Generalized quantum mechanical two-Coulomb-center problem (Demkov problem)*

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We present a new exactly solvable quantum problem for which the Schrödinger equation allows for separation of variables in oblate spheroidal coordinates. Namely, this is the quantum mechanical two-Coulomb-center problem for the case of an imaginary intercenter parameter and complex conjugate charges are considered. Since the potential is defined by the two-sheeted mapping whose singularities are concentrated on a circle rather than at separate points, there arise additional possibilities in the choice of boundary conditions. A detailed classification of the various types of boundary-value problems is given. The quasi-radial equation leads to a new type of boundary value problem which has never been considered before. Results of the numerical calculations, which allow conclusions to be drawn about the structure of the energy spectrum, are shown. Possible physical applications are discussed.

Keywords: two-Coulomb-center problem, potential models

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1. Introduction

The quantum mechanical two-Coulomb-center problem (Z_1eZ_2) plays a fundamental role in various questions of atomic physics, quantum chemistry of diatomic molecules, and collision theory. The problem is to determine the wave functions and terms of an electron moving in a field of two fixed charges Z_1 and Z_2 located at a distance R from each other. The Hamiltonian of the system, in atomic units ($\hbar = m_e = e = 1$), is given by

$$\widehat{H} = -\frac{1}{2}\Delta - \frac{Z_1}{|\boldsymbol{r}+\boldsymbol{R}/2|} - \frac{Z_2}{|\boldsymbol{r}-\boldsymbol{R}/2|}. \tag{1}$$

Due to the high symmetry of Eq. (1), the corresponding Schrödinger equation allows for the separation of variables in prolate spheroidal coordinates. As early as in the 1930s, Jaffe,[1] Baber, and Hasse[2] offered expressions for one-dimensional eigenfunctions in the form of series whose coefficients satisfy three-term recurrence relations.[3] Thereafter, based on these expansions, algorithms were developed to calculate the terms with a relative accuracy of 10^{-12}, and the wave functions $\sim 10^{-10}$.[3,4] All of this led to considerations of various generalizations of the problem (Z_1eZ_2) (see, for example, Ref. [5]).

Application of the two-Coulomb-center problem in the atomic and molecular scattering theory is based on the fact that the motion of the electrons and nuclei can be considered adiabatically due to the large difference in their masses. In other words, the potential curves $E(R)$ or quasimolecular terms are introduced for the colliding particles. These curves are analytic functions of the internuclear distance R. Transitions between two terms $E_1(R)$ and $E_2(R)$ are related to their common complex branch point R_c in the vicinity of which the energy surface looks like a corkscrew

$$\Delta E(R) = E_2(R) - E_1(R) \sim \text{const}(R - R_c)^{1/2}.$$

In the case of slow collisions ($v \ll 1$ a.u. (atomic units), v is the velocity), the branch points located near the real axis play a dominant role. Then, in the framework of the adiabatic approximation, it is possible to obtain a simple expression for the transition probability in such inelastic processes as ionization.[6] More recently, in the 1980s, in connection with the needs of thermonuclear fusion physics, a range of velocities $v \approx 1$ a.u. attracted interest, that is, the positions of the singular points in the two-Coulomb-center problem, throughout the complex plane of the intercenter (internuclear) distance R, needed to be studied, For the first time, such calculations were started by Solov'ev E A[7] and then continued by his coauthors.[8,9] The main result of these studies is that the various types of "hidden" quasicrossings of the terms were found, and approximate expressions relating quasicrossing parameters to quasi-molecule characteristics and quantum numbers were obtained. Note that in Refs. [5] and [7]–[9], the consideration was conducted in prolate spheroidal coordinates. In other words, a solution of the problem (Z_1eZ_2) for real R was

*Dedicated to the memory of Professor Dr. Yu. N. Demkov (12.04.1926–15.11.2010).

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taken as a basis for the generalizations, and the terms for complex R were obtained by their analytic continuation from the real axis.

