THE RELATIVISTIC TWO-COULOMB-CENTER PROBLEM AT SMALL AND LARGE INTERCENTER SEPARATIONS[1]

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By perturbation theory, the asymptotic behaviours of the adiabatic energy terms of the relativistic two-Coulomb-center problem are constructed in the limiting cases of small and large inter-nuclear distances R. On the basis of the boundary-layer method of Fock—Leontovich, the relativistic version of the quasiclassical approximation is elaborated for the Dirac equation with an arbitrary axially symmetric potential, unpermitting the complete separation of variables. The quasiclassical asymptotics of the two-Coulomb-center wave function of a Dirac electron is found in a classically forbidden region. The first two terms of the asymptotic (at large inter-nuclear distance) expansion of the exchange interaction potential of an ion with an atom are calculated.

Introduction

At the present time, a severe asymmetry exists in the development of the theories of non-relativistic and relativistic quantum-mechanical problems of two Coulomb centers (the so-called Z_1eZ_2 problem). Numerous effective asymptotic and numerical methods of solving the two-Coulomb-center problem for the Schrodinger equation (see, for instance, [1 and references therein]) can be opposed only by seldom examples of the consideration of the same problem for the Dirac equation within various approximations [2—5] (the Galerkin method, diagonalization, variational method, perturbation theory, Furry—Sommerfeld—Maue approximation). Such a situation is a surprising example of passivity of the theory under 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.

Besides, with the recent creation of powerful accelerators of highly charged ions in many laboratories [6,7] the need of the consistent Dirac theory of the quantum mechanical problem Z_1eZ_2 is more and more urgent in different fields of physics. Previously, this problem was applied in the theory of supercritical atoms for description of the 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 [8] and in the series of papers of Popov [3,9], though this retrospective list can be incomplete. Note that the intense experimental investigations of the processes of positron generation at slow collisions of heavy ions being carried out in the recent years can essentially complement our knowledge about the vacuum shell of a supercritical atom and verify the status of quantum electrodynamics in the range of strong external fields [3—9], provided that the theory of these processes is equivalently developed.

According to the indicated applications of the Z_1eZ_2 problem, the main interest was attracted by the lower potential curves of the Z_1eZ_2 system with the total charge of both nuclei $Z = Z_1 + Z_2$ exceeding the critical value $Z_{\rm cr} \cong 173$ at the inter-center distances R of the order of the critical value $R_{\rm cr}$ [9] (the model of united atom). Rather recently [10], this problem was used as a model approximation in the investigations of elementary processes of collisions (excitation, charge exchange, ionization) of multiply charged ions. Thus, the relativistic problem was [11] 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 Z_1eZ_2 in the theory of collisions become specially significant in connection with the recent communications [6] appeared from a group of Dr. Gould (Berkeley, USA), who had obtained and detected H- 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 essentially

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determine the orders of spectral characteristics. Here, the approach, based on the Breit—Pauli Hamiltonian, apparently becomes inapplicable, and the necessity of employing the modern methods of relativistic quantum mechanics and quantum electrodynamics arises. This problem can be solved only by comparison of the results of energy structure calculation with the experimental data. Other application of the relativistic problem in the theory of collisions is more traditional and is reduced to using the model functions of a continuous spectrum for the analysis of scattering of relativistic electrons by heavy diatomic molecules [10]. The further references about some other applications of the relativistic Z_1eZ_2 model in atomic and mesoatomic physics can be found in [10], and we should only mark that systematic studies of relativistic effects in atoms and molecules, which often appear rather essential for the explanation of chemical properties of many chemical, especially heavy [12], elements have been started recently. The difficulty in considering the problem consists in the fact that the Dirac equation with the potential of two Coulomb centers does not permit a complete separation of variables in any orthogonal system of coordinates and, thus, one has to deal with first-order partial differential equations. This highly complicates the whole specific problem of finding the electron wave function and potential curves. Unfortunately, the numerical solving of this system of differential equations is a rather complicated and cumbersome problem [4,5,13] requiring rather complicated calculations for each specific system Z_1eZ_2. This causes the necessity of creating and investigating approximate methods of solving this problem, which are based on clear physical ideas and a well-elaborated mathematical device and have a clear area of application. As a suitable method for calculating the wave functions and other quantities in Z_1eZ_2 problem, we propose to employ the relativistic version of the WKB approximation. This approach together with the boundary layer method [14,15], found by M. A. Leontovich and V. A. Fock, allow us to construct the quasiclassical solutions of the Dirac equation with an arbitrary axially symmetric potential, unpermitting the complete separation of variables and to analyze the discrete spectrum of the given problem at large internuclear distances.

