

Quantal Two-Centre Coulomb Problem treated by means of the Phase-Integral Method II. Quantization Conditions in the Symmetric Case Expressed in Terms of Complete Elliptic Integrals. Numerical Illustration.

N. Athavan,^{1,*} N. Fröman,² and M. Lakshmanan¹

¹*Centre for Nonlinear Dynamics, Department of Physics,
Bharathidasan University, Tiruchirapalli 620 024, India*

²*Department of Theoretical Physics, University of Uppsala, Box 803, S-751 05 Uppsala, Sweden*

The contour integrals, occurring in the arbitrary-order phase-integral quantization conditions given in a previous paper, are in the first- and third-order approximations expressed in terms of complete elliptic integrals in the case that the charges of the Coulomb centres are equal. The evaluation of the integrals is facilitated by the knowledge of quasiclassical dynamics. The resulting quantization conditions involving complete elliptic integrals are solved numerically to obtain the energy eigenvalues and the separation constants of the $1s\sigma$ and $2p\sigma$ states of the hydrogen molecule ion for various values of the internuclear distance. The accuracy of the formulas obtained is illustrated by comparison with available numerically exact results.

PACS numbers: 03.65.Sq, 31.15.-p, 31.15.Gy

1. INTRODUCTION

In a previous paper [1] the general two-centre Coulomb problem was treated according to the phase-integral method, briefly described in the appendix of that paper, and arbitrary-order quantization conditions were given, valid uniformly for all energies.

The symmetric case, where the charge numbers Z_1 and Z_2 of the two Coulomb centres are equal, represents for $Z_1 = Z_2 = 1$ the hydrogen molecule ion H_2^+ . This case has for natural reasons been studied more extensively than the general two-centre problem. Thus, the H_2^+ ion was the subject of treatments already with the aid of the old quantum theory [2] and in the early days of quantum mechanics [3, 4]. The simplicity of the hydrogen molecule ion grants it an analogous unique position in molecular physics as the hydrogen atom possesses in atomic physics. For instance, H_2^+ plays a role of fundamental significance in the theory of chemical bonding, and it is also of importance in the study of stellar atmospheres.

For the background of the present paper we refer to [1]. In sec. 2 of the present paper we present the quasiclassical dynamics of the associated particle system by setting up the equation of motion for a particle moving in the relevant potential and express the solution in terms of Jacobian elliptic functions. In sections 3 and 4 we express the quantization conditions given in [1] in terms of complete elliptic integrals by using the solution in sec. 2. We introduce, analogously as Lakshmanan and Kaliappan [5], Lakshmanan *et al.* [6] and Lakshmanan *et al.* [7], convenient transformations to elliptic functions, in order to be able to express both the real and the complex contour integrals, occurring in the quantization conditions, in terms of complete elliptic integrals. In choosing our transformations we exploit the symmetry of the functions $R(\eta)$ and $Q^2(\eta)$, introduced in [1], already from the beginning of the calculations, since this is much simpler than to particularize formulas for the general case of arbitrary nuclear charge numbers Z_1 and Z_2 to the case $Z_1 = Z_2$. Thus we obtain simple expressions for the quantities appearing in the quantization conditions in [1]. It should be remarked that if one particularizes the η -quantization conditions involving complete elliptic integrals that are valid for arbitrary charge numbers Z_1 and Z_2 (to be derived in the subsequent paper [8]) to the case $Z_1 = Z_2$, one must in general make further cumbersome transformations in order to bring the quantization conditions in question into the same form as those obtained by assuming from the beginning that $Z_1 = Z_2$. The functions $\tilde{R}(\xi)$ and $\tilde{Q}^2(\xi)$, introduced in [1], do not display an analogous symmetry as $R(\eta)$ and $Q^2(\eta)$ when $Z_1 = Z_2$. The treatment of the ξ -equation is thus the same whether $Z_1 = Z_2$ or $Z_1 \neq Z_2$, and it is analogous to the treatment of the η -equation in the general case when Z_1 may be different from Z_2 , which is treated in the third paper [8] in our series of papers concerning the phase-integral treatment of the quantal two-centre Coulomb problem. All the contour integrals needed in the calculations are expressed in terms of complete elliptic integrals, corresponding to the use of the first- and third-order phase-integral approximations. Since complete elliptic integrals can easily be

*Present address: Department of Physics, Government Arts College, Ariyalur - 621 713, India.

evaluated by means of standard computer programs, computational difficulties that may arise in direct numerical calculations (especially of higher-order terms) are thereby eliminated. One achieves also the possibility of being able to utilize well-known properties of complete elliptic integrals, for instance series expansions, for analytic studies on the basis of the quantization conditions. Some of the first-order contour integrals have been given in terms of complete elliptic integrals previously by Strand and Reinhardt [9], but to the best knowledge of the present authors, even in the first-order approximation only partial results have been given.

The phase-integral formulas derived in this paper are quite flexible due to the presence of two arbitrary parameters C and \tilde{C} introduced in the base functions $Q(\eta)$ and $\tilde{Q}(\xi)$ in eqs. (3.2b) and (3.2a), respectively, in [1]. In accordance with the discussion in sec. 3.1 of [1] it is appropriate to choose C and \tilde{C} such that the first-order results are exactly equal to the third-order results, and we confirm in sec. 5 the convenience of this approach by investigating for the $1s\sigma$ and $2p\sigma$ states of the hydrogen molecule ion the accuracy of our phase-integral quantization conditions.

2. QUASICLASSICAL DYNAMICS

We have seen in sec. 3 of [1] that the quantization conditions require the evaluation of various contour integrals. In the present section we shall restrict ourselves to the η -equation. The shape of the contours depends on the choice of Λ and on the real or complex nature of the zeros of $Q^2(\eta)$; see Figs. 2 - 4 in [1].

Letting, when $-Q^2(\eta)$ is a double-well potential, the zeros of $Q^2(\eta)$ be $\eta_1, \eta_2, \eta_3, \eta_4$ when $\Lambda = |m| \neq 0$ and η_2, η_3 when $\Lambda = 0$, we shall evaluate the integrals $\alpha = \beta$ and \bar{K} in the following cases separately.

1. $\Lambda = |m| \neq 0$:

- (a) Subbarrier case ($\eta_1 = -\eta_4$ and $\eta_2 = -\eta_3$ are real)
- (b) Superbarrier case (η_1, η_4 are real and η_2, η_3 are complex conjugate)

2. $\Lambda = 0$:

- (a) Subbarrier case (only two zeros, $\eta_2 = -\eta_3$; they are real)
- (b) Superbarrier case (only two zeros, η_2 and η_3 ; they are complex conjugate)

In each one of these cases the evaluation of the contour integrals in terms of complete elliptic integrals is facilitated by the knowledge of the associated quasiclassical dynamics. In particular the relevant substitution for the integration variable in the various contour integrals can be obtained with the help of, for example, Byrd and Friedman [10]. However, the meaning of these substitutions can be attributed to the associated solution of the equation of motion of the corresponding classical problem as in the case of three-dimensional anharmonic oscillators [7].

To illustrate what has been said above, we shall consider the subbarrier case of $\Lambda = |m| \neq 0$. (For the other cases the analysis can be carried out in a similar way.) The base function $Q(\eta)$ for this case is

$$Q(\eta) = p \frac{[(a^2 - \eta^2)(\eta^2 - b^2)]^{\frac{1}{2}}}{1 - \eta^2}, \quad (2.1)$$

where $a = \eta_4 = -\eta_1$, $b = \eta_3 = -\eta_2$ and $p^2 = -\frac{1}{2}Er_{12}^2$. Let us define a new integration variable \bar{u} by writing

$$\bar{u} = \int^{\eta} \frac{d\eta}{(1 - \eta^2)Q(\eta)}; \quad (2.2)$$

then

$$\frac{d\eta}{d\bar{u}} = (1 - \eta^2)Q(\eta) = \hat{Q}(\eta). \quad (2.3)$$

Before solving (2.3), we shall relate this differential equation to the equation of motion for the quasiclassical motion of a particle with a mass μ in a certain potential by differentiating (2.3) with respect to \bar{u} , getting

$$\frac{d^2\eta}{d\bar{u}^2} = \frac{1}{2} \frac{d\hat{Q}^2}{d\eta}. \quad (2.4)$$

Defining now the “time” variable u as

$$u = \bar{u}\sqrt{\mu}, \quad (2.5)$$

we obtain the equation of quasiclassical motion

$$\mu \frac{d^2 \eta}{du^2} = -\frac{dU(\eta)}{d\eta}, \quad (2.6a)$$

$$U(\eta) = -\frac{1}{2}\hat{Q}^2(\eta). \quad (2.6b)$$

We can consider (2.6a) as representing the motion of a particle in the potential $U(\eta)$. We shall now solve the differential equation (2.3) in terms of Jacobian elliptic functions when $Q^2(\eta)$ is given by (2.1). The potential $U(\eta)$ is then given by

$$\begin{aligned} U(\eta) &= -\frac{1}{2}\hat{Q}^2(\eta) = -\frac{1}{2}(1-\eta^2)^2 Q^2(\eta) \\ &= -\frac{1}{2}p^2(a^2-\eta^2)(\eta^2-b^2) \\ &= \frac{1}{2}p^2(\eta^2-a^2)(\eta^2-b^2), \end{aligned} \quad (2.7)$$

and according to (2.3) and (2.1)

$$\frac{d\eta}{d\bar{u}} = p\sqrt{(a^2-\eta^2)(\eta^2-b^2)}. \quad (2.8)$$

By solving (2.8) with respect to η we obtain

$$\eta(\bar{u}) = \frac{b}{dn\left[\frac{p}{a}(\bar{u}-\bar{u}_0)\right]}, \quad (2.9)$$

where \bar{u}_0 is an integration constant, and the modulus k of the Jacobian elliptic function is given by

$$k^2 = 1 - \frac{b^2}{a^2}. \quad (2.10)$$

Similarly we can for all other cases interpret the corresponding quasiclassical dynamics by the above type of treatment.

3. CASE $\Lambda = |m| \neq 0$

In order to express the contour integrals, occurring in the quantization conditions pertaining to the ξ -equation and the η -equation, in terms of complete elliptic integrals, we transform the integrals in question from the ξ - or η -plane to another complex plane, the u -plane, on which the Jacobian elliptic functions $\text{cn}u$, $\text{sn}u$ and $\text{dn}u$ are defined. We make frequent use of formulas in [10]. As mentioned above the transformation in question can be attributed to quasiclassical dynamics.

