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1997 J. Phys. A: Math. Gen. 30 559

(http://iopscience.iop.org/0305-4470/30/2/019)

J. Phys. A: Math. Gen. **30** (1997) 559–571. Printed in the UK PII: S0305-4470(97)76420-5

Problem of two Coulomb centres at large intercentre separation: asymptotic expansions from analytical solutions of the Heun equation

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Received 11 July 1996

Abstract. The case of large intercentre distance in the two Coulomb centres problem is studied by solving separated wave equations with the help of a series of confluent hypergeometric functions. By considering the confluence of two singularities in an auxiliary equation with four regular singularities, new relations between the solutions of the quasi-angular equation are found and used to obtain exponentially small terms in the asymptotic expansion for energy eigenvalues. For some electronic states, energy splittings at pseudocrossings are evaluated, and results are compared with those of earlier asymptotic and numerical calculations.

1. Introduction

The motion of an electron in the field of two Coulomb charges is one of the basic quantum mechanical problems which has been of great importance for the progress of quantum theory and is still of significant interest because of its numerous applications.

This problem is separable in the prolate spheroidal coordinates. Various numerical methods have been used for the solution of the separated two-centre equations (see, e.g., [1] and references therein, and [2, 3]). The separability of the problem is also helpful for obtaining some general analytic results in the regions of large and small intercentre distances R by applying perturbative or asymptotical methods [1, 4–14]. In this paper the case of large R is discussed.

The Schrödinger equation for the two Coulomb centres problem (in atomic units, $m = e = \hbar$) is

$$\left(-\frac{1}{2}\Delta - \frac{Z_1}{r_1} - \frac{Z_2}{r_2}\right)\psi = E\psi \tag{1}$$

where r_1 and r_2 are distances from the electron to charges Z_1 and Z_2. Introducing the prolate spheroidal coordinates

$$\begin{array}{lll} \xi = \dfrac{r_1 + r_2}{R} & \eta = \dfrac{r_1 - r_2}{R} & \varphi = \arctan\dfrac{y}{x} \\ 1 \leqslant \xi < \infty & -1 \leqslant \eta \leqslant 1 & 0 \leqslant \varphi < 2\pi \end{array} \tag{2}$$

and presenting the wavefunction in the form $\psi = u(\xi)v(\eta)\exp(\mathrm{i}m\varphi)$ we obtain the equations

$$\frac{\mathrm{d}}{\mathrm{d}\xi}(\xi^2 - 1)\frac{\mathrm{d}u}{\mathrm{d}\xi} + \left[-\lambda - p(\xi^2 - 1) + a\xi - \frac{m^2}{\xi^2 - 1}\right]u = 0 \tag{3}$$

$$\frac{\mathrm{d}}{\mathrm{d}\eta}(1-\eta^2)\frac{\mathrm{d}v}{\mathrm{d}\eta}+\left[\lambda-p(1-\eta^2)+b\eta-\frac{m^2}{1-\eta^2}\right]v=0 \tag{4}$$

where $p = R(-E/2)^{1/2}$, $a = R(Z_1+Z_2)$, $b = R(Z_1-Z_2)$, and λ is the separation constant. We only consider bound states with $E < 0$.

Different techniques have been used to derive the large R asymptotic expansions for eigenvalues of energy from the separated equations. Komarov and Slavyanov [4] developed a comparison-equation method and applied it to find expansions in powers of $1/R$ for eigenvalues of energy as well as exponentially small corrections to these eigenvalues for both cases $Z_1 = Z_2$ and $Z_1 \neq Z_2$. On the other hand, Damburg and Propin [5, 6] and Power [7] used expansions of solutions of the separated equations in series of confluent hypergeometric functions to determine $1/R$ expansions for energy. Damburg and Propin [5] have also found, with the help of such an expansion, exponentially small splittings between even and odd states for the case $Z_1 = Z_2$. In the case $Z_1 \neq Z_2$, this expansion of solutions has not been used for evaluation of exponentially small corrections to eigenvalues of energy because of difficulties arising in matching solutions of the quasi-angular equation which are defined on different intervals. Power [7] and Greenland [10] have used the comparison-equation method of Komarov and Slavyanov to find expansions of these corrections in powers of $1/R$. Calculations in this method become intricate in higher orders of approximation, and only terms up to and including $\mathrm{O}(1/R^2)$ have been obtained.

In this paper, we develop a new approach to the evaluation of exponentially small terms in the large R asymptotic expansion for energy eigenvalues of the two Coulomb centres problem. We consider the quasi-angular equation (4) as a limiting (confluent) case of the equation

$$(\gamma^2-\eta^2)\frac{\mathrm{d}}{\mathrm{d}\eta}(1-\eta^2)\frac{\mathrm{d}v}{\mathrm{d}\eta}+\left[\Lambda-\frac{2E\rho^2\gamma^2(1-\eta^2)}{\gamma^2-\eta^2}+\frac{2(Z_2-Z_1)\rho\gamma(\gamma^2-1)\eta}{\gamma^2-\eta^2}-\frac{m^2(\gamma^2-\eta^2)}{1-\eta^2}\right]v=0. \tag{5}$$

This equation arises by separating variables in the Schrödinger equation for a particle moving in the field of two Coulomb charges in the space of constant negative curvature [15]. In (5), ρ denotes radius of curvature, Λ is the separation constant, and $\gamma = \coth(\mathcal{R}/2\rho)$, where $\mathcal{R}$ is the distance between charges in the curved space. In the limit of vanishing curvature, that is for $\rho \to \infty$, when $\mathcal{R} \to R$, $2\rho/\gamma \to R$, and $\Lambda/\gamma^2 \to \lambda$, equation (4) is obtained from equation (5). By taking this limit in relations between solutions of equation (5) we find new asymptotic relations between solutions of the quasi-angular equation (4). Then we apply these relations to the computation of splittings of potential curves at pseudocrossings. These splittings are important in the study of charge exchange reactions between atomic hydrogen and heavy ions [16].

2. Solutions of separated equations and connection relations

Following Power [7], we take solutions of the quasiradial equation (3) in the form due to Hyleraas [17]

$$u=(\xi^2-1)^{m/2}\mathrm{e}^{-p(\xi-1)}\sum_{k=-n_1}^{\infty}c_kL_{n_1+k}(2p(\xi-1)) \tag{6}$$

where $L^m_{n_1+k}$ are Laguerre polynomials, and n_1 is a parabolic quantum number. Coefficients c_k obey the three-term recurrence relation

$$\alpha_k^{(\xi)} c_{k+1} + \beta_k^{(\xi)} c_k + \gamma_k^{(\xi)} c_{k-1} = 0 \tag{7}$$

where

$$\begin{aligned}
\alpha_k^{(\xi)} &= (n_1 + k + m + 1)(n_1 + k + 1 - a/2p) \\
\beta_k^{(\xi)} &= -2p(2n_1 + 2k + m + 1) + a + (m+1)(n_1 + m + k) - (2n_1 + 2k + m + 1) \\
&\quad \times (n_1 + k + m + 1 - a/2p) - \lambda \\
\gamma_k^{(\xi)} &= (n_1 + k)(n_1 + k + m - a/2p)
\end{aligned} \tag{8}$$

with boundary condition $c_{-n_1-1} = 0$.