In this work, we consider the generalization of a different kind. Some time ago, Demkov Y N expressed the following idea (private communication). In going to an imaginary parameter R and complex-conjugate charges in the Hamiltonian (1), it remains Hermitian. The Schrödinger equation in this case will also allow a separation of variables in oblate spheroidal coordinates but not in prolate. Because the potential is two-sheeted, there are additional possibilities in the choice of boundary conditions and the formulation of boundary-value problems. Thus, a new exactly solvable quantum problem (integrable system) whose solution can not be reduced to the special case arises.[7–9]

The rest of this paper is organized as follows. In the next section, we briefly describe the properties of the potential relating to our problem. Section 3 deals with the separation of variables and the formulation of boundary-value problems. Particular attention should be paid to the appearance of a new type of the boundary-value problems for the quasi-radial equation. Such types of problems have never been considered before, which is connected to a configuration of the equation singular points and the configuration of the region in which the eigenfunctions are found. The description of the solutions to these problems is the subject of a separate mathematical work; in this article, we restrict ourselves to presenting the results of numerical calculations. In the fourth part, the asymptotics of the eigenfunctions and terms are presented. In Section 5, the results of the numerical calculations are given. In the Conclusions, we discuss possible physical applications.

Note also that the classical analogue of our problem is known as the generalized two fixed centers problem and refers to celestial mechanics.[10] The problem first arose in 1961, when it was necessary to consider the effect of the non-sphericity of the Earth's gravitational field on satellites trajectories.

2. Potential and its properties

The substitutions of $R \to \mathrm{i}R$, $Z_1 \to q_1 + \mathrm{i}q_2$, $Z_2 \to q_1 - \mathrm{i}q_2$ for the Hamiltonian (1), where q_1, q_2, R are real numbers, reduce it to a Hermitian operator again, inasmuch as the last two terms are complex-conjugate. This operator can be considered as a new Hamiltonian whose coordinate part is called the potential of the generalized two-Coulomb-center problem. For clarity, we use the Cartesian coordinate system. Then

$$V = \frac{q_1 + \mathrm{i}q_2}{\sqrt{x^2 + y^2 + (z - \mathrm{i}R/2)^2}} + \frac{q_1 - \mathrm{i}q_2}{\sqrt{x^2 + y^2 + (z + \mathrm{i}R/2)^2}}. \quad (2)$$

It is evident that parameters q_1 and q_2 in the expression (2) are linear, so we represent it as a sum

$$V = V_1(x, y, z; q_1, R) + V_2(x, y, z; q_2, R). \quad (3)$$

Each member of the sum (3) has the following types of symmetry.

i) symmetry with respect to rotations around the z axis by an arbitrary angle;

ii) symmetry (antisymmetry) with respect to reflection in the xy plane: $(x, y, z) \to (x, y, -z)$;

iii) symmetry (antisymmetry) with respect to inversion: $(x, y, z) \to (-x, -y, -z)$;

iv) scale symmetry:

$$x, y, z, R, q_1, q_2 \to \lambda x, \lambda y, \lambda z, \lambda R, \lambda q_1, \lambda q_2 \quad \lambda \in \{\mathbb{R}\} \backslash 0.$$

The property iii) is a consequence of i) and ii). The last property indicates that there are only two non-trivial parameters in the generalized quantum mechanical two-Coulomb-center problem: R and the ratio of q_1/q_2 or q_2/q_1.

Now, let us turn our attention to the fact that the expression (2) defines two-sheeted mapping, which is singular on the circle $C : x^2 + y^2 = R^2/4,\ z = 0$, and not at the points $z_{1,2} = \pm R/2$ as it was in the problem $(Z_1 e Z_2)$. Thus, the space in which the wave functions will be determined becomes two-sheeted, and the potential V does not already allow a simple electrostatic interpretation.

The way to solve this difficulty is the following. First, the regular branches (sheets) can be glued along the singular circle C to a certain analog of the Riemann surface and the potential V can be considered as the electrostatic potential on the extended space. Second, if we use the fact that any multiple connected space can be made simply connected by inserting proper barriers, and keep one or another branch in Eq. (2) fixed, we can interpret the potential V, in such space with the barrier, as a certain electrostatic potential. It should be emphasized that the topological considerations allow considerable arbitrariness in choosing form of the barrier, it is only important that its boundary coincides with the singular circle C. However, the requirement of the variables separation (as shown below) leaves only three basic variants. They are the circle $C_1 : x^2 + y^2 \leqslant R^2/4,\ z = 0$, its exterior $C_2 : x^2 + y^2 \geqslant R^2/4,\ z = 0$ and their union $C_1 \bigcup C_2$, that is, the entire xy plane.