3.1. Four real zeros of $Q^2(\eta)$ and $\tilde{Q}^2(\xi)$

3.1.1. The quantities $\alpha = \beta$ and \bar{K} pertaining to the η -equation: Subbarrier case [Fig. 3(a) in Ref. 1]

Putting $\eta_4 = -\eta_1 = a$ and $\eta_3 = -\eta_2 = b$, we have the base function (2.1), that is,

$$Q(\eta) = p \frac{[(a^2-\eta^2)(\eta^2-b^2)]^{\frac{1}{2}}}{1-\eta^2}. \quad (3.1)$$

Using the appropriate transformation on p. 54 in [10], or equivalently the quasiclassical solution given in sec. II, we put

$$\eta = \frac{b}{dnu} = \frac{b}{(1 - k^2 sn^2 u)^{\frac{1}{2}}}, \quad k^2 = 1 - \frac{b^2}{a^2}. \quad (3.2)$$

Noting that the loop $\eta_2 \rightarrow \eta_1 \rightarrow \eta_2$, that is $-b \rightarrow -a \rightarrow -b$, in the η -plane, denoted by $\Gamma_{-b, -a}$, represents the contour Λ_α in Fig. 3(a) of [1] which corresponds in the u plane to $0 \rightarrow K \rightarrow 2K$, where K is the complete elliptic integral of the first kind, we obtain for the first-order contribution to α the following transformation of the original integral in the η -plane into an integral in the u -plane:

$$\begin{aligned} \alpha^{(1)} &= \frac{1}{2} \int_{\Lambda_\alpha} Q(\eta) d\eta = \frac{1}{2} \int_{\Gamma_{-b, -a}} Q(\eta) d\eta \\ &= \frac{p}{g} \frac{1}{2} \int_0^{2K} \left(\frac{d\eta}{du} \right)^2 \frac{du}{1 - \eta^2} \\ &= p \frac{k^4 b^2}{1 - b^2} \frac{1}{2} \int_0^{2K} \frac{sn^2 u (1 - sn^2 u)}{(1 - k^2 sn^2 u)(1 - \nu^2 sn^2 u)} du, \end{aligned} \quad (3.3)$$

which, after decomposition of the integrand into partial fractions and use of recurrence formulas in [10], yields

$$\alpha^{(1)} = \frac{p}{g} \left[E(k) - \left(1 - \frac{k^2}{\nu^2} \right) K(k) + k^2 \left(1 - \frac{1}{\nu^2} \right) \Pi(\nu^2, k) \right], \quad (3.4a)$$

where

$$\nu^2 = \frac{a^2 - b^2}{a^2(1 - b^2)} = \frac{k^2}{1 - b^2}, \quad g = \frac{1}{a}, \quad k^2 = \frac{a^2 - b^2}{a^2}. \quad (3.5)$$

Here $K(k)$, $E(k)$ and $\Pi(\nu^2, k)$ are complete elliptic integrals of first, second and third kind, respectively. Similarly we obtain for the third-order contribution to α (see eqs. (3.13b), (A.5b), (A.6b), (A3), (2.9b) and (3.2b) of [1]),

$$\begin{aligned} \alpha^{(3)} &= \frac{1}{2} \int_{\Lambda_\alpha} q^{(3)}(\eta) d\eta \\ &= \frac{1}{2} \int_{\Lambda_\alpha} \left[\left(-C + \frac{1}{1 - \eta^2} \right) \frac{1}{2Q(1 - \eta^2)} - \frac{1}{8} Q^{-3}(\eta) \left(\frac{dQ(\eta)}{d\eta} \right)^2 \right] d\eta, \end{aligned} \quad (3.6)$$

where C is the parameter introduced in the base function $Q(\eta)$ in eq. (3.2b) of [1]. After evaluation of the integrals we obtain

$$\begin{aligned} \alpha^{(3)} &= -\frac{gC}{2p} K(k) + \frac{g}{2p(1 - b^2)\nu^2} [k^2 K(k) + (\nu^2 - k^2) \Pi(\nu^2, k)] \\ &\quad - \frac{g(1 - b^2)}{8pb^2k^4} [P_1 K(k) + P_2 E(k) + P_3 \Pi(\nu^2, k)], \end{aligned} \quad (3.4b)$$

where

$$P_1 = \frac{1}{3} [-9k^4 + k^2(8 + 5\nu^2) + 4\nu^2 - 8], \quad (3.7a)$$

$$P_2 = \frac{1}{3} [k^2(-4 - \nu^2) + (8 - 4\nu^2)] \quad (3.7b)$$

and

$$P_3 = 4(\nu^2 - k^2)^2. \quad (3.7c)$$

Analogous calculations can be performed to evaluate the quantity \bar{K} . For this purpose we make use of the appropriate transformation on p. 58 in [10], that is

$$\eta^2 = b^2 sn^2 u. \quad (3.8)$$

The first-order (see eqs.(3.15b), (A5b) and (A6a) of [1]) and the third-order (see eqs. (3.15b), (A5b), (A6b), A(3), (2.9b) and (3.2b) of [1]) contributions to K ($= \pi\bar{K}$) are

$$\begin{aligned}\pi\bar{K}_0 &= \frac{i}{2} \int_{\Lambda_K} Q(\eta) d\eta \\ &= \frac{p\nu^2}{g} \int_0^{2K} \frac{cn^2 u dn^2 u}{1 - \nu^2 sn^2 u} du \\ &= \frac{p}{g} \left[E(k) + k^2 \left(1 - \frac{1}{\nu^2}\right) K(k) + (\nu^2 - k^2) \left(1 - \frac{1}{\nu^2}\right) \Pi(\nu^2, k) \right],\end{aligned}\quad (3.9a)$$

and

$$\begin{aligned}\pi\bar{K}_2 &= \frac{i}{2} \int_{\Lambda_K} q^{(3)}(\eta) d\eta \\ &= -2\text{Im} \frac{1}{2} \int_{\Lambda_K} \left[\left(-C + \frac{1}{1 - \eta^2}\right) \frac{1}{2Q(1 - \eta^2)} - \frac{1}{8} Q^{-3}(\eta) \left(\frac{dQ(\eta)}{d\eta}\right)^2 \right] d\eta \\ &= \frac{Cg}{p} K(k) - \frac{g}{p} \Pi(\nu^2, k) + \frac{g}{4b^2 p} \left[\frac{1}{3k'^6} (-3\nu^2 k^6 - k^4 + 8\nu^2 k^2 - 7\nu^2 + 1) E(k) \right. \\ &\quad \left. + \frac{3\nu^2 - 1}{3k'^2} K(k) + 4\nu^2 \Pi(\nu^2, k) \right],\end{aligned}\quad (3.9b)$$

where

$$\nu^2 = b^2, \quad g = \frac{1}{a}, \quad k^2 = \frac{b^2}{a^2}, \quad k'^2 = 1 - k^2 = \frac{a^2 - b^2}{a^2}.\quad (3.10)$$

The integrals α' and β' for the contours $\Lambda_{\alpha'}$ and $\Lambda_{\beta'}$ in Fig. 3(a) in [1] are obtained from the formulas $\alpha' = \alpha + \frac{\Delta\pi}{2}$ and $\beta' = \beta + \frac{\Delta\pi}{2}$; see eq. (3.18a) in [1].

3.1.2. The quantities \tilde{L} and \tilde{L}' pertaining to the ξ -equation [Fig. 1(a) in Ref. 1]

Denoting the four real zeros $\xi_1 < \xi_2 < 1 < \xi_3 < \xi_4$ of $\tilde{Q}^2(\xi)$ by the simpler notations $d < c < 1 < b < a$, respectively, used in [10], we have

$$\tilde{Q}(\xi) = p \frac{[(a - \xi)(\xi - b)(\xi - c)(\xi - d)]^{\frac{1}{2}}}{\xi^2 - 1}.\quad (3.11)$$

Using the appropriate transformation on p. 120 in [10], we obtain (cf. sec. II)

$$\xi = \frac{b - c\nu_1^2 sn^2 u}{1 - \nu_1^2 sn^2 u}, \quad \nu_1^2 = \frac{a - b}{a - c} < 1.\quad (3.12)$$

Noting that the loop $\xi_3 \rightarrow \xi_4 \rightarrow \xi_3$, that is $b \rightarrow a \rightarrow b$, in the ξ -plane, denoted by $\Gamma_{b,a}$, represents the contour $\Lambda_{\tilde{L}}$ in Fig. 1(a) of [1] and corresponds to $0 \rightarrow K \rightarrow 2K$ in the u -plane, and using the transformation (3.12), we obtain the first-order contribution to \tilde{L} through the following transformation of the original integral in the ξ -plane to the u -plane:

$$\begin{aligned}\tilde{L}^{(1)} &= \frac{1}{2} \int_{\Lambda_{\tilde{L}}} \tilde{Q}(\xi) d\xi \\ &= \frac{1}{2} \int_{\Gamma_{b,a}} \tilde{Q}(\xi) d\xi \\ &= \frac{p}{2g} \int_0^{2K} \left(\frac{d\xi}{du}\right)^2 \frac{du}{\xi^2 - 1} \\ &= \frac{2p(\nu_2^2 - \nu_1^2)(\nu_3^2 - \nu_1^2)}{g} \int_0^{2K} \frac{sn^2 u (1 - sn^2 u)(1 - k^2 sn^2 u)}{(1 - \nu_1^2 sn^2 u)^2 (1 - \nu_2^2 sn^2 u)(1 - \nu_3^2 sn^2 u)} du,\end{aligned}\quad (3.13)$$

where

$$\nu_1^2 = \frac{a-b}{a-c}, \quad \nu_2^2 = \frac{1+c}{1+b}\nu_1^2, \quad \nu_3^2 = \frac{1-c}{1-b}\nu_1^2, \quad (3.14)$$

$$g = \frac{2}{[(a-c)(b-d)]^{\frac{1}{2}}}, \quad k^2 = \frac{(a-b)(c-d)}{(a-c)(b-d)}. \quad (3.15)$$

