Two-particle atomic coalescences: Boundary conditions for the Fock coefficient components

Evgeny Z. Liverts
Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel
(Received 5 May 2016; published 15 August 2016)

The exact values of the presently determined components of the angular Fock coefficients at the two-particle coalescences were obtained and systematized. The Green's-function approach was successfully applied to simplify the most complicated calculations. The boundary conditions for the Fock coefficient components in hyperspherical angular coordinates, which follow from the Kato cusp conditions for the two-electron wave function in the natural interparticle coordinates, were derived. The validity of the obtained boundary conditions was verified with examples of all the presently determined components. The additional boundary conditions not arising from the Kato cusp conditions were obtained as well. Wolfram's *Mathematica* was used extensively to obtain these results.

DOI: 10.1103/PhysRevA.94.022506

I. INTRODUCTION

Investigation of the wave functions of heliumlike isoelectronic systems has been the subject of a great number of articles. However, only a few of them (see, e.g., [1–7]) were devoted to studying these wave functions at two-particle coalescences, where the two electrons or one of the electrons and the nucleus occupy the same point of the usual three-dimensional space. An interest in such specific situations is caused by the fact that they can serve as effective physical and mathematical models for the description of various physical processes, such as, e.g., two-electron photoionization [8].

The analytical treatment of the two-particle coalescences is based on the Fock expansion [9] for the ^1S-state wave functions of a two-electron atom and/or ion

$$\chi(r_1,r_2,r_{12}) \equiv \Psi(r,\alpha,\theta) = \sum_{k=0}^{\infty} r^k \sum_{p=0}^{[k/2]} \psi_{k,p}(\alpha,\theta)(\ln r)^p, \quad (1)$$

where the hyperspherical angles α and θ and the hyperspherical radius r are related to the interparticle distances r_1,r_2 and r_{12} as follows:

$$\alpha = 2\arctan(r_2/r_1), \quad \theta = \arccos\left[\left(r_1^2+r_2^2-r_{12}^2\right)/(2r_1r_2)\right], \quad (2)$$

$$r = \sqrt{r_1^2+r_2^2}. \quad (3)$$

References [10–18] were devoted to investigating the properties and to calculating the angular Fock coefficients (AFCs) $\psi_{k,p}(\alpha,\theta)$. It has been proven that the AFCs satisfy (see, e.g., [15] or [19]) the Fock recurrence relation (FRR)

$$[\Lambda^2 - k(k+4)]\psi_{k,p} = h_{k,p}, \quad (4a)$$

$$\begin{aligned} h_{k,p} &= 2(k+2)(p+1)\psi_{k,p+1} \\ &\quad + (p+1)(p+2)\psi_{k,p+2} \\ &\quad - 2V\psi_{k-1,p} + 2E\psi_{k-2,p}, \end{aligned} \quad (4b)$$

where E is the energy and

$$V \equiv V(\alpha,\theta) = (1-\sin\alpha\cos\theta)^{-1/2} - Z\left[\csc\left(\frac{\alpha}{2}\right) + \sec\left(\frac{\alpha}{2}\right)\right] \quad (5)$$

is the dimensionless Coulomb interaction for the two-electron atom and/or ion with an infinitely massive nucleus of charge Z. The well-known hyperspherical harmonics $Y_{kl}(\alpha,\theta)$ (HH) are the eigenfunctions of the (S-state) hyperspherical angular momentum operator Λ^2.

It was shown in Ref. [19] that any AFC $\psi_{k,p}$ can be separated into independent parts (components)

$$\psi_{k,p}(\alpha,\theta) = \sum_{j=p}^{k-p} \psi_{k,p}^{(j)}(\alpha,\theta) Z^j \quad (6)$$

associated with definite powers of Z, according to separation of the right-hand side (rhs) (4b) of the FRR. Accordingly, each of the FRRs (4) can be separated into the individual FRR equations (IFRRs) for each component,

$$[\Lambda^2 - k(k+4)]\psi_{k,p}^{(j)}(\alpha,\theta) = h_{k,p}^{(j)}(\alpha,\theta), \quad (7)$$

where $h_{k,p}^{(j)}$ corresponds to the separation of the rhs (4b) in powers of Z, which is similar to the separation formula (6).

II. THE EXACT VALUES OF THE AFC COMPONENTS AT THE TWO-PARTICLE COALESCENCES

In Ref. [19] all of the AFC components $\psi_{k,p}^{(j)}(\alpha,\theta)$ were presented for $k \leqslant 2$. For $k > 2$ the components $\psi_{3,0}^{(0)}, \psi_{3,0}^{(3)}, \psi_{3,1}^{(j_1)}, \psi_{4,1}^{(j_2)}$, and $\psi_{4,2}^{(j_3)}$ with all possible j_1, j_2, and j_3 and the subcomponents $\psi_{3,0}^{(1a)}, \psi_{3,0}^{(1b)}, \psi_{3,0}^{(1c)}, \psi_{3,0}^{(2a)}, \psi_{3,0}^{(2b)}, \psi_{3,0}^{(2c)}$ were presented as well. The edge components $\psi_{k,0}^{(0)}$ and $\psi_{k,0}^{(k)}$ with $k \geqslant 4$ as well as subcomponent $\psi_{3,0}^{(2e)}$ were derived in [20].

In Tables I–IV we present the exact values of the presently determined AFC components at the two-particle coalescences. By "exact value" we mean representations expressed through mathematical constants (like π, ln 2, or Catalan's constant $G \simeq 0.915965\ldots$) and rational numbers. The electron-nucleus coalescence (ENC) corresponds to the hyperspherical angles

TABLE I. The components of the AFC at the two-particle coalescences.

k	p	j	$\psi_{k,p}^{(j)}(0,\frac{\pi}{2})$	$\psi_{k,p}^{(j)}(\frac{\pi}{2},0)$
0	0	0	1	1
2	0	1	$\frac{\ln 2-3}{6}$	$\frac{48G-62+\pi(5+12\ln 2)}{72\pi}$
2	1	1	0	$\frac{2-\pi}{3\pi}$
3	1	1	$\frac{2-\pi}{36\pi}$	0
3	1	2	0	$\frac{\pi-2}{3\pi\sqrt{2}}$
4	1	1	$\frac{2-\pi}{576\pi}$	$\frac{(\pi-2)(32E-15)}{960\pi}$
4	1	2	$\frac{(\pi-2)[424-600G+25\pi(12\ln 2-7)]}{5400\pi^2}$	$\frac{(\pi-2)[11536-8400G+\pi(2205\pi-17294+2100\ln 2)]}{75600\pi^2}$
4	1	3	0	$\frac{3(2-\pi)}{40\pi}$
4	2	2	$\frac{(\pi-2)(5\pi-14)}{180\pi^2}$	$\frac{(\pi-2)(5\pi-14)}{180\pi^2}$

$\alpha=0$ and $\theta=\pi/2$, whereas $\alpha=\pi/2$ and $\theta=0$ at the electron-electron coalescence (EEC).

There is no problem with performing the above-mentioned calculations in cases where the considered component is derived in the form of an explicit analytical expression. However, in cases where the component or subcomponent is represented by a single series of the form

$$\psi_{k,p}^{(j)}(\alpha,\theta)=\sum_{l=0}^{\infty}P_l(\cos\theta)(\sin\alpha)^l\omega_l^{(k,p;j)}(\alpha), \tag{8}$$

(e.g., $\psi_{2,0}^{(1)},\psi_{3,0}^{(2c)},\psi_{3,0}^{(2e)},\psi_{4,1}^{(2d)}$), the calculation of its exact value, at least at the EEC, is not a simple problem. Therefore, we shall consider those calculations in detail.