If equation (2) is placed symmetrically relative to the top and bottom sides of the barrier: $V_+ = V_-$, we get an analog of the simple-layer potential; when the branches are placed antisymmetrically: $V_+ = -V_-$, we get an analog of the double-layer potential.

Now, let us agree on the terminology: in future, the spectral problem in the extended space will be referred to as two-sheeted problem, and in the ordinary space with a barrier - one-sheeted problem.

3. Separation of variables and formulation of boundary-value problems

It is known[3] that the potential in which the Schrödinger equation is separable in oblate spheroidal coordinates (ξ,η,φ) must be presented in the form of

$$V=-\frac{2}{R^2}\Big[\frac{a(\xi)-b(\eta)}{\xi^2+\eta^2}+\frac{c(\varphi)}{(\xi^2+1)(1-\eta^2)}\Big].$$

The connection of these coordinates with Cartesian coordinates is given by the following relations:

$$\begin{aligned} x&=\frac{R}{2}\sqrt{(\xi^2+1)(1-\eta^2)}\cos\varphi,\\ y&=\frac{R}{2}\sqrt{(\xi^2+1)(1-\eta^2)}\sin\varphi,\\ z&=\frac{R}{2}\xi\eta, \end{aligned} \tag{4}$$

where the variables domain D is traditionally chosen by one of the two alternative methods

$$\text{I)}\ \ \xi\in[0,\infty),\quad \eta\in[-1,1],\quad \varphi\in[0,2\pi); \tag{5}$$

$$\text{II)}\ \ \xi\in(-\infty,\infty),\quad \eta\in[0,1],\quad \varphi\in[0,2\pi). \tag{6}$$

Note that the cases (5) and (6) are related to the one-sheeted problem, since the relation (4) determines a biunivocal mapping (bijection) $f:D\to\mathbb{R}^3$.

If we proceed to consider the two-sheeted problem, the variables domain $\tilde{D}$ should be chosen as follows:

$$\text{III)}\ \ \xi\in(-\infty,\infty),\quad \eta\in[-1,1],\quad \varphi\in[0,2\pi). \tag{7}$$

Then, the mapping $f:\tilde{D}\to\mathbb{R}^3$ will be single-valued, and the inverse $f^{-1}:\mathbb{R}^3\to\tilde{D}$ – double-valued.

Let us change the variables in Eq. (2) according to Eq. (4) and recall that the potential of the generalized two Coulomb centers problem can be constructed in different ways. A simple analysis shows that there exists a total of nine variants of such structures allowing the separation of variables. The most physically meaningful ones are

$$V=-\frac{4(q_1\xi+q_2\eta)}{R(\xi^2+\eta^2)}, \tag{8}$$

$$V=-\frac{4[q_1\xi+q_2\eta\ \mathrm{sign}(\eta)]}{R(\xi^2+\eta^2)}, \tag{9}$$

$$V=-\frac{4[q_1\xi\ \mathrm{sign}(\xi)+q_2\eta]}{R(\xi^2+\eta^2)}. \tag{10}$$

The variant (8) refers to the double-sheeted problem with the variables domain $\tilde{D}$, as well as to a one-sheeted problem with the domain D according to Eq. (5) or (6). When the domain D is determined by Eq. (5), the impermeable barrier must be the circle C_1. Then V_1 is interpreted as an analog of the simple-layer potential, and V_2-double-layer. If the domain D is determined by Eq. (6), the barrier must be the exterior of the circle C_2. Then V_1 is interpreted as an analog of the double-layer potential, and V_2-simple-layer. The variants (9) and (10) are derivatives from Eq. (8) and refer to one-sheeted problems where V_1 and V_2 are analogs of the simple-layer potential. In the case of Eq. (9), the domain D is determined by Eq. (5), and in the case of Eq. (10), it is determined by Eq. (6).

