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The two Coulomb centres problem at small intercentre separations in the space of arbitrary dimension

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Abstract
The case of small intercentre distance in the D-dimensional two Coulomb centres problem $(Z_1eZ_2)_D$ $(D \geqslant 2)$ is studied by solving the wave equations using the separations of variables. Asymptotic expansions for the electronic terms and the quantum defect are obtained. Results obtained are compared with previous asymptotic and numerical treatments. Correspondence between energy terms of the three-dimensional system $(Z_1eZ_2)_3$ and the D-dimensional system $(Z_1eZ_2)_D$ is found.

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1. Introduction

It was shown by Ehrenfest [1, 2] that the generalization of physical theories to space with an arbitrary dimension D often resulted in a new and unexpected understanding of the problem examined. During the past years such an approach received a considerable development and is widely used in theoretical physics. The $1/D$-expansion or size scaling, a new method of quantum mechanics and quantum field theory, was used in particular to study the properties of atoms in strong electric and magnetic fields, the three bodies problem, the two Coulomb centres problem and many other problems [3–5, 7]. A review of this method, its different variants and its applications to the theory of atoms, molecules and quantum chemistry can be found in [7].

This work is devoted to the generalization of the results of the asymptotic theory for the quantum mechanical two Coulomb centre problem Z_1eZ_2 [8, 9] by inflating the number of spacial dimension (denoted as the $(Z_1eZ_2)_D$ problem). Separating the Schrödinger equation

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in hyperspheroidal coordinates [10] leads to two coupled confluent Heun equations [11, 12], the singularities of which are located at ± 1 and at infinity. To calculate the energy levels of the two Coulomb centre system, a two-parameter boundary-eigenvalue problem must be solved. We solve this problem for the case of small intercentre separations by means of an asymptotic method that has been proposed in [9] and developed in [11]. The $1/D$-expansion of the energy levels for the $(Z_1 e Z_2)_D$ problem was calculated in [6] for the first time. But this expansion gives poor results for the case of small separations. We have obtained an expansion for the energy levels, which is convergent not only for small intercentre separations but also large spatial dimension D. The two-dimensional two centres problem $(Z_1 e Z_2)_2$ at small intercentre separation has been studied in [13], and the same results are presented in this paper.

The solutions of the Schrödinger equation with two-centre potential are of considerable interest in various problems of few-body systems. They describe the bound states of light particles in the field of two heavy particles. Usually such type of systems arises in molecular physics. However, in the past years other systems were also described by the two-centre Schrödinger equation; for example, baryons containing heavy quarks (QQq baryons) [14] and heavy-flavoured hybrid mesons (QQg mesons) are now becoming subjects of extensive investigation. There is a close connection between the $(Z_1 e Z_2)_D$ problem and $SU(2)$ monopole [15, 16]. The five-dimensional bound system of 'charge-dion' with $SU(2)$—Yang monopole [17] is also described by equations obtained by the separation of variables of equation (1) (see below) in hyperspheroidal coordinates. Furthermore, equation (1) is connected to the well-known Teukolsky equation [18].

The organization of the paper is as follows. In the following section we give an outline of the general scheme for solving $(Z_1 e Z_2)_D$ problem. In section 3, we construct and study the B-functions. In sections 4 and 5, we have constructed the asymptotic expansions for the radial Coulomb hyperspheroidal functions and the angular Coulomb hyperspheroidal functions using the ideas in [9, 11, 19]. In section 6, we obtain asymptotic expansion for the energy levels and the quantum defect. Finally, we discuss our results in section 7.

2. Formulation of the problem

The Schrödinger equation for the $(Z_1 e Z_2)_D$ problem in atomic units ($m = e = \hbar = 1$) reads

$$\left(-\frac{1}{2}\triangle - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right)\Psi(\mathbf{r}; R) = E\Psi(\mathbf{r}; R), \tag{1}$$

where r_1 and r_2 are distances from the electron to charges Z_1 and Z_2 and R is the intercentre distance. Introducing the hyperspheroidal coordinate system [10]

$$\begin{aligned}
x_1 &= \frac{R}{2}\cosh u \cos v,\\
x_2 &= \frac{R}{2}\sinh u \sin v \cos\beta_{D-2},\\
x_3 &= \frac{R}{2}\sinh u \sin v \sin\beta_{D-2}\cos\beta_{D-3},\\
&\vdots\\
x_{D-1} &= \frac{R}{2}\sinh u \sin v \sin\beta_{D-2}\ldots\sin\beta_2\cos\beta_1,\\
x_D &= \frac{R}{2}\sinh u \sin v \sin\beta_{D-2}\ldots\sin\beta_2\sin\beta_1,
\end{aligned} \tag{2}$$

where

$$\begin{array}{ll} 0 \leqslant v < 2\pi, & \text{if} \quad D = 2, \\ 0 \leqslant v < \pi, & \text{if} \quad D > 2, \\ 0 \leqslant u < \infty, & \\ \beta_0 = 0, & 0 \leqslant \beta_1 < 2\pi, \\ 0 \leqslant \beta_k < \pi, & k = 2, 3, \ldots, D-2, \end{array}$$

and writing the wavefunction in the form $\Psi(\mathbf{r}) = \Xi^{(D)}(v)\Pi^{(D)}(u)\prod_{k=1}^{D-2} F_k(\beta_k)$, we obtain the equations

$$\left[\frac{1}{\sinh^{D-2} u}\frac{\partial}{\partial u}\sinh^{D-2} u\frac{\partial}{\partial u} - \frac{m_{D-2}(m_{D-2}+D-3)}{\sinh^2 u} + 2p\alpha\cosh u + p^2(\cosh^2 u - 1) - \lambda\right]\Pi^{(D)} = 0, \tag{3}$$

$$\left[\frac{1}{\sin^{D-2} v}\frac{\partial}{\partial v}\sin^{D-2} v\frac{\partial}{\partial v} - \frac{m_{D-2}(m_{D-2}+D-3)}{\sin^2 v} + 2p\beta\cos v - p^2(1-\cos^2 v) + \lambda\right]\Xi^{(D)} = 0, \tag{4}$$

$$\left[\frac{\partial^2}{\partial\beta_1^2} + m_1^2\right]F_1(\beta_1) = 0, \tag{5}$$

$$\left[\frac{1}{\sin^{k-1}\beta_k}\frac{\partial}{\partial\beta_k}\sin^{k-1}\beta_k\frac{\partial}{\partial\beta_k} - \frac{m_{k-1}(m_{k-1}+k-2)}{\sin^2\beta_k} + m_k(m_k+k-1)\right]F_k(\beta_k) = 0, \qquad k = 2, 3, \ldots, D-2, \tag{6}$$

where $\lambda, m_1, m_2, \ldots, m_{D-2}$ are the separation constants, and

$$p = (R/2)(-2E)^{1/2}, \qquad \alpha = (Z_2 + Z_1)(-2E)^{-1/2}, \qquad \beta = (Z_2 - Z_1)(-2E)^{-1/2}. \tag{7}$$

We only consider bound states with $E < 0$.