Note that a, b, c, d , and hence also $\nu_1, \nu_2, \nu_3, g, k$, depend on the choice of the parameter \tilde{C} in the base function $\tilde{Q}(\xi)$; cf. (3.2a) in [1]. Decomposing the integrand in (3.13) into partial fractions, and using recurrence formulas in [10], we obtain the final formula

$$\tilde{L}^{(1)} = -H^{(1)}(\nu_1, \nu_2, \nu_3, g, k, \tilde{C}) \quad (3.16a)$$

$$\begin{aligned} &= \frac{2p}{g} \left[\left(1 - 2k^2 + \frac{3k^2}{\nu_1^2} \right) K(k) - 3E(k) \right. \\ &\quad \left. + \left(2(1+k^2) - \nu_1^2 - \frac{3k^2}{\nu_1^2} \right) \Pi(\nu_1^2, k) - \sum_{i=1}^3 C_i S_i \right], \end{aligned} \quad (3.16b)$$

where we have introduced the ‘‘universal’’ function $H^{(1)}$, and

$$C_1 = \frac{2[2\nu_2^2\nu_3^2 - \nu_1^2\nu_2^2 - \nu_1^2\nu_3^2]}{(\nu_2^2 - \nu_1^2)(\nu_1^2 - \nu_3^2)}, \quad (3.17a)$$

$$C_2 = \frac{2\nu_2^2(\nu_3^2 - \nu_1^2)}{(\nu_2^2 - \nu_1^2)(\nu_3^2 - \nu_2^2)}, \quad (3.17b)$$

$$C_3 = \frac{2\nu_3^2(\nu_2^2 - \nu_1^2)}{(\nu_3^2 - \nu_1^2)(\nu_2^2 - \nu_3^2)}, \quad (3.17c)$$

$$\begin{aligned} S_i &= \frac{1}{3k^2} [(\nu_i^2 + 2\nu_i^2 k^2 - 3k^2)K(k) - (\nu_i^2 + \nu_i^2 k^2 - 3k^2)E(k) \\ &\quad + \frac{3k^2}{\nu_i^2} (1 - \nu_i^2)(k^2 - \nu_i^2)[\Pi(\nu_i^2, k) - K(k)]] , \quad i = 1, 2, 3, \end{aligned} \quad (3.18)$$

which can also be written as

$$S_i = \frac{k'^2}{3} \left[\nu_i^2 \frac{K(k) - E(k)}{k^2} + \frac{(3 - 2\nu_i^2)E(k)}{k'^2} - 3\Pi\left(\frac{k^2 - \nu_i^2}{1 - \nu_i^2}, k\right) \right], \quad i = 1, 2, 3, \quad (3.18')$$

the last formula being valid if ν_i^2 and k^2 fulfil the conditions stated in section 117.03 in [10].

Similarly we get for the third-order contribution to \tilde{L} :

$$\tilde{L}^{(3)} = \frac{1}{2} \int_{\Lambda_{\tilde{L}}} \left[\left(\tilde{C} + \frac{1}{\xi^2 - 1} \right) \frac{1}{2\tilde{Q}(\xi)(\xi^2 - 1)} - \frac{1}{8}\tilde{Q}^{-3}(\xi) \left(\frac{d\tilde{Q}}{d\xi} \right)^2 \right] d\xi,$$

that is

$$\tilde{L}^{(3)} = -H^{(3)}(\nu_1, \nu_2, \nu_3, g, k, \tilde{C}) \quad (3.16c)$$

$$\begin{aligned} &= -\frac{g}{64p(\nu_2^2 - \nu_1^2)(\nu_3^2 - \nu_1^2)} \left[\sum_{i=1}^4 C'_i K(k) + \sum_{i=1}^4 D_i E(k) \right] \\ &\quad - \frac{g}{4p} \left[\tilde{C} + \frac{\nu_1^2(\nu_2^2 - \nu_3^2)}{4\nu_2^2(\nu_1^2 - \nu_3^2)} + \frac{\nu_1^2(\nu_2^2 - \nu_3^2)}{4\nu_3^2(\nu_2^2 - \nu_1^2)} \right] K(k), \end{aligned} \quad (3.16d)$$

where $H^{(3)}$ is another “universal” function, \tilde{C} is the parameter in the base function $\tilde{Q}(\xi)$ (cf. eq. (3.2a) in [1]), and

$$C'_1 = \frac{4}{3k'^2} [k^4 + 2k^2 - 2 + (2\nu_1^2 + \nu_2^2 + \nu_3^2)(1 - 2k^2) + \{2\nu_1^2(\nu_2^2 + \nu_3^2) + \nu_2^2\nu_3^2 + \nu_1^4\}(4 - 3k^2)] \\ + \frac{4}{3k'^2} \left[-\{2\nu_1^2\nu_2^2\nu_3^2 + \nu_1^4(\nu_2^2 + \nu_3^2)\} \frac{11 - 10k^2}{k^2} + \frac{\nu_1^4\nu_2^2\nu_3^2}{k^4} (14 - 6k^2 - 7k^4) \right], \quad (3.19a)$$

$$C'_2 = \frac{4}{\nu_2^2\nu_3^2} \left[2\nu_2^4\nu_3^4 + \nu_1^4\nu_2^4 + \nu_1^4\nu_3^4 - 2\nu_1^4\nu_2^2\nu_3^2 - \frac{2\nu_1^2\nu_2^4\nu_3^4}{k^2} \left(2 - \frac{\nu_1^2}{3} \right) + \frac{4\nu_1^4\nu_2^4\nu_3^4}{3k^4} \right], \quad (3.19b)$$

$$C'_3 = \frac{8\nu_2^2\nu_3^2}{3k^4} (3k^4 - 6\nu_1^2k^2 + 2\nu_1^4 + k^2\nu_1^4), \quad (3.19c)$$

$$C'_4 = 16 \left[-(\nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2) - \frac{\nu_1^4\nu_2^2\nu_3^2}{k^4} (2 + k^2) + \frac{\nu_1^2}{k^2} (\nu_1^2\nu_2^2 + \nu_1^2\nu_3^2 + 4\nu_2^2\nu_3^2) \right], \quad (3.19d)$$

$$D_1 = \frac{4}{3k'^4} [2 - 3k^2 - 3k^4 + 2k^6 - (2\nu_1^2 + \nu_2^2 + \nu_3^2)(1 - 4k^2 + k^4)] \\ + \frac{4}{3k'^4} [-\{2\nu_1^2(\nu_2^2 + \nu_3^2) + \nu_2^2\nu_3^2 + \nu_1^4\}(1 + k^2)] \\ + \frac{4}{3k'^4} \left[\frac{(11 - 20k^2 + 11k^4)\{2\nu_1^2\nu_2^2\nu_3^2 + \nu_1^4(\nu_2^2 + \nu_3^2)\}}{k^2} - \frac{\nu_1^4\nu_2^2\nu_3^2}{k^4} (14 - 13k^2 - 13k^4 + 14k^6) \right], \quad (3.20a)$$

$$D_2 = \frac{16\nu_1^2\nu_2^2\nu_3^2}{3k^4} [3k^2 - \nu_1^2(1 + k^2)], \quad (3.20b)$$

$$D_3 = D_2, \quad (3.20c)$$

$$D_4 = \frac{16\nu_1^2}{k^2} \left[-(\nu_1^2\nu_2^2 + \nu_1^2\nu_3^2 + 4\nu_2^2\nu_3^2) + \frac{2\nu_1^2\nu_2^2\nu_3^2}{k^2} (1 + k^2) \right]. \quad (3.20d)$$

The integral \tilde{L}' for the contour $\Lambda_{\tilde{L}'}$ in Fig. 1(a) in [1] is obtained from the formula $\tilde{L}' = \tilde{L} + \frac{|m|}{2}\pi$. Therefore $\tilde{L}'^{(1)}$ and $\tilde{L}'^{(3)}$ can be obtained from (3.16a,b) and (3.16c,d).

3.2. Two real and two complex conjugate zeros of $Q^2(\eta)$ and $\tilde{Q}^2(\xi)$

3.2.1. *The quantities $\alpha = \beta$, \bar{K} , L and L' pertaining to the η -equation: Superbarrier case [Fig. 4(a) or Fig. 2 in Ref. 1]*

Putting $\eta_4 = -\eta_1 = a$, $\eta_2 = \eta_3^* = -ia_1$, we have

$$Q(\eta) = p \frac{[(a^2 - \eta^2)(a_1^2 + \eta^2)]^{\frac{1}{2}}}{1 - \eta^2}. \quad (3.21)$$

Using the appropriate transformation on p. 133 in [10], that is,

$$\eta^2 = a^2 cn^2 u, \quad (3.22)$$

we now utilize the fact that the Jacobian elliptic functions are doubly periodic, one of the periods being complex. Thus, the loop $\eta_1 \rightarrow \eta_2 \rightarrow \eta_1$, that is $-a \rightarrow -ia_1 \rightarrow -a$, in the η -plane, denoted by $\Gamma_{-a, -ia_1}$, represents the contour Λ_α in Fig. 4(a) of [1], and it corresponds in the u -plane to $0 \rightarrow K + iK' \rightarrow 2K + 2iK'$ where $K' = K(k')$. Denoting by $2\bar{G}^{(2n+1)}$ the integral occurring in the definitions (3.13b) and (3.15b') in [1] when $Z_1 = Z_2$, we have the following first-order expression:

$$\bar{G}^{(1)} = \frac{1}{2} \int_{\Lambda_\alpha} Q(\eta) d\eta \\ = \frac{1}{2} \int_{\Gamma_{-a, -ia_1}} Q(\eta) d\eta, \quad (3.23)$$

which when transformed to the variable u becomes

$$\bar{G}^{(1)} = \frac{pa^2}{2g} \int_0^{2K+2iK'} \frac{sn^2 u dn^2 u}{1-a^2 cn^2 u} du. \quad (3.24)$$

After evaluation of the integral in (3.24) we obtain

$$\begin{aligned} \bar{G}^{(1)} &= \frac{p}{g} \left[E(k) + \frac{k^2}{a^2} (1-a^2) K(k) - \left(\frac{k^2}{a^2} + k'^2 \right) \Pi(\nu^2, k) \right] \\ &\quad - \frac{p}{g} i \left\{ E(k') + (k^2 + a^2 k'^2) [\Pi(1-\nu^2, k') - K(k')] \right\}, \end{aligned} \quad (3.25a)$$

where

$$\nu^2 = \frac{a^2}{a^2-1}, \quad g = \frac{1}{(a^2+a_1^2)^{\frac{1}{2}}}, \quad k^2 = \frac{a^2}{a^2+a_1^2}, \quad k'^2 = 1-k^2. \quad (3.26)$$