A. Component $\psi_{2,0}^{(1)}$

There are three representations for the component $\psi_{2,0}^{(1)P}$ containing different admixtures of the unnormalized HH $Y_{21}(\alpha,\theta)=\sin\alpha\cos\theta$. A superscript P marks the particular solution which is not single valued ("pure" [19]) in the general case. The first representation is the closed analytic expression presented by Eq. (22) of Ref.[19]. Others are of the form

$$\psi_{2,0}^{(1)P}=-\tfrac{1}{3}[\sin(\alpha/2)+\cos(\alpha/2)]\sqrt{1-\sin\alpha\cos\theta}+\chi_{20}(\alpha,\theta), \tag{9}$$

where the function χ_{20} can be represented either by the single series (second representation)

$$\chi_{20}(\alpha,\theta)=\sum_{l=0}^{\infty}P_l(\cos\theta)(\sin\alpha)^l\sigma_l(\rho) \tag{10}$$

of the form (8) or by a double series expansion in HHs. The variable

$$\rho=\tan(\alpha/2) \tag{11}$$

was introduced for convenience. Only the first two cases are of interest to us. For the ENC, both representations give the same results,

$$\lim_{\theta\to\frac{\pi}{2}}\lim_{\alpha\to 0}\psi_{2,0}^{(1)}(\alpha,\theta)=\tfrac{1}{6}(\ln 2-3), \tag{12}$$

because $Y_{21}(0,\pi/2)=0$. One should emphasize that according to definition (8) of the single-series representation, the values of the corresponding component or subcomponent at the ENC ($\alpha=0$) equals $\omega_0^{(k,p;j)}(0)$.

At the EEC, one obtains

$$\lim_{\theta\to 0}\lim_{\alpha\to\frac{\pi}{2}}\psi_{2,0}^{(1)P}(\alpha,\theta)=\tfrac{1}{6}(1-\ln 2) \tag{13}$$

for the analytic representation (22) of Ref. [19]. To obtain the "pure" solution (see Ref. [19]), one needs to subtract the coefficient $\widetilde{C}_{21}^{(P)}\simeq 0.315837352$ from the result (13), taking into account that $Y_{21}(\frac{\pi}{2},0)=1$. This admixture coefficient was

TABLE II. The lower edge components $\psi_{k,0}^{(0)}$ of the logarithmless AFC at the two-particle coalescences.

k	$\psi_{k,0}^{(0)}(0,\frac{\pi}{2})$	$\psi_{k,0}^{(0)}(\frac{\pi}{2},0)$
1	$\frac{1}{2}$	0
2	$\frac{1}{12}(1-2E)$	$\frac{1}{12}(1-2E)$
3	$\frac{1-5E}{72}$	0
4	$\frac{12E^2-11E+1}{1152}$	$\frac{20E^2-21E+7}{1920}$
5	$\frac{160E^2-47E-6}{43200}$	0
6	$\frac{-1260E^3+1595E^2-189E-62}{3628800}$	$\frac{-10080E^3+16460E^2-11361E+3007}{29030400}$
7	$\frac{-786240E^3+261908E^2+100023E-27233}{7315660800}$	0
8	$\frac{16934400E^4-26481840E^3+3072680E^2+2788023E-325061}{2341011456000}$	$\frac{30481920E^4-68266800E^3+72613544E^2-39544113E+8871475}{4213820620800}$

TABLE III. The higher edge components $\psi_{k,0}^{(k)}$ of the logarithmless AFC at the two-particle coalescences.

k	$\psi_{k,0}^{(k)}(0,\frac{\pi}{2})$	$\psi_{k,0}^{(k)}(\frac{\pi}{2},0)$
1	-1	$-\sqrt{2}$
2	$\frac{1}{3}$	$\frac{5}{6}$
3	$-\frac{1}{18}$	$-\frac{7\sqrt{2}}{36}$
4	$\frac{7}{288}+\frac{2}{45\pi}$	$\frac{5}{96}-\frac{2}{135\pi}$
5	$-\frac{43}{4320}-\frac{46}{2025\pi}$	$\frac{1}{\sqrt{2}}\left(-\frac{1}{180}+\frac{32}{2025\pi}\right)$
6	$\frac{89}{45360}+\frac{28}{6075\pi}$	$-\frac{83}{120960}-\frac{47}{12150\pi}$
7	$-\frac{139}{635040}-\frac{22}{42525\pi}$	$\frac{1}{\sqrt{2}}\left(\frac{377}{1016064}+\frac{13}{11340\pi}\right)$
8	$\frac{25507}{390168576}+\frac{2524019}{9601804800\pi}+\frac{412}{1607445\pi^2}$	$-\frac{21871}{650280960}-\frac{679193}{9601804800\pi}+\frac{412}{8037225\pi^2}$

computed by numerical integration with the integrand containing the complicated analytic expression (22) of Ref. [19]. Then, making use of expressions (63)–(65) from Ref. [19] for $\sigma_l(\rho)$, one obtains for the subcomponent (10) at the EEC line

$$\chi_{20}\left(\frac{\pi}{2},0\right) = s_0 + s_1, \tag{14}$$

with

$$s_0 = \lim_{\rho\to 1}[\sigma_0(\rho)+\sigma_1(\rho)]$$
$$= \frac{48G+\pi(3\pi-19-12\ln 2)-14}{72\pi}, \tag{15}$$
$$s_1 = \sum_{l=2}^{\infty}\sigma_l(1), \tag{16}$$

where

$$\sigma_l(1) = \frac{1}{2(l^2+l-2)} - \frac{(2l+1)\Gamma\left(\frac{l-1}{2}\right)\Gamma\left(\frac{l+1}{2}\right)}{48\Gamma\left(\frac{l}{2}+1\right)\Gamma\left(\frac{l}{2}+2\right)} \quad (l \geqslant 2) \tag{17}$$

and G on the rhs of Eq. (15) is Catalan's constant. Separating the summation (16) into parts, one obtains

$$\sum_{l=2}^{\infty}\frac{1}{2(l^2+l-2)} = \frac{11}{36}, \tag{18}$$

$$\sum_{l=2(2)}^{\infty}\frac{(2l+1)\Gamma\left(\frac{l-1}{2}\right)\Gamma\left(\frac{l+1}{2}\right)}{48\Gamma\left(\frac{l}{2}+1\right)\Gamma\left(\frac{l}{2}+2\right)} = \frac{\pi}{24}, \tag{19}$$

$$\sum_{l=3(2)}^{\infty}\frac{(2l+1)\Gamma\left(\frac{l-1}{2}\right)\Gamma\left(\frac{l+1}{2}\right)}{48\Gamma\left(\frac{l}{2}+1\right)\Gamma\left(\frac{l}{2}+2\right)} = \frac{2}{9\pi}. \tag{20}$$

The number in parentheses following the lower limit of summation denotes the step of summation (by default the step is 1). Combining results (14)–(20), one obtains

$$\chi_{20}\left(\frac{\pi}{2},0\right) = \frac{16G+\pi(1-4\ln 2)-10}{24\pi}. \tag{21}$$

The "pure" component can be obtained by subtracting the admixture coefficient $C_{21}^{(P)} = (\pi+4)/9\pi$ (see the end of Sec. VI in Ref. [19]) from the rhs of Eq. (21). Thus, the final

TABLE IV. The subcomponents of the AFC with $k > 2$ at the two-particle coalescences.

k	p	j	$\psi_{k,p}^{(j)}(0,\frac{\pi}{2})$	$\psi_{k,p}^{(j)}(\frac{\pi}{2},0)$
3	0	$1a$	$\frac{5(\pi-2)}{72\pi}$	0
3	0	$1b$	$\frac{4E-1}{36}$	$\frac{5E-2}{18\sqrt{2}}$
3	0	$1c$	$\frac{5(2-\pi)(20+3\pi)}{1728\pi}$	$\frac{25(\pi-2)}{288\sqrt{2}}$
3	0	$2a$	$\frac{1}{9}$	0
3	0	$2b$	0	$\frac{(2-\pi)(36+5\pi)}{144\pi\sqrt{2}}$
3	0	$2c$	$\frac{1}{18}(2-\pi-2\ln 2)$	$\frac{\sqrt{2}}{27}$
3	0	$2d$	$\frac{24-48G+\pi(16-3\pi)}{288}$	
3	0	$2e$	$\frac{1}{8}$	$\frac{5-6G}{12\sqrt{2}}$
3	0	2	$\frac{124-48G-3\pi^2-32\ln 2}{288}$	
4	1	$2b$	$\frac{(\pi-2)(5\pi-14)}{1080\pi^2}$	$\frac{(\pi-2)(5\pi-14)}{3240\pi^2}$
4	1	$2c$	0	$-\frac{37(\pi-2)(5\pi-14)}{8100\pi^2}$
4	1	$2d$	$\frac{(\pi-2)[247-300G+50\pi(3\ln 2-2)]}{2700\pi^2}$	$\frac{(\pi-2)[7028-8400G+3\pi(735\pi-5228+700\ln 2)]}{75600\pi^2}$
4	1	2	$\frac{(\pi-2)[424-600G+25\pi(12\ln 2-7)]}{5400\pi^2}$	$\frac{(\pi-2)[11536-8400G+\pi(2205\pi-17294+2100\ln 2)]}{75600\pi^2}$

result for the EEC is

$$\psi_{2,0}^{(1)}\left(\frac{\pi}{2},0\right) = \frac{48G - 62 + \pi(5 + 12\ln 2)}{72\pi}. \quad (22)$$