Asymptotic expansion for $p \gg 1$ of the solution of the quasi-angular equation (4) which is valid near $\eta = -1$ may be presented in the form [5, 7]

$$v_1 = (1-\eta^2)^{m/2} \mathrm{e}^{-p(1+\eta)} \sum_{k=-\infty}^{\infty} d_k \Phi(-\nu_2 - k, m+1; 2p(1+\eta)) \tag{9}$$

where Φ denotes the confluent hypergeometric function [18], and ν_2 is some parameter. As ν_2 is not integer, series (9) is infinite on both sides. Coefficients d_k satisfy the recurrence relation

$$\alpha_k^{(\eta)} d_{k+1} + \beta_k^{(\eta)} d_k + \gamma_k^{(\eta)} d_{k-1} = 0 \tag{10}$$

where

$$\begin{aligned}
\alpha_k^{(\eta)} &= (\nu_2 + k + 1)(\nu_2 + k + 1 + b/2p) \\
\beta_k^{(\eta)} &= 2p(2\nu_2 + 2k + m + 1) + b + (m+1)(\nu_2 + m + k) - (2\nu_2 + 2k + m + 1) \\
&\quad \times (\nu_2 + k + m + 1 + b/2p) - \lambda \\
\gamma_k^{(\eta)} &= (\nu_2 + k + m)(\nu_2 + k + m + b/2p).
\end{aligned} \tag{11}$$

Asymptotic expansion for the solution of (4) near $\eta = 1$ is given by

$$v_1' = (1-\eta^2)^{m/2} \mathrm{e}^{-p(1-\eta)} \sum_{k=-\infty}^{\infty} d_k \Phi(-\nu_2' - k, m+1; 2p(1-\eta)) \tag{12}$$

where $\nu_2' = \nu_2 + b/2p$. Note that the recurrence relation (10) can be expressed in terms of ν_2' instead of ν_2,

$$\begin{aligned}
\alpha_k^{(\eta)} &= (\nu_2' + k + 1)(\nu_2' + k + 1 - b/2p) \\
\beta_k^{(\eta)} &= 2p(2\nu_2' + 2k + m + 1) - b + (m+1)(\nu_2' + m + k) - (2\nu_2' + 2k + m + 1) \\
&\quad \times (\nu_2' + k + m + 1 - b/2p) - \lambda \\
\gamma_k^{(\eta)} &= (\nu_2' + k + m)(\nu_2' + k + m - b/2p).
\end{aligned} \tag{13}$$

Series (9) and (12) are supposed to represent the same wavefunction, but matching of these series for the case $Z_1 \neq Z_2$ has never been accomplished.

We are going to find relations which connect series (9) and (12) with the help of relations between solutions of equation (5). This equation has four regular singularities $\eta = \pm 1$, $\eta = \pm\gamma$ (the point at infinity is an ordinary point), and can be reduced to the Heun equation [18, vol 3, p 57]. This reduction is effected by a linear fractional transformation of the independent variable, such as

$$\eta = -\gamma[z(\gamma - 1) + 2]/[2\gamma - z(\gamma - 1)] \tag{14}$$

or

$$\eta = \gamma[y(\gamma - 1) + 2]/[2\gamma - y(\gamma - 1)] \tag{15}$$

and a suitable transformation of the dependent variable,

$$v = z^{m/2}(1 - z)^{\mu_+}(z - a)^{m/2} g \tag{16}$$

or

$$v = z^{m/2}(1 - z)^{\mu_-}(z - a)^{m/2} g' \tag{17}$$

where

$$\mu_\pm = \tfrac{1}{2}\{1 - [-2E\rho^2 \mp 2(Z_2 - Z_1)\rho + 1]^{1/2}\} \qquad a = -4\gamma/(\gamma - 1)^2$$
$$z = 2\gamma(\eta + 1)/[(\gamma - 1)(\eta - \gamma)] \qquad y = 2\gamma(\eta - 1)/[(\gamma - 1)(\eta + \gamma)]. \tag{18}$$

As a result, we obtain the Heun equation for g

$$\frac{\mathrm{d}^2 g}{\mathrm{d}z^2} + \left(\frac{m+1}{z} + \frac{2\mu_+}{z-1} + \frac{m+1}{z-a}\right)\frac{\mathrm{d}g}{\mathrm{d}z} + \frac{ABz - q}{z(z-1)(z-a)} g = 0 \tag{19}$$

where

$$A = \mu_+ + \mu_- + m \qquad B = 1 + \mu_+ - \mu_- + m$$
$$q = (m + 1)(\mu_+ a + m) + \rho(Z_1 - Z_2)a/2 - \Lambda a/4\gamma \tag{20}$$

and the equation for g' can be obtained by replacements $\mu_+ \rightleftharpoons \mu_-$ and $Z_1 \rightleftharpoons Z_2$ in (19) and (20).

Solutions of the Heun equation in the form of a series of hypergeometric functions were studied by Erdelyi [19]. We will consider solutions of equation (5) which have solutions of (4) as their limiting cases,

$$v_{1(\rho)} = \phi(z, \mu_+) \sum_{k=-\infty}^{\infty} d_k^{(\rho)} {}_2F_1(-\nu_{(\rho)} - k, m + \nu_{(\rho)} + k + 2\mu_+; m + 1; z) \tag{21}$$

$$v'_{1(\rho)} = \phi(y, \mu_-) \sum_{k=-\infty}^{\infty} d_k^{(\rho)} {}_2F_1(-\nu'_{(\rho)} - k, m + \nu'_{(\rho)} + k + 2\mu_-; m + 1; y) \tag{22}$$

where

$$\phi(x, \mu) = (\gamma/2)^m(-x)^{m/2}(1 - x)^\mu(x - a)^{m/2} \qquad \nu'_{(\rho)} = \nu_{(\rho)} + \mu_+ - \mu_- \tag{23}$$