Similarly one obtains

$$\begin{aligned} \bar{G}^{(3)} &= -\frac{Cg}{2p} K(k) + \left\{ \frac{g}{2p(1-a^2)} + \frac{(\nu^2-1)g}{4p} \right\} \left[\Pi(\nu^2, k) - \frac{\pi}{2} \sqrt{\frac{a^2(1-a^2)}{k'^2 a^2 + k^2}} \right] \\ &\quad - \frac{g}{8\nu^2 p} \left[\frac{1}{3} (-4k^2 + 4\nu^2 - 1) K(k) + \frac{1}{3k'^2} (-8k^4 + 8k^2(1-\nu^2) + 1 + 7\nu^2) E(k) \right] \\ &\quad + i \left\{ -\frac{Cg}{2p} K(k') + \left[\frac{g}{2p(1-a^2)} + \frac{(\nu^2-1)g}{4p} \right] \left[(1-a^2) K(k') - \nu^2 \Pi(\nu^2-1, k') - \frac{\pi}{2} \right] \right\} \\ &\quad - i \frac{g}{8\nu^2 p} \left[\frac{1}{3} (-4k^2 + 4\nu^2 - 1) K(k') + \frac{1}{3k'^2} (-8k^4 + 8k^2(1-\nu^2) + 1 + 7\nu^2) [K(k') - E(k')] \right]. \end{aligned} \quad (3.25b)$$

Recalling the definition of $\bar{G}^{(2n+1)}$ above (3.23) in the present paper, one sees that according to (3.13b) in [1] the first- and third-order contributions to α are

$$\alpha^{(1)} = \text{Re} \bar{G}^{(1)}, \quad (3.27a)$$

$$\alpha^{(3)} = \text{Re} \bar{G}^{(3)}, \quad (3.27b)$$

and that according to (3.15b') in [1] the first- and third-order contributions to $K(=\pi\bar{K})$ are

$$\pi\bar{K}_0 = -2\text{Im} \bar{G}^{(1)}, \quad (3.28a)$$

$$\pi\bar{K}_2 = -2\text{Im} \bar{G}^{(3)}. \quad (3.28b)$$

The integrals $\alpha' = \beta'$ associated with the contours $\Lambda_{\alpha'}$ and $\Lambda_{\beta'}$ in Fig. 4 in [1] are obtained from the integrals $\alpha = \beta$ by means of the relations (3.18a) in [1], that is, $\alpha' = \beta' = \alpha + \frac{\Lambda\pi}{2} = \beta + \frac{\Lambda\pi}{2}$. The integrals L and L' associated with the contours Λ_L and $\Lambda_{L'}$ in Fig. 4(a) in [1] can be obtained from the integrals $\alpha = \beta$ by means of the formulas $L = \alpha + \beta = 2\alpha$ and $L' = L + |m|$.

The only essential difference between $-Q^2(\eta)$ in Fig. 4(a) in [1] and $-Q^2(\eta)$ in Fig. 2 in [1] is that in the former figure there is an underdense barrier of $-Q^2(\eta)$, while in the latter figure $-Q^2(\eta)$ has a single minimum. For the case in Fig. 2 one has therefore the formula $L^{(2n+1)} = \alpha^{(2n+1)} + \beta^{(2n+1)} = 2\alpha^{(2n+1)}$, with the expansions (3.27a) and (3.27b) for $\alpha^{(1)}$ and $\alpha^{(3)}$, and the formula $L'^{(2n+1)} = L^{(2n+1)} + |m|\delta_{m,0}$. The case in Fig. 2 has, however not appeared in our applications.

3.2.2. The quantities \tilde{L} and \tilde{L}' pertaining to the ξ -equation [Fig. 1(a) in Ref. 1]

Denoting by $\xi_3 = b$ and $\xi_4 = a$ the real zeros of $\tilde{Q}^2(\xi)$, and by c and c^* the complex conjugate zeros ξ_1 and ξ_2 of $\tilde{Q}^2(\xi)$, we have

$$\tilde{Q}(\xi) = p \frac{[(a - \xi)(\xi - b)(\xi - c)(\xi - c^*)]^{\frac{1}{2}}}{\xi^2 - 1}. \quad (3.29)$$

Defining

$$c = b_1 - ia_1, \quad c^* = b_1 + ia_1, \quad (3.30)$$

$$A = [(a - b_1)^2 + a_1^2]^{\frac{1}{2}}, \quad B = [(b - b_1)^2 + a_1^2]^{\frac{1}{2}}, \quad (3.31)$$

and using the appropriate transformation on p. 133 in [10], we get

$$\xi = \frac{aB + bA + (bA - aB)cnu}{A + B + (A - B)cnu}. \quad (3.32)$$

Noting that the loop $b \rightarrow a \rightarrow b$ in the ξ -plane (denoted by $\Gamma_{b,a}$ for the contour $\Lambda_{\tilde{L}}$) corresponds to the path $0 \rightarrow 2K \rightarrow 4K$ in the u -plane, and using the transformation (3.32), we obtain for the first-order contribution to \tilde{L} the formula (see Fig. 1(a) in [1]),

$$\begin{aligned} \tilde{L}^{(1)} &= \frac{1}{2} \int_{\Lambda_{\tilde{L}}} \tilde{Q}(\xi) d\xi \\ &= \frac{1}{2} \int_{\Gamma_{b,a}} \tilde{Q}(\xi) d\xi \\ &= \frac{p(\nu_1 - \nu_2)(\nu_1 - \nu_3)}{g} \int_0^{4K} \frac{sn^2 u dn^2 u}{(1 + \nu_1 cnu)^2 (1 + \nu_2 cnu)(1 + \nu_3 cnu)} du, \end{aligned} \quad (3.33)$$

where

$$\nu_1 = \frac{A - B}{A + B}, \quad \nu_2 = \frac{(1 + b)A - (1 + a)B}{(1 + b)A + (1 + a)B}, \quad \nu_3 = \frac{(1 - b)A - (1 - a)B}{(1 - b)A + (1 - a)B}, \quad (3.34)$$

$$g = \frac{1}{\sqrt{AB}}, \quad k^2 = \frac{(a - b)^2 - (A - B)^2}{4AB}. \quad (3.35)$$

By evaluating the last integral in (3.33), and introducing a new ‘‘universal’’ function $\bar{H}^{(1)}$, given by eqs. (2.19), (2.20a-c) and (2.21) in [8] with $j = 0$, we obtain

$$\tilde{L}^{(1)} = -2\text{Re}\bar{H}^{(1)}(\nu_1, \nu_2, \nu_3, g, k, \tilde{C})[\text{with } j=0] \quad (3.36a)$$

$$\begin{aligned} &= \frac{2p}{g} \left\{ \frac{1}{\nu_1^2} \left[\left(2k^2 + \frac{\nu_1^2}{1 - \nu_1^2} \right) \Pi \left(\frac{\nu_1^2}{\nu_1^2 - 1}, k \right) \right. \right. \\ &\quad \left. \left. + (\nu_1^2 - 2k^2)K(k) - 2\nu_1^2 E(k) + \nu_1 k\pi \right] + \sum_{i=1}^3 \bar{C}_i \bar{J}_i \right\}, \end{aligned} \quad (3.36b)$$

where

$$\bar{C}_1 = \frac{\nu_1^2(2\nu_3\nu_2 - \nu_1\nu_3 - \nu_1\nu_2)}{(\nu_1 - \nu_2)(\nu_1 - \nu_3)}, \quad (3.37a)$$

$$\bar{C}_2 = \frac{(\nu_1 - \nu_3)\nu_2^3}{(\nu_1 - \nu_2)(\nu_2 - \nu_3)}, \quad (3.37b)$$

$$\bar{C}_3 = \frac{(\nu_1 - \nu_2)\nu_3^3}{(\nu_1 - \nu_3)(\nu_3 - \nu_2)}, \quad (3.37c)$$

$$\begin{aligned} \bar{J}_i &= \text{Re}\bar{S}_i(\text{with } j = 0) \\ &= \frac{1}{\nu_i^4} \left[k^2(1 - \nu_i^2)K(k) + \nu_i^2 E(k) - (k^2 + \nu_i^2 k'^2) \Pi \left(\frac{\nu_i^2}{\nu_i^2 - 1}, k \right) \right] \\ &\quad + \frac{1}{2k\nu_i^3} \left[k^2(\nu_i^2 - 1) - \frac{\nu_i^2}{2} \right] \pi, \quad i = 1, 2, 3; \end{aligned} \quad (3.38)$$

cf. for the definition of \bar{S}_i eq. (2.21) in [8]. The third-order contribution to \tilde{L} is

$$\begin{aligned} \tilde{L}^{(3)} &= -2\text{Re}\bar{H}^{(3)}(\nu_1, \nu_2, \nu_3, g, k, \tilde{C})[\text{with } j=0] \\ &= -\frac{g}{8p} \left\{ \left(4\tilde{C} + \frac{\nu_1^2(\nu_2 - \nu_3)^2}{\nu_2\nu_3(\nu_1 - \nu_3)(\nu_2 - \nu_1)} \right) K(k) \right. \\ &\quad \left. + \frac{1}{(\nu_1 - \nu_3)(\nu_1 - \nu_2)} [XK(k) + YE(k)] \right\}, \end{aligned} \quad (3.39a)$$

$$(3.39b)$$

where $\bar{H}^{(3)}$ is another ‘‘universal’’ function, given by eqs. (2.22) and (2.23a-c) in [8] with $j = 0$, and where thus

$$\begin{aligned} X &= -\frac{(1 + 4k^2)}{3} + \frac{(3 + 4k'^2)}{3}(\nu_1^2 + 2\nu_1\nu_2 + 2\nu_1\nu_3 + \nu_2\nu_3) - \frac{k'^2}{3k^2}(17 - 4k^2)\nu_1^2\nu_2\nu_3 \\ &\quad - 2\nu_1(\nu_1 + \nu_2 + \nu_3) + 2\nu_2\nu_3 + \nu_1^2 \left(\frac{\nu_2}{\nu_3} + \frac{\nu_3}{\nu_2} \right), \end{aligned} \quad (3.40a)$$

$$\begin{aligned} Y &= \frac{1}{3k'^2}(1 + 8k^2 - 8k^4) + \frac{4}{3}(2k^2 - 1)(\nu_1^2 + 2\nu_1\nu_2 + 2\nu_1\nu_3 + \nu_2\nu_3) \\ &\quad + \frac{\nu_1^2\nu_2\nu_3}{3k^2}(17 - 8k^2 + 8k^4). \end{aligned} \quad (3.40b)$$

The integral \tilde{L}' associated with the contour $\Lambda_{\tilde{L}'}$ in Fig. 1(a) in [1] is obtained from the formula $\tilde{L}' = \tilde{L} + \frac{|m|}{2}\pi$. One has therefore the formulas $\tilde{L}'^{(1)} = \tilde{L}^{(1)} + \frac{|m|}{2}\pi$ and $\tilde{L}'^{(3)} = \tilde{L}^{(3)}$ with $\tilde{L}^{(1)}$ and $\tilde{L}^{(3)}$ given by (3.39a) and (3.39b).