It should be noted that if we consider the generalized quantum mechanical two-Coulomb-center problem in the half-space, the barrier must be the xy plane. The domain D is determined as follows:

$$\text{IV)}\ \ \xi\in[0,\infty),\quad \eta\in[0,1],\quad \varphi\in[0,2\pi).$$

In this case, the differences among Eqs. (8), (9), and (10) vanish. Let us follow the variable separation procedure and the formulation of boundary-value problems by using the example of Eq. (8), since this variant is basic.

Let us represent the wave function Ψ_j, corresponding to the term $E_j(R)$, in the form of

$$\begin{aligned} \Psi_j &= \Psi_{kqm}(\xi,\eta,\varphi;R)\\ &= N_{kqm}(R)X_{mk}(\xi;R)Y_{mq}(\eta;R)\,\mathrm{e}^{\mathrm{i}m\varphi}, \end{aligned} \tag{11}$$

where the multiindex $j=\{kqm\}$ denotes the quantum number set in which k and q coincide with the numbers of zeros of the corresponding functions in the variables ξ and η, and the number m takes the values $0,\pm1,\pm2,\ldots$. The normalization constant $N_{kqm}(R)$ is determined by the condition

$$\int_V \Psi^*_{kqm}(\xi,\eta,\varphi;R)\Psi_{k'q'm'}(\xi,\eta,\varphi;R)\,\mathrm{d}V=\delta_{kk'}\delta_{qq'}\delta_{mm'},$$

where $\mathrm{d}V=R^3(\xi^2+\eta^2)\,\mathrm{d}\xi\,\mathrm{d}\eta\,\mathrm{d}\varphi/8$ is a volume element in the oblate spheroidal coordinates. After substituting Eqs. (8) and (11) in the Schrödinger equation

$$\Delta\Psi+2(E-V)\Psi=0.$$

we obtain the ordinary differential system

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\xi}(\xi^2+1)\frac{\mathrm{d}}{\mathrm{d}\xi}X_{mk}(\xi;R)\\ &-\left[\lambda^{(\xi)}_{mk}+p^2(\xi^2+1)-a\xi-\frac{m^2}{\xi^2+1}\right]X_{mk}(\xi;R)=0, \end{aligned} \tag{12}$$

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}\eta}(1-\eta^2)\frac{\mathrm{d}}{\mathrm{d}\eta}Y_{mq}(\eta;R)\\ &+\left[\lambda^{(\eta)}_{mq}+p^2(1-\eta^2)+b\eta-\frac{m^2}{1-\eta^2}\right]Y_{mq}(\eta;R)=0. \end{aligned} \tag{13}$$

Here, $p_j^2=-E_jR^2/2$ $(p>0)$, $a=2q_1R$, $b=-2q_2R$, p means the energy parameter; a and b are the charge parameters; $\lambda^{(\xi)}_{mk}=\lambda^{(\xi)}_{mk}(p,a)$ and $\lambda^{(\eta)}_{mq}=\lambda^{(\eta)}_{mq}(p,b)$ are the separation constants.

Equations (12) and (13) supplemented by the boundary conditions form the boundary value problems that must be solved simultaneously, and the energy spectrum can be obtained from the condition

$$\lambda^{(\xi)}_{mk}(p,a)=\lambda^{(\eta)}_{mq}(p,b). \tag{14}$$

The general theory of Sturm–Liouville-type one-dimensional boundary problems implies that the quantum numbers k, q, m remain constant for the continuous variation of the intercenter parameter R, and the eigenvalues $\lambda_{mk}^{(\xi)}(p,a)$ or $\lambda_{mq}^{(\eta)}(p,b)$ are non-degenerate. Consequently, if the solution of Eq. (14) exists, it is unique.