Comparing the exact EEC value of the above component derived using the single series and the closed analytic representations, one obtains the exact value of the admixture coefficient

$$\widetilde{C}_{21}^{(P)} = \frac{62 + 17\pi - 48G}{72\pi} \simeq 0.315837352. \quad (23)$$

B. Component $\psi_{4,1}^{(2)}$

In Ref. [19] the component $\psi_{4,1}^{(2)}$ was separated into the parts

$$\psi_{4,1}^{(2)} = \psi_{4,1}^{(2b)} + \psi_{4,1}^{(2c)} + \psi_{4,1}^{(2d)}, \quad (24)$$

where $\psi_{4,1}^{(2b)}$ is presented in Table 1 of Ref. [19] and $\psi_{4,1}^{(2c)}$ is defined by Eq. (92) of Ref. [19]. For the values of these subcomponents calculated at the two-particle coalescences, one easily obtains

$$\psi_{4,1}^{(2b)}\left(0,\frac{\pi}{2}\right) = \frac{(\pi-2)(5\pi-14)}{1080\pi^2},$$
$$\psi_{4,1}^{(2b)}\left(\frac{\pi}{2},0\right) = \frac{(\pi-2)(5\pi-14)}{3240\pi^2}, \quad (25)$$

$$\psi_{4,1}^{(2c)}\left(0,\frac{\pi}{2}\right) = 0, \;\; \psi_{4,1}^{(2c)}\left(\frac{\pi}{2},0\right) = -\frac{37(\pi-2)(5\pi-14)}{8100\pi^2}. \quad (26)$$

The subcomponent $\psi_{4,1}^{(2d)}$ was represented by a single series of the form (8) with the function $\omega_l^{(4,1;2d)}(\alpha) \equiv \tau_l(\rho)$ defined by Eqs.(94)– (96) of Ref. [19] for $l = 0,1,2$. The explicit analytic expression for τ_l with $l \geqslant 3$ was calculated in Ref. [20]. According to representation (8) and Eq. (94) of Ref. [19], one obtains

$$\psi_{4,1}^{(2d)}\left(0,\frac{\pi}{2}\right) = \tau_0(0) = \frac{(\pi-2)[247-300G+50\pi(3\ln 2-2]}{2700\pi^2} \quad (27)$$

at the ENC and

$$\psi_{4,1}^{(2d)}\left(\frac{\pi}{2},0\right) = \sum_{l=0}^{\infty}\tau_l(1) \quad (28)$$

at the EEC. The explicit representations (see Sec. VII of Ref. [19]) for $l = 0,1,2$ yield

$$\tau_0(1) = \frac{(2-\pi)[247-300G+5\pi(15\ln 2-16)]}{8100\pi^2}, \quad (29)$$

$$\tau_1(1) = \frac{(\pi-2)(735\pi-5788)}{50400\pi}, \quad (30)$$

$$\tau_2(1) = \frac{(\pi-2)[4592-16800G+5\pi(109+840\ln 2)]}{113400\pi^2}. \quad (31)$$

The most effective way to calculate $\tau_l(1)$ with $l > 2$ is by use of the formula

$$\tau_l(1) = \frac{u_{4,l}(1)}{2l+1}\int_0^1 \frac{v_{4,l}(t)h_l(t)t^{2l+2}}{(1+t^2)^{2l+3}}dt + A_2(l)v_{4,l}(1) \quad (32)$$

of Ref. [19], where

$$u_{4,l}(\rho) = \rho^{-2l-1}(\rho^2+1)^{l+4}\,{}_2F_1\left(\frac{7}{2},3-l;\frac{1}{2}-l;-\rho^2\right), \quad (33a)$$

$$v_{4,l}(\rho) = (\rho^2+1)^{l+4}\,{}_2F_1\left(\frac{7}{2},4+l;l+\frac{3}{2};-\rho^2\right), \quad (33b)$$

$$h_l(\rho) = -\frac{(\pi-2)(\rho+1)(\rho^2+1)^{l-1}}{3\pi(2l-1)(2l+3)2^{l+1}}\left[\frac{15-4l(l+1)(4l+11)}{(2l-3)(2l+5)\rho} + 4l(2l+3) + 2\rho + 4(l+1)(2l-1)\rho^2 + \frac{(2l-1)(4l+5)\rho^3}{2l+5}\right]. \quad (34)$$

The coefficient $A_2(l)$ equals zero for odd l, whereas for even l (see Ref. [20])

$$A_2(l) = \frac{(2-\pi)}{360l(l-2)\Gamma(l+\frac{1}{2})\pi^{3/2}}\left\{\frac{\left[l(l+1)(688l^4+1376l^3-2480l^2-3168l+465)+450\right]\Gamma\left(\frac{l-1}{2}\right)\Gamma\left(\frac{l+1}{2}\right)}{(2l-3)(2l-1)(2l+1)(2l+3)(2l+5)} - \frac{56}{l-1}\left(\frac{l}{2}!\right)^2\right\}. \quad (35)$$

The easiest method of finding a simple representation for $\tau_l(1)$ with $l \geqslant 3$ involves the use of the *Mathematica* operator FindSequenceFunction (see examples in [20]). In particular, using Eqs. (32)–(35), we have calculated $\tau_l(1)$ for $2 < l < 30$. It was found that

$$\tau_l(1) = \frac{\pi-2}{\pi}\begin{cases}(a_l+\pi b_l), & \text{for odd } l,\\ (\widetilde{a}_l+\pi\widetilde{b}_l)/\pi, & \text{for even } l,\end{cases} \quad (36)$$

where $a_l, b_l, \widetilde{a}_l, \widetilde{b}_l$ are rational numbers. Making use of the calculated sequences for each of the coefficients $a_l, b_l, \widetilde{a}_l$, and $\widetilde{b}_l$, the *Mathematica* operator FindSequenceFunction enables us to find the general forms of these coefficients as functions of l. Notice that for a given sequence there is a minimal number of terms needed for *Mathematica* to find the formula for the general term. In particular, for the coefficients a_l and $\widetilde{b}_l$ this minimal number is 16, whereas for $\widetilde{a}_l$ and b_l it equals 10. Thus, one finally obtains

$$\tau_l(1) = \frac{2-\pi}{180\pi(l+1)(l+3)}\left\{\frac{l(l+1)\{16l(l+1)[43l(l+1)-198]+465\}+450}{(l-2)l(2l-3)(2l-1)(2l+3)(2l+5)} - \frac{7(2l+1)\Gamma\left(\frac{l}{2}-1\right)\Gamma\left(\frac{l}{2}+1\right)}{\Gamma^2\left(\frac{l+1}{2}\right)}\right\}. \quad (37)$$

The summation by *Mathematica* gives

$$\sum_{l=3}^{\infty}\frac{l(l+1)\{16l(l+1)[43l(l+1)-198]+465\}+450}{(l-2)l(l+1)(l+3)(2l-3)(2l-1)(2l+3)(2l+5)}=\frac{675}{35}, \tag{38}$$

$$\sum_{l=3(2)}^{\infty}\frac{(2l+1)\Gamma\left(\frac{l}{2}-1\right)\Gamma\left(\frac{l}{2}+1\right)}{(l+1)(l+3)\Gamma^2\left(\frac{l+1}{2}\right)}=\frac{3\pi}{8}, \tag{39}$$

$$\sum_{l=4(2)}^{\infty}\frac{(2l+1)\Gamma\left(\frac{l}{2}-1\right)\Gamma\left(\frac{l}{2}+1\right)}{(l+1)(l+3)\Gamma^2\left(\frac{l+1}{2}\right)}=\frac{32}{15\pi}. \tag{40}$$