In particular, for $D = 2$ and $m_0 = 0$, the following ordinary differential equations for the functions $\Pi^{(2)}(u)$ and $\Xi^{(2)}(v)$ are obtained:

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}u^2} + 2p\alpha\cosh u - p^2(\cosh^2 u - 1) - \lambda\right]\Pi^{(2)}(u) = 0, \tag{8}$$

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}v^2} + 2p\beta\cos v - p^2(1-\cos^2 v) + \lambda\right]\Xi^{(2)}(v) = 0. \tag{9}$$

The physically correct solutions $\Pi^{(2)}(u)$, $\Xi^{(2)}(v)$ of equations (8) and (9) must satisfy the conditions

$$\Pi^{(2)}(u + 2\pi\mathrm{i}) = \Pi^{(2)}(u), \qquad |\Pi^{(2)}(0)| < \infty, \qquad |\Pi^{(2)}(u)| \xrightarrow{u\to\infty} 0, \tag{10}$$

$$\Xi^{(2)}(v + 2\pi) = \Xi^{(2)}(v). \tag{11}$$

It is expedient to introduce new variables ξ, η for the case $D \geqslant 3$ by

$$\xi = \cosh u, \qquad 1 \leqslant \xi < \infty, \qquad \eta = \cos v, \qquad -1 \leqslant \eta \leqslant 1,$$

so that the radial equation (3) and the angular equation (4) are transformed into

$$\left[\frac{1}{(\xi^2-1)^{\frac{D-3}{2}}}\frac{\mathrm{d}}{\mathrm{d}\xi}(\xi^2-1)^{\frac{D-1}{2}}\frac{\mathrm{d}}{\mathrm{d}\xi}-\lambda-p^2(\xi^2-1)+2p\alpha\xi-\frac{m(m+D-3)}{\xi^2-1}\right]\Pi^{(D)}=0, \tag{12}$$

$$\left[\frac{1}{(1-\eta^2)^{\frac{D-3}{2}}}\frac{\mathrm{d}}{\mathrm{d}\eta}(1-\eta^2)^{\frac{D-1}{2}}\frac{\mathrm{d}}{\mathrm{d}\eta}+\lambda-p^2(1-\eta^2)+2p\beta\eta-\frac{m(m+D-3)}{1-\eta^2}\right]\Xi^{(D)}=0, \tag{13}$$

where

$$m = m_{D-2}.$$

The functions $\Pi(\xi)$ and $\Xi(\eta)$ obey the boundary conditions

$$|\Pi^{(D)}(1)| < \infty, \qquad |\Pi^{(D)}(\xi)| \xrightarrow{\xi\to\infty} 0, \tag{14}$$

$$|\Xi^{(D)}(\pm 1)| < \infty. \tag{15}$$

Both equations (12) and (13) are singly confluent Heun equations [11, 12].

We introduce the radial Coulomb hyperspheroidal functions (RCHF) $\Pi_{mk}^{(D)}(p,\alpha;\xi)$ ($D \geqslant 3$) as solutions of the Sturm–Liouville problem described by (12) and (14) on the ray $\xi \in [1,\infty)$, where k is the number of zeros inside $[1,\infty)$. In the case of $D = 2$, instead of the RCHF, we introduce the radial Coulomb elliptic functions (RCEF) $\Pi_k^{(2)}(p,\alpha;u)$ as the solution of the boundary problems (8) and (10), where now k is the number of zeros inside $[0,\infty)$.

Next, we introduce the angular Coulomb hyperspheroidal functions (ACHF) $\Xi_{mq}^{(D)}(p,\beta;\eta)$ ($D \geqslant 3$) as solutions of the Sturm–Liouville problem of (13) and (15) on the interval $\eta \in [-1,1]$, where q is the number of zeros inside $[-1,1]$. In the case of $D = 2$ instead of the ACHF, we introduce the angular Coulomb elliptic functions (ACEF) $\Xi_l^{(2)}(p,\beta;v)$ as solutions of (9) and (11), where l determines the number of zeros. In the case of equal charges ($Z_1 = Z_2$), l is the number of zeros in the interval $[0,\pi)$. In the case of $Z_1 \neq Z_2$, the number of zeros of the ACEF in the interval $[0,\pi)$ is equal to $2l$.

It can be seen that in the limiting case $p \to 0$ the angular equation (13) can be converted to the following form:

$$\left[\frac{1}{(1-z^2)^{\frac{D-3}{2}}}\frac{\mathrm{d}}{\mathrm{d}z}(1-z^2)^{\frac{D-1}{2}}\frac{\mathrm{d}}{\mathrm{d}z}+n(n+D-2)-\frac{m(m+D-3)}{1-z^2}\right]B=0. \tag{16}$$

Solutions of equation (16) bounded at the singularities $z = \pm 1$ are denoted by $\mathbf{B}_n^{(D),m}(z)$, and in this work we name them the B-functions. The B-functions are expressible in terms of the hypergeometric function, and they will be considered in the following section.

The situation is more complicated for the case of the radial equation (12). In the chosen scale, this equation appears to be a perturbed equation of (16). Actually the proper radial scale in the united atom limit ($p \to 0$) is $p\xi$. The principal scheme of further calculations is the following:

- the use of two different scales;
- perturbation calculations of the solutions;
- the matching of the solutions obtained on different subintervals.

As a final step, the dispersive equation for the eigenvalues of the energy is solved by means of successive approximations. All calculations are rather cumbersome and can be carried out with a symbolic computation system like Maple[4].

[4] Maple Waterloo Software, Inc. See http://www.maplesoft.com

The existence of two scales leads to the fact that the expansions for the separation constant and for the energy levels have more complicated structures than simple power series.

3. The B-functions

The B-functions are solutions of differential equation (16) where n and z are unrestricted. We will restrict ourselves $D = 3, 4, 5, \ldots$ and $m = 0, 1, 2, \ldots$ in the further deductions. If $D = 3$, then equation (16) simplifies to Legendre's equation [20] and we suppose that

$$\mathbf{B}_n^{(3),m}(z) = P_n^m(z), \tag{17}$$

where $P_n^m(z)$ are Legendre functions. For $m = 0$, equation (16) reduces to Gegenbauer's equation [20] and we suppose that

$$\mathbf{B}_n^{(D),0}(z) = \text{const} \cdot C_n^{\frac{D-2}{2}}(z), \tag{18}$$

where $C_n^a(z)$ are Gegenbauer functions [20]. The differential equation (16) remains unchanged if m is replaced by $-m - D + 3$, z by $-z$, and n by $-n - D + 2$. Therefore,

$$\mathbf{B}_n^{(D),m}(\pm z), \qquad \mathbf{B}_n^{(D),-m-D+3}(\pm z), \qquad \mathbf{B}_{-n-D+2}^{(D),m}(\pm z), \qquad \mathbf{B}_{-n-D+2}^{(D),-m-D+3}(\pm z)$$

are solutions of (16). We follow relation (17) and introduce the B-functions by

$$\mathbf{B}_n^{(D),m}(z) = \frac{\Gamma(n + m + D - 2)}{\Gamma(n - m + 1)}(z^2 - 1)^{\frac{3-D}{4}} P_{n+\frac{D-3}{2}}^{-m-\frac{D-3}{2}}(z). \tag{19}$$

Hence, the following relation between the B-functions and Gegenbauer functions is valid:

$$\mathbf{B}_n^{(D),m}(z) = 2^{-m-\frac{D-3}{2}} \frac{\Gamma(2m + D - 2)}{\Gamma\left(m + \frac{D-1}{2}\right)}(z^2 - 1)^{\frac{m}{2}} C_{n-m}^{m+\frac{D-2}{2}}(z), \tag{20}$$

and it is easily seen that condition (18) is fulfilled. Relation (19) leads to the important symmetry property

$$\mathbf{B}_{-n-D+2}^{(D),m}(z) = (-1)^{D-3}\mathbf{B}_n^{(D),m}(z). \tag{21}$$

The recurrent formulae for the B-functions may be derived by applying recurrence relations between the contiguous Legendre functions

$$(2n + D - 2)z\mathbf{B}_n^{(D),m}(z) = (n - m + 1)\mathbf{B}_{n+1}^{(D),m}(z) + (n + m + D - 3)\mathbf{B}_{n-1}^{(D),m}(z), \tag{22}$$

$$\begin{aligned}&(2n + D - 2)(1 - z^2)\frac{\mathrm{d}}{\mathrm{d}z}\mathbf{B}_n^{(D),m}(z) \\ &\qquad = (m - n - 1)n\mathbf{B}_{n+1}^{(D),m}(z) + (n + D - 2)(n + m + D - 3)\mathbf{B}_{n-1}^{(D),m}(z).\end{aligned} \tag{23}$$

