exchange part of the interaction, which is determined by the region of large distances of the electron from its own atom. As a suitable method for calculating the wavefunctions and exchange interaction, we propose to employ a quasi-classical approach. This approach is the relativistic generalization of the well-known Fock–Leontovich method [24], elaborated for diffraction problems, and allows us to calculate the exchange splitting of potential curves in a double potential well, when binding energies have the same order as $m_e c^2$. The main ideas and principles of this method can be found in [24, 25].

The paper is organized as follows. In section 2, the method of constructing the asymptotic expansions of the energy of the Z_1eZ_2 system at small and large internuclear distances R is proposed. For this we use the scheme of perturbation theory, which does not require the separation of variables. As a result of the calculations performed, the asymptotic expressions for the energy levels of the Z_1eZ_2 system are obtained at $R \to 0$ ($R \to \infty$) to within terms $O(R^3)$ ($O(R^{-3})$). In section 3 we analytically solve the Dirac equation with an axially symmetrical potential by the WKB method in the below-barrier range in the vicinity of the potential symmetry axis. In section 4, we employ the approach elaborated to the two-Coulomb-centre problem when the internuclear distances R are large, and obtain the two-Coulomb-centre wavefunction. Using this function, in section 5 we calculate the first two terms of the asymptotic behaviour of the exchange interaction potential of an ion with an atom for the general nonresonance case. In the last section of the paper, we discuss and compare the results obtained with the data from similar nonrelativistic approximations.

2. Asymptotic behaviour of potential curves of the relativistic two-Coulomb-centre problem in the united- and separated-atom limits

When the total charge of the Coulomb centres $Z = Z_1 + Z_2$ is positive and the internuclear distance R tends to zero, it is possible to consider the relativistic Z_1eZ_2 problem within perturbation theory, which does not require the separation of variables. The Dirac Hamiltonian of the Z_1eZ_2 problem is of the form ($m_e = e = \hbar = 1$)

$$\hat{H} = c\vec{\alpha} \cdot \hat{\vec{p}} + c^2\beta + V \qquad V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2} \tag{2.1}$$

where $r_{1,2}$ is the distance between the electron and the corresponding nucleus, $\hat{\vec{p}} = -i\vec{\nabla}$ is the momentum operator, and c is the velocity of light. In the standard representation [27],

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}. \tag{2.2}$$

Here $\vec{\sigma}$ are Pauli matrices, and 0 and I are, respectively, 2×2 zero and identity matrices. Let us represent the complete Hamiltonian of the two-Coulomb-centre problem, $\hat{H}$, by the Hamiltonian of the zero approximation $\hat{H}^{UA}$ and a perturbation $\hat{W}$:

$$\hat{H} = \hat{H}^{UA} + \hat{W}. \tag{2.3}$$

The Dirac Hamiltonian of the united relativistic atom is taken as $\hat{H}^{UA}$:

$$\hat{H}^{UA} = c\vec{\alpha} \cdot \hat{\vec{p}} + c^2\beta - \frac{Z}{r_0} \tag{2.4}$$

where the atom is placed on the z-axis, directed from the centre of Z_1 to the centre Z_2, at the point $z = z_0$:

$$z_0 = \left(-\frac{1}{2} + \frac{Z_2}{Z}\right) R = \left(\frac{1}{2} - \frac{Z_1}{Z}\right) R. \tag{2.5}$$

The point z_0 is at the centre of the electric charges, because it divides the internuclear distance into two segments:

$$R_1 = \frac{Z_2}{Z}R \qquad R_2 = \frac{Z_1}{Z}R. \tag{2.6}$$

We consider a spherical system of coordinates r_0, θ_0, φ_0: the origin is at the point $(0, 0, z_0)$ and the angle θ_0 is measured from the z-axis.

Now we construct the unperturbed wavefunction of a united atom. The eigenvalues of the operator $\hat{H}^{UA}$ are characterized by spherical quantum numbers n, j, l, m, where n is the principal quantum number, j and l are the total electron and orbital angular moments, respectively, m is the projection of j onto the internuclear axis z. For the given j and l there are two types of solution, distinguished by a parity $P = (-1)^l$—instead of which we shall use the orbital moment $l = j \pm 1/2$. For continuous approach of nuclei ($R \to 0$), the solutions of the Dirac equation with the potential of two Coulomb centres should tend to the respective solution of the spherically symmetric Coulomb problem. Therefore in the Z_1eZ_2 problem it is also necessary to distinguish two types of potential curve and two types of solution of the Dirac equation, which for continuous approach of nuclei Z_1 and Z_2 transform into the states with $l = j + 1/2$ and $j - 1/2$ for the united atom with the nuclear charge $Z = Z_1 + Z_2$. The eigenfunctions of the operator $\hat{H}^{UA}$ for both types are represented in the form [27]

$$\Psi^{UA}_{njlm}(\vec{r}_0) = \begin{pmatrix} f(r_0)\Omega_{jlm}(\theta_0, \varphi_0) \\ (-1)^{\frac{1+l-l'}{2}} g(r_0)\Omega_{jl'm}(\theta_0, \varphi_0) \end{pmatrix} \qquad l = j \pm \tfrac{1}{2} \qquad l' = 2j - l. \tag{2.7}$$

The radial functions f and g, respectively, are the large and small components of the Dirac bispinor wavefunctions [27]:

$$\left.\begin{matrix} f \\ g \end{matrix}\right\} = \pm\frac{\sqrt{\Gamma(2\gamma + n' + 1)}}{\Gamma(2\gamma + 1)\sqrt{n'!}}\sqrt{\frac{1 \pm \varepsilon}{4N(N - \chi)}}\left(\frac{2Z}{N}\right)^{3/2} \mathrm{e}^{-\frac{Zr_0}{N}}\left(\frac{2Zr_0}{N}\right)^{\gamma - 1}$$
$$\times\left[(N - \aleph)F\left(-n', 2\gamma + 1, \frac{2Zr_0}{N}\right) \mp n'F\left(-n' + 1, 2\gamma + 1, \frac{2Zr_0}{N}\right)\right] \tag{2.8}$$

where

$$n' = n - j - \tfrac{1}{2} \qquad \aleph = (-1)^{k-l}k \qquad k = j + \tfrac{1}{2} \tag{2.9a}$$

$$N = \sqrt{n^2 - 2n'(k - \gamma)} \qquad \gamma = \sqrt{k^2 - (\alpha_0 Z)^2} \qquad \varepsilon = \left[1 + \left(\frac{\alpha_0 Z}{n' + \gamma}\right)^2\right]^{-1/2}. \tag{2.9b}$$

Here $\alpha_0 = 1/c \approx 1/137$ is the fine-structure constant. The eigenvalues of the operator $\hat{H}^{UA}$ are determined by the well-known Bohr–Sommerfeld formula [27]:

$$E^{UA}_{nj} = \varepsilon c^2 = \frac{c^2}{\sqrt{1 + \left(\frac{\alpha_0 Z}{n' + \gamma}\right)^2}}. \tag{2.10}$$

Since the spectrum of the operator $\hat{H}^{UA}$ is degenerated for l and m, for application of perturbation theory first of all it is necessary to construct exact functions of the zero approximation, for which the matrix of the perturbation operator $\hat{W}$ is diagonal. We can show that the matrix $\left\| W^{njl'm'}_{njlm} \right\|$ of the perturbation operator will be diagonal for the functions of united atom (2.7)–(2.9), if z_0 is determined by the relation (2.5). Now we determine the matrix elements of the perturbation operator of the system:

$$\hat{W} = \frac{Z}{r_0} - \frac{Z_1}{\left|\vec{r}_0 + \vec{R}_1\right|} - \frac{Z_2}{\left|\vec{r}_0 - \vec{R}_2\right|}. \tag{2.11}$$