Recall that (2) following the lower limit of summation denotes its step. Combining the results (28)–(40), one obtains

$$\psi_{4,1}^{(2d)}\left(\frac{\pi}{2},0\right)=\frac{\pi-2}{75\,600\pi^2}[7028-8400G+3\pi(735\pi-5228+700\ln 2)]. \tag{41}$$

Finally, summation of the individual subcomponents in Eq. (24) yields

$$\psi_{4,1}^{(2)}\left(0,\frac{\pi}{2}\right)=\frac{(\pi-2)[424-600G+25\pi(12\ln 2-7)]}{5400\pi^2} \tag{42}$$

at the ENC and

$$\psi_{4,1}^{(2)}\left(\frac{\pi}{2},0\right)=\frac{\pi-2}{75600\pi^2}[11536-8400G+\pi(2205\pi-17294+2100\ln 2)] \tag{43}$$

at the EEC.

C. Subcomponent $\psi_{3,0}^{(2c)}$

In Ref. [19] the subcomponent $\psi_{3,0}^{(2c)}$ was represented by a single series of the form (8) with the function $\omega_l^{(3,0;2c)}(\alpha)\equiv\phi_l(\rho)$ defined as follows:

$$\phi_l(\rho)=\phi_l^{(P)}(\rho)+c_l v_{3,l}(\rho). \tag{44}$$

The functions included in the rhs of Eq. (44) are

$$v_{3,l}(\rho)=(\rho^2+1)^{l-\frac{3}{2}}\left[\frac{(2l-3)(2l-1)}{(2l+3)(2l+5)}\rho^4+\frac{2(2l-3)}{2l+3}\rho^2+1\right], \tag{45}$$

$$\phi_l^{(P)}(\rho)=\frac{2^{-l}(\rho^2+1)^{l-\frac{3}{2}}}{3(2l-3)(2l-1)(2l+3)(2l+5)}\times\left[2f_{1l}(\rho)+\frac{2f_{2l}(\rho)+f_{3l}(\rho)}{2l+1}\right], \tag{46}$$

where

$$f_{1l}(\rho)=[9-4l(l+2)]\rho+(13-4l^2)\rho^3, \tag{47}$$

$$f_{2l}(\rho)=[(2l-3)(2l-1)\rho^4+2(2l-3)(2l+5)\rho^2+(2l+3)(2l+5)]\arctan(\rho), \tag{48}$$

$$f_{3l}(\rho)=-[(2l+3)(2l+5)\rho^4+2(2l-3)(2l+5)\rho^2+(2l-3)(2l-1)]\frac{\rho}{l+1}\,{}_2F_1(1,l+1;l+2;-\rho^2). \tag{49}$$

A simple representation of the coefficient c_l was derived in Ref. [20] in the form

$$c_l=\frac{2(2l+1)-\pi-H_{\frac{l}{2}}+H_{\frac{l-1}{2}}}{6(2l-3)(2l-1)(2l+1)2^l}, \tag{50}$$

where H_z denote the harmonic numbers with primary definition of the form

$$H_z=\gamma+\psi(z+1), \tag{51}$$

where $\psi(\bar{z})$ is the digamma function and γ is the Euler-Mascheroni constant.

According to the single-series representation (8) and making use of Eqs. (44)–(50), one obtains

$$\psi_{3,0}^{(2c)}\left(0,\frac{\pi}{2}\right)=\phi_0(0)=\frac{1}{18}(2-\pi-2\ln 2) \tag{52}$$

at the ENC and

$$\psi_{3,0}^{(2c)}\left(\frac{\pi}{2},0\right)=\sum_{l=0}^{\infty}\phi_l(1) \tag{53}$$

at the EEC. To obtain a simple representation for $\phi_l(1)$, we use again the *Mathematica* operator FindSequenceFunction (see the previous section and Ref. [20]). The *Mathematica* calculations of $\phi_l(1)$ with $l\geqslant 0$, performed on the expressions in Eqs. (44)–(50), show that

$$\phi_l(1)=\sqrt{2}(a_l+b_l\ln 2), \tag{54}$$

where a_l and b_l are rational numbers. It is enough to use the sequence of a_l with $0\leqslant l\leqslant 27$ and the sequence of b_l with $0\leqslant l\leqslant 6$ to find

$$a_l=\frac{1}{3(2l-3)(2l+1)(2l+5)}\times\left[\frac{8(2l+1)}{4l(l+1)-3}+H_{\frac{l-1}{2}}-H_{\frac{l}{2}}+(-1)^l 2\ln 2\right], \tag{55}$$

$$b_l=-\frac{2(-1)^l}{3(2l-3)(2l+1)(2l+5)}; \tag{56}$$

hence, one easily obtains

$$\phi_l(1)=\frac{\sqrt{2}}{3(2l-3)(2l+1)(2l+5)}\times\left[\frac{8(2l+1)}{4l(l+1)-3}+H_{\frac{l-1}{2}}-H_{\frac{l}{2}}\right]. \tag{57}$$

Mathematica summations yield

$$\sum_{l=0}^{\infty}\frac{1}{(2l-3)(2l+5)[4l(l+1)-3]}=0, \tag{58}$$

$$\sum_{l=0}^{\infty}\frac{1}{(2l-3)(2l+1)(2l+5)}\Big(H_{\frac{l-1}{2}}-H_{\frac{l}{2}}\Big)=\frac{1}{9}. \tag{59}$$

Thus, finally for the EEC, one obtains

$$\psi_{3,0}^{(2c)}\Big(\frac{\pi}{2},0\Big)=\frac{\sqrt{2}}{27}. \tag{60}$$

D. Subcomponent $\psi_{3,0}^{(2e)}$

In Ref. [20] the subcomponent $\psi_{3,0}^{(2e)}$ was derived in the form of the single series (8) with the function $\omega_l^{(3,0;2e)}(\alpha)\equiv\lambda_l(\rho)$ defined as

$$\lambda_l(\rho)=\frac{1}{2l+1}\{u_{3,l}(\rho)\mathcal{V}_{3,l}(\rho)-v_{3,l}(\rho)[\mathcal{U}_{3,l}(\rho)-(2l+1)s_l]\}, \tag{61}$$

where

$$s_l=\frac{2^{-l-3}}{(2l-3)(2l-1)(2l+1)}\Big[2l(l+1)\Big(H_{\frac{l+1}{2}}-H_{\frac{l}{2}}-\pi\Big)+2l+3\Big], \tag{62}$$

$$u_{3,l}(\rho)=\frac{(\rho^2+1)^{l-\frac{3}{2}}}{\rho^{2l+1}}\left[\frac{(2l+3)(2l+5)}{(2l-3)(2l-1)}\rho^4+\frac{2(2l+5)}{2l-1}\rho^2+1\right], \tag{63}$$

$$\mathcal{U}_{3,l}(\rho)=-\frac{l(l+1)\big[(\rho^2+1)^4\arctan(\rho)+\rho^7-\rho\big]+(l^2-7l-10)\rho^5-(l^2+9l-2)\rho^3}{2^l(2l-3)(2l-1)(\rho^2+1)^4}, \tag{64}$$

$$\mathcal{V}_{3,l}(\rho)=-\big[(-2)^l(l-2)(l-1)(2l+3)(2l+5)\big]^{-1}\big\{12\big[B_{-\rho^2}(l+1,-3)-B_{-\rho^2}(l+1,-4)\big]$$
$$+(2l-3)\rho^2\big[2l^2+l-7+(l-2)(2l-1)\rho^2\big]\big[(3-l)B_{-\rho^2}(l+1,-3)-4B_{-\rho^2}(l+1,-4)\big]\big\}. \tag{65}$$

Here $B_z(a,b)$ is the Euler beta function with the basic definition

$$B_z(a,b)=\int_0^z t^{a-1}(1-t)^{b-1}dt,\quad \mathrm{Re}(a)>0,\ \mathrm{Re}(b)>0,\ |z|\leqslant 1. \tag{66}$$

It is seen that expression (65) cannot be applied directly for $l=1$ or 2. For these values of l, we have

$$\mathcal{V}_{3,1}(\rho)=\frac{1}{140}\left[\frac{3+10\rho^2+11\rho^4-20\rho^6}{(1+\rho^2)^4}+2\ln(1+\rho^2)\right], \tag{67}$$

$$\mathcal{V}_{3,2}(\rho)=-\frac{1}{84}\left[\frac{5+14\rho^2+9\rho^4-6\rho^6+24\rho^8+6\rho^{10}}{6(1+\rho^2)^4}+\ln(1+\rho^2)\right]. \tag{68}$$

The function $v_{3,l}(\rho)$ is defined by Eq. (45).