By means of the transformation relationship of the hypergeometric function ${}_2F_1(a, b; c; x)$ [20], expression (19) is expressible in the form

$$\begin{aligned}\mathbf{B}_n^{(D),m}(z) &= (-1)^{D-3}2^{n+\frac{D-1}{2}}(z + 1)^{\frac{m}{2}-n-\frac{D-1}{2}}(z - 1)^{-\frac{m}{2}-\frac{D-3}{2}} \\ &\quad\times \frac{\Gamma(-2n - D + 2)}{\Gamma(-n - \frac{D-3}{2})\Gamma(-n - m - D + 3)} \\ &\quad\times {}_2F_1\left(n + \frac{D-1}{2}, n - m + 1; 2n + D - 1; \frac{2}{z + 1}\right) \\ &\quad+ 2^{-n-\frac{D-3}{2}}(z + 1)^{\frac{m}{2}+n+\frac{D-3}{2}}(z - 1)^{-\frac{m}{2}-\frac{D-3}{2}} \frac{\Gamma(2n + D - 2)}{\Gamma(n + \frac{D-1}{2})\Gamma(n - m + 1)} \\ &\quad\times {}_2F_1\left(-n - \frac{D-3}{2}, -n - m - D + 3; -2n - D + 3; \frac{2}{z + 1}\right).\end{aligned} \tag{24}$$

In our applications of the B-functions $z = x$, where $-1 \leqslant x \leqslant 1$. If $m + \frac{D-3}{2}$ is an even integer and D is an odd integer, we see from equation (19) that the values of $\mathbf{B}_n^{(D),m}(z)$ on both sides of the cut are equal, so in this case it is sufficient to take the branch cut along the real axis from -1 to $-\infty$. In all other cases, $\mathbf{B}_n^{(D),m}(x - \mathrm{i}0)$ and $\mathbf{B}_n^{(D),m}(x + \mathrm{i}0)$ are different [$f(x \pm \mathrm{i}0)$ means $\lim_{\varepsilon \to 0} f(x \pm \mathrm{i}\varepsilon)$, $\varepsilon > 0$]. In order to avoid ambiguity, it is usual to introduce slightly modified solutions of (16). These will be denoted by $\mathbb{B}_n^{(D),m}(x)$:

$$\mathbb{B}_n^{(D),m}(x) = \frac{1}{2}\left[\mathrm{e}^{-\mathrm{i}\pi\frac{m}{2}}\mathbf{B}_n^{(D),m}(x + \mathrm{i}0) + \mathrm{e}^{\mathrm{i}\pi\frac{m}{2}}\mathbf{B}_n^{(D),m}(x - \mathrm{i}0)\right]. \tag{25}$$

With this definition, formulae for the $\mathbb{B}_n^{(D),m}(x)$ corresponding to that for the $\mathbf{B}_n^{(D),m}(z)$ (19) may be obtained as

$$\mathbb{B}_n^{(D),m}(x) = \frac{\Gamma(n + m + D - 2)}{\Gamma(n - m + 1)}(1 - x^2)^{\frac{3-D}{4}}\mathbb{P}_{n+\frac{D-3}{2}}^{-m-\frac{D-3}{2}}(x), \tag{26}$$

where $\mathbb{P}_n^m(x)$ are Legendre functions on the cut [20]. If $n = 0, 1, 2, 3, \ldots$ and $n \geqslant m$, equation (26) is valid, and the hypergeometric series involved are polynomials of degree $n - m$ in x and $\left\{\mathbb{B}_n^{(D),m}(x)\right\}$ is a system of orthogonal polynomials. The orthogonal relationship for these polynomials reads

$$\begin{aligned}
&\int_{-1}^{1} \mathbb{B}_n^{(D),m}(x)\mathbb{B}_r^{(D),m}(x)(1 - x^2)^{\frac{D-3}{2}}\,\mathrm{d}x = 0, \qquad n \neq r, \\
&\int_{-1}^{1} \left[\mathbb{B}_n^{(D),m}(x)\right]^2 (1 - x^2)^{\frac{D-3}{2}}\,\mathrm{d}x = \frac{(n + m + D - 3)!}{(n - m)!\left(n + \frac{D-2}{2}\right)}.
\end{aligned} \tag{27}$$

4. The asymptotic expansions for the ACHF, ACEF and for the separation constants

Setting $p = 0$ in equation (13), we obtain the B-functions equation (16). This suggests to present an expansion for the eigenfunction $\Xi^{(D)}(\eta)$ of boundary problem (13) and (15) in the form

$$\Xi^{(D)}(\eta) = \sum_{n=m-l}^{\infty} g_n \mathbb{B}_{l+n}^{(D),m}(\eta). \tag{28}$$

The coefficients g_n satisfy the system of recurrent equations

$$\begin{aligned}
&p^2\Omega_n\Omega_{n+1}g_{n+2} + 2p\beta\Omega_n g_{n+1} \\
&\quad + [\lambda^{(\eta)} - (l + n)(l + n + D - 2) - p^2 + p^2(\Omega_{n-1}\Gamma_n + \Omega_n\Gamma_{n+1})]g_n \\
&\quad + 2p\beta\Gamma_n g_{n-1} + p^2\Gamma_n\Gamma_{n-1}g_{n-2} = 0, \qquad g_{m-l-1} = 0, \qquad g_{m-l-2} = 0,
\end{aligned} \tag{29}$$

where

$$\Omega_n = \frac{l + n + m + D - 2}{2l + 2n + D}, \qquad \Gamma_n = \frac{l + n - m}{2n + 2l + D - 4}. \tag{30}$$

The coefficients Ω_n and Γ_n are symmetrical, corresponding to the substitution $l \to -l - D + 2$:

$$\Omega_n(l) = \Gamma_{-n}(-l - D + 2), \qquad \Gamma_n(l) = \Omega_{-n}(-l - D + 2) \tag{31}$$

that leads to the symmetry of g_n

$$g_n(l) = g_{-n}(-l - D + 2), \qquad n \geqslant m - l, \tag{32}$$

and to the invariance of the separation constant

$$\lambda^{(\eta)}(l) = \lambda^{(\eta)}(-l - D + 2). \tag{33}$$

The asymptotic procedure of getting the succeeding coefficients g_n in expansion (28) and separation constant $\lambda^{(\eta)}$ is based on the formal series

$$g_n = p^{|n|}\sum_{j=0}^{\infty}[g_n]_{2j}p^{2j}, \qquad g_0 \equiv 1, \qquad \lambda^{(\eta)} = \sum_{j=0}^{\infty}[\lambda]_{2j}p^{2j}. \tag{34}$$

Firstly, expansions (34) are inserted into recurrent equations (29). Then we equate coefficients of alike powers of p. On the first step of the recursive procedure, $[\lambda]_0$ is obtained. On the next step the coefficients $[g_{\pm 1}]_0$ are obtained, then $[\lambda]_2$ and so on. We give some final results

$$[\lambda]_0 = l(l+D-2), \tag{35}$$

$$[\lambda]_2 = 1 - \Omega_0\Gamma_1\left(1 + \frac{2\beta^2}{l+\frac{D-1}{2}}\right) - \Gamma_0\Omega_{-1}\left(1 - \frac{2\beta^2}{l+\frac{D-3}{2}}\right), \tag{36}$$

$$\begin{aligned}[\lambda]_4 = &-\frac{\Omega_0\Gamma_1\Omega_1\Gamma_2}{2(2l+D)}\left(1+\frac{2\beta^2}{l+\frac{D-1}{2}}\right)^2 - \frac{\beta^2}{\left(l+\frac{D-1}{2}\right)^2}\Omega_0\Gamma_1\Omega_1\Gamma_2 \\ &- \frac{\beta^2(2l+D-2)}{\left(l+\frac{D-1}{2}\right)^2}\Gamma_0\Omega_{-1}\Omega_0\Gamma_1 + \frac{2\beta^4}{\left(l+\frac{D-1}{2}\right)^3}\Omega_0^2\Gamma_1^2 \\ &+ \frac{\beta^4}{\left(l+\frac{D-3}{2}\right)^2\left(l+\frac{D-1}{2}\right)^2}\Gamma_0\Omega_{-1}\Omega_0\Gamma_1 + \{\quad\}_{l\to -l-D+2}.\end{aligned} \tag{37}$$

For the sake of brevity, we denote with the brace all terms in (37) that are symmetrical to the given ones in accordance with the substitution $l \to -l-D+2$ and the property (31).