For this purpose we use the expansion of $\hat{W}$ in Legendre polynomials:

$$\hat{W} = \frac{Z}{r_0} - \left\{ \begin{array}{l} Z_1 \sum_{l=0}^{\infty} (-1)^l R_1^l r_0^{-l-1} P_l(\cos\theta_0),\ r_0 > \left|\vec{R}_1\right| \\ Z_1 \sum_{l=0}^{\infty} (-1)^l R_1^{-l-1} r_0^l P_l(\cos\theta_0),\ r_0 < \left|\vec{R}_1\right| \end{array} \right\} - \left\{ \begin{array}{l} Z_2 \sum_{l=0}^{\infty} R_2^l r_0^{-l-1} P_l(\cos\theta_0),\ r_0 > \left|\vec{R}_2\right| \\ Z_2 \sum_{l=0}^{\infty} R_2^{-l-1} r_0^l P_l(\cos\theta_0),\ r_0 < \left|\vec{R}_2\right| \end{array} \right\}. \tag{2.12}$$

The coefficient of $r_0^{-2} P_1$ for $r_0 > \max\left\{\left|\vec{R}_1\right|, \left|\vec{R}_2\right|\right\}$ is equal to $Z_2 R_2 - Z_1 R_1$ and, according to equation (2.6), this is equal to zero. The estimates of all radial and angular integrals made with functions (2.7)–(2.9) show that at $R \to 0$ the matrix $\|W_{njlm}^{njl'm'}\|$ is diagonal with respect to each group of mutually degenerate states, i.e.

$$W_{njlm}^{njl'm'} = \int \left(\Psi_{njlm}^{UA}(\vec{r}_0)\right)^{+} \hat{W} \Psi_{njl'm'}^{UA}(\vec{r}_0)\, \mathrm{d}\vec{r}_0 = \delta_{ll'}\delta_{mm'}\left[W_{njlm}^{njl'm'}\right]_2 + \mathrm{O}(R^3). \tag{2.13}$$

The leading term $[W_{njlm}^{njl'm'}]_2$ of the expansion of the diagonal matrix element of $\hat{W}$ is determined by the expansion (2.12) for $r_0 \rangle \max\left\{\left|\vec{R}_1\right|, \left|\vec{R}_2\right|\right\}$, in which the integration over r_0 is carried out from the zero point:

$$\begin{aligned} \left[W_{njlm}^{njl'm'}\right]_2 &= -\left(Z_1 R_1^2 + Z_2 R_2^2\right) \int \left|\Psi_{njlm}^{UA}(\vec{r}_0)\right| r_0^{-3} P_2(\cos\theta_0)\, \mathrm{d}\vec{r}_0 \\ &= \frac{Z_1 Z_2}{2N^3} \frac{[3m^2 - j(j+1)]}{j(j+1)} \frac{[3\varepsilon\aleph(\varepsilon\aleph - 1) - \gamma^2 + 1](ZR)^2}{\gamma(\gamma^2 - 1)(4\gamma^2 - 1)}. \end{aligned} \tag{2.14}$$

The formulae (2.10), (2.14) determine the two first terms of the expansion in small R of a total energy (which includes the rest energy of an electron) of the $Z_1 e Z_2$ system:

$$E_{njlm}(Z_1, Z_2, R) = \varepsilon c^2 + \left[W_{njlm}^{njlm}\right]_2 \qquad l = j \pm 1/2. \tag{2.15}$$

Proceeding in (2.14) to the nonrelativistic limit ($\alpha_0 \to 0$) we arrive at the result, which can be achieved on the basis of the Breit–Pauli equation. The formulae obtained have the compact form

$$\left[\bar{W}_{njlm}^{njlm}\right] = \lim_{\alpha_0 \to 0} \left[W_{njlm}^{njlm}\right]_2 = Z_1 Z_2 \frac{[3m^2 - j(j+1)](2\aleph - 1)(\aleph - 1)(ZR)^2}{n^3 j^2 (j+1)^2 (2j-1)(2j+1)(2j+3)}. \tag{2.16}$$

For $j = 1/2$ one should take $m = j$ in (2.16), then reduce by $(2j - 1)$ and take $j = 1/2$. The calculated result is given by

$$\left[\bar{W}_{n\frac{1}{2}0\frac{1}{2}}^{n\frac{1}{2}0\frac{1}{2}}\right] = \frac{2}{3n^3} Z_1 Z_2 (ZR)^2. \tag{2.17}$$

Equation (2.17) coincides with the expression obtained in the nonrelativistic case [1] for the states with $l = 0$.

We have compared (see figure 1) the binding energies of some bound states of the Pb–Pb system calculated using the asymptotic formula (2.15) with results of the paper [8]. The difference ∼5% is connected with the finite extent of the Pb nuclei in [8].

To estimate the contribution of the relativistic effects in potential curves in the united-atom limit, we consider the relation $Q1(Z_1, R) = E_{\mathrm{bin}}/E_{\mathrm{bin}}^{(n)}$ (figure 2) between the relativistic ($E_{\mathrm{bin}} = (E_{njlm}^2 - c^4)/(2c^2)$ (see (2.15))) and nonrelativistic ($E_{\mathrm{bin}}^{(n)}$) [1] expressions for the binding energy, when $Z_1 = Z_2$.

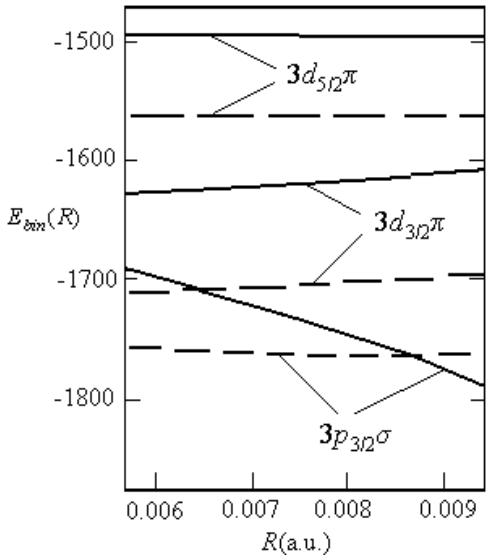

Figure 1. The binding energies of some bound states of the Pb–Pb system obtained in this paper (full curves) and in [8] (dashed curves).

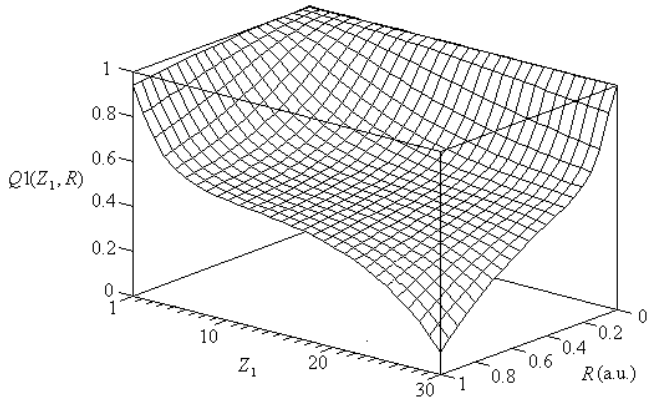

Figure 2. The relative contribution $Q1(Z_1, R)$ of the relativistic effects to the binding energy in the resonance case for the $2P_{3/2}\sigma$ state.

Now we shall determine the energy $E(R)$ and the wavefunctions $\Psi(\vec{r}; R)$ of an electron in the asymptotic region when the distance R between the Coulomb centres is large. This distance should be so large that the quantum penetrability of the potential barrier separating the atomic particles is much smaller than unity. When atoms 1 and 2 are different, the eigenvalues (potential curves) $E(R)$ of the two-Coulomb-centre problem, dependent on the internuclear distance R as a parameter, are divided into two classes in the asymptotic limit $R \to \infty$: $E_{\rm I}$ and $E_{\rm II}$—potential curves that, for $R \to \infty$, transform into the energy levels of isolated atoms 1 and 2, respectively. The criterion of applicability of the expansion given below is the requirement that the wavefunction of the Ψ_1-state, for instance, of atom 1, should not be strongly perturbed by the other particle. The distortion of the dependence of this function on the coordinates should be small. This is related to the energy shift of the state induced by the interaction with perturbing particle 2. The external (Coulomb) field of the latter has to be weak compared to the typical intra-atomic fields in order for perturbation theory to be applicable.