4. CASE $\Lambda = 0$

4.1. Two real zeros of $Q^2(\eta)$ and $\tilde{Q}^2(\xi)$

4.1.1. *The quantities $\alpha = \beta$ and \bar{K} pertaining to the η -equation: Subbarrier case [Fig. 3(b) in Ref. 1]*

Putting $\eta_3 = -\eta_2 = b$ as before, we have

$$Q(\eta) = p \left[\frac{(\eta^2 - b^2)}{1 - \eta^2} \right]^{\frac{1}{2}}. \quad (4.1)$$

Using (3.2) with $a = 1$, the first- and third-order contributions to α become

$$\alpha^{(1)} = p[E(k) - (1 - k^2)K(k)], \quad (4.2a)$$

$$\alpha^{(3)} = \frac{1}{2pk^2} \left[(1 - Ck^2)K(k) - E(k) - \frac{1}{12} \left((3k^2 - 8)K(k) - (7k^2 - 8)\frac{E(k)}{k'^2} \right) \right], \quad (4.2b)$$

where $k^2 = 1 - b^2$.

The first- and third-order contributions to $K(= \pi\bar{K})$ are

$$\pi\bar{K}_0 = 2p[E(k) - (1 - k^2)K(k)], \quad (4.3a)$$

$$\pi\bar{K}_2 = \frac{1}{p} \left[CK(k) - \frac{E(k)}{k'^2} + \frac{1}{12k^2} \left(\frac{7k^2 + 1}{k'^2} E(k) - (3k^2 + 1)K(k) \right) \right], \quad (4.3b)$$

where $k^2 = b^2$.

4.1.2. *The quantities \tilde{L} and \tilde{L}' pertaining to the ξ -equation [Fig. 1 in Ref. 1]*

If the real zeros of $\tilde{Q}^2(\xi)$ are $\xi_3 = c (< a)$ and $\xi_4 = a$, we have

$$\tilde{Q}(\xi) = p \left[\frac{(\xi - c)(a - \xi)}{(\xi + 1)(\xi - 1)} \right]^{\frac{1}{2}}. \quad (4.4)$$

We shall treat the three cases $1 < c < a$, $-1 < c < 1 < a$ and $c < -1 < 1 < a$ separately.

Case $1 < c < a$ [Fig. 1(a) in Ref. 1]

For this case we use in [10] the transformation on p. 120 and the formula in section 256.19 with a suitable choice of parameters to obtain the first- and third-order contributions to \tilde{L} as

$$\begin{aligned} \tilde{L}^{(1)} &= \int_c^a \tilde{Q}(\xi) d\xi \\ &= p \frac{(a - c)(c - 1)g}{2\nu^2(\nu^2 - k^2)} [(2\nu^2 - \nu^4 - k^2)\Pi(\nu^2, k) - \nu^2 E(k) - (\nu^2 - k^2)K(k)], \end{aligned} \quad (4.5a)$$

$$\begin{aligned} \tilde{L}^{(3)} &= \frac{\tilde{C}gK(k)}{2p} + \frac{g}{2(c^2 - 1)p} \left[\frac{2\nu^2}{k^4} (k^2 - \nu^2)K(k) + \frac{1}{k^4 k'^2} (k^2(k^2 - \nu^4 - 2\nu^2) + 2\nu^4) E(k) \right] \\ &\quad - \frac{g}{24\nu^4 p(c - 1)} [(-2 + k^2 + 2\nu^2 - \nu^4)K(k) + 2(k^4 - (1 + \nu^2 + \nu^4)k^2 - \nu^2 + 2\nu^4 + 1) E(k)], \end{aligned} \quad (4.5b)$$

where

$$\nu^2 = \frac{a - c}{a - 1}, \quad g = \frac{2}{[(a - 1)(c + 1)]^{\frac{1}{2}}}, \quad k^2 = \frac{2(a - c)}{(a - 1)(c + 1)}. \quad (4.6)$$

To obtain \tilde{L}' one can use the formula $\tilde{L}'^{(2n+1)} = \tilde{L}^{(2n+1)} + \frac{|m|}{2} \delta_{m,0}$ with $\tilde{L}^{(1)}$ and $\tilde{L}^{(3)}$ given by (4.5a) and (4.5b).
Case $-1 < c < 1 < a$ [Fig. 1(b) in Ref. 1]

We use in [10] the appropriate transformation on p. 120 and the formula in section 256.17 (with $b = 1$ and $d = -1$) to obtain the first- and third-order contributions to \tilde{L}' (see Fig.1(b) in [1]) as

$$\tilde{L}'^{(1)} = \frac{2p}{g} \left[\left(1 - \frac{k^2}{\nu^2} \right) K(k) - E(k) + \left(\nu^2 - 2k^2 + \frac{k^2}{\nu^2} \right) \Pi(\nu^2, k) \right], \quad (4.7a)$$

$$\begin{aligned} \tilde{L}'^{(3)} &= \frac{g\tilde{C}K(k)}{2p} + \frac{g}{4p\nu^2(1 - c)} \left[\left(1 - \frac{\nu^4}{k^2} \right) K(k) + (k^2(2k^2 - 1 - 2\nu^2) + \nu^4) \frac{E(k)}{k^2 k'^2} \right] \\ &\quad - \frac{g}{16(1 - c)p\nu^2} \left[\frac{4}{3k^2} ((2 + \nu^4 + 2\nu^2)k^2 - 3k^4 - 2\nu^4) K(k) \right. \\ &\quad \left. + \frac{8}{3k'^2} \left(-(\nu^4 + \nu^2 - 1) + k^2(\nu^4 - \nu^2 + 2) + \frac{\nu^4}{k^2} \right) E(k) \right], \end{aligned} \quad (4.7b)$$

where

$$\nu^2 = \frac{a-1}{a-c}, \quad g = \left(\frac{2}{a-c}\right)^{\frac{1}{2}}, \quad k^2 = \frac{(1+c)(a-1)}{2(a-c)}. \quad (4.8)$$

Case $c < -1 < 1 < a$ [Fig. 1(b) in Ref. 1]

Using in [10] the transformation on p. 120 and the formula in section 256.20 with a suitable choice of parameters, we obtain the first- and third-order contributions to \tilde{L}' as

$$\tilde{L}'^{95(1)} = \frac{(a-c)(1-c)gp}{2\nu^4} [-\nu^2 E(k) + (\nu^2 + k^2)K(k) + (\nu^4 - k^2)\Pi(\nu^2, k)], \quad (4.9a)$$

$$\begin{aligned} \tilde{L}'^{(3)} = & \frac{\tilde{C}gK(k)}{p} + \frac{g}{4p\nu^2} \left[(1 - 2\nu^2 + \frac{\nu^4}{k^2})K(k) - (1 + \frac{\nu^4}{k^2})E(k) \right] \\ & - \frac{g}{32p\nu^2} \left\{ \frac{4}{3k^2k'^2} [-k^4 + k^2(2 - \nu^4 - 2\nu^2) - \nu^4] K(k) \right. \\ & \left. + \frac{8}{3k^2k'^4} [-k^6 + k^4(\nu^2 - \nu^4) + k^2(\nu^4 + \nu^2 - 1) - \nu^4] E(k) \right\}, \end{aligned} \quad (4.9b)$$

with

$$\nu^2 = \frac{a-1}{a+1}, \quad g = \frac{2}{[(a+1)(1-c)]^{\frac{1}{2}}}, \quad k^2 = \frac{(a-1)(-c-1)}{(a+1)(1-c)}. \quad (4.10)$$

4.2. Two complex conjugate zeros of $Q^2(\eta)$

The case of two complex conjugate zeros of the square of the base function occurs only for the η -equation.

4.2.1. *The quantities $\alpha = \beta$ and \bar{K} pertaining to the η -equation: Superbarrier case [Fig. 4(b) in Ref. 1]*

With $\eta_2 = -ia_1$ and $\eta_3 = ia_1$ we have

$$Q(\eta) = p \frac{[(1-\eta^2)(a_1^2 + \eta^2)]^{\frac{1}{2}}}{1-\eta^2} = p \left(\frac{a_1^2 + \eta^2}{1-\eta^2} \right)^{\frac{1}{2}}. \quad (4.11)$$

Specializing to the case $a = 1$ in (3.27a,b) and (3.28a,b) along with (3.25a,b), we obtain the first- and third-order contributions to α as

$$\alpha^{(1)} = \text{Re}\bar{G}^{(1)}, \quad \alpha^{(3)} = \text{Re}\bar{G}^{(3)} \quad (4.12)$$

and the first- and third-order contributions to $K(=\pi\bar{K})$ as

$$\pi\bar{K}_0 = -2\text{Im}\bar{G}^{(1)}, \quad \pi\bar{K}_2 = -2\text{Im}\bar{G}^{(3)}, \quad (4.13)$$

where

$$\bar{G}^{(1)} = \frac{p}{g} \{E(k) + i[K(k') - E(k')]\}, \quad (4.14a)$$

$$\begin{aligned} \bar{G}^{(3)} = & \frac{g}{2p} \left[(1-C)K(k) - E(k) - \frac{1}{12} \left(4K(k) + \frac{(8k^2-7)}{k'^2} E(k) \right) \right] \\ & + i \frac{g}{2p} \left[-CK(k') + E(k') - \frac{1}{12} \left(4K(k') + \frac{(8k^2-7)}{k'^2} \{K(k') - E(k')\} \right) \right] \end{aligned} \quad (4.14b)$$

with

$$g = \frac{1}{(1+a_1^2)^{\frac{1}{2}}}, \quad k^2 = \frac{1}{1+a_1^2}. \quad (4.15)$$

The integral L' associated with the contour $\Lambda_{L'}$ in Fig. 4(b) in [1] is obtained from the formula $L' = \alpha + \beta = 2\alpha$.