The paper is organized as follows. In the first two sections, the method of constructing the asymptotic expansions of the energy of the system Z_1eZ_2 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. In Sec. 3, we analytically solve the Dirac equation with an axially symmetric potential by the WKB method in the below-barrier range in the vicinity of the potential symmetry axis. In Sec. 4, we employ the elaborated approach to the two-Coulomb-center problem, when the internuclear distances R are large, and obtain the two-Coulomb-center wave function. Using this function, we calculate the first two terms of the asymptotic behaviour of the exchange interaction potential of an ion with an atom for the general non-resonance case. In the last section of the paper, we discuss and compare the obtained results with the data of similar non-relativistic approximations.

1. Asymptotic Behaviour of Potential Curves of the Relativistic Z_1eZ_2 Problem at $R \to 0$

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

$$\hat{H} = c\vec{\alpha}\hat{\vec{p}} + c^2\beta - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}, \tag{1}$$

where r_i is the distance between the electron and the corresponding nucleus ($i = 1, 2$); $\hat{\vec{p}} = -i\vec{\nabla}_r$ is the momentum operator, and c is the velocity of light. In the standard representation [16],

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}. \tag{2}$$

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

$$\hat{H} = \hat{H}^{UA} + \hat{W}, \qquad \hat{H}^{UA} = c\vec{\alpha}\hat{\vec{p}} + c^2\beta - \frac{Z}{r_0},$$
$$Z = Z_1 + Z_2. \tag{3}$$

We consider the spherical system of coordinates r_0, θ_0, φ_0, whose origin is at the electric center $(0, 0, z_0)$, and the angle θ_0 is measured from the axis Oz, directed from the center Z_1 to center Z_2. Now we construct the unperturbed wave function of an 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. For the given j and l, there are two types of the solutions, distinguishing by a parity $P = (-1)^l$, instead of which we shall use the orbital moment $l = j \pm 1/2$. At continuous approaching of nuclei ($R \longrightarrow 0$), the solutions of the Dirac equation with the potential of two Coulomb centers should tend to the respective solutions of the spherically symmetric Coulomb problem. Therefore, in the Z_1eZ_2 problem it is also necessary to distinguish two types of potential curves and two types of solutions of the Dirac equation, which at the continuous approaching of the nuclei Z_1 and Z_2 transit into the states with $l = j + 1/2$ and $l = j - 1/2$ for the united atom with the nuclear charge $Z = Z_1 + Z_2$. The explicit form of the eigenfunctions of the operator $\hat{H}^{UA}$ for both types can be found in [16]. Expanding $\hat{W}$ in Legendre polynomials and calculating the elements of the matrix $\left\| W_{njlm}^{njl'm'} \right\|$ to within $O\left(R^3\right)$, we see that it is diagonal with respect to each group of mutually degenerate states $l = j \pm 1/2$ and m. The final formula for the energy of the Z_1eZ_2 system has the form:

$$E_{njlm}(Z_1, Z_2, R) = \varepsilon c^2 + \frac{Z_1 Z_2}{2N^3} \frac{\left[3m^2 - j(j+1)\right]}{j(j+1)} \times$$

$$\times \frac{\left[3\varepsilon\aleph(\varepsilon\aleph - 1) - \gamma^2 + 1\right] \cdot (ZR)^2}{\gamma(\gamma^2 - 1)(4\gamma^2 - 1)} + O\left(R^3\right), \qquad (4)$$

$$\begin{aligned} n' &= n - j - \frac{1}{2}, \qquad \aleph = (-1)^{k-l} k, \\ k &= j + \frac{1}{2}, \qquad l = j \pm 1/2, \end{aligned} \qquad (5)$$

$$\begin{aligned} N &= \sqrt{n^2 - 2n'(k - \gamma)}, \qquad \gamma = \sqrt{k^2 - (\alpha_0 Z)^2}, \\ \varepsilon &= \left[1 + \left(\frac{\alpha_0 Z}{n' + \gamma}\right)^2\right]^{-1/2}. \end{aligned} \qquad (6)$$

Here $\alpha_0 = 1/c \approx 1/137$ is the fine structure constant.