Having placed the origin at the position of the hydrogen-like ion eZ_1 with nuclear charge Z_1 and run the polar axis along the R-axis, we represent a complete Hamiltonian of the two-Coulomb-centre problem (2.1) by a Hamiltonian of the zero-approximation $\hat{H}^{SA}$ and perturbation $\hat{V}$:

$$\hat{H} = \hat{H}^{SA} + \hat{V}. \tag{2.18}$$

The Hamiltonian of the relativistic hydrogen-like atom with charge Z_1 is taken as $\hat{H}^{SA}$:

$$\hat{H}^{SA} = c\vec{\alpha} \cdot \hat{\vec{p}} + c^2\beta - \frac{Z_1}{r_1}. \tag{2.19}$$

At large internuclear distances the operator of the interaction between the electron and the Z_2-nucleus $\hat{V} = -Z_2/|\vec{R} - \vec{r}|$ can be considered as a small perturbation of the Hamiltonian $\hat{H}^{SA}$. In a spherical coordinate system, the wavefunctions $\Psi^{SA}_{n_1 j_1 l_1 m_1}(\vec{r}_1)$ of the eZ_1 atom, belonging to a discrete energy spectrum, are represented by formulae which are obtained from (2.7)–(2.9) by making the substitutions $Z \to Z_1$, $\vec{r}_0 \to \vec{r}_1 = (r_1, \theta_1, \varphi_1)$, $\varepsilon, \aleph, N, \gamma \to \varepsilon_1, \aleph_1, N_1, \gamma_1$, and (the set of quantum numbers) $n, j, l, m \to n_1, j_1, l_1, m_1$. By means of the same substitutions, the eigenvalues E_1 of $\hat{H}^{SA}$ are obtained from (2.10).

We can write the following expression for the operator $\hat{V}$:

$$\hat{V} = -\begin{cases} Z_2 \displaystyle\sum_{s=0}^{\infty} R^s r_1^{-s-1} P_s(\cos\theta_1) & r_1 > \left|\vec{R}\right| \\ Z_2 \displaystyle\sum_{s=0}^{\infty} R^{-s-1} r_1^s P_s(\cos\theta_1) & r_1 < \left|\vec{R}\right|. \end{cases} \tag{2.20}$$

For the wavefunctions of the zero-order approximation we can write

$$\Psi_0 = \sum_{l'_1 m'_1} C^{l_1 m_1}_{l'_1 m'_1}(R) \Psi^{SA}_{n_1 j_1 l'_1 m'_1}(\vec{r}_1). \tag{2.21}$$

By substituting expansion (2.21) into the Dirac equation with Hamiltonian $\hat{H}$, multiplying by $\Psi^{SA^+}_{n_1 j_1 l_1 m_1}(\vec{r}_1)$, and integrating over the electron coordinates, we find expansion coefficients given by

$$\sum_{l'_1 m'_1} \left[\left(E_{\mathrm{I}} - E^{SA}_{n_1 j_1}\right) \delta_{l_1 l'_1} \delta_{m_1 m'_1} - V^{n_1 j_1 l'_1 m'_1}_{n_1 j_1 l_1 m_1} \right] C^{l_1 m_1}_{l'_1 m'_1}(R) = 0. \tag{2.22}$$

Here $V^{n_1 j_1 l'_1 m'_1}_{n_1 j_1 l_1 m_1}$ are the matrix elements of the perturbation operator (2.20):

$$V^{n_1 j_1 l'_1 m'_1}_{n_1 j_1 l_1 m_1} = \int \Psi^{SA^+}_{n_1 j_1 l_1 m_1}(\vec{r}_1) \hat{V} \Psi^{SA}_{n_1 j_1 l'_1 m'_1}(\vec{r}_1)\, \mathrm{d}r_1 \tag{2.23}$$

where the integral over r_1 is taken from zero, using the expansion (2.20) for $r_1 < |\vec{R}|$. In the basis of the spherical functions $\Psi^{SA}_{n_1 j_1 l_1 m_1}(\vec{r}_1)$, the first term of the perturbation operator (2.20) is diagonal with respect to each group of mutually degenerate states and the second term has nonzero off-diagonal matrix elements

$$V^{n_1 j_1 j_1 + 1/2 m_1}_{n_1 j_1 j_1 + 1/2 m_1} = V^{n_1 j_1 j_1 - 1/2 m_1}_{n_1 j_1 j_1 - 1/2 m_1} = -\frac{Z_2}{R} \tag{2.24}$$

$$V^{n_1 j_1 j_1 - 1/2 m_1}_{n_1 j_1 j_1 + 1/2 m_1} = -V^{n_1 j_1 j_1 + 1/2 m_1}_{n_1 j_1 j_1 - 1/2 m_1} = \frac{3\mathrm{i}}{4} \sqrt{N_1^2 - \aleph_1^2}\, \frac{(n'_1 + \gamma_1) m_1}{j_1(j_1+1)} \frac{Z_2}{Z_1 R^2}. \tag{2.25}$$

By using matrix elements (2.24), (2.25) and solving the equation obtained from the condition that the determinant in (2.22) should be equal to zero, we obtain the expression for the energy terms in first-order perturbation theory:

$$E_{\mathrm{I}}(R) = \varepsilon_1 c^2 - \frac{Z_2}{R} + \frac{Z_2 \xi_1}{R^2} + \mathrm{O}(R^{-3}) \tag{2.26}$$

where

$$\xi_1 = \pm\frac{3}{4}\sqrt{N_1^2 - \aleph_1^2}\,\frac{(n_1' + \gamma_1)m_1}{j_1(j_1+1)Z_1}. \tag{2.27}$$

'$\pm$' corresponds to the state with $l_1 = j_1 \pm 1/2$. Formula (2.26) gives the expansion in the multipoles of the energy of the electrostatic interaction of the atom eZ_1 with the distant point charge Z_2. The last term in (2.26) coincides with the Stark shift of level in the weak electric field with the intensity $-Z_2/R^2$ [28].

The asymptotic expansion of the potential curve E_{II} is obtained from E_{I} by making the substitutions $\varepsilon_1 \to \varepsilon_2$, $Z_{1,2} \to Z_{2,1}$, $n_1, \aleph_1, j_1, m_1 \to n_2, \aleph_2, j_2, m_2$.

3. Quasi-classical approximation for the Dirac equation with an axially symmetrical potential

Consider an axially symmetrical problem, where two classically allowed regions are separated by a potential barrier. Then the direction of the most probable tunnelling is the potential symmetry axis z, the axis ρ is perpendicular to z, φ is a azimuth angle.

For the bispinor Ψ the stationary Dirac equation is of the form ($m_{\mathrm{e}} = e = \hbar = 1$)

$$\begin{aligned} c\vec{\sigma}\,\vec{p}\xi &= (E - V + c^2)\eta \\ c\vec{\sigma}\,\vec{p}\eta &= (E - V - c^2)\xi \end{aligned} \qquad \Psi = \begin{pmatrix} \xi \\ \eta \end{pmatrix} \tag{3.1}$$

where $\vec{p} = -\mathrm{i}\vec{\nabla}$ is the momentum operator, c is the velocity of light, $\vec{\sigma}$ are the Pauli matrices, E is the electron energy including c^2, $V = V(z, \rho)$ is the effective potential energy of the interaction of the electron with the external field not allowing complete separation of variables in the Dirac equation.