5. ACCURACY OF THE PHASE-INTEGRAL QUANTIZATION CONDITIONS FOR THE $1s\sigma$ AND $2p\sigma$ STATES OF THE HYDROGEN MOLECULE ION

For the $1s\sigma$ and $2p\sigma$ states of the hydrogen molecule ion one has to put $\Lambda = 0$. The quantization conditions in [1] for the $1s\sigma$ state are (3.5a) with $\tilde{s} = 0$ [Fig. 1(a) in Ref. 1] and (3.9) with $s = m = 0$ [Fig. 4(b) in Ref. 1] when r_{12} is sufficiently small, but (3.5b) with $\tilde{s} = m = 0$ [Fig. 1(b) in Ref. 1] and (3.25b) with $s_\alpha = s_\beta = m = 0$ [Fig. 3(b) in Ref. 1] when r_{12} is sufficiently large. The quantization conditions in [1] for the $2p\sigma$ state are (3.5a) with $\tilde{s} = 0$ [Fig. 1(a) in Ref. 1] and (3.9) with $s = 1$ and $m = 0$ [Fig. 4(b) in Ref. 1] when r_{12} is sufficiently small, but (3.5b) with $\tilde{s} = m = 0$ [Fig. 1(b) in Ref. 1] and (3.25a) with $s_\alpha = s_\beta = m = 0$ [Fig. 3(b) in Ref. 1] when r_{12} is sufficiently large. After having expressed these quantization conditions in the first and third order of the phase-integral approximation in terms of complete elliptic integrals, as described in the previous sections, we have used these quantization conditions to calculate the energy E and the reduced separation constant A' . In subsection 5.1 we determine C and \tilde{C} as functions of r_{12} such that the first- and third-order quantization conditions give the same values of both E and A' . For the values of C and \tilde{C} thus obtained, the choice of the base functions $Q(\eta)$ and $\tilde{Q}(\xi)$ is optimal in the sense that the most accurate first-order values of E and A' are obtained, since the first- and third-order approximations give the same values of E and A' . In this connection we remark that there are quantal systems for which one can obtain exact values of the energy by choosing the base function such that the first- and third-order results coincide; see p. 1826 in [11] and p. 16 in [12]. In subsection 5.2 we determine C and \tilde{C} such that the phase-integral quantization conditions give the numerically exact values of E and A' obtained by Murai and Takatsu [13, 14] and establish that the values of C and \tilde{C} thus obtained are in qualitative agreement with the values of C and \tilde{C} determined in subsection 5.1.

5.1. Determination of $C(r_{12})$ and $\tilde{C}(r_{12})$ such that the first- and third-order quantization conditions give the same results

By determining C and \tilde{C} for each value of r_{12} such that the first- and third-order quantization conditions give the same value of E as well as of A' , we have obtained the results in Table I for the $1s\sigma$ state and in Table II for the $2p\sigma$ state of the hydrogen molecule ion; see also Figs. 1 and 2. The phase-integral values of E and A' in these tables are in reasonable agreement with the numerically exact values obtained by Murai and Takatsu [13, 14], as is best seen from Fig.1 for the state $1s\sigma$ and from Fig. 2 for the state $2p\sigma$.

It is seen that in Figs. 1 and 2 there are sometimes some irregularities in the values of C , \tilde{C} , $|E - E_{MT}|$ and $|A' - A'_{MT}|$ for low r_{12} values. It should also be noted that C and \tilde{C} approach the correct limiting value $\frac{1}{4}$ as $r_{12} \rightarrow 0$.

5.2. Determination of $C(r_{12})$ and $\tilde{C}(r_{12})$ such that the first-order phase-integral quantization conditions reproduce numerically exact values of E and A'

By determining C and \tilde{C} for each value of r_{12} such that the first-order quantization conditions reproduce the numerically exact values of E and A' calculated by Murai and Takatsu [13, 14] we have obtained the values of C and \tilde{C} presented in Table III for the $1s\sigma$ state and in Table IV for the $2p\sigma$ state. In Figs. 3 and 4, we have shown the dependence of C and \tilde{C} on r_{12} for the states $1s\sigma$ and $2p\sigma$, respectively. One can carry out a similar calculation using the third-order phase-integral quantization condition also and determine the appropriate C and \tilde{C} . However, the numerical analysis becomes too laborious and time consuming and so we have not presented the results here.

To obtain the numerical results in subsections V.A and V.B a general FORTRAN computer program using very rapid library routines was written at the Centre for Nonlinear Dynamics, Department of Physics, Bharathidasan University, Tiruchirapalli, India. We have carried out the numerical calculations by Silicon Graphics Power Indigo 2 XZ Graphics Workstation (R8000, 64bit processor) using FORTRAN 77 compiler.

Some years ago, a direct numerical integration of the contour integrals in the phase-integral quantization conditions for the hydrogen molecule ion was carried out by Fil. lic. Anders Hökback at the Department of Theoretical Physics, University of Uppsala, Sweden. By means of this numerical material it was possible to make valuable checks of the correctness of the phase-integral quantization conditions expressed in terms of complete elliptic integrals.

Acknowledgments

The authors are much indebted to Fil. lic. Anders Hökback for placing his unpublished numerical material at their

disposal. The authors are extremely grateful to Professor Per Olof Fröman for very critical reading of the manuscript and for making numerous comments which resulted in a much improved presentation. The work of M.L. forms part of a Department of Science and Technology, Government of India, research project. Support from the Swedish Natural Science Research Council for M. Lakshmanan's visits to Uppsala is gratefully acknowledged.

-
- [1] N. Athavan, P.O. Fröman, N. Fröman, and M. Lakshmanan, *J. Math. Phys.*, submitted for publication (Paper I).
 - [2] W. Pauli, Jr., *Annalen der Physik (Leipzig)* **68**, 177 (1922).
 - [3] W. Alexandrow, *Annalen der Physik (Leipzig)* **81**, 603 (1926); **82**, 683 (1927).
 - [4] O. Burrau, *Det Kgl. Danske Videnskabernes Selskab. Matematisk-fysiske Meddelelser*. **VII**, 14, 1 (1927).
 - [5] M. Lakshmanan and P. Kaliappan, *J. Phys. A: Math. Gen.* **13**, L299 (1980).
 - [6] M. Lakshmanan, F. Karlsson, and P.O. Fröman, *Phys. Rev.* **D24**, 2586 (1981).
 - [7] M. Lakshmanan, P. Kaliappan, K. Larsson, F. Karlsson, and P.O. Fröman, *Phys. Rev.* **A49**, 3296 (1994).
 - [8] N. Athavan, M. Lakshmanan, and N. Fröman, *J. Math. Phys.*, submitted for publication (Paper III).
 - [9] M.P. Strand and W.P. Reinhardt, *J. Chem. Phys.* **70**, 3812 (1979).
 - [10] P.F. Byrd and M.D. Friedman, *Handbook of Elliptic Integrals for Engineers and Scientists*. Die Grundlehren der Mathematischen Wissenschaften in Einzeldarstellungen, Band 67, Second Edition, Revised (Springer-Verlag, Berlin, Heidelberg, New York, 1971)
 - [11] N. Fröman and P.O. Fröman, *J. Math. Phys.* **19**, 1823 (1978).
 - [12] N. Fröman, P.O. Fröman, and K. Larsson, *Phil. Trans. Roy. Soc. Lond.* **A347**, 1 (1994).
 - [13] T. Murai and H. Takatsu, *Tables of Electronic Energy of H_2^+* . Contributions from the Research Group on Atoms and Molecules No. 10, Progress Report VII, March 1974, PP74-111. Research Group on Atoms and Molecules, c/o Department of Physics, Faculty of Science, Ochanomizu University, 1-1, Otsuko 2 chome, Bunkyo-ku, Tokyo 112, Japan.
 - [14] T. Murai and H. Takatsu, Private communication in 1976 of numerical results concerning the hydrogen molecule ion.

TABLE I: For the state $1s\sigma$ of H_2^+ the values of C and \tilde{C} have been obtained from the requirement that the first- and third-order phase-integral results coincide for E as well as for A' . With the use of these values of C and \tilde{C} , the values of E and A' have then been obtained from the quantization conditions that are appropriate depending on whether r_{12} is sufficiently small or sufficiently large. The numerically exact values obtained by Murai and Takatsu [13,14] are given in the columns called E_{MT} and A'_{MT} .

r_{12}	C	\tilde{C}	E	E_{MT}	$E - E_{MT}$	A'	A'_{MT}	$A' - A'_{MT}$
Sufficiently small r_{12}								
0.6	0.4091767180	0.4953643560	-1.618424439	-1.6714847145	0.053060275	-0.1992407489	-0.1992300000	-0.000010748
0.8	0.4431528990	0.4884579844	-1.545199993	-1.5544800915	0.009280098	-0.3249142019	-0.3279000000	0.002985799
1.0	0.4681771744	0.4902081420	-1.455314042	-1.4517863130	-0.003527729	-0.4706879721	-0.4759469161	0.005258944
Sufficiently large r_{12}								
2.0	0.5255080000	0.5057903368	-1.109450173	-1.1026342150	-0.006815958	-1.385866329	-1.393538844	0.007672515
3.0	0.5347955900	0.5146860140	-0.9146268870	-0.9108961974	-0.00373069	-2.451736492	-2.458030452	0.00629396
4.0	0.5255436520	0.5191506880	-0.7981985544	-0.7960848837	-0.002113671	-3.564275870	-3.569090310	0.00481444
5.0	0.5095344153	0.5210276591	-0.7256775451	-0.7244202952	-0.00125725	-4.673981394	-4.677559936	0.003578542
6.0	0.4942331566	0.5213617485	-0.6794162838	-0.6786357151	-0.000780568	-5.759202308	-5.761839130	0.002636822
7.0	0.4829917740	0.5208505340	-0.6489619089	-0.6484511471	-0.000510761	-6.817236218	-6.819239945	0.002003727
8.0	0.4758245700	0.5199462800	-0.6279265372	-0.6275703886	-0.000356149	-7.854452399	-7.856077820	0.001625421
9.0	0.4715076730	0.5189057600	-0.6125711074	-0.6123065640	-0.000264543	-8.878337258	-8.879752233	0.001414975
10.0	0.4688953184	0.5178568616	-0.6007859807	-0.6005787289	-0.000207251	-9.894343735	-9.895643269	0.001299534
15.0	0.4641710460	0.5135686450	-0.5668106207	-0.5667156052	-0.000095015	-14.93203345	-14.93315205	0.00111865
20.0	0.4625834317	0.5107892808	-0.5500740452	-0.5500142593	-0.000059786	-19.94891764	-19.94996067	0.00104303
25.0	0.4617350800	0.5089200200	-0.5400488855	-0.5400058008	-0.000043085	-24.95899430	-24.95998443	0.00099013

TABLE II: For the state $2p\sigma$ of H_2^+ the values of C and \tilde{C} have been obtained from the requirement that the first- and third-order phase-integral results coincide for E as well as for A' . With the use of these values of C and \tilde{C} , the values of E and A' have then been obtained from the quantization conditions that are appropriate depending on whether r_{12} is sufficiently small or sufficiently large. The numerically exact values obtained by Murai and Takatsu [13,14] are given in the columns called E_{MT} and A'_{MT} .

