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Asymptotic Expansions of the Potential Curves of the Relativistic Quantum-Mechanical Two-Coulomb-Centre Problem

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The asymptotic expansions (at small and large internuclear distances R) of the eigenvalues (potential curves) $E(R)$ of the two-Coulomb-centre problem by the perturbation theory are obtained.

1 Introduction

In the present time a severe asymmetry exists in development of the theories of nonrelativistic and relativistic quantum-mechanical problems of two Coulomb centres (the so-called Z_1eZ_2 problem). Numerous effective asymptotic and numerical methods of solving the two-Coulomb-centre problem for the Schrödinger equation (see, for instance, [1] and references therein) can be opposed only by seldom examples of the consideration of same problem for the Dirac equation within various approximations [2, 3, 4, 5] (the Galerkin method, diagonalization, variational method, perturbation theory, Furry–Sommerfeld–Maue approximation). Such situation is a surprising example of passivity of the theory at 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.

Besides, with the recent erection of powerful accelerators of highly charged ions in many laboratories [6, 7] the need of the consistent Dirac theory of the quantum mechanical problem is more and more urgent in different fields of physics. Previously, this problem was applied, 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 $Z_1 + Z_2 > 173$ [3, 8, 9]. Rather recently [10], Z_1eZ_2 problem was used as a model approximation in the investigations of elementary processes of collisions (excitation, charge exchange, ionization) of multiply charged ions. Other application of the relativistic problem in 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 on heavy diatomic molecules [10].

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 highly complicates the whole specific problem of finding the electron wave function and potential curves. Unfortunately, numerical solving this system of differential equations is rather complicated and cumbersome problem [4, 5] requiring complicated calculations for each specific system Z_1eZ_2. This causes the necessity of creating and investigating approximative methods of solving this problem, which are based on clear physical ideas and well elaborated mathematical device and have a clear area of application.

In the present paper we determine the energy of an electron for two asymptotic cases, when the distance R between the Coulomb centres is rather small or rather large. For this we use the scheme of the perturbation theory which does not require the separation of variables. As

a result of the performed calculations, the asymptotic expressions for levels of energy of system Z_1eZ_2 are obtained at $R \to 0$ ($R \to \infty$) up to the terms $O(R^3)$ ($O(R^{-3})$).

2 Asymptotic expansions of the solutions of the problem at $R \to 0$

When the total charge of Coulomb centres $Z = Z_1 + Z_2$ is positive and internuclear distance R tends to zero, it is possible to consider the relativistic problem within the perturbation theory. The Dirac Hamiltonian of the problem Z_1eZ_2 is of the form ($m_e = e = \hbar = 1$):

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

where $r_{1,2}$ is the distance between the electron and the corresponding nucleus, $\widehat{\vec{p}} = -i\hbar$ is the momentum operator, and c is the velocity of light. In standard representation [11],

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

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 $\widehat{H}$ by the Hamiltonian of zero approximation $\widehat{H}^{UA}$ and perturbation $\widehat{W}$:

$$\widehat{H} = \widehat{H}^{UA} + \widehat{W}.$$

As $\widehat{H}^{UA}$ the Dirac Hamiltonian of the united relativistic atom

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

is taken, the atom being placed on the axis z, directed from centre Z_1 to centre Z_2, in the point $z = z_0$ that is the centre of electric charges and divides the internuclear distance into two segments:

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

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

Now we construct the unperturbed wave function of an united atom. The eigenvalues of the operator 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, is the projection of j onto the internuclear axis z. The explicit form of the eigenfunctions of the operator $\widehat{H}^{UA}$ can be found in [11]. Expanding the perturbation operator $\widehat{W}$ in the Legendre polynomials and calculating the matrix elements of the matrix $\left\|W^{njl'm'}_{njlm}\right\|$ to the first (within the terms $O\left(R^3\right)$) nonzero term we see that at $R \to 0$ the matrix $\left\|W^{njl'm'}_{njlm}\right\|$ is diagonal with respect to each group of mutually degenerated (on l and m) states. The residual result for energy of Z_1eZ_2 system at is $R \to 0$

$$E_{njlm}(R) = \varepsilon c^2 + \frac{Z_1Z_2}{2N^3} \cdot \frac{3m^2 - j(j+1)}{j(j+1)} \cdot \frac{\left[3\varepsilon\aleph(\varepsilon\aleph - 1) - \gamma^2 + 1\right] \cdot (ZR)^2}{\gamma(\gamma^2 - 1)(4\gamma^2 - 1)} + O\left(R^3\right), \tag{2}$$