For the ENC one obtains

$$\psi_{3,0}^{(2e)}\Big(0,\frac{\pi}{2}\Big)=\lambda_0(0)=\frac{1}{8}, \tag{69}$$

whereas for the ENC, the single-series representation (8) yields

$$\psi_{3,0}^{(2e)}\Big(\frac{\pi}{2},0\Big)=\sum_{l=0}^{\infty}\lambda_l(1). \tag{70}$$

Using formulas (61)–(68), one obtains

$$\lambda_l(1)=\frac{2l(l+1)\Big(H_{\frac{l+1}{2}}-H_{\frac{l}{2}}\Big)-6l-1}{2\sqrt{2}(2l-3)(2l+1)(2l+5)}. \tag{71}$$

Then using the integral representation for the harmonic numbers

$$H_z=\int_0^1\frac{1-t^z}{1-t}dt,\qquad \mathrm{Re}(z)>-1, \tag{72}$$

and making use of the change of variable $x=\sqrt{t}$, one obtains

$$\sum_{l=0}^{\infty}\lambda_l(1)=\frac{1}{2\sqrt{2}}(4S_1-S_2), \tag{73}$$

where

$$S_2=\sum_{l=0}^{\infty}\frac{6l+1}{(2l-3)(2l+1)(2l+5)}=\frac{1}{6}, \tag{74}$$

$$S_1=\frac{1}{2}\sum_{l=0}^{\infty}\frac{l(l+1)\Big(H_{\frac{l+1}{2}}-H_{\frac{l}{2}}\Big)}{(2l-3)(2l+1)(2l+5)}=\int_0^1\left(\sum_{l=0}^{\infty}\frac{l(l+1)x^{l+1}}{(2l-3)(2l+1)(2l+5)}\right)\frac{dx}{x+1}$$
$$=\int_0^1\frac{\mathrm{arctanh}(\sqrt{x})(15x^4+2x^2+15)-5\sqrt{x}(3x^3+x^2+x+3)}{128x^{3/2}}\left(\frac{dx}{x+1}\right)=\frac{1-G}{4}. \tag{75}$$

G, as before, denotes Catalan's constant. Inserting the results (73)–(75) into the rhs of Eq. (70), one finally obtains

$$\psi_{3,0}^{(2e)}\left(\frac{\pi}{2},0\right) = \frac{5-6G}{12\sqrt{2}}. \tag{76}$$

III. GREEN'S-FUNCTION APPROACH

The Green's-function approach to calculating the AFCs was presented in Refs. [9,21]. It follows from the general formulas that any component or subcomponent of the AFC at the electron-nucleus coalescence can be calculated in the following simple way:

$$\psi_{k,p}^{(j)}\left(0,\frac{\pi}{2}\right) = \frac{1}{8}\int_0^\pi d\alpha \sin\alpha \cos\left[\left(\frac{k}{2}+1\right)\alpha\right]\zeta(\alpha) \times \int_0^\pi d\theta(\sin\theta) h_{k,p}^{(j)}(\alpha,\theta), \tag{77}$$

where

$$\zeta(\alpha) = \begin{cases} 1, & k \text{ odd}, \\ 1-\frac{\alpha}{\pi}, & k \text{ even}. \end{cases} \tag{78}$$

For the electron-electron coalescence, one obtains the more complicated formula

$$\psi_{k,p}^{(j)}\left(\frac{\pi}{2},0\right) = \frac{1}{8}\int_0^\pi d\alpha \sin^2\alpha \int_0^\pi d\theta(\sin\theta) h_{k,p}^{(j)}(\alpha,\theta) \times \cos\left[\left(\frac{k}{2}+1\right)\gamma\right]\frac{\zeta(\gamma)}{\sin\gamma}, \tag{79}$$

where the angle γ is defined by the relation

$$\cos\gamma = \sin\alpha\cos\theta \qquad (0 \leqslant \gamma \leqslant \pi). \tag{80}$$

It is clear that $h_{k,p}^{(j)}$ in Eqs. (77) and (79) represents the rhs of the corresponding IFRR (7). It is seen that Eq. (77) can be obtained by changing γ to α in Eq. (79). Notice that the above formulas with even k are correct only for the so-called "pure" components or subcomponents (see Ref. [19]). Using Eqs. (77)–(80), we have recalculated all of the AFCs (presented in Refs. [19,20]) at the two-particle coalescences. The results coincide with direct derivations based on the explicit representations (including single-series ones) of the AFC.

The component $\psi_{3,0}^{(2)}(\alpha,\theta)$ was not obtained previously because of the difficulties with calculations of the subcomponent $\psi_{3,0}^{(2d)}$, which represents the physical solution of the IFRR

$$\left(\Lambda^2-21\right)\psi_{3,0}^{(2d)}(\alpha,\theta) = h_{3,0}^{(2d)}(\alpha,\theta), \tag{81}$$

with the rhs

$$h_{3,0}^{(2d)}(\alpha,\theta) = \frac{4}{\sin\alpha}\left[\sin\left(\frac{\alpha}{2}\right)+\cos\left(\frac{\alpha}{2}\right)\right]\chi_{20}(\alpha,\theta), \tag{82}$$

where the function χ_{20} is defined by the single series (10). The use of Eq. (77) enables us to obtain the exact value of the mentioned subcomponent at the ENC as follows:

$$\begin{aligned}\psi_{3,0}^{(2d)}\left(0,\frac{\pi}{2}\right) &= \frac{1}{8}\int_0^\pi d\alpha \sin\alpha\cos\left(\frac{5\alpha}{2}\right)\int_0^\pi d\theta(\sin\theta) h_{3,0}^{(2d)}(\alpha,\theta) \\ &= \int_0^{\pi/2}\left[\sin\left(\frac{\alpha}{2}\right)+\cos\left(\frac{\alpha}{2}\right)\right]\cos\left(\frac{5\alpha}{2}\right)\sigma_0(\alpha)d\alpha + \int_{\pi/2}^{\pi}\left[\sin\left(\frac{\alpha}{2}\right)+\cos\left(\frac{\alpha}{2}\right)\right]\cos\left(\frac{5\alpha}{2}\right)\sigma_0(\pi-\alpha)d\alpha \\ &= \frac{1}{288}[24-48G+\pi(16-3\pi)],\end{aligned} \tag{83}$$

where (see Ref. [19])

$$\sigma_0(\alpha) = \frac{1}{12}\left\{\left(2\sin\alpha - \frac{1}{\sin\alpha}\right)\alpha + \cos\alpha[2\ln(\cos\alpha+1)+1] - \sin\alpha - 2\right\}, \quad 0 \leqslant \alpha \leqslant \pi/2. \tag{84}$$

To use $\sigma_0(\alpha)$ in the range $\pi/2 < \alpha \leqslant \pi$, one should replace α by $\pi-\alpha$ in the rhs of Eq. (84).

On the other hand, the exact value of subcomponent $\psi_{3,0}^{(2d)}$ at the ENC can be derived by using the single-series representation

$$\psi_{3,0}^{(2d)}(\alpha,\theta) = \sum_{l=0}^{\infty} P_l(\cos\theta)(\sin\alpha)^l g_l(\rho), \tag{85}$$

which gives

$$\psi_{3,0}^{(2d)}(0,\frac{\pi}{2}) = g_0(0). \tag{86}$$

We have obtained the exact analytic representation (see the Appendix) for the function $g_0(\rho)$, which at the ENC ($\rho \to 0$) coincides with the result (83).