Instead of expansion (28), we can use the expansions of the form

$$\begin{aligned}\Xi^{(D)}(\eta) &= \mathrm{e}^{-p\eta}\sum_{n=m-l}^{\infty} d_n \mathbb{B}_{l+n}^{(D),m}(\eta), \\ d_n &= p^{|n|}\sum_{j=0}^{\infty}[d_n]_{2j}p^{2j}, \qquad d_0 \equiv 1,\end{aligned} \tag{38}$$

where the coefficients d_n satisfy the three-term recurrent equation system

$$\begin{aligned}2pd_{n-1}&\frac{(l+n-m)\left(\beta+l+n+\frac{D-3}{2}\right)}{2l+2n+D-4} - d_n[(l+n)(l+n+D-2)-\lambda^{(\eta)}] \\ &+2pd_{n+1}\frac{(l+n+m+D-2)\left(\beta-l-n-\frac{D-1}{2}\right)}{2l+2n+D} = 0, \qquad d_{-1}=0.\end{aligned} \tag{39}$$

It is easy to obtain from equation (39) the following limiting ratio:

$$\left|\frac{d_{n+1}}{d_n}\right| \sim \frac{p}{n}, \qquad n \to +\infty. \tag{40}$$

Thus, series (38) converges on the interval $-1 \leqslant \eta \leqslant 1$. The successive approximation procedure leads to an expansion for the eigenvalues $\lambda^{(\eta)}$:

$$\begin{aligned}\lambda^{(\eta)} = l(l+D-2) &+ 2p^2\frac{\left(l+\frac{D-3}{2}\right)^2 + l + \frac{D-5}{2} + \left(m+\frac{D-3}{2}\right)^2}{(2l+D-4)(2l+D)} \\ &+2p^2\beta^2\frac{\left(l+\frac{D-3}{2}\right)^2 + l + \frac{D-3}{2} - 3\left(m+\frac{D-3}{2}\right)^2}{\left(l+\frac{D-3}{2}\right)\left(l+\frac{D-1}{2}\right)(2l+D-4)(2l+D)} + O(p^4).\end{aligned} \tag{41}$$

Now, we obtain the asymptotic expansion of the ACEF. The differential equation (9) belongs to the class of equations with periodic coefficients. In the case of the equal charges ($Z_1 = Z_2$) parameter β is equal to zero, and the angular equation (9) transforms to the Mathieu equation (see [20] vol 3). From condition (11) follows that these solutions of equation (9) are

$$\Xi_l^{(2),(+)}(p, 0; \upsilon) = ce_l\left(\upsilon, -\frac{p^2}{4}\right), \qquad \Xi_l^{(2),(-)}(p, 0; \upsilon) = se_l\left(\upsilon, -\frac{p^2}{4}\right), \tag{42}$$

where $ce_l(\nu, q)$ and $se_l(\nu, q)$ are the well-known Mathieu's functions (see again [20] vol 3).

In the case $Z_1 \neq Z_2$, we introduce the new function $\Xi^{(2)}(p, \beta; \upsilon) = \mathrm{e}^{-p\cos\upsilon} W(p, \beta; \upsilon)$ and the new variable $\upsilon = 2\zeta$. In these terms, the angular equation (9) is transformed to Ince's equation [21]

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\zeta^2} + 4p\sin(2\zeta)\frac{\mathrm{d}}{\mathrm{d}\zeta} + 4p(1+2\beta)\cos(2\zeta) + 4\lambda\right] W(p, \beta; \upsilon) = 0. \tag{43}$$

Formal solutions of problems (43) and (11) are obtainable as trigonometric series

$$W_l^{(+)}(p, \beta; \upsilon) = \sum_{n=0}^{\infty} a_n \cos(2n\zeta), \qquad (l \geqslant 0), \tag{44}$$

$$a_n(l) = p^{|n-l|} \sum_{j=0}^{\infty} [a_n(l)]_{2j} p^{2j}, \qquad a_l(l) = 1, \qquad (l \geqslant 0),$$

$$W_l^{(-)}(p, \beta; \upsilon) = \sum_{n=0}^{\infty} b_n \sin[(2n+2)\zeta], \qquad (l \geqslant 1), \tag{45}$$

$$b_n(l) = p^{|n-l+1|} \sum_{j=0}^{\infty} [b_n(l)]_{2j} p^{2j}, \qquad b_{l-1}(l) = 1, \qquad (l \geqslant 1).$$

The eigenfunctions $W_l^{(+)}(p, \beta; \upsilon)$ and $W_l^{(-)}(p, \beta; \upsilon)$ correspond to the eigenvalues $\lambda_l^{(+)}$ and $\lambda_l^{(-)}$. The three-term recurrence relation for the coefficients a_n and b_n and the perturbation procedure for obtaining $\lambda_l^{(\pm)}$ are studied in [13]. The eigenvalues $\lambda_l^{(\pm)}$ and $\lambda^{(\eta)}$ are connected with relation

$$\lambda_l^{(\pm)} = \lambda^{(\eta)}\Big|_{\substack{D=2\\ m=0,}} \qquad (l \geqslant 2). \tag{46}$$

5. The asymptotic expansions for the RCHF and RCEF

When the values of ξ are finite, the radial equation (12) is like perturbed equation (16). This suggests to represent an expansion for the solution $\Pi_<^{(D)}(\xi)$, which is finite at $\xi = 1$, in the form

$$\Pi_<^{(D)}(\xi) = \mathrm{e}^{-p\xi} \sum_{n=-\infty}^{\infty} d_n(\nu)\mathbf{B}_{\nu+n}^{(D),m}(\xi),$$
$$d_0(\nu) \equiv 1, \qquad d_n(\nu) = p^{|n|} \sum_{j=0}^{\infty} [d_n(\nu)]_{2j} p^{2j}. \tag{47}$$

The coefficients $d_n(\nu)$ satisfy the recurrent equations that coincide with relation (39) by changing l into ν and β into $-\alpha$. The expansion for the eigenvalues $\lambda^{(\xi)}$ of boundary problems (12) and (14) is equivalent to series (41) after substituting $l \to \nu$ and $\beta \to -\alpha$

$$\lambda^{(\xi)} = \lambda^{(\eta)} \bigg|_{\substack{l \to \nu, \\ \beta \to -\alpha.}} \tag{48}$$

The convergence of series (47) is determined (and ensured) by the behaviour of ratios $d_{n+1}(\nu)\mathbf{B}^{(D),m}_{\nu+n+1}(\xi) \big/ d_n(\nu)\mathbf{B}^{(D),m}_{\nu+n}(\xi)$ at large positive n, and $d_n(\nu)\mathbf{B}^{(D),m}_{\nu+n}(\xi) \big/ d_{n+1}(\nu)\mathbf{B}^{(D),m}_{\nu+n+1}(\xi)$ at large negative n. From the recurrence relations for coefficients $d_n(\nu)$ and from equation (22) we obtain

$$\left| \frac{d_{n+1}(\nu)\mathbf{B}^{(D),m}_{\nu+n+1}(\xi)}{d_n(\nu)\mathbf{B}^{(D),m}_{\nu+n}(\xi)} \right| \sim \frac{p}{n}\left(\xi - \sqrt{\xi^2 - 1}\right), \qquad n \to +\infty, \tag{49}$$

$$\left| \frac{d_n(\nu)\mathbf{B}^{(D),m}_{\nu+n}(\xi)}{d_{n+1}(\nu)\mathbf{B}^{(D),m}_{\nu+n+1}(\xi)} \right| \sim \frac{p}{n\left(\xi - \sqrt{\xi^2 - 1}\right)}, \qquad n \to -\infty. \tag{50}$$

Thus, series (47) converges in the complex plane cut from +1 to $-\infty$.