$\nu_{(\rho)}$ is a parameter and ${}_2F_1$ denotes the hypergeometric function. Coefficients $d_k^{(\rho)}$ satisfy the recurrence relation

$$\alpha_k^{(\eta,\rho)} d_{k+1}^{(\rho)} + \beta_k^{(\eta,\rho)} d_k^{(\rho)} + \gamma_k^{(\eta,\rho)} d_{k-1}^{(\rho)} = 0 \tag{24}$$

where

$$\alpha_k^{(\eta,\rho)} = \frac{(\nu_{(\rho)} + k + 1)(\nu'_{(\rho)} + k + 1)(\nu'_{(\rho)} + 2\mu_- + k)(\nu_{(\rho)} + 2\mu_+ + k)}{(2\nu_{(\rho)} + 2\mu_+ + 2k + m + 1)(2\nu_{(\rho)} + 2\mu_+ + 2k + m + 2)}$$

$$\beta_k^{(\eta,\rho)} = \left(a - \frac{1}{2}\right)\left[\frac{\Lambda}{4\gamma} + \frac{E\rho^2}{2} + (\nu_{(\rho)} + \mu_+ + k + m)(\nu_{(\rho)} + \mu_+ + k)\right]$$
$$+ \frac{5m^2 - 1}{8} + \frac{\Lambda}{8\gamma} + \frac{E\rho^2}{4}$$
$$- \frac{[(2\mu_+ - 1)^2 - m^2][(2\mu_- - 1)^2 - m^2]}{8(2\nu_{(\rho)} + 2\mu_+ + 2k + m + 1)(2\nu_{(\rho)} + 2\mu_+ + 2k + m - 1)}$$

$$\gamma_k^{(\eta,\rho)} = (\nu_{(\rho)} + k + m)(\nu'_{(\rho)} + k + m)$$
$$\times \frac{(\nu_{(\rho)} + 2\mu_+ + k + m - 1)(\nu'_{(\rho)} + 2\mu_- + k + m - 1)}{(2\nu_{(\rho)} + 2\mu_+ + 2k + m - 1)(2\nu_{(\rho)} + 2\mu_+ + 2k + m - 2)}. \quad (25)$$

Introducing the continued fractions

$$R_k^{(\rho)} = \frac{d_k^{(\rho)}}{d_{k-1}^{(\rho)}} = \frac{-\gamma_k^{(\eta,\rho)}}{\beta_k^{(\eta,\rho)} + \alpha_k^{(\eta,\rho)} R_{k+1}^{(\rho)}} \qquad L_k^{(\rho)} = \frac{d_k^{(\rho)}}{d_{k+1}^{(\rho)}} = \frac{-\alpha_k^{(\eta,\rho)}}{\beta_k^{(\eta,\rho)} + \gamma_k^{(\eta,\rho)} L_{k-1}^{(\rho)}} \quad (26)$$

we can write down a transcendental equation

$$R_1^{(\rho)} L_0^{(\rho)} = 1. \quad (27)$$

Now, convergence of series (21) and (22) can be examined following the approach of Erdelyi [19], with the difference that in our case series are infinite in two directions like the series solutions of the equation of spheroidal wavefunctions [18, vol 3, p 135]. In this way it can be shown that if (27) is satisfied, then the series (21) is convergent inside the ellipse in the complex z plane which has foci at $z = 0$ and $z = 1$ and which passes through $z = a$, and series (22) is convergent inside the similar ellipse in the y plane. From (14) and (15) we can see that $\eta = -1$ lies inside the domain of convergence of the series (21) and on the boundary of the domain of convergence of the series (22); the point $\eta = 1$ lies inside the domain of convergence of the series (22) and on the boundary of the domain of convergence of the series (21).

Coefficients $\alpha_k^{(\eta,\rho)}$, $\beta_k^{(\eta,\rho)}$, and $\gamma_k^{(\eta,\rho)}$ of (25) in the recurrence relation (24) have as their limits, when $\rho \to \infty$, coefficients $\alpha_k^{(\eta)}$, $\beta_k^{(\eta)}$, and $\gamma_k^{(\eta)}$ of (11), respectively, and equation (27) for parameter $\nu_{(\rho)}$ has equation

$$R_1 L_0 = 1 \quad (28)$$

as its limiting case. In (28)

$$R_k = \frac{d_k}{d_{k-1}} = \frac{-\gamma_k^{(\eta)}}{\beta_k^{(\eta)} + \alpha_k^{(\eta)} R_{k+1}} \qquad L_k = \frac{d_k}{d_{k+1}} = \frac{-\alpha_k^{(\eta)}}{\beta_k^{(\eta)} + \gamma_k^{(\eta)} L_{k-1}}. \quad (29)$$

Hence for $\rho \to \infty$ we can take parameter $\nu_{(\rho)} = \nu_2 + \mathrm{O}(1/\rho)$, and coefficients $d_k^{(\rho)} = d_k + \mathrm{O}(1/\rho)$. In this limit hypergeometric functions occurring in expansions (21) and (22) also go over into confluent hypergeometric functions which enter (9) and (12). It follows that as, $\rho \to \infty$,

$$v_{1(\rho)} \to v_1 \qquad v'_{1(\rho)} \to v'_1. \quad (30)$$

Domains of convergence of series (9) and (12) can be determined as limits to which domains of convergence of series (21) and (22) tend, respectively, as $\rho \to \infty$. In this way we find that series (9) and (12) converge in the halfplanes $-\infty < \mathrm{Re}\,\eta < 1$ and $-1 < \mathrm{Re}\,\eta < \infty$, respectively, provided (28) is satisfied.

Using relations between Kummer's series solutions of the hypergeometric equation [18, vol 1, p 105], we can present solutions (21) and (22) of equation (5) as linear combinations of further solutions of this equation

$$v_{1(\rho)} = \Gamma(m+1)(v_{2(\rho)} + v_{3(\rho)}) \qquad v'_{1(\rho)} = \Gamma(m+1)(v'_{2(\rho)} + v'_{3(\rho)}) \quad (31)$$