Let us now discuss the formulation of boundary-value problems. On the one hand, it follows from the most common requirements for the wave function that

$$\Psi_j \in \mathscr{L}_2\left(\mathbb{R}^3\right) \subset \mathscr{L}_2^{(\xi)}(\mathbb{R}) \cup \mathscr{L}_2^{(\eta)}([-1,1]) \cup \mathscr{L}_2^{(\varphi)}([0,2\pi)) . \tag{15}$$

On the other hand, in the spatial domain where the potential becomes infinite, the particle can not penetrate at all, that is, there must be $\Psi_j = 0$. The continuity of Ψ_j requires that Ψ_j becomes zero on the boundary of this domain; generally speaking, in this case, the derivative of Ψ_j has a jump.[11] Thus, in the one-sheeted problem, where the circle C_1 is the barrier for the wave function, we have

$$\Psi_+|_{C_1} = \Psi_-|_{C_1} = 0. \tag{16}$$

The normal derivative must jump

$$\left.\frac{\partial\Psi}{\partial n_+}\right|_{C_1} - \left.\frac{\partial\Psi}{\partial n_-}\right|_{C_1} = g(\eta;q_1,q_2,R), \tag{17}$$

where $g(\eta;q_1,q_2,R)$ is a smooth function of η and parameters q_1, q_2, and R. From the conditions (15) and (16), we obtain the boundary conditions for quasi-radial function

$$X_{mk}(0;R) = 0, \quad |X_{mk}(\xi;R)| \xrightarrow[\xi\to\infty]{} 0. \tag{18}$$

In the quasi-angular equation (13), the boundary points are simultaneously singular, therefore, in order to satisfy the condition (15), it should be required that the function be limited in

$$|Y_{mq}(\pm 1;R)| < \infty. \tag{19}$$

If Eqs. (18) and (19) are satisfied, then Eq. (16) holds, and the condition (17) is satisfied automatically.

In the one-sheeted problem with the barrier C_2, it is necessary to impose on the wave function the following condition:

$$\Psi_+|_{C_2} = \Psi_-|_{C_2} = 0. \tag{20}$$

For the normal derivative, we obtain

$$\left.\frac{\partial\Psi}{\partial n_+}\right|_{C_2} - \left.\frac{\partial\Psi}{\partial n_-}\right|_{C_2} = h(\eta;q_1,q_2,R),$$

where $h(\eta;q_1,q_2,R)$ is a smooth function of η and parameters q_1, q_2 and R. From Eq. (19), we obtain the boundary conditions for the quasi-radial and quasi-angular functions

$$|X_{mk}(\xi;R)| \xrightarrow[\xi\to\pm\infty]{} 0, \; Y_{mq}(0;R) = 0, \; |Y_{mq}(+1;R)| < \infty. \tag{21}$$

In the two-sheeted problem, no barrier appears, but there is a circle C on which the potential is singular, therefore, the following condition must be satisfied:

$$\Psi|_C = \Psi(0,0,\varphi;R) = 0, \tag{22}$$

which is in contradiction with the expression (11). Indeed, if expressions (11) and (22) are valid, we have the alternative

i) $X_{mk}(0;R) = 0$, or $Y_{mq}(0;R) = 0$;

ii) $X_{mk}(0;R) = 0$ and $Y_{mq}(0;R) = 0$ simultaneously,

which, generally speaking, does not follow from any physical considerations. The contradiction arises particularly acutely when we consider the ground state.

It is apparent that both cases are not satisfied. The way out of the situation is to separate factors (factorization)

$$\Psi_j = \overline{N}_{kqm}(R)(\xi^2+\eta^2)\overline{X}_{mk}(\xi;R)\overline{Y}_{mq}(\eta;R)\,\mathrm{e}^{\mathrm{i}m\varphi}. \tag{23}$$

Here, the overline means that we are dealing with one-dimensional functions of the two-sheeted problem. Although the functions satisfy Eqs. (12) and (13), but they essentially different from the corresponding functions of the one-sheeted problem.

The boundary conditions in the two-sheeted problem are formulated as follows:

$$|\overline{X}_{mk}(\xi;R)| \xrightarrow[\xi\to\pm\infty]{} 0, \; |\overline{Y}_{mq}(\pm 1;R)| < \infty, \tag{24}$$

because the boundary points are singular.