2. Asymptotic Behaviour of Potential Curves of the Relativistic Z_1eZ_2 Problem at $R \to \infty$

Now we shall determine the energy $E(R)$ of an electron in the asymptotic region, when the distance R between the Coulomb centers 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) of the two-Coulomb-center problem, dependent on the internuclear distance R as a parameter, are divided into two classes in the asymptotic limit $R \to \infty$: E_I- and $E_{II}-$ potential curves that, for $R \to \infty$, transform into the energy levels of isolated atoms eZ_1 and eZ_2, respectively. The criterion of the applicability of the below expansion is the requirement that the wave function 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 is considered to be weak compared to the typical intraatomic fields in order the perturbation theory to be applied. Having placed the origin of the spherical coordinate system r_1, θ_1, φ_1 at the position of the hydrogen-like ion eZ_1 with nuclear charge Z_1 and run the polar axis along the $\vec{R}$ axis, we represent the complete Hamiltonian of the two-Coulomb-center problem (1) by the Hamiltonian of the zero-approximation $\hat{H}^{SA}$ and perturbation $\hat{V}$,

$$\hat{H} = \hat{H}^{SA} + \hat{V}. \qquad (7)$$

As $\hat{H}^{SA}$, the Hamiltonian of the relativistic hydrogen-like atom with charge Z_1,

$$\hat{H}^{SA} = c\vec{\alpha}\hat{\vec{p}} + c^2\beta - \frac{Z_1}{r_1}, \qquad (8)$$

is taken. The eigenstates of the operator $\hat{H}^{SA}$ are characterized by the set of quantum numbers n_1, j_1, l_1, m_1. Similarly to the previous case, we expand the perturbation operator $\hat{V} = -Z_2/|\vec{r}_1 - \vec{R}|$ in Legendre polynomials and calculate the matrix $\left\| V_{n_1 j_1 l_1 m_1}^{n_1 j_1 l_1' m_1'} \right\|$ to within the first undisappearing non-diagonal term, inclusively.

Diagonalizing the complete matrix with respect to each group of mutually degenerate states ($l = j \pm 1/2$ and m), in the first-order of perturbation theory, we obtain an analytic expression in the form of the asymptotic (on R^{-1}) expansion:

$$E_I(R) = \varepsilon_1 c^2 - \frac{Z_2}{R} \pm \frac{3}{4}\sqrt{N_1^2 - \aleph_1^2} \frac{(n_1' + \gamma_1) m_1}{j_1(j_1 + 1)} \frac{Z_2}{Z_1 R^2} +$$

$$+ O\left(R^{-3}\right), \qquad (9)$$

where the quantities n_1', $\aleph_1$, k_1, l_1, N_1, γ_1, ε_1 are obtained from (6) by entering index 1, "$\pm$" correspond to the state with $l_1 = j_1 \pm 1/2$. The last term in (9) coincides with the Stark shift of a level in the weak electric field with the intensity $-Z_2/R^2$ [18]. The obtained formulae

can be applied, in particular, for constructing the one-electron relativistic correlation diagrams of heavy quasi-molecules in the region between the limits of united and separated atoms. The asymptotic expansion of the potential curve E_{II} is obtained from E_I by the substitutions $\varepsilon_1 \longrightarrow \varepsilon_2$, $Z_{1,2} \longrightarrow Z_{2,1}$, $n_1, \aleph_1, j_1, m_1 \longrightarrow n_2, \aleph_2, j_2, m_2$.

3. Quasi-classical Approximation for the Dirac Equation with an Axially Symmetric Potential

For the solution of a quantum-mechanical problem, it is often enough to find a wave function not in the whole configurational space, but only in the vicinity of some manifold M of smaller dimensionality, where the wave function is localized. The states described by such wave functions are called "localized". The example of such states is the problem of exchange interaction of atomic particles at large internuclear distances resulting in splitting the potential curves at the point of quasi-crossing. Exchange splitting is known [17] to be mainly determined by the electron distribution region lying in the vicinity of the internuclear axis $\vec{R}$ (M is a straight line). Another example of localized state is the process of tunneling ionization of a hydrogen atom in a rather weak constant electric field when the probability flux is localized in the below-barrier range in the vicinity of the symmetry axis (M is a straight line, too).