Series (48) for the separation constant is invariant under the substitution $\nu \to -\nu - D + 2$. This leads to the symmetry of the coefficients $d_n(\nu)$:

$$d_{-n}(\nu) = d_n(-\nu - D + 2). \tag{51}$$

From equations (51) and (21), we can see that the solution $\Pi^{(D)}_{<}(\xi)$ has the symmetry property

$$\Pi^{(D)}_{<}(\xi)\big|_{\nu \to -\nu - D + 2} = (-1)^{D-3}\Pi^{(D)}_{<}(\xi). \tag{52}$$

Another series is needed in the region of large ξ ($\xi = O(p^{-1})$), where the new scale for the independent variable is introduced:

$$x = p(\xi + 1), \tag{53}$$

and the new function

$$\widetilde{\Pi}^{(D)}(x) = \frac{(\xi + 1)^{\frac{m+D-3}{2}}}{(\xi - 1)^{\frac{m}{2}}}\Pi^{(D)}(\xi). \tag{54}$$

Thus, instead of (12) we obtain

$$\begin{aligned}
&\left[\frac{\mathrm{d}}{\mathrm{d}x}x^2\frac{\mathrm{d}}{\mathrm{d}x} - x^2 + 2\alpha x - \tau(\tau+1)\right]\widetilde{\Pi}^{(D)}(x) + \frac{p}{x - 2p}\left[2\left(m + \frac{D-1}{2}\right)x\frac{\mathrm{d}}{\mathrm{d}x}\right. \\
&\qquad + \left(\tau(\tau+1) - \frac{(D-3)(D-1)}{4} - \lambda^{(\xi)}\right)\frac{x}{p} \\
&\qquad \left. + 2\alpha x - 2\tau(\tau+1)\right]\widetilde{\Pi}^{(D)}(x) \equiv \widehat{T}\widetilde{\Pi}^{(D)}(x) + p\widehat{Q}\widetilde{\Pi}^{(D)}(x) = 0,
\end{aligned} \tag{55}$$

where $\tau = \nu + \frac{D-3}{2}$.

Here ν is a parameter which will be determined later on. The motivation for introducing the new variable x and the new function (54) can be clearly seen now: it allows a useful partitioning of differential operators, such that the operator $\widehat{T}$, in equation (55), coincides with the three-dimensional radial Schrödinger operator in spherical coordinates for the Coulomb field of a united atom with charge $Z_1 + Z_2$ and an effective orbital momentum τ. The two linearly independent solutions of the equation $\widehat{T}R(x) = 0$ are functions $R_\tau(x)$ and $R_{-\tau-1}(x)$, where

$$R_\tau(x) = x^\tau \mathrm{e}^{-x}{}_1F_1(-\alpha + \tau + 1; 2\tau + 2; 2x). \tag{56}$$

Here ${}_1F_1(a; c; x)$ is the regular in the origin solution of the confluent hypergeometric equation. The recurrence relation for the function $R_\tau(x)$ can be obtained either by using the corresponding relations between the adjacent confluent functions [20], or by using the well-elaborated techniques of integral transformation [9]. Here we shall give only the final result

$$\frac{R_\tau(x)}{x} = R_{\tau-1}(x) + \frac{\alpha}{\tau(\tau+1)} R_\tau(x) + \frac{\alpha^2 - (\tau+1)^2}{(\tau+1)^2(2\tau+1)(2\tau+3)} R_{\tau+1}(x), \tag{57}$$

$$\frac{\mathrm{d}R_\tau(x)}{\mathrm{d}x} = \tau R_{\tau-1}(x) - \frac{\alpha^2 - (\tau+1)^2}{(\tau+1)(2\tau+1)(2\tau+3)} R_{\tau+1}(x). \tag{58}$$

According to property (52), we shall construct the function $\Pi_>^{(D)}(\xi)$ that is the continuation of the function $\Pi_<^{(D)}(\xi)$ to large ξ in the form

$$\Pi_>^{(D)}(\xi) = g(\nu) y_\nu^{(1)}(\xi) + (-1)^{D-3} g(-\nu - D + 2) y_{-\nu-D+2}^{(1)}(\xi), \tag{59}$$

$$y_\nu^{(1)}(\xi) = \frac{(\xi-1)^{\frac{m}{2}}}{(\xi+1)^{\frac{m+D-3}{2}}} \sum_{n=-\infty}^{\infty} h_n(\nu) R_{\tau+n}(x), \tag{60}$$

$$\begin{aligned} y_{-\nu-D+2}^{(1)}(\xi) &= \frac{(\xi-1)^{\frac{m}{2}}}{(\xi+1)^{\frac{m+D-3}{2}}} \sum_{n=-\infty}^{\infty} h_n(-\nu - D + 2) R_{-\tau-1+n}(x), \\ h_n(\nu) &= p^{|n|} \sum_{j=0}^{\infty} [h_n(\nu)]_{2j} p^{2j}, \qquad h_0(\nu) \equiv 1. \end{aligned} \tag{61}$$

Here $g(\nu)$ and $g(-\nu - D + 2)$ will be found later by matching expansions (47) and (59). Both functions (60) and (61) have to satisfy equation (55) separately. The coefficients $h_n(\nu)$ obey the three-term recurrence relation

$$\begin{aligned} 2ph_{n-1} &\frac{\left[\left(\nu + \frac{D-3}{2}\right)^2 - \alpha^2\right](\nu + n + m + D - 3)}{\left(\nu + n + \frac{D-3}{2}\right)(2\nu + 2n + D - 4)(2\nu + 2n + D - 2)} \\ &+ h_n \left[\left(\nu + n + \frac{D-3}{2}\right)\left(\nu + n + \frac{D-1}{2}\right) - \lambda^{(\xi)}\right] \\ &- 2ph_{n+1}\left(\nu + n + \frac{D-1}{2}\right)(\nu + n - m + 1) = 0. \end{aligned} \tag{62}$$

From recurrence relations (57) and (62), we can obtain the following limiting ratios:

$$\left|\frac{h_{n+1}(\nu) R_{\tau+n+1}(x)}{h_n(\nu) R_{\tau+n}(x)}\right| \sim \frac{px}{2n^2}, \qquad n \to +\infty, \tag{63}$$

$$\left|\frac{h_n(\nu) R_{\tau+n}(x)}{h_{n+1}(\nu) R_{\tau+n+1}(x)}\right| \sim \frac{2p}{x}, \qquad n \to -\infty. \tag{64}$$

Thus, series (59) converges whenever $|\xi| > 1$. The coefficients $d_n(\nu)$ (47) and $h_n(\nu)$ (59) are connected with the relation

$$h_n(\nu) = d_n(\nu)(-2)^n \frac{\left(\alpha + \nu + \frac{D-1}{2}\right)_n (\nu + m + D - 2)_n}{(2\nu + D - 1)_{2n}(\nu - m + 1)_n}, \tag{65}$$

where $(a)_n = \frac{\Gamma(a+n)}{\Gamma(a)}$ is the Pochhammer symbol.

Using relation (24), we can present solution (47) of the radial equation (12) as linear combinations of further solutions of this equation

$$\Pi_{<}^{(D)}(\xi) = y_\nu^{(2)}(\xi) + (-1)^{D-3} y_{-\nu-D+2}^{(2)}(\xi), \tag{66}$$

where

$$\begin{aligned} y_\nu^{(2)}(\xi) = \mathrm{e}^{-p\xi}\left(\frac{\xi+1}{\xi-1}\right)^{\frac{m+D-3}{2}} & \sum_{n=-\infty}^{\infty} d_n(\nu) 2^{-n-\nu-\frac{D-3}{2}} \\ & \times \frac{(\xi+1)^{n+\nu}\Gamma(2n+2\nu+D-2)}{\Gamma\left(n+\nu+\frac{D-1}{2}\right)\Gamma(n+\nu-m+1)} \\ & \times {}_2F_1\left(-n-\nu-\frac{D-3}{2}, -n-\nu-m-D+3; -2n-2\nu-D+3; \frac{2}{\xi+1}\right). \end{aligned} \tag{67}$$