Now we can calculate the exact value of the component $\psi_{3,0}^{(2)}$ at the ENC. Gathering the subcomponents, one obtains

$$\begin{aligned}\psi_{3,0}^{(2)}\left(0,\frac{\pi}{2}\right) &= \left(\psi_{3,0}^{(2a)}+\psi_{3,0}^{(2b)}+\psi_{3,0}^{(2c)}+\psi_{3,0}^{(2d)}+\psi_{3,0}^{(2e)}\right)\Big|_{\alpha=0} \\ &= \frac{124-48G-3\pi^2-32\ln 2}{288}.\end{aligned} \tag{87}$$

All the subcomponents along with the resulting component (87) at the ENC are presented in Table IV. The exact calculation of the component $\psi_{3,0}^{(2)}$ at the EEC is still difficult.

IV. THE BOUNDARY CONDITIONS FOR THE AFC COMPONENTS

The Kato cusp condition (KCC) [1] for the two-electron atomic wave function (1) at the ENC reads

$$\left.\frac{\partial\chi(r_1,r_2,r_{12})}{\partial r_2}\right|_{r_2=0}=-Z\chi(r,0,r), \tag{88}$$

where, according to definition (3), $r=r_1=r_{12}$ is the hyperspherical radius (3) at the ENC line. The chain-rule relation yields

$$\frac{\partial\Psi(r,\alpha,\theta)}{\partial r_2}=\frac{\partial\Psi}{\partial r}\frac{\partial r}{\partial r_2}+\frac{\partial\Psi}{\partial\alpha}\frac{\partial\alpha}{\partial r_2}+\frac{\partial\Psi}{\partial\theta}\frac{\partial\theta}{\partial r_2}, \tag{89}$$

where, according to Eqs.(2) and (3), one obtains for the ENC

$$\left.\frac{\partial r}{\partial r_2}\right|_{r_2=0}=0, \tag{90a}$$

$$\left.\frac{\partial\alpha}{\partial r_2}\right|_{r_2=0}=\frac{2}{r}, \tag{90b}$$

$$\left.\frac{\partial\theta}{\partial r_2}\right|_{r_2=0}=-\frac{1}{2r}. \tag{90c}$$

Inserting the Fock expansion (1) into the KCC (88), transforming to hyperspherical coordinates using Eqs. (89) and (90), and using the Z-power separation (6), one obtains

$$\sum_{k=0}^{\infty}r^{k-1}\sum_{p=0}^{[k/2]}\ln^p r\sum_{j=p}^{k-p}Z^j\left.\times\left(2\frac{\partial\psi_{k,p}^{(j)}(\alpha,\theta)}{\partial\alpha}-\frac{1}{2}\frac{\partial\psi_{k,p}^{(j)}(\alpha,\theta)}{\partial\theta}\right)\right|_{\alpha=0,\theta=\pi/2}$$
$$=-\sum_{k=0}^{\infty}r^k\sum_{p=0}^{[k/2]}\ln^p r\sum_{j=p}^{k-p}Z^{j+1}\psi_{k,p}^{(j)}\left(0,\frac{\pi}{2}\right). \tag{91}$$

Equating coefficients for the same powers of r, $\ln r$, and Z on both sides of Eq. (91), one obtains the following equation:

$$\psi_{k,p}^{(j)}\left(0,\frac{\pi}{2}\right)=\frac{1}{2}\left.\frac{\partial\psi_{k+1,p}^{(j+1)}(\alpha,\theta)}{\partial\theta}\right|_{\alpha=0,\theta=\pi/2}-2\left.\frac{\partial\psi_{k+1,p}^{(j+1)}(\alpha,\theta)}{\partial\alpha}\right|_{\alpha=0,\theta=\pi/2} \tag{92}$$

for the AFC components at the ENC line.

In its turn, the KCC for the two-electron atomic wave function (1) at the EEC is

$$\left.\frac{\partial\chi(r_1,r_2,r_{12})}{\partial r_{12}}\right|_{r_{12}=0}=\frac{1}{2}\chi\left(\frac{r}{\sqrt{2}},\frac{r}{\sqrt{2}},0\right), \tag{93}$$

where $r_1=r_2=r/\sqrt{2}$. Transforming to hyperspherical coordinates, one obtains

$$\frac{\partial\Psi(r,\alpha,\theta)}{\partial r_{12}}=\frac{\partial\Psi}{\partial r}\frac{\partial r}{\partial r_{12}}+\frac{\partial\Psi}{\partial\alpha}\frac{\partial\alpha}{\partial r_{12}}+\frac{\partial\Psi}{\partial\theta}\frac{\partial\theta}{\partial r_{12}}, \tag{94}$$

where according to Eqs. (2) and (3), we have for the EEC line

$$\left.\frac{\partial r}{\partial r_{12}}\right|_{r_{12}=0}=0, \tag{95a}$$

$$\left.\frac{\partial\alpha}{\partial r_{12}}\right|_{r_{12}=0}=0, \tag{95b}$$

$$\left.\frac{\partial\theta}{\partial r_{12}}\right|_{r_{12}=0}=\frac{\sqrt{2}}{r}. \tag{95c}$$

Inserting the Fock expansion (1) into the KCC (93), transforming to hyperspherical coordinates by Eqs. (94) and (95), and using the Z-power separation (6), one obtains

$$\sqrt{2}\sum_{k=0}^{\infty}r^{k-1}\sum_{p=0}^{[k/2]}\ln^p r\sum_{j=p}^{k-p}Z^j\left.\frac{\partial\psi_{k,p}^{(j)}(\alpha,\theta)}{\partial\theta}\right|_{\alpha=\pi/2,\theta=0}$$
$$=\frac{1}{2}\sum_{k=0}^{\infty}r^k\sum_{p=0}^{[k/2]}\ln^p r\sum_{j=p}^{k-p}Z^j\psi_{k,p}^{(j)}\left(\frac{\pi}{2},0\right). \tag{96}$$

Equating coefficients for the same powers of r, $\ln r$, and Z on both sides of Eq. (96), one obtains the relation

$$\psi_{k,p}^{(j)}\left(\frac{\pi}{2},0\right)=2\sqrt{2}\left.\frac{\partial\psi_{k+1,p}^{(j)}(\alpha,\theta)}{\partial\theta}\right|_{\alpha=\pi/2,\theta=0} \tag{97}$$

for the AFC components at the EEC line.

The important features of the limits under consideration have to be reported. It can be verified that any subcomponent $\psi(\alpha,\theta)\equiv\psi_{k,p}^{(j)}(\alpha,\theta)$ can be represented in the form (8), where some of the functions $\omega_l^{(k,p;j)}(\alpha)$ can be constants, including zero. For example, using representation (19) of Ref. [19] for $\psi_{4,2}(\alpha,\theta)$, one can write

$$\omega_l^{(4,2;2)}(\alpha)=\frac{(\pi-2)(5\pi-14)}{180\pi^2}\left[\left(1-\frac{4}{3}\sin^2\alpha\right)\delta_{l,0}+\frac{4}{3}\delta_{l,2}\right],$$

where $\delta_{l,m}$ is the Kronecker delta. It follows from the form of the rhs of Eq. (8) that the partial derivative of the function represented by Eq. (8) possesses the property

$$\left.\frac{\partial\psi(\alpha,\theta)}{\partial\theta}\right|_{\alpha=\alpha_0,\theta=\theta_0}=\lim_{\theta\to\theta_0}\frac{d\psi(\alpha_0,\theta)}{d\theta}. \tag{98}$$

It is clear that equations like (98) for the partial derivatives (but not mixed) of the higher orders can be written. Therefore, one can conclude that the AFC components or subcomponents possess the property (98). Consequently, since the hyperspherical angle θ is nonnegative, the relation (98) for $\theta_0=0$ reduces to the form

$$\left.\frac{\partial\psi(\alpha,\theta)}{\partial\theta}\right|_{\alpha=\alpha_0,\theta=0}=\lim_{\theta\to 0^+}\frac{d\psi(\alpha_0,\theta)}{d\theta}. \tag{99}$$

It will be shown that the right-hand-side limit on the rhs of Eq. (99) is of special importance for the single series (8).