Next, we discuss the specific of the boundary-value problems related to the quasi-radial equation. In the problem (Z_1eZ_2), the corresponding equation was considered on the interval $[1,\infty)$, that is, between the singular points. Then, using the Jaffe transformation[1] for the independent variable $x = (\xi-1)/(\xi+1)$, the interval is transferred to the unit segment, and the additional singular point –1 goes to $-\infty$ and does not effect the convergence of series representing the eigenfunction. In our problem, equation (12) on the complex $\xi-$plane has three singular points: two finite regular point $\xi_1 = +\mathrm{i}, \xi_2 = -\mathrm{i}$ and one irregular at infinity.

It is clear that the points ξ_1 and ξ_2 are "on different sides" of the real axis, and so any attempt to present $X_{mk}(\xi;R)$ in the form of series faces the problem of the circle of convergence. Use of standard techniques, such as the transformation of Jaffe[1] or Jaffe–Lay,[12] are no longer possible here, and therefore it is necessary to look for a more general method including the standard methods as special cases. Note that the problem of the circle of convergence will always appear in the boundary-value problems after separation of variables in the Schrödinger equation in oblate spheroidal coordinates (it is typical for these coordinates).

In conclusion, for this section, we note that the separation of the factors in Eq. (23), without changing the structure of Eqs. (12) and (13), can affect the convergence of the series for the one-dimensional functions.

4. Asymptotic behavior of the eigenfunctions and terms as $R \to 0$.

In the context of possible practical applications of the model under consideration, the pattern of the terms is of the most interest. In order to correctly identify the individual terms it is necessary to know the initial approximation or asymptotic of $E_j(R)$ as $R \to 0$. In this limit, the difference between the one-sheeted and two-sheeted problems disappears and, in addition, the spherical symmetry arises, therefore it is natural to go to spherical coordinates (r, θ, φ).

Let us expand the potential (2) in powers of the small parameter (R/r) using the formula (see, for example, Ref. [13]):

$$\frac{1}{\sqrt{1-2tu+t^2}} = \sum_{k=0}^{\infty} t^k P_k(u), \quad |t| < \min|u \pm \sqrt{u^2-1}|,$$

where $P_k(u)$ are Legendre polynomials. As a result of the transformations, we obtain the expression

$$V = \frac{2q_1}{r}\sum_{n=0}^{\infty}(-1)^n\left(\frac{R}{2r}\right)^{2n} P_{2n}(\cos\theta) + \frac{2q_2}{r}\sum_{n=0}^{\infty}(-1)^{n+1}\left(\frac{R}{2r}\right)^{2n+1} P_{2n+1}(\cos\theta), \quad (25)$$

where odd multipole moments are associated with the parameter q_1, and the even multipoles with q_2. It is clear that only one term $2q_1/r$ in Eq. (25) does not vanish as $R \to 0$. This term is naturally chosen as the unperturbed potential while the perturbation will be the first term of the second sum $-q_2 R/r^2 \cos\theta$. Then the terms $E_j(R)$ must continuously transit to N^2-fold degenerate energy levels of the hydrogen atom with a charge $2q_1$

$$E_j(R) \xrightarrow[R\to 0]{} E_{Nlm} = -\frac{2q_1^2}{N^2}, \quad (26)$$

where $i = \{Nlm\}$ is a set of spherical quantum numbers which are related to the numbers of zeros of the one-dimensional eigenfunctions by the relations

$$N = k+q+m+1, \quad l = q+m.$$

The radial $X_{mk}(\xi;R)$ and angular $Y_{mq}(\eta;R)$ parts of the eigenfunction Ψ_j are reduced to into the radial $R_{Nl}(r)$ and angular $Y_{lm}(\theta,\varphi)$ parts of one-center problem

$$\Psi_{kqm}(\xi,\eta,\varphi;0) = N_{kqm}(0)X_{mk}(\xi;0)Y_{mq}(\eta;0)\,\mathrm{e}^{\mathrm{i}m\varphi} = \tilde{N}R_{Nl}(r)Y_{lm}(\theta,\varphi), \quad (27)$$

that will be the correct function of the zero approximation. Arguments similar to those in Ref. [3] give the following expression for the energy in the first non-vanishing order:

$$E_{Nlm}(q_1,q_2,R) = -\frac{2q_1^2}{N^2} - \frac{8q_1^2(q_1^2+q_2^2)[l(l+1)-3m^2]R^2}{N^3 l(l+1)(2l-1)(2l+1)(2l+3)} + O((R)^2). \quad (28)$$

Note that formula (28) reduces to Baber and Hasse's result[2] by means of the substitution $q_1 \to (Z_1+Z_2)/2$, $q_2 \to \mathrm{i}(Z_1 - Z_2)/2$. The calculation of the energy in the following order of the perturbation theory becomes quite cumbersome and, in addition, one can expect logarithmic corrections similar to those obtained in Ref. [14] for the problem $(Z_1 e Z_2)$.