In such cases it is natural to expand the potential into the powers of the coordinate perpendicular to M. This allows us to carry out the approximate separation of variables, to find approximate analytic solutions of the obtained system of matrix partial differential equations in the vicinity of the manifold M and to consider the wide range of problems of the theory of slow atomic collisions.

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

For the bispinor $\Psi = \begin{pmatrix} \xi \\ \eta \end{pmatrix}$, the stationary Dirac equation is of the form

$$c\vec{\sigma}\vec{p}\xi = \left(E - V + c^2\right)\eta, \qquad c\vec{\sigma}\vec{p}\eta = \left(E - V - c^2\right)\xi, \tag{10}$$

where $V = V(z,\rho)$ is the effective potential energy of the interaction of the electron with the external field not allowing the complete separation of variables in the Dirac equation. By inserting the first equation of (10) into second one and using the substitution

$$\xi = (W^+)^{1/2}\Phi, \qquad W^{\pm} = E - V \pm c^2, \tag{11}$$

we arrive at the matrix equation

$$\Delta\Phi + k^2\Phi = 0, \tag{12}$$

$$k^2 = \frac{1}{\hbar^2 c^2}\left[(E-V)^2 - c^4\right] - \frac{\Delta V}{2W^+} -$$

$$-\frac{3}{4}\left(\frac{\vec{\nabla}V}{W^+}\right) + \frac{i}{W^+}\vec{\sigma}\left[\vec{\nabla}V, \vec{\nabla}\right]. \tag{13}$$

Since the potential V is axially symmetric, the Hamiltonian commutes with the projection operator of the total angular momentum of the electron onto the potential symmetry axis Oz, and Eq. (12) permits the separation of the variable φ. For this purpose, we represent a solution of (12) in the form

$$\Phi = \begin{pmatrix} F_1(z,\rho)\exp\left[i\left(m - 1/2\right)\varphi\right] \\ F_2(z,\rho)\exp\left[i\left(m + 1/2\right)\varphi\right] \end{pmatrix}, \tag{14}$$

where $F_{1,2}$ are new unknown functions, m is the projection of the total angular momentum of the electron onto the potential symmetry axis z. By substituting (14) in (12), we obtain the matrix differential equation

$$\begin{aligned} (\Delta \; + \; \widehat{\partial})F &= (q^2 + \gamma)F, \\ F \; &= \; \begin{pmatrix} F_1 \\ F_2 \end{pmatrix}, \\ q \; &= \; \frac{1}{c}\left[c^4 - (E-V)^2\right]^{1/2}, \end{aligned} \tag{15}$$

$$\begin{aligned} \widehat{\partial} \; &= \; \frac{1}{W^+}\left(\frac{\partial V}{\partial\rho}\frac{\partial}{\partial z} - \frac{\partial V}{\partial z}\frac{\partial}{\partial\rho}\right)\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \\ \gamma \; &= \; \begin{pmatrix} a_{m-1/2} & b_{m+1/2} \\ b_{m-1/2} & a_{-m-1/2} \end{pmatrix}, \end{aligned} \tag{16}$$

$$\begin{aligned} a_\mu(z,\rho) \; &= \; \frac{\mu^2}{\rho^2} + \frac{1}{W^+}\left[\frac{\mu}{\rho}\frac{\partial V}{\partial\rho} + \frac{\Delta V}{2} + \frac{3}{4}\frac{\left(\vec{\nabla}V\right)^2}{W^+}\right], \\ b_\mu(z,\rho) \; &= \; -\frac{\mu}{\rho W^+}\frac{\partial V}{\partial z}. \end{aligned} \tag{17}$$

Substituting a solution of this equation in the form of the WKB expansion

$$F = \varphi\exp(\hbar^{-1}S), \qquad \varphi = \sum_{n=0}^{\infty}\hbar^n\varphi^{(n)} \tag{18}$$

and equating the coefficients of each power of $\hbar$ to zero, we arrive at the system of the first-order differential equations for the unknown function S and spinor component $\varphi^{(n)}$:

$$(\vec{\nabla}S)^2 - q^2 = 0, \tag{19}$$

$$2\vec{\nabla}S\vec{\nabla}\varphi^{(0)} + \Delta S\varphi^{(0)} + \widehat{\partial}S\varphi^{(0)} = 0, \ldots \tag{20}$$