By inserting the first equation of (3.1) into the second one and using the substitution

$$\xi = (W^+)^{1/2}\Phi \qquad W^{\pm} = E - V \pm c^2 \tag{3.2}$$

we arrive at the matrix equation

$$\Delta\Phi + k^2\Phi = 0 \qquad k^2 = \frac{1}{\hbar^2 c^2}\left[(E-V)^2 - c^4\right] - \frac{\Delta V}{2W^+} - \frac{3}{4}\left(\frac{\vec{\nabla}V}{W^+}\right) + \frac{\mathrm{i}}{W^+}\vec{\sigma}\left[\vec{\nabla}V, \vec{\nabla}\right]. \tag{3.3}$$

Here we have restored in an obvious way the reduced Planck constant $\hbar$. Since the potential V is axially symmetrical, the Hamiltonian commutes with the operator of projection of total angular momentum of the electron onto a potential symmetry axis z, and equation (3.3) permits separation of a variable φ. For this purpose we represent the solution of (3.3) in the form

$$\Phi = \begin{pmatrix} F_1(z, \rho)\exp\left[\mathrm{i}(m - 1/2)\varphi\right] \\ F_2(z, \rho)\exp\left[\mathrm{i}(m + 1/2)\varphi\right] \end{pmatrix} \tag{3.4}$$

where $F_{1,2}$ are new unknown functions, m is the projection of the total angular momentum of the electron onto a potential symmetry axis z. By substituting (3.4) into (3.3), we obtain the matrix differential equation

$$(\Delta + \partial)F = (\hbar^{-2}q^2 + \gamma)F \qquad F = \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} \qquad q = \frac{1}{c}\left[c^4 - (E-V)^2\right]^{1/2} \tag{3.5}$$

$$\partial = \frac{1}{W^+}\left(\frac{\partial V}{\partial\rho}\frac{\partial}{\partial z} - \frac{\partial V}{\partial z}\frac{\partial}{\partial\rho}\right)\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \qquad \gamma = \begin{pmatrix} a_{m-1/2} & b_{m+1/2} \\ b_{m-1/2} & a_{-m-1/2} \end{pmatrix} \tag{3.6}$$

$$a_\mu(z, \rho) = \frac{\mu^2}{\rho^2} + \frac{1}{W^+}\left[\frac{\mu}{\rho}\frac{\partial V}{\partial\rho} + \frac{\Delta V}{2} + \frac{3}{4}\frac{\left(\vec{\nabla}V\right)^2}{W^+}\right] \qquad b_\mu(z, \rho) = -\frac{\mu}{\rho W^+}\frac{\partial V}{\partial z}. \tag{3.7}$$

We seek a solution of equation (3.5) in the form of a WKB expansion:

$$F = \varphi \exp(\hbar^{-1} S) \qquad \varphi = \sum_{n=0}^{\infty} \hbar^n \varphi^{(n)}. \tag{3.8}$$

Here $\varphi^{(n)}$ is a bispinor (the upper component corresponds to the function F_1, the lower to F_2). Having substituted F, determined by (3.8), into (3.5) and equated to zero the coefficients of each power of $\hbar$, we arrive at the hierarchy of equations

$$\left(\vec{\nabla} S\right)^2 - q^2 = 0 \tag{3.9}$$

$$2\vec{\nabla} S \cdot \vec{\nabla}\varphi^{(0)} + \Delta S \varphi^{(0)} + \hat{\partial} S \varphi^{(0)} = 0 \tag{3.10}$$

$$2\vec{\nabla} \cdot S\vec{\nabla}\varphi^{(n+1)} + \Delta S \varphi^{(n+1)} + \hat{\partial} S \varphi^{(n+1)} + \Delta\varphi^{(n)} + \hat{\partial}\varphi^{(n)} - \gamma\varphi^{(n)} = 0 \tag{3.11}$$

where $n = 0, 1, 2, \ldots$. Unfortunately, equations (3.9)–(3.11), similarly to the initial equation (3.1), do not permit exact separation of variables. In order to solve this problem, we use the idea of the boundary-layer method.

We seek the solutions of equations (3.9)–(3.11) in the below-barrier range, where, unlike for the classically allowed range, the wavefunction is often localized in the vicinity of the most probable tunnelling direction, which substantially simplifies the whole problem: it is natural to expand all the quantities in equations (3.9)–(3.11), including the solutions, in the vicinity of the z-axis.

Consider equation (3.9) and assume that

$$q^2(z, \rho) = q_0^2(z) + \sum_{k=1}^{\infty} Q_k(z)\rho^{2k} \qquad q_0^2(z) = q^2(z, 0) \qquad Q_k = \frac{1}{(2k)!}\frac{\partial^{2k} q^2(z, 0)}{\partial\rho^{2k}}. \tag{3.12}$$

According to the above speculation, the solution of equation (3.9) can also be represented in the form of an expansion in powers of coordinate the ρ:

$$S(z, \rho) = \sum_{n=0}^{\infty} S_n(z)\rho^{2n}. \tag{3.13}$$

By inserting (3.13) into (3.9) and equating to zero the coefficients of each power of ρ, we obtain the recurrent system of first-order differential equations

$$(S_0')^2 - q_0^2 = 0 \tag{3.14}$$

$$2S_0'S_1' + 4S_1^2 - Q_1 = 0 \tag{3.15}$$

$$2S_0'S_2' + 16S_1S_2 + (S_1')^2 - Q_2 = 0 \tag{3.16}$$

and so on, from which the values S_n ($n = 0, 1, 2, \ldots$) are successively determined. Here the prime means the derivative with respect to z. Note that if in the expansion (3.13) the coefficients of negative and odd powers of ρ are taken into account, after substitution of (3.13) into (3.9) they will be equal to zero. A similar situation will arise later for the functions $\varphi^{(n)}$. We shall consider the first three equations of the given system. It is easy to show that the solution of equation (3.14) is

$$S_0 = \pm \int q_0 \, \mathrm{d}z + C_0 \qquad C_0 = \text{constant}. \tag{3.17}$$

Since in the below-barrier range the wavefunction should decrease exponentially with increasing z, in (3.17) we select the negative sign.

Equation (3.15) is the nonlinear Riccati differential equation and are not solvable analytically in the general case. However, by making the substitution

$$S_1 = \frac{q_0(z)}{2}\left(\frac{1}{2}\frac{q_0'(z)}{q_0(z)} - \frac{\sigma'(z)}{\sigma(z)}\right) \tag{3.18}$$

one can proceed from (3.15) to the linear second-order equation

$$\sigma'' + \left[\frac{1}{4}\left(\frac{q_0'}{q_0}\right)^2 - \frac{1}{2}\frac{q_0''}{q_0} - \frac{Q_1}{q_0^2}\right]\sigma = 0. \tag{3.19}$$

Note that in the nonrelativistic limit $c \to \infty$ equation (3.19) is transformed into a similar equation, obtained by Sumetsky [29] by solving the Schrödinger equation with an axially symmetrical potential by the parabolic equation method.

Taking into account (3.17) and (3.18), we obtain the solution of the ordinary first-order differential equation (3.16):

$$S_2 = \frac{q_0^2}{2\sigma^4}\left\{\int \frac{\sigma^4}{q_0^3}\left[(S_1')^2 - Q_2\right]\mathrm{d}z + C_1\right\} \qquad C_1 = \text{constant}. \tag{3.20}$$

The solutions of the equations (3.10), (3.11) are sought in the form

$$\varphi^{(n)}(z,\rho) = \begin{pmatrix} \rho^{|m-1/2|}\sum_{k=0}^{\infty}\varphi_{1k}^{(n)}(z)\,\rho^{2k} \\ \rho^{|m+1/2|}\sum_{k=0}^{\infty}\varphi_{2k}^{(n)}(z)\,\rho^{2k} \end{pmatrix}. \tag{3.21}$$

By substituting (3.21) into the corresponding equations and equating to zero the coefficients of each power of ρ in the each of the two components, we obtain a system of ordinary first-order differential equations, which is solvable. For $m > 0$ the solutions are expressed as integrals:

$$\varphi_{10}^{(0)} = \frac{C_2^+}{\sigma}\left(\frac{\sqrt{q_0}}{\sigma}\right)^{p-2} \qquad \varphi_{20}^{(0)} = \frac{C_2^{(+)}}{\sigma}\left(\frac{\sqrt{q_0}}{\sigma}\right)^{p-1}\left[\int \frac{\sigma A_1(z)}{q_0\sqrt{q_0}}\,\mathrm{d}z + C_3^+\right] \tag{3.22}$$

$$\varphi_{11}^{(0)} = -\frac{1}{\sigma}\left(\frac{\sqrt{q_0}}{\sigma}\right)^{p}\left\{\int \frac{1}{\sqrt{q_0}}\left(\frac{\sigma}{\sqrt{q_0}}\right)^{p+1} \times\left[S_1'\varphi_{10}^{(0)'} + \tfrac{1}{2}S_1''\varphi_{10}^{(0)} + 4pS_2\varphi_{10}^{(0)} + A_1(z)\varphi_{20}^{(0)}\right]\mathrm{d}z + C_4^+\right\} \tag{3.23}$$