r_{12}	C	\tilde{C}	E	E_{MT}	$E - E_{MT}$	A'	A'_{MT}	$A' - A'_{MT}$
Sufficiently small r_{12}								
0.2	0.2633959780	0.246516819	-0.5020720303	-0.5026800000	-0.00060797	-2.005074078	-2.004020000	0.001054078
0.4	0.2688550280	0.234829974	-0.5091302928	-0.5107900000	-0.001659708	-2.018393631	-2.016330000	0.002063631
0.6	0.2750685470	0.209525191	-0.5231745581	-0.5243050000	-0.001130442	-2.041072959	-2.037690000	0.003382959
0.8	0.2826340310	0.1470935880	-0.5524257935	-0.5427400000	0.009685793	-2.075482537	-2.069270000	0.006212537
2.0	0.3435728404	0.5524319489	-0.6571837692	-0.6675343922	-0.010350623	-2.523233873	-2.521958177	0.001275696
3.0	0.3915235980	0.5260048459	-0.7015678961	-0.7014183334	0.000149563	-3.202554526	-3.196382289	0.006172237
Sufficiently large r_{12}								
4.0	0.4279941950	0.5249345450	-0.6960011808	-0.6955506394	0.000450542	-4.029227017	-4.025940635	0.003286382
5.0	0.4481616320	0.5238924640	-0.6777410414	-0.6772916132	0.000449428	-4.942443752	-4.941274459	0.001169293
6.0	0.4591233730	0.5226760960	-0.6577104664	-0.6573105590	0.000399907	-5.903631412	-5.903659889	-0.000028477
7.0	0.4644579210	0.5214162480	-0.6394674183	-0.6391288554	0.000338563	-6.890343283	-6.890997919	-0.000654636
8.0	0.4666144860	0.5201789140	-0.6238870346	-0.6236060156	0.000280969	-7.889744744	-7.890707161	-0.000962417
9.0	0.4671264910	0.5189985500	-0.6108876012	-0.6106549406	0.00023266	-8.894778515	-8.895880333	-0.001101818
10.0	0.4668770890	0.5178931230	-0.6000950569	-0.5999010686	0.000193989	-9.901798495	-9.902954530	-0.001156035
15.0	0.4641395400	0.5135689400	-0.5668036046	-0.5667087290	0.000094875	-14.93214472	-14.93326111	-0.00111639
20.0	0.4625830500	0.5107892800	-0.5500739820	-0.5500141977	0.000059785	-19.94891896	-19.94996191	-0.00104295
25.0	0.4617350700	0.5089200100	-0.5400488850	-0.5400058003	0.000043085	-24.95899432	-24.95998445	-0.00099013

TABLE III: For the state $1s\sigma$ of H_2^+ the values of C and \tilde{C} have been obtained from the requirement that the first-order phase-integral results, obtained from quantization conditions that are appropriate depending on whether r_{12} is sufficiently small or sufficiently large, coincide for E as well as for A' with the numerically exact results obtained by Murai and Takatsu [13,14] and quoted in this table as E_{MT} and A'_{MT} .

r_{12}	E_{MT}	A'_{MT}	C	\tilde{C}
Sufficiently small r_{12}				
0.2	-1.9286203017	-0.0256900000	0.3148379823	0.3506512286
0.4	-1.8007540595	-0.0957300000	0.3477075009	0.4296524070
0.6	-1.6714847145	-0.1992300000	0.3681917193	0.4607730539
0.8	-1.5544800915	-0.3279000000	0.3807005347	0.4777532944
1.0	-1.4517863130	-0.4759469161	0.1120058693	0.4885447845
Sufficiently large r_{12}				
2.0	-1.1026342150	-1.393538844	0.5095379703	0.5120864521
3.0	-0.9108961974	-2.458030452	0.5196342600	0.5202577750
4.0	-0.7960848837	-3.569090310	0.5131695740	0.5235297064
5.0	-0.7244202952	-4.677559936	0.5001127420	0.5243749920
6.0	-0.6786357151	-5.761839130	0.4872379220	0.5239023990
7.0	-0.6484511471	-6.819239945	0.4776859510	0.5227893710
8.0	-0.6275703886	-7.856077820	0.4715798270	0.5214462830
9.0	-0.6123065640	-8.879752233	0.4679041020	0.5200867890
10.0	-0.6005787289	-9.895643269	0.4656852040	0.5188037440
15.0	-0.5667156052	-14.93315205	0.4617106320	0.5139609640
20.0	-0.5500142593	-19.94996067	0.4603989670	0.5109975070
25.0	-0.5400058008	-24.95998443	0.4597077000	0.5090477000

TABLE IV: For the state $2p\sigma$ of H_2^+ the values of C and \tilde{C} have been obtained from the requirement that the first-order phase-integral results, obtained from quantization conditions that are appropriate depending on whether r_{12} is sufficiently small or sufficiently large, coincide for E as well as for A' with the numerically exact results obtained by Murai and Takatsu [13,14] and quoted in this table as E_{MT} and A'_{MT} .

r_{12}	E_{MT}	A'_{MT}	C	\tilde{C}
Sufficiently small r_{12}				
0.2	-0.5026800000	-2.004020000	0.264492583	0.2439809316
0.4	-0.5107900000	-2.016330000	0.2712715280	0.2275797176
0.6	-0.5243050000	-2.037690000	0.2795333746	0.2071325406
0.8	-0.5427400000	-2.069270000	0.2897524086	0.1952877316
1.0	-0.5648136251	-2.112417232	0.3022903142	0.2116506664
2.0	-0.6675343922	-2.521958177	0.4118503542	0.5180809640
3.0	-0.7014183334	-3.196382289	-0.7005640546	0.5327867225
Sufficiently large r_{12}				
4.0	-0.6955506394	-4.025940635	0.4300576700	0.5304281261
5.0	-0.6772916132	-4.941274459	0.4476172910	0.5276798434
6.0	-0.6573105590	-5.903659889	0.4571245682	0.5253680730
7.0	-0.6391288554	-6.890997919	0.4617645750	0.5234038890
8.0	-0.6236060156	-7.890707161	0.4636608160	0.5216941120
9.0	-0.6106549406	-8.895880333	0.4641349950	0.5201842000
10.0	-0.5999010686	-9.902954530	0.4639483020	0.5188413890
15.0	-0.5667087290	-14.93326111	0.4616835060	0.5139612540
20.0	-0.5500141977	-19.94996191	0.4603986900	0.5109975560
25.0	-0.5400058003	-24.95998445	0.4597076900	0.5090476900

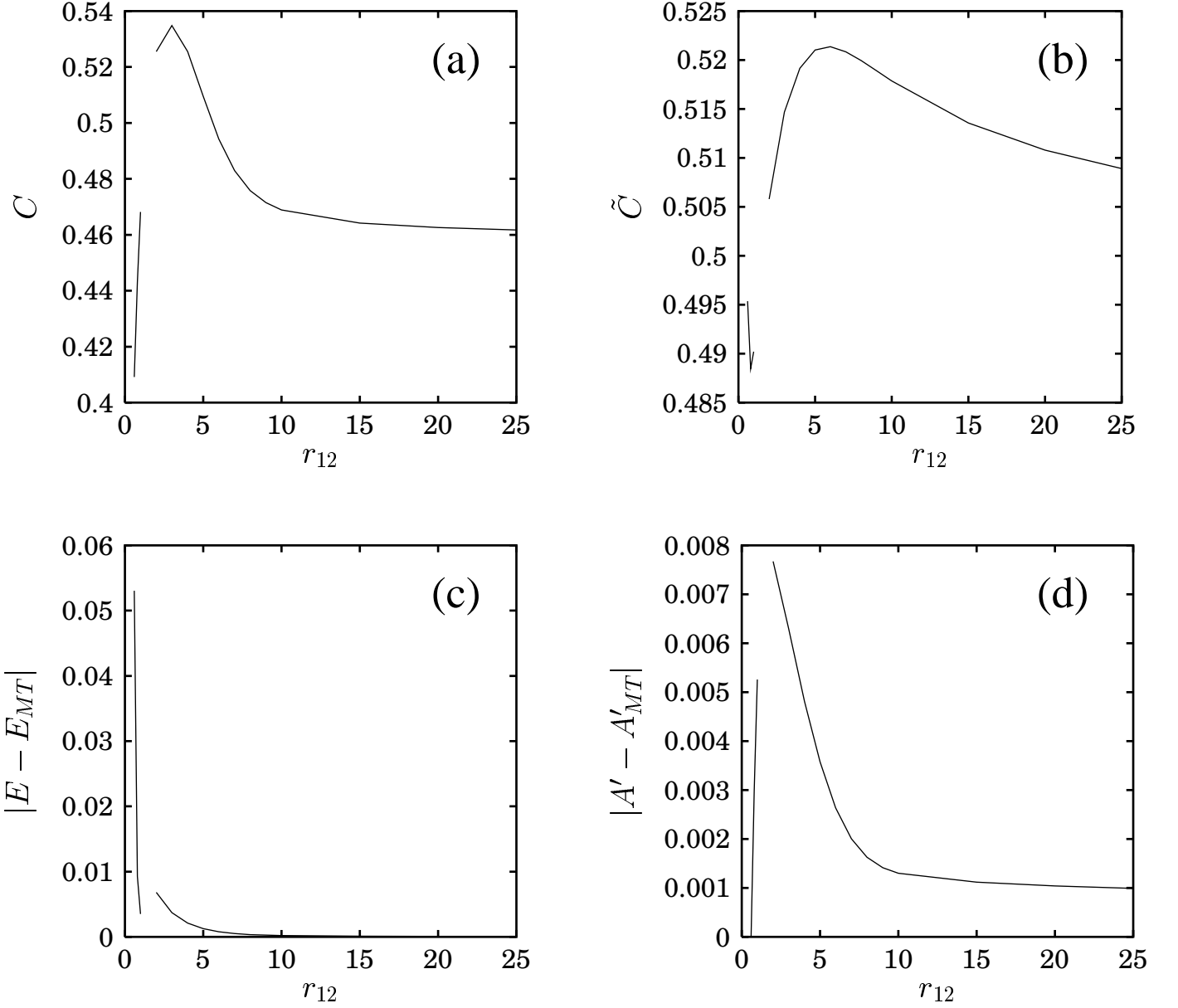


FIG. 1: Plots for the $1s\sigma$ state of the ion H_2^+ of (a) C versus r_{12} , (b) \tilde{C} versus r_{12} , (c) $|E - E_{MT}|$ versus r_{12} and (d) $A' - A'_{MT}$ versus r_{12} , when C and \tilde{C} are determined as functions of r_{12} from the requirement that the first-order phase-integral results coincide with the third-order results. Here E and A' are the phase-integral values obtained in Table I, while E_{MT} and A'_{MT} are the corresponding numerically exact values obtained by Murai and Takatsu [13,14] and quoted in the same table. There is a break in each curve between the regions where the quantization conditions for sufficiently small and sufficiently large values of r_{12} have been used.