where

$$v_{2(\rho)} = \phi(z,\mu_+)\sum_{k=-\infty}^{\infty}\frac{d_k^{(\rho)}\Gamma(2\nu_{(\rho)}+2k+2\mu_+ +m)(-z)^{\nu_{(\rho)}+k}}{\Gamma(\nu_{(\rho)}+k+2\mu_+ +m)\Gamma(\nu_{(\rho)}+k+m+1)}$$
$$\times {}_2F_1(-\nu_{(\rho)}-k,-\nu_{(\rho)}-k-m;1-2\nu_{(\rho)}-2k-2\mu_+ -m;1/z)$$
$$v_{3(\rho)} = (1-z)^{1-2\mu_+}\phi(z,\mu_+)\sum_{k=-\infty}^{\infty}\frac{d_k^{(\rho)}\Gamma(-2\nu_{(\rho)}-2k-2\mu_+ -m)(-z)^{-\nu_{(\rho)}-k-m-1}}{\Gamma(-\nu_{(\rho)}-k-2\mu_+ +1)\Gamma(-\nu_{(\rho)}-k)}$$
$$\times {}_2F_1(\nu_{(\rho)}+k+1,\nu_{(\rho)}+k+m+1;1+2\nu_{(\rho)}+2k+2\mu_+ +m;1/z) \quad (32)$$
$$v'_{2(\rho)} = \phi(y,\mu_-)\sum_{k=-\infty}^{\infty}\frac{d_k^{(\rho)}\Gamma(2\nu'_{(\rho)}+2k+2\mu_+ +m)(-y)^{\nu'_{(\rho)}+k}}{\Gamma(\nu'_{(\rho)}+k+2\mu_+ +m)\Gamma(\nu'_{(\rho)}+k+m+1)}$$
$$\times {}_2F_1(-\nu'_{(\rho)}-k,-\nu'_{(\rho)}-k-m;1-2\nu'_{(\rho)}-2k-2\mu_- -m;1/y)$$
$$v'_{3(\rho)} = (1-y)^{1-2\mu_-}\phi(y,\mu_-)\sum_{k=-\infty}^{\infty}\frac{d_k^{(\rho)}\Gamma(-2\nu'_{(\rho)}-2k-2\mu_- -m)(-y)^{-\nu'_{(\rho)}-k-m-1}}{\Gamma(-\nu'_{(\rho)}-k-2\mu_- +1)\Gamma(-\nu'_{(\rho)}-k)}$$
$$\times {}_2F_1(\nu'_{(\rho)}+k+1,\nu'_{(\rho)}+k+m+1;1+2\nu'_{(\rho)}+2k+2\mu_- +m;1/y). \quad (33)$$

Now, let us describe a closed circuit in the complex plane of η making positive loops around points $\eta = 1$ and $\eta = \gamma$, which is equivalent to describing negative loops around points $\eta = -1$ and $\eta = -\gamma$, then by (18) we have

$$y \to e^{2\pi i}y \qquad 1-y \to e^{2\pi i}(1-y) \qquad z \to e^{-2\pi i}z \qquad 1-z \to e^{-2\pi i}(1-z)$$

and it is easily seen that the effect of this circulation on the solutions (32) and (33) of equation (5) is

$$v_{2(\rho)} \to \exp[-2\pi i(\nu_{(\rho)}+\mu_+)]v_{2(\rho)} \qquad v'_{2(\rho)} \to \exp[2\pi i(\nu_{(\rho)}+\mu_+)]v'_{2(\rho)}$$
$$v'_{3(\rho)} \to \exp[-2\pi i(\nu_{(\rho)}+\mu_+)]v'_{3(\rho)} \qquad v_{3(\rho)} \to \exp[2\pi i(\nu_{(\rho)}+\mu_+)]v_{3(\rho)}. \quad (34)$$

Since $v_{2(\rho)}, v'_{2(\rho)}, v_{3(\rho)}$, and $v'_{3(\rho)}$ are solutions of an ordinary differential equation of the second order, equation (34) implies that

$$v'_{3(\rho)} = K_{(\rho)}v_{2(\rho)} \qquad v_{3(\rho)} = K'_{(\rho)}v'_{2(\rho)} \quad (35)$$

where $K_{(\rho)}$ and $K'_{(\rho)}$ are some constants.

Taking the limit $\rho \to \infty$ in equations (31)–(33) we find

$$v_{i(\rho)} \to v_i \qquad v'_{i(\rho)} \to v'_i \qquad i = 2,3 \quad (36)$$

and

$$v_1 = \Gamma(m+1)(v_2+v_3) \qquad v'_1 = \Gamma(m+1)(v'_2+v'_3) \quad (37)$$

where

$$v_2 = (1-\eta^2)^{m/2}e^{-p(1+\eta)}\sum_{k=-\infty}^{\infty}\frac{d_k\exp[-i\epsilon\pi(\nu_2+k)]}{\Gamma(m+\nu_2+k+1)}\Psi(-\nu_2-k,m+1;2p(1+\eta))$$
$$v_3 = (1-\eta^2)^{m/2}e^{-p(1+\eta)}\sum_{k=-\infty}^{\infty}\frac{d_k\exp[-i\epsilon\pi(\nu_2+k+m+1)]}{\Gamma(-\nu_2-k)}$$
$$\times\Psi(m+\nu_2+k+1,m+1;-2p(1+\eta)) \quad (38)$$
$$v'_2 = (1-\eta^2)^{m/2}e^{-p(1-\eta)}\sum_{k=-\infty}^{\infty}\frac{d_k\exp[-i\epsilon'\pi(\nu'_2+k)]}{\Gamma(m+\nu'_2+k+1)}\Psi(-\nu'_2-k,m+1;2p(1-\eta))$$

$$v_3' = (1-\eta^2)^{m/2} \mathrm{e}^{-p(1-\eta)} \sum_{k=-\infty}^{\infty} \frac{d_k \exp[-\mathrm{i}\epsilon' \pi(\nu_2' + k + m + 1)]}{\Gamma(-\nu_2' - k)} \times \Psi(m + \nu_2' + k + 1, m + 1; -2p(1-\eta)). \tag{39}$$

Here Ψ denotes the second solution of the confluent hypergeometric equation [18], $\epsilon = \mathrm{sign}(\mathrm{Im}(2p(1+\eta)))$, and $\epsilon' = \mathrm{sign}(\mathrm{Im}(2p(1-\eta)))$. Ψ is defined in the complex plane with the cut from 0 to infinity, and its argument in (38) and (39) should be taken on the shore of this cut. For real η from the interval $-1 \leqslant \eta \leqslant 1$ we have $\epsilon' = \epsilon = \mathrm{sign}(\mathrm{Im} 2p)$.

From relations (35) we obtain, in the limit $\rho \to \infty$, relations between series (38) and (39)

$$v_3' = K v_2 \qquad v_3 = K' v_2' \tag{40}$$

where K and K' are constants. Relations (37), (38), and (39) can also be obtained from (9) and (12) by making use of properties of confluent hypergeometric functions. However, it would be difficult to derive relations (40) without the use of the limiting procedure, since the circuit which we have used to obtain (35) passes between singularities γ and $-\gamma$ which coalesce as $\rho \to \infty$.

From (37) and (40) it is seen that equation

$$K K' = 1 \tag{41}$$

is the necessary condition for solutions of the quasi-angular equation (4) to be finite for $-1 \leqslant \eta \leqslant 1$.