$$\varphi_{21}^{(0)} = -\frac{1}{\sigma}\left(\frac{\sqrt{q_0}}{\sigma}\right)^{p+1}\left\{\int \frac{1}{\sqrt{q_0}}\left(\frac{\sigma}{\sqrt{q_0}}\right)^{p+2}\left[S_1'\varphi_{20}^{(0)'} + \frac{1}{2}S_1''\varphi_{20}^{(0)} + 4(p+1)S_2\varphi_{20}^{(0)} - A_1(z)\left(\varphi_{11}^{(0)} + \frac{V_1}{W_0^+}\varphi_{10}^{(0)}\right) + A_2(z)\varphi_{10}^{(0)}\right]\mathrm{d}z + C_5^+\right\} \tag{3.24}$$

$$\varphi_{10}^{(1)} = \frac{1}{\sigma}\left(\frac{\sqrt{q_0}}{\sigma}\right)^{p-2}\left\{\int \frac{1}{2\sqrt{q_0}}\left(\frac{\sigma}{\sqrt{q_0}}\right)^{p-1} \times\left[\varphi_{10}^{(0)''} - B_1(z)\varphi_{10}^{(0)} + 2(p-1)\left(2\varphi_{11}^{(0)} + \frac{V_0'\varphi_{20}^{(0)}}{W_0^+}\right)\right]\mathrm{d}z + C_6^+\right\} \tag{3.25}$$

$$\varphi_{20}^{(1)} = \frac{1}{\sigma}\left(\frac{\sqrt{q_0}}{\sigma}\right)^{p-1}\left\{\int \frac{1}{2\sqrt{q_0}}\left(\frac{\sigma}{\sqrt{q_0}}\right)^{p}\left[\varphi_{20}^{(0)''} - B_2(z)\varphi_{20}^{(0)} + 4p\varphi_{21}^{(0)'} + \frac{2V_1}{W_0^+}\varphi_{10}^{(0)'} - \frac{2V_0'}{W_0^+}\varphi_{11}^{(0)} + 2A_1(z)\varphi_{10}^{(1)}\right]\mathrm{d}z + C_7^+\right\} \tag{3.26}$$

where

$$A_1(z) = \left(S_1V_0' - q_0V_1\right)/W_0^+ \qquad A_2(z) = \left(S_1'V_1 - S_1V_1' + 2q_0V_2 - 2S_2V_0'\right)/W_0^+ \tag{3.27}$$

$$B^{\pm}(z)=\frac{1}{W_0^+}\left[(1\pm 2|m|)\,V_1+\frac{1}{2}V_0''+\frac{3}{4}\frac{\left(V_0'\right)^2}{W_0^+}\right]\qquad p=|m|+3/2 \tag{3.28}$$

$$V_0(z)=V(z,0)\qquad V_k(z)=\frac{1}{(2k)!}\frac{\partial^{2k}V(z,0)}{\partial\rho^{2k}}\qquad W_0^{\pm}=W^{\pm}(z,0). \tag{3.29}$$

For $m<0$ these solutions are obtained from (3.22)–(3.26) by making the replacements $\varphi_{1i}^{(j)}\to\varphi_{2i}^{(j)}$, $\varphi_{2i}^{(j)}\to-\varphi_{1i}^{(j)}$, $C_k^+\to C_k^-$ $(i,j=0,1,k=2,3,\ldots,7)$.

Note that if it is necessary to find the first l terms of the expansion (3.13), then in each function $\varphi^{(n)}$ of (3.21) one has to take into account the first $l-n-1$ $(n=0,1,\ldots,l-2)$ terms of the expansion in ρ. Here, we take into account the first three terms of (3.13), two terms of $\varphi^{(0)}$, and the leading term of $\varphi^{(1)}$.

The lower component η of Ψ is obtained from the upper one ξ by the operation

$$\xi\underset{W^+\to W^-}{\longrightarrow}\eta. \tag{3.30}$$

Thus we have obtained the solution Ψ of equation (3.1) within constants C_0, C_1, $C_k^{\pm}$ $(k=2,3,\ldots,7)$. To determine these, one should take a certain potential and normalize the wavefunction. In the next section, we shall consider the potential of two Coulomb centres.

4. The relativistic two-Coulomb-centre wavefunction in the below-barrier region

We now find the wavefunction of the Dirac electron placed in a field of two fixed nuclei with charges Z_1 and Z_2, separated by the large distance R. The energy $E_{\rm I}(R)$ in the first approximation of perturbation theory is found in section 2 (see (2.26)).

We search for a solution of the Dirac equation with potential (2.1) under the boundary condition

$$\Psi_{\rm I}\underset{z\ll R}{\longrightarrow}\Psi_1 \tag{4.1}$$

$$\Psi_1=\begin{pmatrix} f_1(r_1)\Omega_{j_1l_1m_1}(\vec{n}_1)\\ (-1)^{\frac{1+l_1-l_1'}{2}}g_1(r_1)\Omega_{j_1l_1'm_1}(\vec{n}_1)\end{pmatrix}\qquad \begin{matrix} l_1=j_1\pm 1/2,\\ l_1'=2j_1-l_1\end{matrix}\qquad \vec{n}_1=\frac{\vec{r}_1}{r_1} \tag{4.2}$$

which means that when the electron approaches atom 1, the two-Coulomb-centre function $\Psi_{\rm I}$ tends to the unperturbed atomic wavefunction Ψ_1 (see section 2). For the radial wavefunctions f_1 and g_1, equation (2.8), of the discrete spectrum of the Dirac electron, it is worthwhile to take the asymptotic expansions

$$\left.\begin{matrix} f_1\\ g_1\end{matrix}\right\}=\pm\sqrt{1\pm\varepsilon_1^2}A_1r_1^{\varepsilon_1Z_1/\lambda_1-1}{\rm e}^{-\lambda_1r_1}\left[1+B_1^{(\pm)}r_1^{-1}+\cdots\right]\qquad r_1\lambda_1^2\gg Z_1 \tag{4.3}$$

$$A_1=\lambda_1(2\lambda_1)^{\varepsilon_1Z_1/\lambda_1}\left(\frac{Z_1/\lambda_1-\aleph_1}{2Z_1\Gamma(\varepsilon_1Z_1/\lambda_1-\gamma_1+1)\Gamma(\varepsilon_1Z_1/\lambda_1+\gamma_1+1)}\right)^{1/2} \tag{4.4}$$

$$B_1^{(\pm)}=\frac{1}{2\lambda_1}\left(\aleph_1+\frac{Z_1}{\lambda_1}\right)\left(\aleph_1\pm 1-\frac{Z_1}{\lambda_1}\right)\qquad \lambda_1=c\sqrt{1-\varepsilon_1^2} \tag{4.5}$$

where '+' corresponds to f_1, '−' corresponds to g_1. To determine all constants in $\Psi_{\rm I}$ we expand Ψ_1 in powers of ρ and match $\Psi_{\rm I}$ and Ψ_1 at $Z_1/\lambda_1^2\ll z\ll R$.

Let us find the wavefunctions $\Psi_{\rm I}$ in the internuclear region $(z\sim R)$ within $\mathrm{O}(R^{-2})$. For this we apply the general scheme elaborated in section 2 to the Dirac equation with the potential (2.1). Using (2.1), (3.5), (3.12), (4.1), calculating the integral (3.17), and neglecting quantities of the order of R^{-2}, we obtain

$$S_0=-\lambda_{\rm I}z-\frac{Z_1^2}{2\lambda_{\rm I}^3z}+\frac{Z_2^2z}{2\lambda_{\rm I}^3R(R-z)}+\frac{\varepsilon_1Z_1}{\lambda_1}\ln z-\frac{\varepsilon_1Z_2}{\lambda_1}\left(1+\frac{Z_1-Z_2}{\varepsilon_1\lambda_1^2R}\right)\ln\left(1-\frac{z}{R}\right) \tag{4.6}$$

where $\lambda_{\rm I}=c\sqrt{1-\varepsilon_{\rm I}^2}$, $\varepsilon_{\rm I}=E_{\rm I}/c^2$.