Now, we describe a closed circuit on the complex plane of ξ, making positive loops around the points $\xi = \pm 1$. This leads to $\xi - 1 \to \mathrm{e}^{2\pi\mathrm{i}}(\xi - 1)$, $\xi + 1 \to \mathrm{e}^{2\pi\mathrm{i}}(\xi + 1)$, and it can easily be seen that the effect of this circulation on solutions (67), (60) and (61) of the radial equation is

$$y_\nu^{(1)}(\xi) \to \mathrm{e}^{2\pi\mathrm{i}\nu} y_\nu^{(1)}(\xi), \qquad y_{-\nu-D+2}^{(1)}(\xi) \to \mathrm{e}^{2\pi\mathrm{i}(-\nu-D+2)} y_{-\nu-D+2}^{(1)}(\xi), \tag{68}$$

$$y_\nu^{(2)}(\xi) \to \mathrm{e}^{2\pi\mathrm{i}\nu} y_\nu^{(2)}(\xi), \qquad y_{-\nu-D+2}^{(2)}(\xi) \to \mathrm{e}^{2\pi\mathrm{i}(-\nu-D+2)} y_{-\nu-D+2}^{(2)}(\xi). \tag{69}$$

Since $y_\nu^{(1)}(\xi)$, $y_\nu^{(2)}(\xi)$, $y_{-\nu-D+2}^{(1)}(\xi)$ and $y_{-\nu-D+2}^{(2)}(\xi)$ are solutions of an ordinary differential equation of the second order, relations (68) and (69) imply that

$$y_\nu^{(2)}(\xi) = g(\nu) y_\nu^{(1)}(\xi), \qquad y_{-\nu-D+2}^{(2)}(\xi) = g(-\nu-D+2) y_{-\nu-D+2}^{(1)}(\xi). \tag{70}$$

The value ν is called the characteristic exponent, and the solutions $y_\nu^{(1)}(\xi)$, $y_\nu^{(2)}(\xi)$ are called Floquet solutions [11, 19]. The characteristic exponent ν is a function of the parameters of the radial equation.

The constant of proportionality $g(\nu)$ may be evaluated by expanding the hypergeometric series representation $y_\nu^{(2)}(\xi)$ and the confluent hypergeometric representation for $y_\nu^{(1)}(\xi)$ and comparing alike terms

$$g(\nu) = \mathrm{e}^p p^{-\nu-j-\frac{D-3}{2}} \frac{2^{j+\nu+\frac{D-3}{2}}\Gamma\left(j+\nu+\frac{D-2}{2}\right)}{\sqrt{\pi}\,\Gamma(1+j+\nu-m)} S(\nu), \tag{71}$$

where

$$\begin{aligned} S(\nu) = \Bigg[& \sum_{k=0}^{\infty} d_{j+k}(\nu) \frac{2^{2k}\left(j+\nu+\frac{D-2}{2}\right)_k}{(1+j+\nu-m)_k} \\ & \times \sum_{l=0}^{k} \frac{\left(-j-k-\nu-\frac{D-3}{2}\right)_l \left(m+\frac{D-3}{2}\right)_{k-l} (-j-k-\nu-m-D+3)_l}{(-2j-2k-2\nu-D+3)_l\, l!\,(k-l)!} \Bigg] \\ & \times \left[\sum_{k=0}^{\infty} h_{j-k}(\nu) \frac{2^k\left(-\alpha+j-k+\nu+\frac{D-1}{2}\right)_k}{(2\nu+2j-2k+D-1)_k\, k!}\right]^{-1}. \end{aligned} \tag{72}$$

In formula (71), j is an arbitrary integer and $g(\nu)$ is independent of j. Here we shall give only the final result for the ratio $S(-\nu-D+2)/S(\nu)$:

$$\frac{S(-\nu-D+2)}{S(\nu)} = 1-4p^2\frac{2\nu+D-2}{(2\nu+D-4)^2(2\nu+D)^2}$$
$$\times\left[\alpha^2\left(1-\frac{3\left(m+\frac{D-3}{2}\right)^2\left[8\left(\nu+\frac{D-3}{2}\right)\left(\nu+\frac{D-1}{2}\right)-3\right]}{4\left(\nu+\frac{D-3}{2}\right)^2\left(\nu+\frac{D-1}{2}\right)^2}\right)\right.$$
$$\left.+\left(m+\frac{D-3}{2}\right)^2-\frac{1}{4}\right]+O(p^4). \tag{73}$$

When α and τ have arbitrary values, the solution $\Pi_>^{(D)}(\xi)$ in the limit $x\to\infty$ has the form of a linear combination of the two exponents, one decreasing and the other increasing. Declaring the coefficient in front of the increasing exponent to be zero, we obtain the dispersive equation that connects the values of the parameters α, τ and p:

$$\tan(\pi\alpha) = \tan\pi\left(\nu+\frac{D-3}{2}\right)\frac{1-\varepsilon}{1+\varepsilon}, \tag{74}$$

where

$$\varepsilon = \left(\frac{p}{4}\right)^{2\nu+D-2}\frac{\Gamma\left(\alpha+\nu+\frac{D-1}{2}\right)(-1)^m\pi^2\Gamma(\nu+m+D-2)}{\Gamma\left(\alpha-\nu-\frac{D-3}{2}\right)\cos^2\left[\pi\left(\nu+\frac{D-3}{2}\right)\right]\left(\nu+\frac{D-2}{2}\right)^2}$$
$$\times\frac{\Gamma(\nu-m+1)}{\Gamma^4\left(\nu+\frac{D-2}{2}\right)\Gamma^2\left(\nu+\frac{D-1}{2}\right)}\frac{\sin(\pi\nu)}{\sin\left[\pi\left(\nu+\frac{D-3}{2}\right)\right]}\frac{S(-\nu-D+2)}{S(\nu)}. \tag{75}$$

In concluding this section, we show the scheme of calculations the asymptotic expansions for the RCEF. Transforming the radial equation (8) into the algebraic form by writing $\xi=\cosh u$, we obtain

$$\left[(\xi^2-1)\frac{\mathrm{d}^2}{\mathrm{d}\xi^2}+\xi\frac{\mathrm{d}}{\mathrm{d}\xi}-p^2(\xi^2-1)+2p\alpha\xi-\lambda\right]\Pi^{(2)}(\xi)=0. \tag{76}$$

Equation (76) is a particular case of the confluent Heun equation [11, 12]. When the values of ξ are finite, the radial equation (76) is like a perturbed equation for the Chebyshev polynomial of the first kind $T_n(\xi)$ (see [20], vol 2). We represent the solution $\Pi_<^{(2)}(\xi)$ which is finite at $\xi=1$ by formal series

$$\Pi_<^{(2)}(\xi) = \mathrm{e}^{-p\xi}\sum_{n=-\infty}^{\infty}\overline{d}_nT_{\nu+n}(\xi). \tag{77}$$

The solution $\Pi_<^{(2)}(\xi)$ and the series for the separation constant are invariant to the substitution $\nu\to-\nu$. According to the symmetry $\nu\to-\nu$, we shall construct the function $\Pi_>^{(2)}(\xi)$, that is the continuation of the function $\Pi_<^{(2)}(\xi)$ to large ξ, in the form

$$\Pi_>^{(2)}(\xi) = \sqrt{\xi+1}\left[\overline{g}(\nu)\sum_{n=-\infty}^{\infty}\overline{h}_n(\nu)R_{\nu-\frac{1}{2}+n}(x)+\overline{g}(-\nu)\sum_{n=-\infty}^{\infty}\overline{h}_n(-\nu)R_{-\nu-\frac{1}{2}+n}(x)\right], \tag{78}$$

where $\overline{g}(\nu)$ and $\overline{g}(-\nu)$ are matching constants. The dispersive equation, that connects the values of the parameters α, ν, and p, reads

$$\tan\pi\left(\alpha+\frac{1}{2}\right) = \tan(\pi\nu)\frac{1-\epsilon}{1+\epsilon}, \tag{79}$$

where

$$\epsilon = p^{2\nu}\frac{\Gamma(-2\nu+1)\Gamma\left(\nu+\alpha+\frac{1}{2}\right)}{\Gamma(2\nu+1)\Gamma\left(-\nu+\alpha+\frac{1}{2}\right)}\left[1-\frac{8\alpha^2\nu}{(4\nu^2-1)^2}p^2+O(p^4)\right]. \tag{80}$$