It is well known that the two-electron wave function (1) and at least its first and second partial derivatives with respect to the interparticle coordinates r_1,r_2, and r_{12} must be finite. Considering the relation (94) at the ENC, one obtains

$$\frac{\partial r}{\partial r_{12}}\bigg|_{r_2=0} = 0, \quad \frac{\partial \alpha}{\partial r_{12}}\bigg|_{r_2=0} = 0, \quad \frac{\partial \theta}{\partial r_{12}}\bigg|_{r_2=0} = \infty. \quad (100)$$

It follows from Eqs. (94) and (100) that one should set

$$\frac{\partial \Psi}{\partial \theta}\bigg|_{\alpha=0,\theta=\pi/2} = 0 \quad (101)$$

in order to preserve the finiteness of the partial derivative $\partial\Psi/\partial r_{12}$ at the ENC. Using the Fock expansion (1), the property (98), and the Z-power separation (6), one obtains for the AFC components

$$\lim_{\theta\to\pi/2} \frac{d\psi_{k,p}^{(j)}(0,\theta)}{d\theta} = 0. \quad (102)$$

Making use of Eqs. (99) and (102), one can rewrite the specific conditions (92) and (97) in the final form

$$\lim_{\theta\to\pi/2}\lim_{\alpha\to 0} \frac{\partial}{\partial\alpha}\psi_{k+1,p}^{(j+1)}(\alpha,\theta) = -\frac{1}{2}\psi_{k,p}^{(j)}\left(0,\frac{\pi}{2}\right), \quad (103)$$

$$\lim_{\theta\to 0^+} \frac{d}{d\theta}\psi_{k+1,p}^{(j)}\left(\frac{\pi}{2},\theta\right) = \frac{1}{2\sqrt{2}}\psi_{k,p}^{(j)}\left(\frac{\pi}{2},0\right). \quad (104)$$

Note that we did not use $d\psi_{k+1,p}^{(j+1)}(\alpha,\pi/2)/d\alpha$ instead of $\lim_{\theta\to\pi/2}\partial\psi_{k+1,p}^{(j+1)}(\alpha,\theta)/\partial\alpha$ in the left-hand side (lhs) of Eq. (103) because, in general, the limit of the angle α must be taken first.

One should emphasize that Eqs. (103) and (104) have been derived for the first time and represent the specific boundary conditions for the AFC components at the two-particle coalescences.

A number of the AFC components derived in Ref. [19], refined and derived in Ref. [20], and supplemented here are at our disposal. We have verified the validity of Eqs. (103) and (104) for examples of all the presently determined components. Notice that the presently calculated subcomponents at the two-particle coalescences are presented in Table IV, whereas the presently determined components (at the two-particle coalescences) on the right-hand sides of Eqs. (103) and (104) are presented in Tables I–III. In all cases where we could provide verification, the correctness of the boundary conditions (103) and (104) was certified.

Note that there are the components or subcomponents that can be placed to the lhs of Eqs. (103) and (104), while the corresponding AFC components or subcomponents in the rhs do not exist. However, when we say that they do not exist, we indeed mean the components $\psi_{k,p}^{(j)} \equiv 0$ for $k < 0$ or $p > [k/2]$ or $j < p$ or $j > k - p$. We have verified that in all those cases Eqs. (103) and (104) remain correct.

To verify the correctness of the conditions (103) and (104), we need to calculate the AFC components or subcomponents and their partial derivatives with respect to the hyperspherical angles α and θ at the two-particle coalescences. There is no problem with performing such calculations for the component or subcomponent represented by explicit analytic functions of α and θ, that is, when only a limited number of the functions $\omega_l(\rho) \equiv \omega_l^{(k,p;j)}(\alpha)$ are different from zero. However, in the case of representation by an infinite single series of the form (8), special consideration is required. For such cases, it is easy to verify the correctness of the following relations:

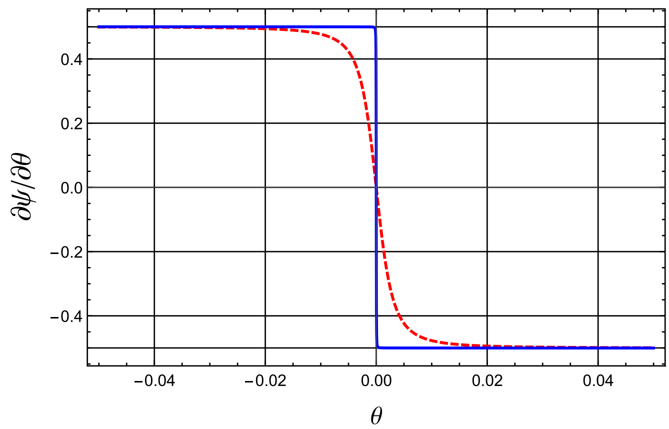

FIG. 1. Partial derivative $\partial\psi/\partial\theta$ for $\psi \equiv \psi_{2,0}^{(1)}(\alpha,\theta)$, with $\alpha = 0.499\pi$ (dashed line) and $\alpha = 0.49999\pi$ (solid line).

$$\psi\left(0,\frac{\pi}{2}\right) = \omega_0(0), \quad (105)$$

$$\psi\left(\frac{\pi}{2},0\right) = \sum_{l=0}^{\infty}\omega_l(1), \quad (106)$$

$$\frac{\partial\psi(\alpha,\theta)}{\partial\alpha}\bigg|_{\alpha=0,\theta=\pi/2} = \frac{d\omega_0(\rho)}{d\alpha}\bigg|_{\alpha=0}, \quad (107)$$

$$\frac{\partial\psi(\alpha,\theta)}{\partial\theta}\bigg|_{\alpha=0,\theta=\pi/2} = 0, \quad (108)$$

where ρ is defined by Eq. (11). Note that Eq. (108) derived for the single-series or HH representations coincides with the general equation (102). The problem is to calculate (performing term-by-term differentiation) the derivative with respect to θ:

$$g(\theta) \equiv \frac{d}{d\theta}\psi\left(\frac{\pi}{2},\theta\right) = \frac{1}{\sin\theta}\sum_{l=1}^{\infty}\omega_l\left(\frac{\pi}{2}\right)(l+1)[P_{l+1}(\cos\theta) - \cos\theta\, P_l(\cos\theta)], \quad (109)$$

which, at first sight, equals zero at the EEC ($\theta = 0$). However, it is not correct in general. Figure 1 (a and b) demonstrates the reason for the possible wrong result. In Fig. 1, we depict the plots of the partial derivative $\partial\psi_{2,0}^{(1)}(\alpha,\theta)/\partial\theta$ in the vicinity of the EEC angle point $\alpha = \pi/2, \theta = 0$. To build the plots we used the analytic representation (22) of Ref. [19]. It is seen that the mentioned derivative has a cusp (singularity) at the EEC point of the hyperspherical angular space. For $\theta \geqslant 0$ we need to calculate the right-hand-side limit.

It can be shown that for the components or subcomponents represented by series of the form (8) the two-sided limits of the partial derivative with respect to θ at the EEC can be calculated using the equation

$$\lim_{\theta\to 0^{\pm}} \frac{d}{d\theta}\psi\left(\frac{\pi}{2},\theta\right) = \lim_{l\to\infty}\{\mp\omega_l(1)l^2\}. \quad (110)$$

Notice that relation (110) remains correct in the absence of the cusp for the derivative $g(\theta)$ at the point $\theta = 0$, that is, in the case where the function $g(\theta)$ is continuous at $\theta = 0$ and the left-hand-side and right-hand-side limits coincide.