To derive explicit expressions for K and K', suitable for asymptotic expansions at large R, we consider solutions of equation (5) of the form

$$\tilde{v}_{(\rho)} = \tilde{y}^{\mu_+} (\tilde{y} - 1)^{m/2} (\tilde{y} - a)^{1-\mu_-} \Gamma(\mu_+ + \mu_- + m) \sum_{k=-\infty}^{\infty} \frac{d_k^{(\rho)} \sigma_k \tilde{y}^{\nu_{(\rho)}+k}}{\Gamma(-\nu'_{(\rho)} - k)\Gamma(\nu_{(\rho)} + k + m + 1)} \times {}_2F_1(-\nu_{(\rho)} - k - 2\mu_+ + 1, -\nu_{(\rho)} - k; 1 - 2\nu_{(\rho)} - 2k - 2\mu_+ - m; 1/\tilde{y}) \tag{42}$$

$$\tilde{v}'_{(\rho)} = \tilde{z}^{\mu_-} (\tilde{z} - 1)^{m/2} (\tilde{z} - a)^{1-\mu_+} \Gamma(\mu_+ + \mu_- + m) \sum_{k=-\infty}^{\infty} \frac{d_k^{(\rho)} \sigma_k \tilde{z}^{\nu'_{(\rho)}+k}}{\Gamma(-\nu_{(\rho)} - k)\Gamma(\nu'_{(\rho)} + k + m + 1)} \times {}_2F_1(-\nu'_{(\rho)} - k - 2\mu_- + 1, -\nu'_{(\rho)} - k; 1 - 2\nu'_{(\rho)} - 2k - 2\mu_- - m; 1/\tilde{z}) \tag{43}$$

where $\tilde{y} = a/y$, $\tilde{z} = a/z$, and

$$\sigma_k = \Gamma(2\nu_{(\rho)} + 2k + 2\mu_+ + m)[\Gamma(\nu_{(\rho)} + k + 2\mu_+ + m)\Gamma(\nu'_{(\rho)} + k + 2\mu_- + m)]^{-1}.$$

Series in (42) and (43) converge inside the ellipses in complex planes $\tilde{y}$ and $\tilde{z}$ similar to those described above. Using the same closed circuit as in the derivation of (35), we find relations

$$\begin{aligned} v'_{3(\rho)} &= K_{1(\rho)} \tilde{v}_{(\rho)} \qquad & \tilde{v}_{(\rho)} &= K_{2(\rho)} v_{2(\rho)} \\ v_{3(\rho)} &= K'_{1(\rho)} \tilde{v}'_{(\rho)} \qquad & \tilde{v}'_{(\rho)} &= K'_{2(\rho)} v'_{2(\rho)} \end{aligned} \tag{44}$$

where $K_{1(\rho)}$, $K_{2(\rho)}$, $K'_{1(\rho)}$, and $K'_{2(\rho)}$ are constants. Obviously,

$$K_{(\rho)} = K_{1(\rho)} K_{2(\rho)} \qquad K'_{(\rho)} = K'_{1(\rho)} K'_{2(\rho)}. \tag{45}$$

In the limit $\rho \to \infty$ we have

$$\tilde{v}_{(\rho)} \to \tilde{v} \qquad \tilde{v}'_{(\rho)} \to \tilde{v}' \tag{46}$$

where

$$\tilde{v} = \mathrm{e}^{p(1-\eta)} 2^{1+b/2p} \sum_{k=-\infty}^{\infty} \frac{d_k (1+\eta)^{\nu_2+k+m/2} (1-\eta)^{-\nu_2'-k-1-m/2}}{\Gamma(\nu_2+k+m+1)\Gamma(-\nu_2'-k)} \tag{47}$$

$$\tilde{v}' = \mathrm{e}^{p(1+\eta)} 2^{1-b/2p} \sum_{k=-\infty}^{\infty} \frac{d_k (1-\eta)^{\nu_2'+k+m/2} (1+\eta)^{-\nu_2-k-1-m/2}}{\Gamma(\nu_2'+k+m+1)\Gamma(-\nu_2-k)}. \tag{48}$$

Domains of convergence of series (42) and (43) shrink as $\rho \to \infty$ and formal series $\tilde{v}$ (47) and $\tilde{v}'$ (48) are divergent. Nevertheless, they are helpful for a short-cut derivation of expressions for K and K'. Taking formal limit $\rho \to \infty$ in (44) and (45) we obtain

$$\begin{aligned} v_3' &= K_1 \tilde{v} \qquad \tilde{v} = K_2 v_2 \\ v_3 &= K_1' \tilde{v}' \qquad \tilde{v}' = K_2' v_2' \end{aligned} \tag{49}$$

and

$$K = K_1 K_2 \qquad K' = K_1' K_2'. \tag{50}$$

Now, expressions for K_1, K_2 and K_1', K_2' can be obtained by expanding confluent hypergeometric functions which enter solutions v_2, v_3 and v_2', v_3' and sums which enter solutions $\tilde{v}$ and $\tilde{v}'$ on both sides of each of the equations (49) in a series of powers of $1+\eta$ or $1-\eta$ and comparing like terms. Finally, using (50), we find

$$\begin{aligned} K = {} & \mathrm{e}^{2p+\mathrm{i}\epsilon\nu_2} (4p)^{-(\nu_2+\nu_2'+m+1)} \Gamma(\nu_2+m+1) [\Gamma(\nu_2'+m+1)\Gamma(\nu_2+1)]^2 [\Gamma(-\nu_2')]^{-1} \\ & \times \sum_{k=0}^{\infty} \frac{(-1)^k d_{-k}}{k!\,\Gamma(\nu_2'-k+m+1)} \sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(\nu_2'-k+1) d_{-k}}{k!\,\Gamma(\nu_2-k+m+1)\Gamma(\nu_2'-k+m+1)} \\ & \times \left[\sum_{k=0}^{\infty} \frac{\Gamma(\nu_2+k+1) d_k}{k!} \sum_{k=0}^{\infty} \frac{\Gamma(\nu_2+k+1)\Gamma(\nu_2'+k+1) d_k}{k!\,\Gamma(\nu_2+k+m+1)} \right]^{-1} \end{aligned} \tag{51}$$

and expression for K' can be obtained from (51) by replacements $\nu_2 \rightleftharpoons \nu_2'$. Series which enter (51) and corresponding expression for K' are divergent. Nevertheless, these expressions are suitable for derivation of asymptotic expansions for energy eigenvalues at large R.