5. Results of numerical calculations

The boundary-value problems, which are Eqs. (12) and (13) supplemented by the boundary conditions (18), (19), and (21), have been solved numerically. As noted above, the condition (14) for the fixed parameters a, b, and $j = \{kqm\}$ has a unique solution

$$p_j^*(2q_1R, -2q_2R) = \frac{R}{2}\sqrt{-2E_j}. \quad (29)$$

Solving it for E_j, we find a discrete spectrum. For the classification of the terms, in addition to $j = \{kqm\}$, we will also use the set of spherical quantum numbers $i = \{Nlm\}$. We keep the traditional spectroscopic notation, when the numbers

$$l = 0,1,2,3,4,5,\ldots \quad \text{and} \quad m = 0,1,2,3,\ldots$$

correspond to the letter rows

$$L = \mathrm{s},\mathrm{p},\mathrm{d},\mathrm{f},\mathrm{g},\mathrm{h},\ldots \quad \text{and} \quad M = \sigma,\pi,\delta,\phi,\ldots$$

Therefore, in order to make any conclusions about the structure of the energy spectrum in the generalized quantum mechanical two-Coulomb-center problem, at least on a qualitative level, it is necessary to find a meaningful collection of the special cases of $E_j(R)$ which covers the transition and asymptotic (as $R \to 0$, $R \to \infty$) domains.

Calculations with different combinations of $q_1 = 1,\ldots 10$ and $q_2 = 1,\ldots 10$, show that such collection is formed from the first ten $E_j(R)$ at $R \in [0;20]$. It can be explained by the fact that there is a scaling (see symmetry property iv) of the potential (2)) in our problem. Thus, in spite of the fact that a total of about two thousand curves have been calculated, the structure of the spectrum was determined in a very wide domain of variation of q_1, q_2, and R.

Analysis of the curves shows that the pattern of the terms varies considerably for $q_1 < q_2$ and $q_1 > q_2$. This statement becomes especially obvious when selecting two systems differing from each other by the permutation $q_1 \leftrightarrow q_2$, for example, $q_1 = 1, q_2 = 3$ (see Fig. 1) and $q_1 = 3$, $q_2 = 1$ (see Fig. 2).

First of all, we pay attention to the fact that the terms in Fig. 1 have distinct local minima at finite R, whereas the terms in Fig. 2 change rather aslope. The availability of the minima of $E_j(R)$ at $q_1 < q_2$ indicates the stable states of a moving charged particle in such systems.

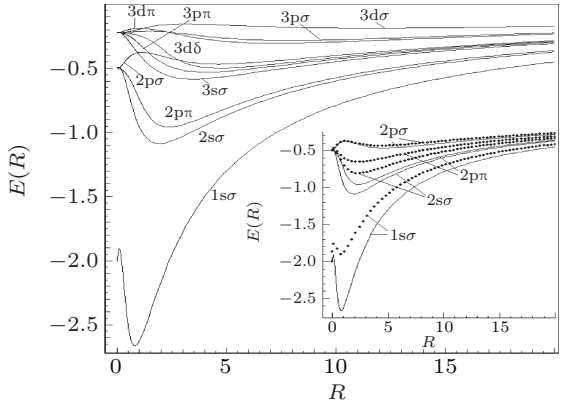


Fig. 1. Terms of system $q_1 = 1$, $q_2 = 3$.