where

$$n_r = n - j - 1/2, \qquad \aleph = (-1)^{k-l}k, \qquad k = j + 1/2, \qquad l = j \pm 1/2, \tag{3}$$

$$N = \sqrt{n^2 - 2n_r(k-\gamma)}, \qquad \gamma = \sqrt{k^2 - (Z\alpha_0)^2},$$
$$\varepsilon = \left[1 + \left(\frac{Z\alpha_0}{n_r + \gamma}\right)^2\right]^{-1/2}, \qquad \alpha_0 = \frac{1}{c}. \tag{4}$$

We have compared (see Fig. 1) the binding energies of some bound states of the Pb-Pb system calculated by asymptotic formula (2) with results of paper [5]. The difference $\approx 5\%$ is connected with the finite extension of the Pb nuclei in [5].

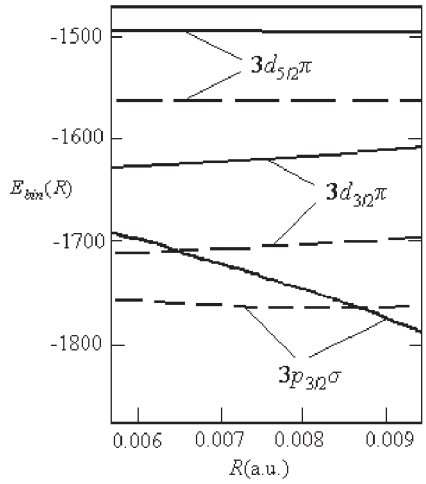

Figure 1.

3 Asymptotic expansions of the solutions of the problem at $R \to \infty$

Now we shall determine the energy $E(R)$ and the wave functions $\Psi(\vec{r}; R)$ 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 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_I- and E_{II}-potential curves that, for $R \to \infty$, transform into the energy levels of isolated atoms 1 and 2, respectively.

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 (1) by a Hamiltonian of zero-approximation $\widehat{H}^{SA}$ and perturbation $\widehat{V}$:

$$\widehat{H} = \widehat{H}^{SA} + \widehat{V}.$$

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

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

is taken. In a spherical coordinate system wave functions $\Psi^{SA}_{n_1 j_1 l_1 m_1}(\vec{r}_1)$ of eZ_1 atom, belonging to a discrete energy spectrum, are characterized by the set quantum numbers n_1, j_1, l_1, m_1. At large internuclear distances the operator of the interaction between the electron and the Z_2 nucleus $\widehat{V} = -Z_2/\left|\vec{R} - \vec{r}\right|$ can be considered as a small perturbation of the Hamiltonian $\widehat{H}^{SA}$. As in previous case we expand the perturbation operator $\widehat{V}$ in the Legendre polynomials and

calculate the matrix $\left\| V^{n_1 j_1 l_1' m_1'}_{n_1 j_1 l_1 m_1} \right\|$ of the perturbation operator to the first non-zero diagonal term.

Diagonalizing the complete matrix of energy with respect to each group of mutually degenerate states we obtain the analytical expression for E_I-potential curves in the first order of the perturbation theory

$$E_I(R) = \varepsilon_1 c^2 - \frac{Z_2}{R} \pm \frac{3}{4}\sqrt{N_1^2 - \aleph_1^2}\frac{(n_{r1} + \gamma_1)\, m_1}{j_1(j_1+1)}\frac{Z_2}{Z_1 R^2} + O\left(R^{-3}\right), \tag{5}$$

where the quantities n_{r1}, $\aleph_1$, k_1, l_1, N_1, γ_1, ε_1 are obtained from (3), (4) by adding index 1. The third term in (5) coincides with the Stark shift of level in the weak electric field with the intensity $-Z_2/R^2$ [12].

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

4 Conclusions

Here we briefly summarize the results obtained in this paper. By means of the 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 to $O\left(R^3\right)$ and $O\left(R^{-3}\right)$, respectively. Note that asymptotic expressions of the potential curves obtained here are applicable under the condition that quantities γ, $\gamma_{1,2}$ are real only, which corresponds to the range of applicability of the Dirac equation solutions for the point-charge.

Acknowledgements

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