3. Asymptotic evaluation of energy splittings at pseudocrossings

The first step in deriving asymptotic expansions for the energy is to obtain expansions of the separation constant λ in powers of $1/p$. Power [7] has given such expansions up to and including $\mathrm{O}(1/p^5)$. For convenience, we write down the first few terms of these. The expansion derived from the recurrence relation (7) reads

$$\lambda_\xi = 2p(S-2\kappa) + 2(\kappa S - \kappa^2 - \omega) + \frac{1}{2p}[2\kappa(\kappa^2+\omega) - (3\kappa^2+\omega)S + \kappa S^2] + \mathrm{O}\left(\frac{1}{p^2}\right) \tag{52}$$

where $S = a/2p$, $\kappa = n_1 + (m+1)/2$, and $\omega = (1-m^2)/4$. From the recurrence relation (10) expansions can be derived which may include either parameter ν_2 or ν_2'

$$\lambda_\eta = 2p(2\chi + D) - 2(\chi D + \chi^2 + \omega) - \frac{1}{2p}[2\chi(\chi^2+\omega) + (3\chi^2+\omega)D + \chi D^2] + \mathrm{O}\left(\frac{1}{p^2}\right) \tag{53}$$

$$\lambda'_\eta = 2p(2\chi' - D) + 2(\chi' D - \chi'^2 - \omega) - \frac{1}{2p}[2\chi'(\chi'^2 + \omega) - (3\chi'^2 + \omega)D + \chi' D^2] + \mathrm{O}\left(\frac{1}{p^2}\right) \quad (54)$$

where $D = b/2p$, $\chi = \nu_2 + (m+1)/2$, and $\chi' = \nu'_2 + (m+1)/2$.

Power [7] also demonstrated how the expansion of the energy in powers of $1/R$ is derived by equating λ_ξ and λ_η (or λ_ξ and λ'_η). From (52) and (53) one obtains

$$E_{n_1\nu_2 m} = -\frac{Z_1^2}{2\nu^2} - \frac{Z_2}{R} + \frac{3\nu(n_1 - \nu_2)Z_2}{2Z_1 R^2} + \mathrm{O}\left(\frac{1}{R^3}\right) \quad (55)$$

and from (52) and (54)

$$E_{n_1\nu'_2 m} = -\frac{Z_2^2}{2\nu'^2} - \frac{Z_1}{R} + \frac{3\nu'(n_1 - \nu'_2)Z_1}{2Z_2 R^2} + O\left(\frac{1}{R^3}\right) \quad (56)$$

where $\nu = n_1 + \nu_2 + m + 1$ and $\nu' = n_1 + \nu'_2 + m + 1$. Expansions (55) and (56) depend on parameters ν_2 and ν'_2 which are not yet determined. From (41) and (51) it is seen that for large p, parameter ν_2 or ν'_2, or both must be close to some integer numbers. We denote $\nu_2 = n_2 + \delta n_2$ and $\nu'_2 = n'_2 + \delta n'_2$. Since spheroidal coordinates become parabolic coordinates as $R \to \infty$, an integer number n_2 (or n'_2) can be identified with a parabolic quantum number of an electronic state in the field of charge Z_1 (or Z_2). If D is not close to an integer number then either δn_2 or $\delta n'_2$ has an order of magnitude $\mathrm{O}(p^{2(n_2+n'_2+m+1)}\mathrm{e}^{-4p})$. In most cases these corrections are negligible, and energy eigenvalues are given by expansion (55) with n_2 substituted instead of ν_2, or by (56) with n'_2 in place of ν'_2. Here we restrict our treatment to the more interesting case when D is close to some integer number for some value of R, and so-called pseudocrossing occurs. Then δn_2 and $\delta n'_2$ have equal orders of magnitude, and keeping in (41) only terms of lowest order in δn_2 and $\delta n'_2$ we obtain

$$\delta n_2 \delta n'_2 = \frac{(4p)^{2(n_2+n'_2+m+1)}\mathrm{e}^{-4p}}{n_2! n'_2! (n_2+m)!(n'_2+m)!} f(n_2, n'_2) f(n'_2, n_2) \quad (57)$$

where

$$f(n_2, n'_2) = \sum_{k=0}^{\infty} \frac{(n_2+1)_k (n'_2+1)_k d_k}{k!(n_2+m+1)_k} \sum_{k=0}^{\infty} \frac{(n_2+1)_k d_k}{k!} \times \left[\sum_{k=0}^{\infty} \frac{(-n_2-m)_k(-n'_2-m)_k d_{-k}}{k!(-n'_2)_k} \sum_{k=0}^{\infty} \frac{(-n'_2-m)_k d_{-k}}{k!}\right]^{-1} \quad (58)$$

and $(a)_k = \Gamma(a+k)/\Gamma(a)$ is Pochgammer's symbol.

Coefficients d_k which enter (58) can be obtained from the recurrence relation (10) by the method of successive approximations. Setting

$$d_{\pm r}/d_0 = \sum_{t=r}^{\infty} d_{\pm r}^{(t)} p^{-t} \quad (59)$$

we obtain

$$d_1^{(1)} = -(2\chi + m + 1)(2\chi' + m + 1)/16$$

$$d_1^{(2)} = -(2\chi + m + 1)(2\chi' + m + 1)(\chi + \chi' + 1)/32$$

$$d_1^{(3)} = (2\chi + m + 1)(2\chi' + m + 1)(-209 + 18m^2 - m^4 - 348\chi - 4m^2\chi - 164\chi^2 + 4m^2\chi^2 - 348\chi' - 4m^2\chi' - 400\chi\chi' + 16\chi^2\chi' - 164\chi'^2 + 4m^2\chi'^2 + 16\chi\chi'^2 - 16(\chi\chi')^2)/8192$$

$$d_{-1}^{(1)} = (2\chi - m - 1)(2\chi' - m - 1)/16$$
$$d_{-1}^{(2)} = (2\chi - m - 1)(2\chi' - m - 1)(\chi + \chi' - 1)/32$$
$$\begin{aligned} d_{-1}^{(3)} = {} & (2\chi - m - 1)(2\chi' - m - 1)(209 - 18m^2 + m^4 - 348\chi - 4m^2\chi + 164\chi^2 \\ & -4m^2\chi^2 - 348\chi' - 4m^2\chi' + 400\chi\chi' + 16\chi^2\chi' + 164\chi'^2 - 4m^2\chi'^2 \\ & +16\chi\chi'^2 + 16(\chi\chi')^2)/8192 \end{aligned}$$
$$d_2^{(2)} = -(2\chi + m + 3)(2\chi + m + 1)(2\chi' + m + 3)(2\chi' + m + 1)/512$$
$$d_2^{(3)} = (2\chi + m + 3)(2\chi + m + 1)(2\chi' + m + 3)(2\chi' + m + 1)(2\chi + 2\chi' + 3)/1024$$
$$d_{-2}^{(2)} = (2\chi - m - 3)(2\chi - m - 1)(2\chi' - m - 3)(2\chi' - m - 1)/512$$
$$d_{-2}^{(3)} = (2\chi - m - 3)(2\chi - m - 1)(2\chi' - m - 3)(2\chi' - m - 1)(2\chi + 2\chi' - 3)/1024,$$
$$\begin{aligned} d_3^{(3)} = {} & -(2\chi + m + 5)(2\chi + m + 3)(2\chi + m + 1)(2\chi' + m + 5)(2\chi' + m + 3) \\ & (2\chi' + m + 1)/24576 \end{aligned}$$
$$\begin{aligned} d_{-3}^{(3)} = {} & (2\chi - m - 5)(2\chi - m - 3)(2\chi - m - 1)(2\chi' - m - 5)(2\chi' - m - 3) \\ & (2\chi' - m - 1)/24576 \end{aligned} \tag{60}$$