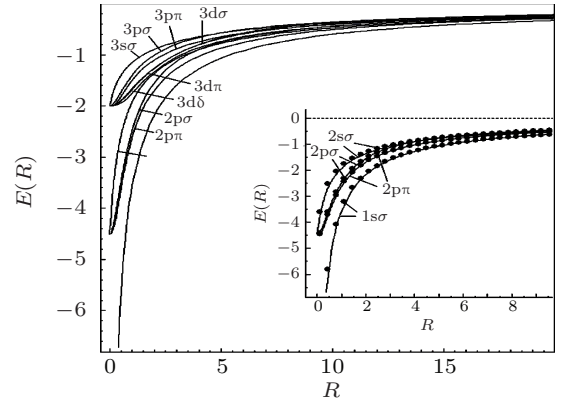


Fig. 2. Terms of system $q_1 = 3$, $q_2 = 1$.

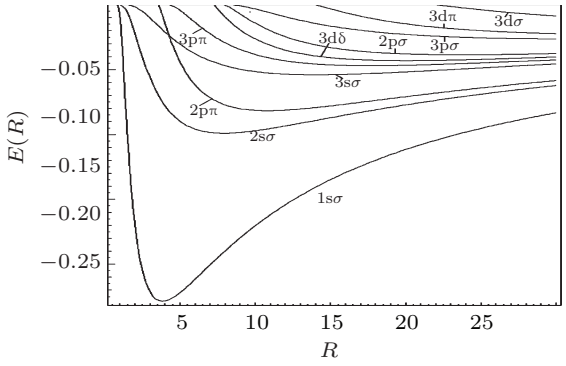


Fig. 3. Terms of system $q_1 = 0$, $q_2 = 1$.

The case of $q_1 = 0$ requires a separate consideration. It is well-known[15] that in the spherically symmetric field Cr^{-2} with $C \leqslant -1/4$ the energy levels exponentially condense to the continuous spectrum border. One can see a similar effect in the Fig. 3. We stress that the continuous spectrum starts at finite values of R.

Note that in all three figures the dashed lines depict the border of the continuous spectrum.

The question of the configuration interaction of the terms or their quasicrossings requires special consideration. In the works of Solov'ev,[7–9] the branch points were found near the imaginary axis R, so we can expect quasicrossings in the spectrum of our problem.

6. Conclusion

We have considered a new exactly solvable quantum problem. Distinct from the $(Z_1 e Z_2)$ problem, our problem allows for various choices of boundary conditions. It gives us additional opportunities in setting the boundary problems. We have shown that the boundary problems associated with the quasi-radial equation belong to a new type. The peculiarity of these problems is related to the fact that the singular points of the differential equation are on different sides of the region in which the eigenfunctions are defined. Analytic representations of such eigenfunctions are not known yet. Even in the famous paper Ref. [16] where an analogous problem for spheroidal equations has arised, the boundary problems were not duly considered and the relevant discussions were largely avoided. Therefore, our paper can be considered as an incentive for mathematical physics experts to analyse problems of this type. In particular, it would be interesting to apply the Nikiforov–Uvarov method[17] and asymptotic iteration method (AIM)[18–20] to these problems.

Note that in a recent paper,[21] an exactly solvable problem was considered with a ring-shaped noncentral potential. Singularities of this potential were located on a plane, instead of a circle as in our work, and the separation of variables in the Schrödinger equation was performed in spherical coordinates. Therefore, the Nikiforov–Uvarov method could be used for determination of the eigenfunctions. Our boundary problems are far more complex. The Nikiforov–Uvarov method has never been applied to such models.

We have shown for the first time that quantum problems can be considered on Riemannian surfaces. Probably, this idea could give some insights into the puzzle of confinement of quarks. At least, one could consider models of Refs. [22]–[24] type on Riemannian surfaces.

Numerical calculations have shown that for $q_1 < q_2$ the terms $E_j(R)$ do have minima at finite values of R. It implies that such systems possess stable states. We believe that the Demkov problem may be viewed as a model for higher excited electron states in the fields of various ring molecules (e.g., aromatic hydrocarbons). In particular, the asymptotic formulas (27) and (28) may be useful for the description of the higher excited states of benzene[25] which have been observed experimentally. Exact quantum mechanical computation of these states is very challenging from a technical point of view. Our work offers a possibility of simple description not only for benzene but for a good number of ring molecules.

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