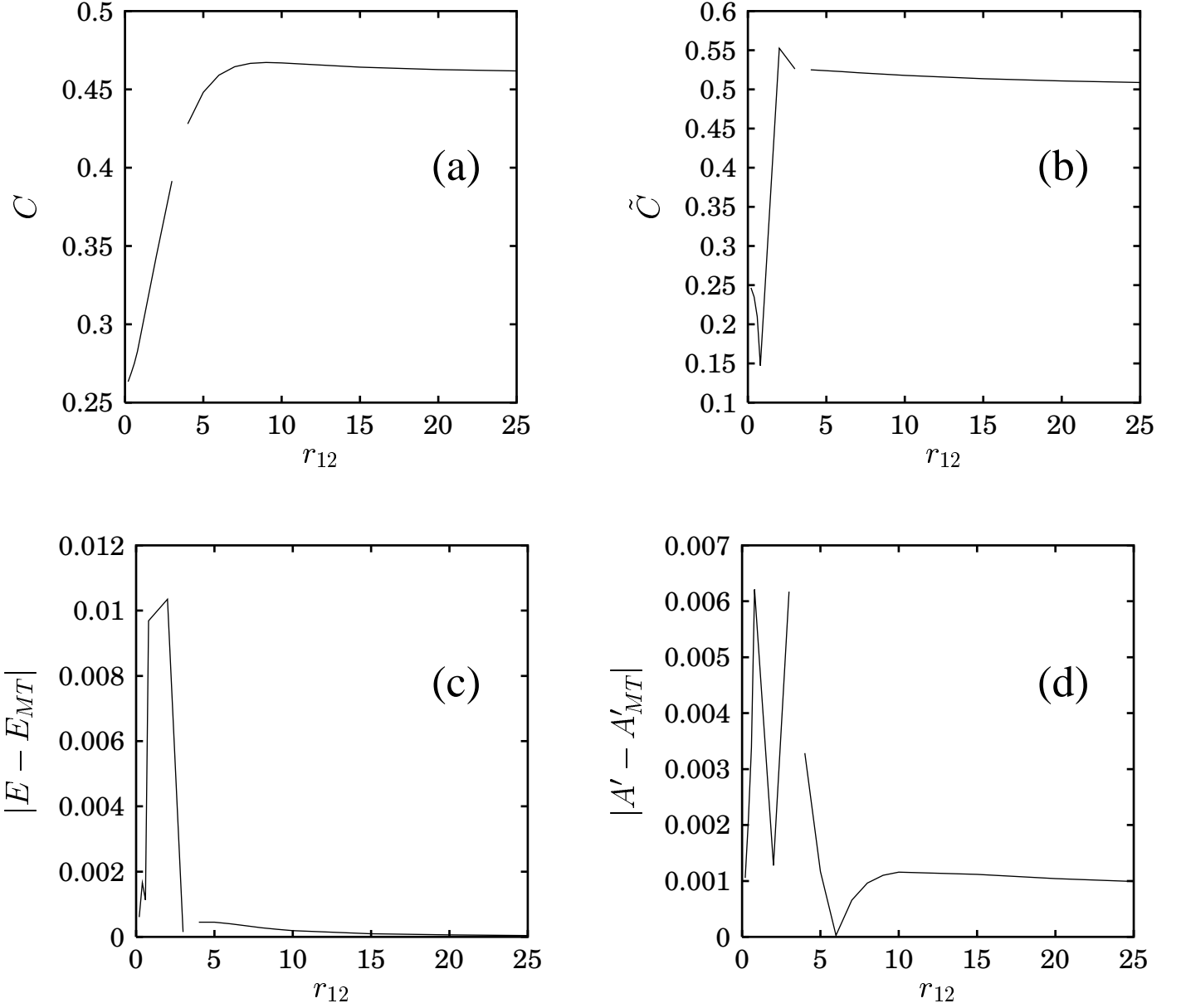


FIG. 2: Plots for the $2p\sigma$ state of the ion H_2^+ of (a) C versus r_{12} , (b) \tilde{C} versus r_{12} , (c) $|E - E_{MT}|$ versus r_{12} and (d) $A' - A'_{MT}$ versus r_{12} , when C and \tilde{C} are determined as functions of r_{12} from the requirement that the first-order phase-integral results coincide with the third-order results. Here E and A' are the phase-integral values obtained in Table II, while E_{MT} and A'_{MT} are the corresponding numerically exact values obtained by Murai and Takatsu [13,14] and quoted in the same table. There is a break in each curve between the regions where the quantization conditions for sufficiently small and sufficiently large values of r_{12} have been used.

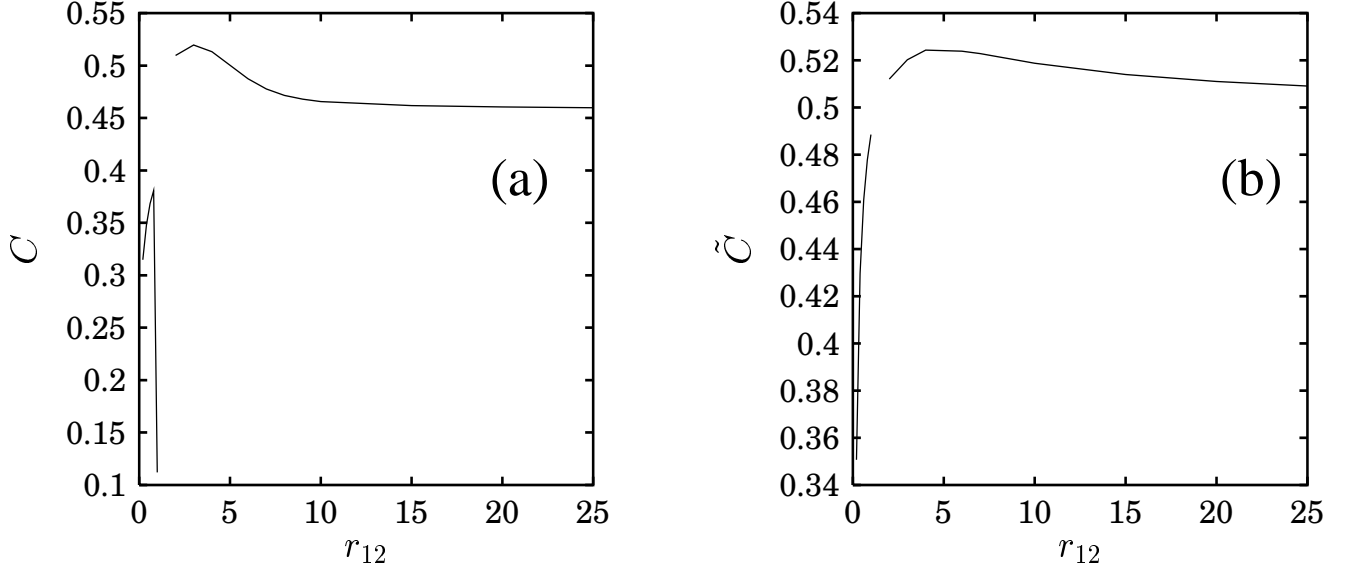


FIG. 3: Plots for the $1s\sigma$ state of the ion H_2^+ of (a) C versus r_{12} and (b) \tilde{C} versus r_{12} , when C and \tilde{C} are determined as functions of r_{12} from the requirement that the first-order phase-integral results coincide with the numerically exact results obtained by Murai and Takatsu [13,14]. There is a break in each curve between the regions where the quantization conditions for sufficiently small and sufficiently large values of r_{12} have been used.

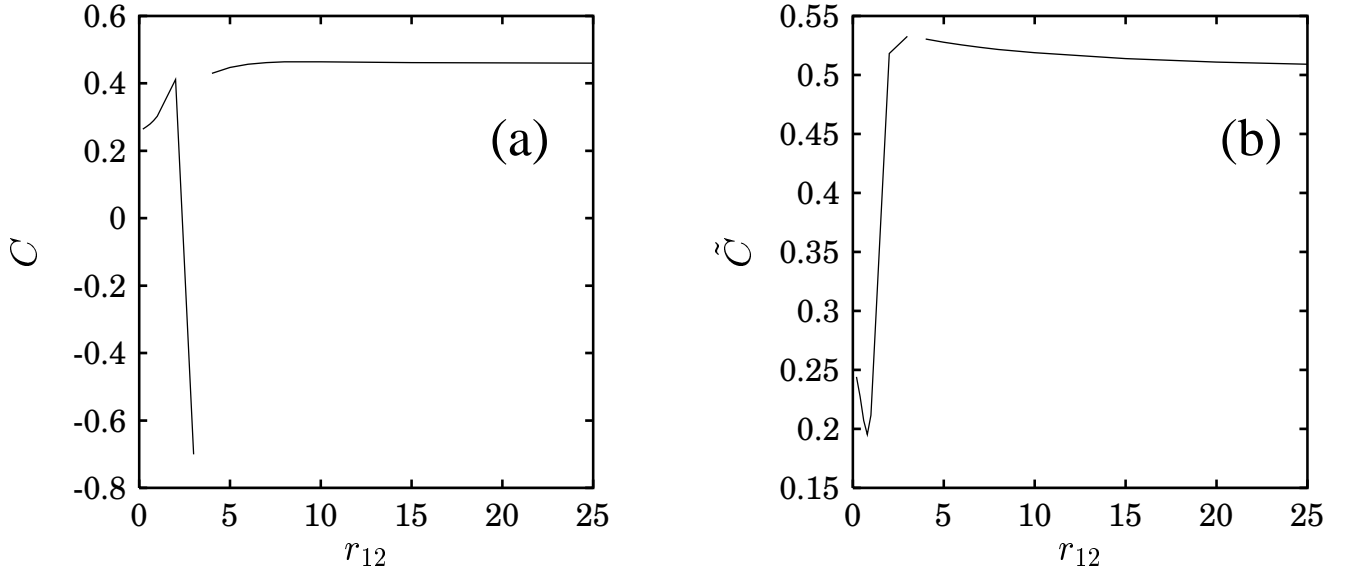


FIG. 4: Plots for the $2p\sigma$ state of the ion H_2^+ of (a) C versus r_{12} and (b) \tilde{C} versus r_{12} , when C and \tilde{C} are determined as functions of r_{12} from the requirement that the first-order phase-integral results coincide with the numerically exact results obtained by Murai and Takatsu [13,14]. There is a break in each curve between the regions where the quantization conditions for sufficiently small and sufficiently large values of r_{12} have been used.