Equation (3.19) with the potential (2.1) is solved by iteration. The solution σ is represented in the form

$$\sigma = \sigma_0(1 + \sigma_1 + \sigma_2 + \cdots). \tag{4.7}$$

Here $\sigma_0 = z\sqrt{q_0}$ is the solution of the equation (3.19) with the model spherically symmetrical potential $V = -Z_1/r_1 - Z_2/(R - r_1)$:

$$\sigma_0'' + \left[\frac{1}{4}\left(\frac{q_0'}{q_0}\right)^2 - \frac{1}{2}\frac{q_0''}{q_0} - \frac{1}{z}\frac{q_0'}{q_0}\right]\sigma_0 = 0. \tag{4.8}$$

Corrections $\sigma_1, \sigma_2, \ldots$ are quantities of the order of $R^{-1}, R^{-2}, \ldots$ which take into account the weak dependence of the potential (2.1) in the vicinity of the internuclear axis $\vec{R}$ on the spherical angle θ_1. By substituting (4.7) into (3.19) and equating to zero the terms of each order of R^{-1}, we obtain the hierarchy of equations

$$\sigma_1'' + 2\frac{\sigma_0'}{\sigma_0}\sigma_1' + H(z) = 0 \tag{4.9a}$$

$$\sigma_{n+1}'' + 2\frac{\sigma_0'}{\sigma_0}\sigma_{n+1}' + H(z)\sigma_n = 0 \qquad n = 1, 2, \ldots \tag{4.9b}$$

$$H(z) = \frac{E_1 - V_0(z)}{c^2 q_0^2}\frac{Z_2 R}{z(R - z)^3}. \tag{4.10}$$

In order to determine $\sigma(z)$ within $O(R^{-2})$, one needs to find σ_1. By solving equation (4.9a) with the boundary condition (4.1), we arrive at the expression

$$\sigma = z\sqrt{q_0}\left[1 + \frac{\varepsilon_1 Z_2}{2\lambda_1^2}\frac{z}{R(R - z)} + O(R^{-2})\right]. \tag{4.11}$$

By inserting (4.11) into (3.19), we obtain the formula

$$S_1 = -\frac{q_0}{2z}\left[1 + \frac{\varepsilon_1 Z_2}{2\lambda_1^2}\frac{z}{(R - z)^2}\right]. \tag{4.12}$$

Having substituted (4.12) into (3.20) and calculated the integral, taking account of the boundary condition (4.1), we find the leading term of the asymptotic behaviour of S_2:

$$S_2 = \frac{\lambda_I}{8z^3}. \tag{4.13}$$

Taking into account the above-determined quantities and restricting ourselves to the first two terms of the asymptotic expansion of $\varphi^{(0)}$ (in the small parameter R^{-1}) and the leading term of the asymptotic expansion of $\varphi^{(1)}$ (a similar procedure was followed for the bispinor η), we obtain the expressions

$$\varphi^{\pm} = \frac{\sqrt{\lambda_1}A_1}{c\sigma}\begin{pmatrix} K^{\pm}\left(\frac{\rho\sqrt{q_0}}{\sigma}\right)^{|m_1|-1/2}\left[1 + L^{\pm}\left(\frac{\rho}{z}\right)^2 + \delta_{-m_1|m_1|}U^{\pm}(z) + \omega^{\pm}(z)\right] \\ M^{\pm}\left(\frac{\rho\sqrt{q_0}}{\sigma}\right)^{|m_1|+1/2}\left[1 + N^{\pm}\left(\frac{\rho}{z}\right)^2 + \delta_{m_1|m_1|}U^{\pm}(z) + \omega^{\pm}(z)\right] \end{pmatrix} \tag{4.14}$$

$$K^{\pm} = (-P^{\pm})^{\frac{1-\operatorname{sgn} m_1}{2}}Q^{\pm} \qquad M^{\pm} = \left(P^{\pm}\right)^{\frac{1+\operatorname{sgn} m_1}{2}}Q^{\pm} \qquad P^{\pm} = \frac{|m_1| \pm \aleph_1 + 1/2}{2|m_1| + 1} \tag{4.15}$$

$$Q^{\pm} = \left[(-1)^{m_1+1/2}\operatorname{sgn}\aleph_1\right]^{\frac{1+\operatorname{sgn} m_1}{2}}(\pm 1)^{\frac{1-\operatorname{sgn} m_1}{2}}\frac{i^{j_1 \pm \frac{\operatorname{sgn}\aleph_1}{2}}}{2^{|m_1|-1/2}\,(|m_1| - 1/2)!}\sqrt{\frac{(j_1 + |m_1|)!}{4\pi\,(j_1 - |m_1|)!}} \tag{4.16}$$

$$L^{\pm} = -\frac{1}{2}\left[|m_1| + 1 - \frac{\operatorname{sgn} m_1}{2} + \frac{\left(\aleph_1 \pm \frac{1}{2}\right)^2 - \left(|m_1| + \frac{1-\operatorname{sgn} m_1}{2}\right)^2}{2|m_1| + 2 - \operatorname{sgn} m_1}\right] \tag{4.17}$$

$$L^{\pm} \underset{\operatorname{sgn} m_1 \to -\operatorname{sgn} m_1}{\longrightarrow} N^{\pm} \qquad U^{\pm}(z) = -\frac{Z_2}{4W_0^{\pm}P^{\pm}}\frac{z(2R - z)}{R(R - z)^2} \qquad \omega^{\pm}(z) = \frac{\aleph_1(\aleph_1 \pm 1)}{2\lambda_1 z} \tag{4.18}$$

where '+' corresponds to the bispinor ξ, '$-$' corresponds to the bispinor η. Thus, we obtain the asymptotic solutions of the Dirac equation with the potential of two Coulomb centres in the internuclear region within $O(R^{-2})$. The term $\omega^{\pm}(z)$ corresponds to centrifugal energy. The approximation given does not take into account terms related to the spin–orbit and spin–spin interactions which are of the order of R^{-2}, though the general scheme elaborated in section 3 allows us to find the higher approximations. The wavefunction Ψ_{II}, corresponding to the potential curve E_{II}-term is obtained from Ψ_I by making the substitutions $\varepsilon_{I,1} \to \varepsilon_{II,2}$, $Z_{1,2} \to Z_{2,1}, z \to R - z, n_1, \aleph_1, j_1, m_1 \to n_2, \aleph_2, j_2, m_2$.

5. The asymptotic method of calculating the exchange interaction potential for an ion with an atom

In a collision of slow bare nuclei of different elements with hydrogen-like atoms, the transition of an electron from one nucleus to the other occurs at large distances between the colliding particles. The value of the energy splitting between the terms of the system, in the range of their pseudocrossing, determines the nonadiabatic transition probability. Now we demonstrate the asymptotic method for calculating the exchange splitting of potential curves of the Z_1eZ_2 problem.

Consider the interaction of atom 1 with atom 2, whose energy level for binding with the electron is close to that of atom 1. In other words, the Dirac energy levels E_1 and E_2 for potentials $-Z_1/r_1$ and $-Z_2/r_2$ happen to be close to each other. The energy difference $|E_1 - E_2|$ is assumed to be small compared to the energy differences between these and all other levels of the fine structure of any of the interacting atoms.