6. Asymptotic expansions for the electronic terms and the quantum defect

The first step in deriving asymptotic expansions for the energy levels is to obtain the expansion of the parameter ν in powers of p. The asymptotic expansion for ν can be derived by equating $\lambda^{(\eta)}$ and $\lambda^{(\xi)}$. From equations (41) and (48) one obtains

$$\nu_{lm}^{(D)} = l + [\nu]_2 p^2 + [\nu]_4 p^4 + [\nu]_6 p^6 + O(p^8). \tag{81}$$

Here

$$\begin{aligned}
[\nu]_2 &= \alpha^2 s \mathcal{A}_{lm}^{(D)}, \\
[\nu]_4 &= \alpha^2 s\big(\alpha^2\big[s\mathcal{B}_{lm}^{(D)} + \mathcal{C}_{lm}^{(D)}\big] + \mathcal{D}_{lm}^{(D)}\big), \\
[\nu]_6 &= \alpha^2 s\big(\alpha^4\big[s^2\mathcal{E}_{lm}^{(D)} + s\mathcal{F}_{lm}^{(D)} + \mathcal{G}_{lm}^{(D)}\big] + \alpha^2\big[s\mathcal{H}_{lm}^{(D)} + \mathcal{I}_{lm}^{(D)}\big] + \mathcal{J}_{lm}^{(D)}\big),
\end{aligned}$$

where $s = \frac{Z_1 Z_2}{(Z_1+Z_2)^2}$. The coefficients $\mathcal{A}_{lm}^{(D)}, \mathcal{B}_{lm}^{(D)}, \mathcal{C}_{lm}^{(D)}$ and $\mathcal{D}_{lm}^{(D)}$ are connected with the coefficients A_{lm}, B_{lm}, C_{lm},[5] and D_{lm} from [9] by the following relations:

$$\mathcal{A}_{lm}^{(D)} = A_{lm}\bigg|_{\substack{l \to l + \frac{D-3}{2} \\ m \to m + \frac{D-3}{2}}}, \qquad \mathcal{B}_{lm}^{(D)} = B_{lm}\bigg|_{\substack{l \to l + \frac{D-3}{2} \\ m \to m + \frac{D-3}{2}}},$$

$$\mathcal{C}_{lm}^{(D)} = C_{lm}\bigg|_{\substack{l \to l + \frac{D-3}{2} \\ m \to m + \frac{D-3}{2}}}, \qquad \mathcal{D}_{lm}^{(D)} = D_{lm}\bigg|_{\substack{l \to l + \frac{D-3}{2} \\ m \to m + \frac{D-3}{2}}}.$$

The other coefficients have rather cumbersome forms and they are not presented here.

Inserting expression (81) into dispersion equation (74) and solving this equation by successive approximations, we obtain the following asymptotic expression for the energy terms:

$$E_{nlm}^{(D)} = -\frac{Z^2}{2\mathfrak{n}^2}\left[1 - \frac{s(ZR)^2}{2\mathfrak{n}}\mathcal{A}_{lm}^{(D)} + \frac{s(ZR)^4}{32\mathfrak{n}^3}[\mathcal{E}]_4 + \frac{s(ZR)^6}{64\mathfrak{n}^5}[\mathcal{E}]_6 + o(ZR)^6\right], \tag{82}$$

where $\mathfrak{n} = n + \frac{D-3}{2}$, $Z = Z_1 + Z_2$, and

$$\begin{aligned}
[\mathcal{E}]_4 &= \mathfrak{n}s\big(6\big[\mathcal{A}_{lm}^{(D)}\big]^2 - 4\mathfrak{n}\mathcal{B}_{lm}^{(D)}\big) - 4\mathcal{D}_{lm}^{(D)} - 4\mathfrak{n}^2\mathcal{C}_{lm}^{(D)}, \\
[\mathcal{E}]_6 &= -4s^2\mathfrak{n}^2\big[\mathcal{A}_{lm}^{(D)}\big]^3 + 6s\mathfrak{n}^3\big(\mathcal{C}_{lm}^{(D)} + s\mathcal{B}_{lm}^{(D)}\big)\mathcal{A}_{lm}^{(D)} + 10s\mathfrak{n}\mathcal{A}_{lm}^{(D)}\mathcal{D}_{lm}^{(D)} \\
&\quad - 2\mathfrak{n}^4\big(\mathcal{G}_{lm}^{(D)} + s\mathcal{F}_{lm}^{(D)}\big) - \mathfrak{n}^2\big(2\mathcal{I}_{lm}^{(D)} - Z^2 s^2 + 2s\mathcal{H}_{lm}^{(D)}\big) - 2\mathcal{J}_{lm}^{(D)}.
\end{aligned}$$

The additional supposition has been made at this step that s is not large.

We define the quantum defect $\Delta_{nlm}^{(D)}$ for the $(Z_1 e Z_2)_D$ system by the following relation:

$$E_{nlm}^{(D)} = -\frac{Z^2}{2\big(n + \Delta_{nlm}^{(D)} + \frac{D-3}{2}\big)}. \tag{83}$$

Expansion for the quantum defect $\Delta_{nlm}^{(D)}$ can be found from the expansion of the energy $E_{nlm}^{(D)}$

$$\Delta_{nlm}^{(D)} = \frac{s(ZR)^2}{4}\mathcal{A}_{lm}^{(D)} + \frac{s(ZR)^4}{16}[\mathcal{D}]_4 + \frac{s(ZR)^6}{64}[\mathcal{D}]_6 + o(ZR)^6, \tag{84}$$

[5] There is a misprint in the coefficient C_{lm} from the original article [9]. The correct form of the coefficient C_{lm} is

$$C_{lm} = \frac{A_{lm}}{2l+1}\left(\frac{(2l+1)^3}{8}A_{lm}^2 - \frac{A_{lm}}{2} - \frac{18m^2(4m^2-1)(2l+1)}{l^2(l+1)^2(2l-1)^2(2l+3)^2}\right) - \frac{B_{lm}}{2}.$$

where

$$[\mathcal{D}]_4 = s\mathcal{B}^{(D)}_{lm} + \mathcal{C}^{(D)}_{lm} + \frac{1}{\mathfrak{n}^2}\mathcal{D}^{(D)}_{lm},$$

$$[\mathcal{D}]_6 = \mathcal{G}^{(D)}_{lm} + s\mathcal{F}^{(D)}_{lm} + \frac{1}{2\mathfrak{n}^2}\left(2\mathcal{I}^{(D)}_{lm} + 2s\mathcal{H}^{(D)}_{lm} - Z^2 s^2\right) - \frac{2s}{\mathfrak{n}^3}\mathcal{A}^{(D)}_{lm}\mathcal{D}^{(D)}_{lm} + \frac{\mathcal{J}^{(D)}_{lm}}{\mathfrak{n}^4}.$$

Solving dispersive equation (74), one can see that expansions (82) and (84) contain only even powers of R up to the power $2l + D - 1$. The next terms are connected with ε in equation (74) and include logarithms. It is possible to connect the existence of these terms with the fact that the wavefunction in the vicinity of both nuclei includes the negative and positive powers of the variables.

In the case of $D = 3$ and arbitrary n, l, m these terms have been found in [9]. The fact, that they cannot be calculated for $D = 2$, has been mentioned in [13]. If we try to compute the logarithmic terms for the most general case (D, n, l, and m are arbitrary), we can easily see that these terms can be obtained for odd values of D only and they have complicated forms. This clarifies the previous statement. Moreover, it is important that the higher a space dimension is, the weaker the influence of the logarithmic terms is on the energy of the system $(Z_1eZ_2)_D$. It can be seen in [13] that the logarithmic terms of the united-atom expansion for the energy levels are the most significant for the case $D = 2$ and $l = 0$.

By going deeper into the details while solving the dispersive equation (74), one can also obtain the exact solution: the D-dimensional one-centre Coulomb functions in hypersphseroidal coordinates.