and so on. Since we are keeping only terms of lowest order in δn_2 and $\delta n_2'$, replacements $\chi \to \chi_0 = n_2 + (m+1)/2$ and $\chi' \to \chi_0' = n_2' + (m+1)/2$ should be done before substituting (60) in (58). We write down, as an illustration, the first few terms of the expansion for $(\delta n_2 \delta n_2')^{1/2}$

$$\begin{aligned} (\delta n_2 \delta n_2')^{1/2} = \delta = {} & \frac{(4p)^{n_2+n_2'+m+1}\mathrm{e}^{-2p}}{[n_2!(n_2+m)!n_2'!(n_2'+m)!]^{1/2}} \left\{ 1 - \frac{1}{4p}[\chi_0^2 + 2\omega + 4\chi_0\chi_0' + \chi_0'^2] \right. \\ & + \frac{1}{32p^2}[(\chi_0^2 + 2\omega + 4\chi_0\chi_0' + \chi_0'^2)^2 - 2(\chi_0 + \chi_0') \\ & \times(1 + \chi_0^2 + 6\omega + 8\chi_0\chi_0' + \chi_0'^2)] + \frac{1}{384p^3}[-(\chi_0^2 + 2\omega + 4\chi_0\chi_0' + \chi_0'^2)^3 \\ & +6(\chi_0 + \chi_0')(\chi_0^2 + 2\omega + 4\chi_0\chi_0' + \chi_0'^2)(1 + \chi_0^2 + 6\omega + 8\chi_0\chi_0' + \chi_0'^2) \\ & -2(17\chi_0^2 + 5\chi^4 + 12\omega + 78\omega\chi_0^2 + 26\omega^2 - 68\chi_0\chi_0' + 76\chi_0^3\chi_0' \\ & +120\omega\chi_0\chi_0' + 17\chi_0'^2 + 168\chi_0^2\chi_0'^2 + 78\omega\chi_0'^2 + 76\chi\chi_0'^3 + 5\chi_0'^4)] \\ & \left. +\mathrm{O}\left(\frac{1}{p^4}\right) \right\} \end{aligned} \tag{61}$$

where $p = R|Z_1 - Z_2|/|n_2 - n_2'|$. Terms up to and including $\mathrm{O}(1/p^2)$ in expansion (61) coincide with the result of Power [7] who assumed $\delta n_2 = \delta n_2'$. Greenland [10] pointed out that two exponentially small corrections are needed to determine eigenvalues of energy when a pseudocrossing occurs. He used the normalization of wavefunctions found with the help of a series analogous to (6), (9), and (12) to determine these corrections separately. This approach leads to the amount of computations rapidly growing with the order of the approximation. We propose a different method. Let us expand expressions for energy eigenvalues from (55) and (56) in a series of powers of δn_2 and $\delta n_2'$, retaining only first powers of these small quantities

$$E_{n_1\nu_2 m} = E_{n_1 n_2 m} + E'_{n_1 n_2 m}\delta n_2 \qquad E_{n_1\nu_2' m} = E_{n_1 n_2' m} + E'_{n_1 n_2' m}\delta n_2' \tag{62}$$

where

$$E'_{n_1 n_2 m} = \left(\frac{\partial E_{n_1\nu_2 m}}{\partial \nu_2}\right)_{\nu_2 = n_2} \qquad E'_{n_1 n_2' m} = \left(\frac{\partial E_{n_1\nu_2' m}}{\partial \nu_2'}\right)_{\nu_2' = n_2'}. \tag{63}$$

Since $E_{n_1n_2m}$ and $E_{n_1n_2'm}$, on the one hand, and δn_2 and $\delta n_2'$ on the other, belong to different scales of smallness, the condition of crossing of two potential curves $E_{n_1\nu_2m} = E_{n_1\nu_2'm}$ implies $E_{n_1n_2m} = E_{n_1n_2'm}$ and $E'_{n_1n_2m}\delta n_2 = E'_{n_1n_2'm}\delta n_2'$. Then, in the frames of the used approximation, we obtain the relation

$$d = \delta n_2/\delta n_2' = E'_{n_1n_2'm}/E'_{n_1n_2m} + \mathrm{O}(p^{2(n_2+n_2'+m+1)}\mathrm{e}^{-4p}). \tag{64}$$

We assume that relation (64) is valid not only at the crossing point, but also in the vicinity of this point. From (61) and (64) we find two solutions for δn_2 and $\delta n_2'$,

$$\delta n_{2(\pm)} = \pm\delta d^{1/2} \qquad \delta n'_{2(\pm)} = \pm\delta d^{-1/2} \tag{65}$$

and, as a consequence, two possibilities for energy curves given by (62):

$$E^{\pm}_{n_1\nu_2m} = E_{n_1n_2m} + E'_{n_1n_2m}\delta n_{2(\pm)} \qquad E^{\pm}_{n_1\nu_2'm} = E_{n_1n_2'm} + E'_{n_1n_2'm}\delta n'_{2(\pm)}. \tag{66}$$