Making use of the general solutions of the Dirac equation in the case under consideration, it is seen that in order to construct stationary functions, one should utilize the linear combinations

$$\Psi_{\pm} = C_1\Psi_I + C_2\Psi_{II} \tag{5.1}$$

where the functions $\Psi_{I,II}$ were constructed in section 4. The coefficients $C_{1,2}$ of the wavefunction can be determined with the help of auxiliary conditions, which are the conditions for obtaining stationary wavefunctions. For this purpose, in this case of two levels $E_{1,2}$ that are close in energy, the two-level approximation can be applied. Since the 'atomic' functions $\Psi_{I,II}$ constructed in section 4 are orthogonal to each other, $C_{1,2}$ can be determined by solutions of the two-level secular equation [28]:

$$\begin{aligned} C_{1,\pm} &= \left\{ \frac{H_{12}}{2|H_{12}|} \left(1 \pm \frac{\tilde{\chi}}{\left(|\tilde{\chi}|^2 + |\Delta|^2\right)^{1/2}} \right) \right\}^{1/2} \\ C_{2,\pm} &= \pm \left\{ \frac{H_{21}}{2|H_{21}|} \left(1 \mp \frac{\tilde{\chi}}{\left(|\tilde{\chi}|^2 + |\Delta|^2\right)^{1/2}} \right) \right\}^{1/2} \\ \tilde{\chi} &= H_{11} - H_{22} = \langle \Psi_I | \hat{H} | \Psi_I \rangle - \langle \Psi_{II} | \hat{H} | \Psi_{II} \rangle \qquad \Delta = 2\langle \Psi_I | \hat{H} | \Psi_{II} \rangle \end{aligned} \tag{5.2}$$

where $H_{ik} = \langle \Psi_i | \hat{H} | \Psi_k \rangle$ are matrix elements of the Dirac Hamiltonian (2.1) connecting the functions $\Psi_{I,II}$. The perturbed energy levels and the difference between them are

$$E_{\pm} = \left(H_{11} + H_{22} \pm \sqrt{|\tilde{\chi}|^2 + |\Delta|^2} \right) \Big/ 2 \qquad E_+ - E_- = \sqrt{|\tilde{\chi}|^2 + |\Delta|^2} \tag{5.3}$$

respectively. The formulae for the two-level approximation (5.2), (5.3) uniquely describe both the resonance and nonresonance cases. At asymptotically large internuclear distances R, the diagonal matrix elements H_{11} and H_{22} of the Hamiltonian (2.1) are close to the nonperturbed eigenenergies: $H_{11} \cong E_1$, $H_{22} \cong E_2$. The nonresonance case considered in the previous

section implies that the condition $|H_{11} - H_{22}| \cong |E_1 - E_2| \gg |H_{12}|$ is valid. As a result, formulae (5.2) are simplified:

$$C_{1,+} \cong 1 - |H_{12}|^2/\left(2|H_{11} - H_{22}|^2\right) + \cdots \qquad C_{2,+} \cong |H_{12}/(H_{11} - H_{22})| + \cdots \ll 1. \quad (5.4)$$

Hence, it can be seen that the function Ψ_+ determined by formula (5.1) is close to Ψ_{I}, whereas the admixture of state Ψ_{II} to it is exponentially small ($C_{2,+} \ll 1$). For Ψ_-, we have a similar result on taking the lower indices in (5.2).

For calculating the exchange splitting of the potential curves $\Delta E(R)$ in the relativistic two-Coulomb-centre problem, we use the representation for $\Delta E(R)$ as the integral over the surface S conditionally separating the domains where the electron is in Ψ_{I}- and Ψ_{II}-states [30]:

$$\Delta E = \Delta = 2\mathrm{i}c \int_S \mathrm{d}\vec{S} \cdot (\Psi_{\mathrm{II}}^+ \vec{\alpha} \Psi_{\mathrm{I}}). \quad (5.5)$$

Here the surface element $\mathrm{d}\vec{S}$ is directed from atom 1 to atom 2. This formula is valid only in the vicinity of the point R_p of the pseudocrossing of the potential curves E_{I} and E_{II}, when the electron transits from level E_1 of atom 1 to the closely spaced level E_2 of the other atom. From the condition $E_{\mathrm{I}} \cong E_{\mathrm{II}}$ we find that

$$R_p = \frac{Z_2 - Z_1 + \sqrt{(Z_2 - Z_1)^2 - 4\,(E_1 - E_2)\,(Z_2\xi_1 - Z_1\xi_2)}}{2\,(E_1 - E_2)}. \quad (5.6)$$

Note that representation (5.5) is a relativistic analogue of the well-known Firsov formula [31] for $\Delta E(R)$ in the nonrelativistic case. The mid-plane between the two nuclei is taken as the surface S. Having calculated the integral (5.5) by the stationary-phase method [32], we arrive at the following expression for the first two terms of the asymptotic expansion of $\Delta E(R)$:

$$\Delta E = \frac{2A_1A_2}{(|m| - 1/2)!(\lambda_1 + \lambda_2)^{|m|-1/2}} D_{j_1 j_2 m} R^{\frac{\varepsilon_1 Z_1}{\lambda_1} + \frac{\varepsilon_2 Z_2}{\lambda_2} - |m| - 1/2} \times \exp\left\{-\frac{R\,(\lambda_1 + \lambda_2)}{2} - \frac{1}{2}\left(\frac{\varepsilon_1 Z_2}{\lambda_1} + \frac{\varepsilon_2 Z_1}{\lambda_2}\right)\right\}\left[1 + \frac{I}{R}\right] \quad (5.7)$$

$$D_{j_1 j_2 m} = \sqrt{\frac{(j_1 + |m|)!\,(j_2 + |m|)!}{(j_1 - |m|)!\,(j_2 - |m|)!}} \qquad m = m_1 = m_2 \quad (5.8)$$

$$I = \frac{1}{\lambda_1 + \lambda_2}\left[\aleph_1^2 + \aleph_2^2 - (|m| + 1/2)^2 - \frac{\aleph_1\aleph_2}{|m| + 1/2}\right] + \frac{|m| + 1/2}{2}\left(\frac{\varepsilon_1 Z_2}{\lambda_1^2} + \frac{\varepsilon_2 Z_1}{\lambda_2^2}\right) + \frac{\varepsilon_1 Z_2 \xi_1}{2\lambda_1} + \frac{\varepsilon_2 Z_1 \xi_2}{2\lambda_2} - \frac{Z_1^2}{4\lambda_1^3} - \frac{Z_2^2}{4\lambda_2^3}. \quad (5.9)$$

In the resonance case, when the parameters of the two atoms coincide ($Z_1 = Z_2$, $\varepsilon_1 = \varepsilon_2$, $\lambda_1 = \lambda_2$, $n_1 = n_2$, $j_1 = j_2$, $\aleph_1 = \aleph_2$), expression (5.7) determines the exchange splitting between the gerade and ungerade potential curves of the system (Z, e, Z).

For applicability of WKB method the internuclear distances should be greater than R_0, where the potential barrier disappears:

$$R_0 = \frac{Z_1 + 2\sqrt{Z_1 Z_2} + \sqrt{(Z_1 + 2\sqrt{Z_1 Z_2})^2 + 4(c^2 - E_1)Z_2\xi_1}}{2(c^2 - E_1)}. \quad (5.10)$$

We stress, however, that analytic expressions derived for the asymptotic expansion of various splittings and shifts of the potential curves can sometimes be used in the region of internuclear distances that are smaller than those given by the formal criteria of applicability of the asymptotic expansions. Qualitatively, this can be explained by the fact that asymptotic

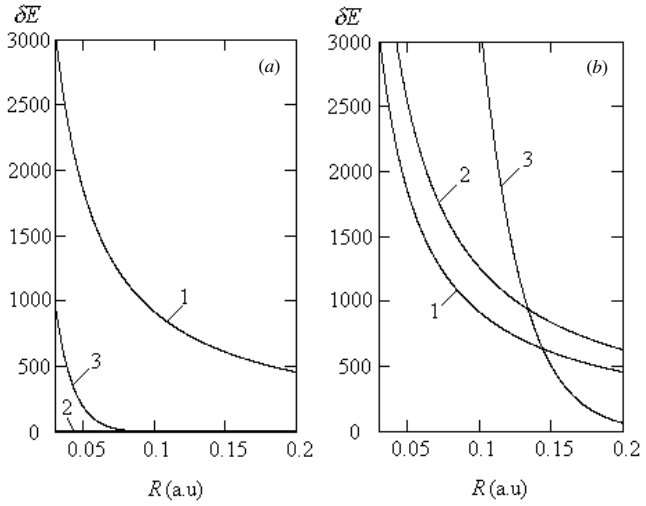

Figure 3. Absolute values of the contributions of the monopole (1), dipole (2), and exchange (3) terms in the resonance case $Z_1 = Z_2 = 92$ corresponding to (*a*) the $1S_{1/2}\sigma$ and (*b*) the $2P_{1/2}\sigma$ states.

solutions of the two-Coulomb-centre problem (even the first term of the wavefunction expansion in powers of R^{-1}, up to sufficiently small R) retain the basic analytic properties of the exact solution [1] rather well, thus reproducing the results of variational calculations [33]. These properties are also conserved for other quantities computed with these functions.