$$2\vec{\nabla}S\vec{\nabla}\varphi^{(n+1)} + \Delta S\varphi^{(n+1)} + \widehat{\partial}S\varphi^{(n+1)} +$$

$$+\Delta\varphi^{(n)} + \widehat{\partial}\varphi^{(n)} - \gamma\varphi^{(n)} = 0, \tag{21}$$

where $n = 0, 1, 2, \ldots$. Unfortunately, Eq. (19)–(21), similarly to the initial equation (12), do not permit the exact separation of variables. In order to solve this problem, we use the idea of the boundary-layer method. We seek the solutions of (19)–(21) in the below-barrier range, where, contrary to the classically allowed range, the wave function is often localized in the vicinity of the most probable way of tunneling, what essentially simplifies the whole problem. So, it is natural to expand all the quantities in (19)–(21), including the solutions in the vicinity of the axis Oz.

Consider Eq. (19) and assume that

$$q^2(z,\rho) = q_0^2(z) + \sum_{k=1}^{\infty} Q_k(z)\rho^{2k}, \quad q_0^2(z) = q^2(z,0),$$

$$Q_k = \frac{1}{(2k)!}\frac{\partial^{2k}q^2(z,0)}{\partial\rho^{2k}}. \tag{22}$$

According to the above speculations, the solution of (19) is also represented as the expansion in powers of the coordinate ρ:

$$S(z,\rho) = \sum_{n=0}^{\infty} S_n(z)\rho^{2n}. \tag{23}$$

After inserting (23) into (19) and equating the coefficients of each power of ρ to zero, we obtain the recurrent system of ordinary first-order differential equations

$$(S_0')^2 - q_0^2 = 0, \tag{24}$$

$$2S_0'S_1' + 4S_1^2 - Q_1 = 0, \tag{25}$$

$$2S_0'S_2' + 16S_1S_2 + (S_1')^2 - Q_2 = 0, \ldots \tag{26}$$

from which values S_n $(n = 0, 1, 2, \ldots)$ are successively determined. Here, prime means the derivative with respect to z. Note that if, in expansion (19), the coefficients of negative and odd powers of ρ are taken into account, they will be equal to zero after substitution of (23) into (19). The similar situation will repeat later for the functions $\varphi^{(n)}$. All the equations of the obtained system, except for the second one, are easy integrated. Equation (25) is the non-linear Riccati differential equation and, as in the non-relativistic case [19], is not solvable analytically in the general case. However, it is approximately solved, when a small parameter exists in the considered problem (for example, in the Z_1eZ_2 problem considered in the next section, such a parameter will be R^{-1}). The solutions of Eqs. (20), (21) are sought in the form

$$\varphi^{(n)}(z,\rho) = \begin{pmatrix} \rho^{|m-1/2|}\sum\limits_{k=0}^{\infty}\varphi_{1k}^{(n)}(z)\rho^{2k} \\ \rho^{|m+1/2|}\sum\limits_{k=0}^{\infty}\varphi_{2k}^{(n)}(z)\rho^{2k} \end{pmatrix}. \tag{27}$$

By substituting (27) into the corresponding equations and equating the coefficients of each power of ρ in the both components to zero, we obtain the system of ordinary first-order differential equations, whose solutions are expressed by integrals. The lower component η of Ψ is obtained from the upper one ξ by operation $W^+ \to W^-$.

4. Quasi-classical Asymptotics of Two-Coulomb-Center Wave Function and Exchange Splitting of Adiabatic Potential Curves

Find the asymptotics (at $z \sim R \gg 1$) of the wave function of a Dirac electron placed in a field of two fixed nuclei with charges Z_1 and Z_2, separated by the large distance R. We search for a solution of the Dirac equation with the potential

$$V = -\frac{Z_1}{r_1} - \frac{Z_2}{\left|\vec{R} - \vec{r}_1\right|} \tag{28}$$

under the boundary condition $\Psi_I \underset{z\ll R}{\longrightarrow} \Psi_1$, which means that, when the electron approaches the atom Z_1, the two-Coulomb-center function Ψ_I tends to the unperturbed wave function Ψ_1 of the eZ_1 atom. Using the obtained expansions (9) and the general method elaborated in the previous section to the Dirac equation with potential (28), we obtain the following expressions for the sought functions:

$$S_0 = -\lambda_I z - \frac{Z_1^2}{2\lambda_I^3 z} + \frac{Z_2^2 z}{2\lambda_I^3 R(R-z)} + \frac{\varepsilon_1 Z_1}{\lambda_1}\ln z -$$

$$-\frac{\varepsilon_1 Z_2}{\lambda_1}\left(1+\frac{Z_1-Z_2}{\varepsilon_1\lambda_1^2 R}\right)\ln\left(1-\frac{z}{R}\right), \tag{29}$$

$$S_1=-\frac{q_0}{2z}\left[1+\frac{\varepsilon_I Z_2}{2\lambda_I^2}\frac{z}{(R-z)^2}\right], \tag{30}$$

$$S_2=\frac{\lambda_1}{8z^3}, \tag{30}$$

$$\varepsilon_{1,I}=\frac{E_{1,I}}{c^2},\quad \lambda_{1,I}=c\sqrt{1-\varepsilon_{1,I}^2}, \tag{31}$$

$$\varphi=\frac{1}{\sigma}\begin{pmatrix} K_1^{\pm}\left(\dfrac{\rho\sqrt{q_0}}{\sigma}\right)^{|m_1-1/2|}\left[1+L_1^{\pm}\cdot\left(\dfrac{\rho}{z}\right)^2+U_1^{\pm}(z)\right] \\ K_2^{\pm}\left(\dfrac{\rho\sqrt{q_0}}{\sigma}\right)^{|m_1+1/2|}\left[1+L_2^{\pm}\cdot\left(\dfrac{\rho}{z}\right)^2+U_2^{\pm}(z)\right] \end{pmatrix}, \tag{32}$$

$$U_{1,2}^{\pm}(z)=\frac{\alpha_{1,2}^{\pm}}{W_0^{\pm}}\frac{z(2R-z)}{(R-z)^2}+\frac{\aleph_1(\aleph_1\pm 1)}{2\lambda_I z}, \tag{33}$$

where $\pm$ correspond to the bispinor ξ and η, respectively. The constants $K_{1,2}^{\pm}$, $L_{1,2}^{\pm}$, $\alpha_{1,2}^{\pm}$ are determined from the boundary condition $\Psi_I \underset{z\ll R}{\longrightarrow} \Psi_1$, but the final expressions for them are very cumbersome and are not given here. The wave function Ψ_{II}, corresponding to the potential curve E_{II}-term is similarly obtained.

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 energy splitting between terms of the system, in the range of their pseudocrossing, determines the non-adiabatic transition probability.

For calculating the exchange splitting of potential curves of the Z_1eZ_2 system, we use the representation for this quantity as the integral over the surface S, conditionally separating the domains where the electron is in Ψ_I- and Ψ_{II}-states [11]:

$$\Delta E=E_I-E_{II}=2ic\int\limits_S d\vec{S}(\Psi_{II}^{+}\vec{\alpha}\Psi_I). \tag{34}$$

Note that the integral representation (34) is valid only in the vicinity of the point R_p of pseudocrossing of the E_I- and E_{II}-terms:

$$R_p=$$

$$=\frac{Z_2-Z_1+\sqrt{(Z_2-Z_1)^2-4(E_1-E_2)(Z_2\xi_1-Z_1\xi_2)}}{2(E_1-E_2)}. \tag{35}$$

Having substituted Ψ_I- i Ψ_{II}-functions into (34) in the explicit form and calculated the surface integral by the stationary phase method, we arrive at the following expression for the first two terms of the asymptotic expansion of $\Delta E(R)$ at large R:

$$\Delta E=\frac{2A_1A_2}{(|m|-1/2)!(\lambda_1+\lambda_2)^{|m|-1/2}}D_{j_1j_2m}R^{a-|m|-1/2}\times$$

$$\times\exp\left\{-\frac{R(\lambda_1+\lambda_2)+a}{2}\right\}\left[1+\frac{I_1+I_2}{R}\right], \tag{36}$$

$$I_1=\frac{1}{\lambda_1+\lambda_2}\left[\aleph_1^2+\aleph_2^2-(|m|+1/2)^2-\right.$$