The expansion for $d^{1/2}$ is easily found from (55) and (56),

$$d^{1/2} = \left(\frac{n^3Z_2^2}{n'^3Z_1^2}\right)^{1/2}\left[1 + \frac{3}{4Z_1^3Z_2^3R^2}(n^4Z_2^4 - n^3n_1Z_2^4 + n^3n_2Z_2^4 - n'^4Z_1^4 + n'^3n_1Z_1^4 - n'^3n_2'Z_1^4)\right] + \mathrm{O}(R^{-3}) \tag{67}$$

where $n = n_1 + n_2 + m + 1$ and $n' = n_1 + n_2' + m + 1$. In order to relate the approximate energy eigenvalues given by equation (66) with exact potential curves, let us recall that each exact potential curve may be labelled by the united atom quantum numbers N, l, m as well as by the separated atom parabolic quantum numbers, n_1, n_2, m if the electron is localized near the centre Z_1 for $R \to \infty$, or n_1', n_2', m in the opposite case. There is one-to-one correspondence between the united atom and separated atom quantum numbers, and potential curves for which $n_1 = n_1'$ cannot cross. On the other hand, some curves defined by $1/R$ expansions (55) and (56) (with exponential corrections neglected) do cross, and different parts of these curves correspond to the exact potential curves of different states [7]. If two curves $E_{n_1n_2m}(R)$ and $E_{n_1n_2'm}(R)$ defined by expansions (55) and (56), where $\delta n_2, \delta n_2'$ are neglected, cross at some point R_c^0, and for $R > R_\mathrm{c}^0$ the curve $E_{n_1n_2m}(R)$ corresponds to the exact curve labelled by the united atom quantum numbers N, l, m, then we have

$$E_{n_1n_2m} = \begin{cases} E_{Nlm} & R > R_\mathrm{c}^0 \\ E_{N-1,l-1,m} & R < R_\mathrm{c}^0 \end{cases}$$
$$E_{n_1n_2'm} = \begin{cases} E_{N-1,l-1m} & R > R_\mathrm{c}^0 \\ E_{Nlm} & R < R_\mathrm{c}^0. \end{cases} \tag{68}$$

Curves $E^{\pm}_{n_1\nu_2m}(R)$ and $E^{\pm}_{n_1\nu_2'm}(R)$ (66) which take into account exponentially small corrections also cross, and only parts of these curves correspond to the exact potential curves labelled by the united atom quantum numbers. In the vicinity of R_c^0 this correspondence is given by

$$E_{Nlm}(R) = \max(E^{+}_{n_1\nu_2m}(R), E^{+}_{n_1\nu_2'm}(R))$$
$$E_{N-1,l-1,m}(R) = \min(E^{-}_{n_1\nu_2m}(R), E^{-}_{n_1\nu_2'm}(R)). \tag{69}$$

Thus energy splitting in the vicinity of the pseudocrossing point is

$$\Delta E(R) = E_{Nlm}(R) - E_{N-1,l-1,m}(R) \tag{70}$$

with $E_{Nlm}(R)$ and $E_{N-1,l-1,m}(R)$ defined by (69). We define the point of the pseudocrossing R_c as the point where ΔE (70) takes its minimum value. (Ambiguities in the definition of this point were discussed in [1, 7].) In order to test our asymptotic formulae, we computed minimal splittings for some σ states of the $(Z_1 = 1, e, Z_2)$ system. Computation has been performed by taking into account exponentially small terms up to and including $O(1/R^4)$, but in some cases (of R not very large) terms of order $O(1/R^4)$ were larger than those of order $O(1/R^3)$ and the expansion was truncated after terms of order $O(1/R^3)$. The results of the computation are given in table 1. They are compared with the data of numerical calculations taken from [16], as well as with results of Greenland's asymptotic treatment [10].

Table 1. Energy splittings ΔE at pseudocrossing points R_c in the system (p, e, Z_2) calculated through $O(1/R^k)$. The states are labelled by the united atom quantum numbers. Numerically obtained values R_c^{num} and ΔE^{num} are taken from [16]. ΔE_G are the data obtained by using the asymptotic series in [10].

Z_2	(Nlm)–$(N'l'm)$	R_c	ΔE	k	ΔE_G	R_c^{num}	ΔE^{num}
5	(5,4,0)–(4,3,0)	13.0	4.16×10^{-3}	4	5.4×10^{-3}	13.0	4.2×10^{-3}
6	(6,5,0)–(5,4,0)	21.4	2.41×10^{-5}	4	—	—	—
	(5,4,0)–(4,3,0)	7.46	10.5×10^{-2}	3	9.8×10^{-2}	8.1	0.10
7	(7,6,0)–(6,5,0)	31.9	2.14×10^{-8}	4	—	—	—
	(6,5,0)–(5,4,0)	11.5	2.44×10^{-2}	4	2.9×10^{-2}	11.6	2.4×10^{-2}
	(5,4,0)–(4,3,0)	6.19	0.277	3	0.16	6.4	0.24
8	(8,7,0)–(7,6,0)	44.3	2.88×10^{-12}	4	—	—	—
	(7,6,0)–(6,5,0)	16.8	1.87×10^{-3}	4	2.3×10^{-3}	16.8	1.96×10^{-3}
	(6,5,0)–(5,4,0)	8.56	10.7×10^{-2}	4	0.11	8.9	0.10
	(5,4,0)–(4,3,0)	4.56	0.395	3	0.22	5.4	0.38
10	(8,7,0)–(7,6,0)	16.2	5.72×10^{-3}	4	8.0×10^{-3}	16.1	6.0×10^{-3}
	(7,6,0)–(6,5,0)	9.76	9.47×10^{-2}	4	0.10	10.0	9.2×10^{-2}
	(6,5,0)–(5,4,0)	5.78	0.324	3	0.24	6.5	0.30
14	(10,9,0)–(9,8,0)	17.4	1.07×10^{-2}	4	1.5×10^{-2}	17.2	1.06×10^{-2}
	(9,8,0)–(8,7,0)	12.3	7.77×10^{-2}	4	9.3×10^{-2}	12.2	7.0×10^{-2}
	(8,7,0)–(7,6,0)	8.08	0.148	3	0.20	8.9	19.6×10^{-2}

4. Discussion

Comparison of our results with those of the previous asymptotic and numerical treatments shows that, as should be expected, evaluation of additional terms of the exponentially small asymptotic subseries improves agreement between asymptotic and numerical results, provided charge separation R is large enough. Agreement is less satisfactory for R not very large, when treatment limited to the first exponentially small order of corrections becomes inadequate. Equation (41) which is basic in our treatment allows for the evaluation of higher exponential orders. In this connection, it should be noted that constants K and K' which enter this equation for real eigenvalues of energy are explicitly complex. In the case $Z_1 = Z_2$, this phenomenon was studied in detail in [12, 13]. Its origin lies in the fact that the divergent $1/R$ expansion has complex Borel sum, and the explicit imaginary series cancels the imaginary part of the Borel sum making the sum of the entire expansion real. The problem of summation of the asymptotic expansion including higher exponentially small subseries in the case $Z_1 \neq Z_2$ needs further investigation.

Acknowledgments

We would like to thank the referee for useful suggestions. This work was supported in part by the Foundation for Basic Research of Belarus.

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