Therefore, at $R \gg 1$ the energy shift is defined by the formula

$$\delta E = E_- - E_1 = -\frac{Z_2}{R} + \frac{Z_2\xi_1}{R^2} - \frac{\Delta E}{2}. \tag{5.11}$$

The dependence of the absolute values of various terms on the rhs of (5.11) on R is shown in figure 3 in the resonance case for uranium.

6. Conclusions

Here we briefly summarize the results obtained in this paper. In this work we have obtained analytical quasi-classical solutions of the Dirac equation with an axially symmetrical potential, which does not permit complete separation of variables. Our method allows the spin–orbit and spin–spin interactions to be taken into account. We have obtained the relativistic two-Coulomb-centre wavefunction of an electron and calculated the exchange splitting of potential curves which are expressed through the known characteristics of the separated atoms: charges of atomic cores Z_1 and Z_2, asymptotic coefficients A_1 and A_2, binding energies $\lambda_{1,2}^2/2$, and quantum numbers of the electron in the states of atoms considered (ions). The expression obtained for ΔE, equation (5.7), and a similar nonrelativistic expression for $\Delta E^{(n)}$ [1] for the exchange splitting between symmetrical (g) and unsymmetrical (u) potential curves of the (Z, e, Z) system can be conveniently written as a ratio $Q2(Z, R) = \Delta E/\Delta E^{(n)}$. The function $Q2(Z, R)$ shows (figure 4) that the role of relativistic effects increases with increasing charge Z and internuclear distance R, and the relative contribution of the relativistic effects amounts to about 50%, even at $Z = 45$. By means of perturbation theory we have calculated the asymptotic expansion of the eigenvalues (potential curves) $E(R)$ of the two-Coulomb-centre problem in the limits of united ($R \to 0$) and separated ($R \to \infty$) atoms with the precision $O(R^3)$ and $O(R^{-3})$, respectively.

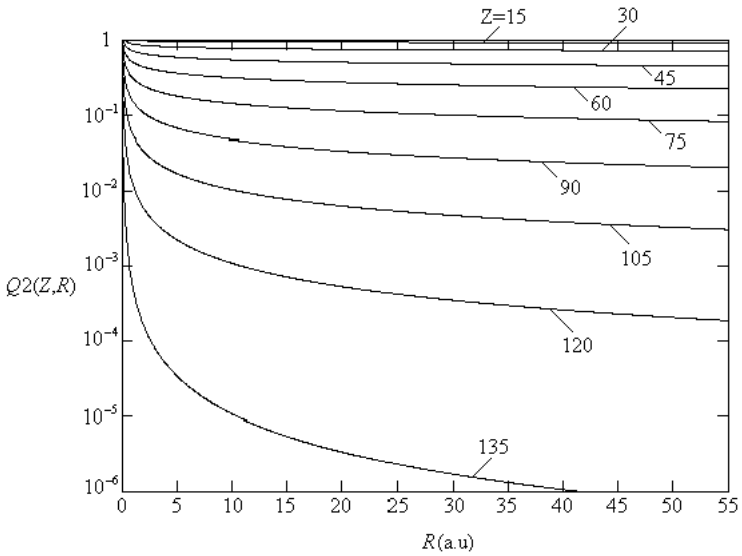

Figure 4. The relative contribution $Q2(Z, R)$ of the relativistic effects in the exchange splitting of potential curves in the resonance case for the $1S_{1/2}\sigma$ state.

Note that asymptotic expressions obtained here for the potential curves are applicable under the condition that the quantities γ, $\gamma_{1,2}$ are purely real, which corresponds to the range of applicability of the Dirac equation solutions for the point charge.

Acknowledgment

The work was partially supported by INTAS (no 99-01326).

References

[1] Komarov I V, Ponomarev L I and Slavyanov S Yu 1976 *Spheroidal and Coulomb Spheroidal Functions* (Moscow: Nauka) (in Russian)
[2] Luke S K, Hunter G, McFachran R P and Cohen M 1969 *J. Chem. Phys.* **50** 1644
[3] Popov V S 1970 *Pis. Zh. Eksp. Teor. Fiz.* **11** 254
[4] Popov V S 1970 *Zh. Eksp. Teor. Fiz.* **59** 965
[5] Popov V S 1970 *Yad. Fiz.* **12** 429
[6] Lyul'ka V A 1976 *Theor. Math. Phys.* **28** 737
[7] Mukherjee S and Chandel S S 1978 *J. Phys. A: Math. Gen.* **11** 1257
[8] Muller B and Greiner W 1976 *Z. Naturf.* a **31** 1
Rafelski J and Muller B 1976 *Phys. Lett.* B **65** 205
[9] Wietschorke K-H *et al* 1987 *Phys. Rev.* A **36** 377
[10] Chauhan H K and Raina P K 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 5889
[11] Gould H and Munger C T 1987 *Phys. Rev.* **36** 476
[12] Pokotilovsky Yu N 1993 *Part. Nucl.* **24** 5
[13] Martinson I 1989 *Rep. Prog. Phys.* **52** 157
[14] Gershtein S S and Zel'dovich Ya B 1969 *Zh. Eksp. Teor. Fiz.* **57** 654
Gershtein S S and Zel'dovich Ya B 1969 *Nuovo Cimento* **1** 835
[15] Pieper W and Greiner W 1969 *Z. Phys.* **218** 327
[16] Voronkov V V and Kolesnikov N N 1960 *Zh. Eksp. Teor. Fiz.* **39** 189
[17] Popov V S, Voskresensky D N, Eletsky V L and Mur V D 1979 *Zh. Eksp. Teor. Fiz.* **76** 431

[18] Soffel M, Müller B and Greiner W 1982 *Phys. Rep.* C **85** 51
[19] Grib A A, Mamaev S G and Mostapenko V M 1988 *Vacuum Quantum Effects in Strong Fields* (Moscow: Energoatomizdat)
[20] Leinberger U *et al* 1998 *Eur. Phys. J.* A **1** 249
[21] Janev R K, Presnyakov L P and Shevelko V P 1985 *Physics of Highly Charged Ions* (Berlin: Springer)
[22] Schuch R 1985 *Collision Physics with Highly Stripped Slow Ions Proc. 4th Int. Conf. on Physics of Electronic and Atomic Collisions* (Stenford: Stenford University) (invited papers)
[23] Marinov M S and Popov V S 1973 *Zh. Eksp. Teor. Fiz.* **65** 2141
Lizin V I, Marinov M S and Popov V S 1976 *Phys. Lett.* B **65** 205
[24] Leontovich M A and Fock V A 1946 *Zh. Eksp. Teor. Fiz.* **16** 647
[25] Babich V M and Kirpichnikova N Y 1985 *The Boundary-Layer Method in the Diffraction Problems* (Berlin: Springer)
[26] Smirnov B M 1973 *Asymptotic Methods in the Theory of Atomic Collisions* (Moscow: Atomizdat) (in Russian)
[27] Berestetskii V B, Lifshitz E M and Pitaevskii L P 1982 *Quantum Electrodynamics* (Oxford: Pergamon)
[28] Zapryagaev S A, Manakov N L and Pal'chikov V G 1985 *Theory of Multiply Charged One- and Two-Electron Ions* (Moscow: Energoatomizdat) (in Russian)
[29] Sumetsky M Yu 1980 *Teor. Mat. Fiz.* **45** 64
[30] Gorvat P P, Lazur V Yu, Migalina S I, Shuba I M and Yanev R K 1996 *Theor. Math. Phys.* **109** 1423
[31] Firsov O B 1951 *Zh. Eksp. Teor. Fiz.* **21** 1001
[32] Demkov Yu N 1973 *Proc. 8th Int. Conf. on Physics of Electronic and Atomic Collisions* (Belgrade: Institute of Physics) *(Invited Lectures and Progress Reports)* p 26
[33] Chibisov M I and Janev R K 1988 *Phys. Rep.* **166** 1