We have calculated one additional term in the expansion for the characteristic exponent ν for the case $D = 3$ and $l = m = 0$:

$$\begin{aligned}\nu^{(3)}_{00} = {}& \frac{8}{3}\alpha^2 s p^2 + \frac{16}{135}\alpha^4 s(9 - 38s)p^4 \\ &+ \frac{16\alpha^2 s}{42\,525}(\alpha^4[+78\,880s^2 + 2160s - 288] + \alpha^2[-2520s + 630] + 63)p^6 \\ &- \frac{32s\alpha^2}{13\,395\,375}(\alpha^6[68\,230\,064s^3 - 17\,236\,464s^2 + 395\,262s - 33\,225] \\ &+ \alpha^4[690\,480s^2 - 350\,280s + 44\,415] \\ &+ \alpha^2[63\,504s - 15\,750] - 165)p^8 + O(p^{10}).\end{aligned} \tag{85}$$

Up to now only the two first terms in expansion (85) have been calculated [9, 22]. Inserting expansion (85) into dispersion equation (74) and solving it by successive approximations procedure, we obtain the following asymptotic expressions for the energy $E^{(3)}_{n00}$ for the case of S states and $D = 3$:

$$E^{(3)}_{n00} = -\frac{Z^2}{2n^2}\left[1 + \mathfrak{E}_1 + \mathfrak{E}_2\right], \tag{86}$$

where

$$\begin{aligned}\mathfrak{E}_1 = {}& -\frac{4s}{3n}(ZR)^2 + \frac{4s}{3n}(ZR)^3 + \frac{4s}{5n}\left[s\left(\frac{5}{3n} + \frac{19}{27}\right) - 1\right](ZR)^4 \\ &+ \frac{16s}{9n}\left[s\left(\ln\frac{2ZR}{n} + \psi(n+1) + 2\gamma - \frac{2}{n} - \frac{139}{60}\right)\right. \\ &\left. + \frac{1}{48n^2} + \frac{43}{240}\right](ZR)^5 - \frac{16s^2}{9n}(ZR)^6\ln\frac{2ZR}{n},\end{aligned}$$

Table 1. Values of $\nu_{ml}^{(3)}$ at $R \to 0$ for $Z_1 = Z_2 = 1$ and $\alpha = \sqrt{2}$; $E = -1$.

R	$(\nu_{00}^{(3)})^{\mathrm{a}}$	$(\nu_{00}^{(3)})^{\mathrm{b}}$	$(\nu_{01}^{(3)})^{\mathrm{a}}$	$(\nu_{01}^{(3)})^{\mathrm{c}}$
0.025	0.000 416 661	0.000 416 661	0.999 917	0.999 917
0.05	0.001 666 58	0.001 666 58	0.999 667	0.999 667
0.10	0.006 665 67	0.006 665 67	0.998 665	0.998 665
0.20	0.026 6741	0.026 6741	0.994 641	0.994 641
0.30	0.060 240	0.060 234	0.987 868	0.987 868
0.40	0.108 375	0.108 268	0.978 242	0.978 243
0.50	0.174 353	0.173 253	0.965 602	0.965 608
0.60	0.269 069	0.260 344	0.949 715	0.949 742

[a] Values for $\nu_{ml}^{(3)}$ obtained by numerical solutions in [22].
[b] Values for $\nu_{00}^{(3)}$ obtained by using expansion (85).
[c] Values for $\nu_{01}^{(3)}$ obtained by using expansion (81).

$$
\begin{aligned}
\mathfrak{E}_2 = \frac{16s}{9n}\Bigg[&-s\left(\psi(n+1) + \frac{1}{2n} + 2\gamma + \frac{1}{n}\left(\frac{19}{30}s - \frac{53}{20}\right) + \frac{1}{n^2}\left(\frac{2}{3}s - \frac{1}{60}\right) + \frac{493}{945}s - \frac{1801}{840}\right) \\
&- \frac{1}{2400n^4} - \frac{1}{40n^2} - \frac{773}{16\,800}\Bigg](ZR)^6 + \frac{32s^3}{27n}(ZR)^7 \ln^2 R \\
&- \frac{s^2}{170\,100n^3}\Bigg[\Bigg(-\frac{253\,680}{s} + 1\,061\,760 - 403\,200 \ln\frac{2Z}{n} - 806\,400\gamma \\
&- 403\,200\psi(n+1)\Bigg)sn^2 + 806\,400sn - 8400\Bigg](ZR)^7 \ln R + O(R^7).
\end{aligned}
$$

Here $\psi(n+1) = \frac{\mathrm{d}\ln\Gamma(x+1)}{\mathrm{d}x}\big|_{x=n}$ is the logarithmic derivative of the gamma function [20] and $\gamma = 0.5772\ldots$ is the Euler constant. The form of the $\mathfrak{E}_1$ has been obtained in [9].

The asymptotic expansions for the energy levels and the quantum defect of the system $(Z_1eZ_2)_2$ are studied in [13]. Asymptotic expansions (81), (82) and (84) are valid for the case of $D = 2$ $(m = 0)$ when $l \geqslant 4$.

7. Discussion

We have checked our approximate results with numerical solutions. In table 1, the comparison of our results for values $\nu_{ml}^{(3)}$ (81), (85) with those of the previous asymptotic and numerical treatments [22] shows that, as expected, the inclusion of additional terms in the asymptotic expansions for $\nu_{ml}^{(3)}$ improves the agreement between asymptotic and numerical results. It can be seen from this table that the agreement of the two sets of values for $\nu_{ml}^{(3)}$ is better for the smaller R and the larger l values. In table 2, we give comparison results obtained from the asymptotic expansion for the three-dimensional (3D) ground state energy level of H_2^+ (86) and from the numerical solution [23]. It can be seen from this table that taking into account the coefficient $\mathfrak{E}_2$ makes the agreement between the asymptotic and numerical results worse. This fact is due to the divergence of the series for the energy levels. The results are better for larger n.

From the asymptotic expansion for the energy $E_{nlm}^{(D)}$ (82), it is easily seen that the series for energy converges at small R and large D. We have compared high energy levels of the two-dimensional (2D) H_2^+ with high energy levels of the 3D H_2^+. In table 3, we can see how the high energy levels of the 2D H_2^+ approach the corresponding energy levels of the 3D H_2^+.

Table 2. Energy for the ground state of 3D H_2^+

R	$(-E_{100}^{(3)})^{a}$	$2[1+\mathfrak{E}_1]$	$2[1+\mathfrak{E}_1+\mathfrak{E}_2]$
0.05	1.993 9765	1.993 9765	1.993 9765
0.10	1.978 2421	1.978 236	1.978 244
0.20	1.928 6202	1.928 37	1.928 89
0.30	1.866 7039	1.8649	1.8704
0.40	1.800 7539	1.7943	1.8228
0.50	1.734 9879	1.714	1.818
0.60	1.671 4846	1.60	1.91

[a] Values for $E_{100}^{(3)}$ obtained by numerical solutions in [23].

Table 3. Comparing high energy levels of 2D H_2^+ and 3D H_2^+ ($R = 0.05$).

n	l	m	$-E_{nlm}^{(3)}$	$-E_{nl}^{(2)}$
		0	0.080 000 230 88	
5	4	3	0.079 999 919 19	0.098 765 867 59
		4	0.079 999 676 77	
		0	0.020 000 002 95	
10	9	5	0.020 000 000 49	0.022 160 668 83
		9	0.019 999 994 99	
		0	0.008 888 889 133	
15	14	7	0.008 888 888 962	0.009 512 485 436
		14	0.008 888 888 450	
		0	0.002 222 222 226	
30	29	15	0.002 222 222 223	0.002 298 190 179
		29	0.002 222 222 215	

This result confirms a well-know fact: the motion of an electron in the Rydberg state becomes approximately planar. The energy terms $E_{nlm}^{(D)}$ of the system $(Z_1eZ_2)_D$ are connected with the energy terms $E_{nlm}^{(3)}$ of Z_1eZ_2 by the following relation:

$$E_{nlm}^{(D)} = E_{nlm}^{(3)}\left|\begin{array}{l} n \to n + \frac{D-3}{2} \\ l \to l + \frac{D-3}{2} \\ m \to m + \frac{D-3}{2}. \end{array}\right. \tag{87}$$

Identical correspondences also exist for the D-dimensional hydrogen atom and the D-dimensional helium isoelectronic sequence [24].

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