$$\left.-\frac{\aleph_1\aleph_2}{|m|+1/2}\right], \tag{37}$$

$$I_2=\frac{|m|+1/2}{2}\left(\frac{\varepsilon_1 Z_2}{\lambda_1^2}+\frac{\varepsilon_2 Z_1}{\lambda_2^2}\right)+\frac{\varepsilon_1 Z_2\xi_1}{2\lambda_1}+\frac{\varepsilon_2 Z_1\xi_2}{2\lambda_2}-$$

$$-\frac{Z_1^2}{4\lambda_1^3}-\frac{Z_2^2}{4\lambda_2^3}, \tag{38}$$

$$D_{j_1j_2m}=\sqrt{\frac{(j_1+|m|)!\,(j_2+|m|)!}{(j_1-|m|)!\,(j_2-|m|)!}},$$

$$a=\frac{\varepsilon_1 Z_2}{\lambda_1}+\frac{\varepsilon_2 Z_1}{\lambda_2},\qquad m=m_1=m_2. \tag{39}$$

We stress, however, that the analytic expressions derived for the asymptotic expansion of various splittings and shifts of the potential curves can be used sometimes 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 the asymptotic solutions of the two-Coulomb-center problem (even the first term

of the wave function 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 [20]. These properties are also conserved for other quantities computed with these functions.

Conclusions

Here we briefly summarize the results obtained in this paper. Within perturbation theory, we have calculated the asymptotic expansion of the eigenvalues (potential curves) $E(R)$ of the two-Coulomb-center problem in the limits of united ($R \longrightarrow 0$) and separated ($R \longrightarrow \infty$) atoms with the precision to $O\left(R^3\right)$ and $O\left(R^{-3}\right)$, respectively. The obtained formulae can be applied, in particular, for constructing the one-electron relativistic correlation diagrams of heavy quasi-molecules in the region between the limits of united and separated atoms. In this work, we have obtained analytic quasi-classical solutions of the Dirac equation with an axially symmetric 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-center wave function of an electron and calculated the exchange splitting of potential curves ΔE, which are expressed through the known characteristics of the separated atoms: the charges of atomic cores Z_1 and Z_2, asymptotic coefficients $A_{1,2}$, binding energies $\lambda_{1,2}^2/2$ and quantum numbers of the electron in the considered states of atoms (ions). Our results and analogous non-relativistic results [1] of the exchange splitting show that the role of relativistic effects increases with increasing the charges Z_1, Z_2 and internuclear distance R, and the relative contribution of relativistic effects amounts to about 50 % even at $Z = Z_1 = Z_2 = 45$.

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РЕЛЯТИВІСТСЬКА ЗАДАЧА ДВОХ КУЛОНІВСЬКИХ ЦЕНТРІВ ДЛЯ МАЛИХ ТА ВЕЛИКИХ МІЖЦЕНТРОВИХ ВІДСТАНЕЙ

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Р е з ю м е

За допомогою теорії збурень побудовано асимптотики адіабатичних термів релятивістської задачі двох кулонівських центрів в граничних випадках малих та великих між'ядерних відстаней R. На основі методу межового шару Фока—Леонтовича розроблено релятивістську версію квазікласичного наближення для рівняння Дірака з довільним аксіально-симетричним потенціалом, що не допускає повного відокремлення змінних. Знайдено асимптотику квазікласичного типу для двоцентрової хвильової функції діраківського електрона в класично забороненій області. Обчислено перші два члени асимптотичного розкладу за оберненими степенями R величини обмінного розщеплення термів в релятивістській двоцентровій задачі.

РЕЛЯТИВИСТСКАЯ ЗАДАЧА ДВУХ КУЛОНОВСКИХ ЦЕНТРОВ ДЛЯ МАЛЫХ И БОЛЬШИХ МЕЖЦЕНТРОВЫХ РАССТОЯНИЙ

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Р е з ю м е

С помощью теории возмущений построены асимптотики адиабатических термов релятивистской задачи двух кулоновских центров в предельных случаях малых и больших межъядерных расстояний R. На основании метода пограничного слоя Фока—Леонтовича разработана релятивистская версия квазиклассического приближения для уравнения Дирака с произвольным аксиально-симметричным потенциалом, недопускающим полного разделения переменных. Найдена асимптотика квазикласического типа для волновой функции дираковского электрона в классически запрещенной области. Вычислены первые два члена асимптотического разложения по обратным степеням R величины обменного расщепления термов в релятивистской двухцентровой задаче.