Only four subcomponents represented by a single series of the form (8) were considered in the previous section and in Refs. [19,20]. These are $\chi_{20}, \psi_{4,1}^{(2d)}, \psi_{3,0}^{(2e)}$, and $\psi_{3,0}^{(2c)}$. Using the representation (109) with the increasing (but finite) upper limits, we can build the sequence of plots for the derivatives $g(\theta)$ to ensure that the corresponding limits are

$$\lim_{l\to\infty}\{-\sigma_l(1)l^2\} = -\tfrac{1}{6}, \quad \lim_{l\to\infty}\{-\tau_l(1)l^2\} = \frac{\pi-2}{12\pi},$$
$$\lim_{l\to\infty}\{-\phi_l(1)l^2\} = 0, \quad (111)$$

where $\sigma_l(1),\tau_l(1)$, and $\phi_l(1)$ are defined by Eqs. (17), (37), and (57), respectively. It is easy to verify that the results (111) confirm the validity of the conditions

$$\lim_{\theta\to 0^{+}} \frac{d}{d\theta}\psi_{2,0}^{(1)}\left(\frac{\pi}{2},\theta\right) = \frac{1}{2\sqrt{2}}\psi_{1,0}^{(1)}\left(\frac{\pi}{2},0\right) = -\frac{1}{2}, \quad (112)$$

$$\lim_{\theta\to 0^{+}} \frac{d}{d\theta}\psi_{4,1}^{(2)}\left(\frac{\pi}{2},\theta\right) = \frac{1}{2\sqrt{2}}\psi_{3,1}^{(2)}\left(\frac{\pi}{2},0\right) = \frac{\pi-2}{12\pi}, \quad (113)$$

corresponding to the general formula (104) for the EEC. The rhs of Eq. (112) can also be obtained directly using the analytic representation (22) of Ref. [19] for the function $\psi_{2,0}^{(1)}$ on the lhs. Moreover, using Eq.(107) and the results in the Appendix, one easily obtains the boundary condition

$$\lim_{\theta\to\pi/2}\lim_{\alpha\to 0}\frac{d\psi_{3,0}^{(2)}(\alpha,\theta)}{d\alpha} = -\frac{1}{2}\psi_{2,0}^{(1)}\left(0,\frac{\pi}{2}\right) = \frac{3-\ln 2}{12} \quad (114)$$

at the ENC.

In analogy to Eqs. (94), (100), and (101) it is easy to write down the chain-rule relation for the second derivative $\partial^2\Psi/\partial r_{12}^2$. This relation, taken at the ENC line, enables us to obtain the condition

$$\lim_{\theta\to\pi/2}\frac{d^2\psi_{k,p}^{(j)}(0,\theta)}{d\theta^2} = 0. \quad (115)$$

The relation

$$2\left.\frac{\partial\chi(r_1,r_2,r_{12})}{\partial r_2}\right|_{r_1=r_2=R} = \frac{\partial\chi(R,R,r_{12})}{\partial R} \quad (116)$$

was obtained previously [see Eq. (40) of Ref. [7]]. Considering the relation (89) at the EEC, one obtains

$$\left.\frac{\partial r}{\partial r_2}\right|_{r_{12}=0} = \frac{1}{\sqrt{2}}, \quad \left.\frac{\partial\alpha}{\partial r_2}\right|_{r_{12}=0} = \frac{\sqrt{2}}{r}, \quad \left.\frac{\partial\theta}{\partial r_2}\right|_{r_{12}=0} = 0. \quad (117)$$

Substituting Eq. (89) taken at the EEC and Eq. (117) into Eq. (116) with $r_{12} = 0$ and $R = r/\sqrt{2}$ yields

$$\left.\left(\frac{\partial\Psi}{\partial r} + \frac{2}{r}\frac{\partial\Psi}{\partial\alpha}\right)\right|_{\alpha=\pi/2,\theta=0} = \frac{d}{dr}\Psi\left(r,\frac{\pi}{2},0\right), \quad (118)$$

from which one obtains the condition

$$\left.\frac{\partial\Psi}{\partial\alpha}\right|_{\alpha=\pi/2,\theta=0} = 0. \quad (119)$$

Substituting the Fock expansion (1) and the relation (6) into Eq. (119) yields, for the derivative of the AFC components at the EEC,

$$\lim_{\theta\to 0}\lim_{\alpha\to\pi/2}\frac{\partial}{\partial\alpha}\psi_{k,p}^{(j)}(\alpha,\theta) = 0. \quad (120)$$

The correctness of the relations (102), (115), and (120) was verified with examples of the presently determined AFC components.

V. CONCLUSIONS

The exact values of all the presently determined AFC components at the two-particle coalescences have been derived and presented in Tables I–IV. The corresponding results for the edge components $\psi_{k,0}^{(0)}$ and $\psi_{k,0}^{(k)}$ with $1 \leqslant k \leqslant 8$ are displayed in Tables II and III, respectively. The infinite series summation by *Mathematica* and the use of the *Mathematica* operator FindSequenceFunction enabled us to obtain the exact results at the EEC even for the components and/or subcomponents represented by infinite single series of the form (8). As a side result, the exact "pure" analytical representation of the subcomponent $\chi_{20}(\alpha,\theta)$ was obtained by using the exact admixture coefficient defined by Eq. (23). The Green's-function approach has proven to be useful as an additional method for calculating the AFC components at the two-particle coalescences.

The boundary conditions (103) and (104) for the AFC components, expressed through the hyperspherical angles α and θ, were derived as a result of application of the Kato cusp conditions for the two-electron (S-state) wave function expressed in the interparticle distances r_1,r_2, and r_{12}. The additional boundary conditions, which have nothing to do with the Kato cusp conditions, were also obtained. The correctness of the obtained boundary conditions was verified for all the presently determined AFC components.

ACKNOWLEDGMENTS

The author acknowledges Prof. N. Barnea for useful discussions. The author is grateful to Prof. P. Abbott for providing his thesis. The author thanks the anonymous referee for improving the presentation of his results in this article. This work was supported by the PAZY Fund.

APPENDIX

It was shown in [19] that to derive the physical solution of the IFRR (81) in the form of the single series (85), one should, first of all, represent the rhs (82) in the similar form

$$h_{3,0}^{(2d)} = \sum_{l=0}^{\infty} P_l(\cos\theta)(\sin\alpha)^l h_l(\rho). \tag{A1}$$

Then, the basis functions $g_l(\rho)$ of the single-series representation (85) can be found as the physical solution of the equation

$$(1+\rho^2)^2 g_l''(\rho) + 2\rho^{-1}\left[1+\rho^2+l(1-\rho^4)\right]g_l'(\rho) + (3-2l)(2l+7)g_l(\rho) = -h_l(\rho). \tag{A2}$$

The individual solutions $u_{3,l}(\rho)$ and $v_{3,l}(\rho)$ of the homogeneous equation associated with Eq. (A2) are represented by Eqs. (63) and (45), respectively. Using the method of variation of parameters, the particular solution [marked by a superscript (P)] of the inhomogeneous equation (A2) can be found in the form (see Ref. [19])

$$g_l^{(P)}(\rho) = \frac{1}{2l+1}\left[u_{3,l}(\rho)\int \frac{v_{3,l}(\rho)h_l(\rho)\rho^{2l+2}}{(\rho^2+1)^{2l+3}}d\rho - v_{3,l}(\rho)\int \frac{u_{3,l}(\rho)h_l(\rho)\rho^{2l+2}}{(\rho^2+1)^{2l+3}}d\rho\right]. \tag{A3}$$

We shall find only the function $g_0(\rho)$ used in the main text of this paper. Making use of the definition (82), one obtains [see also Eq. (63) of Ref. [19]] the expression for the rhs,

$$h_0(\rho) = \frac{1+\rho}{3\rho\sqrt{1+\rho^2}}\left[(1-\rho^2)\ln\left(\frac{2}{1+\rho^2}\right) - \frac{(\rho^4-6\rho^2+1)\arctan(\rho)}{2\rho} - \frac{1}{2}(3\rho^2+2\rho+1)\right], \tag{A4}$$

which is correct for $0 \leqslant \rho \leqslant 1$. For $\rho > 1$ one should replace ρ by $1/\rho$ on the rhs of Eq. (A4). The formula (A3) gives one of the particular solutions [marked by a superscript (P_1)] in the following rather complicated form:

$$\begin{aligned} g_0^{(P_1)}(\rho) = \frac{(\rho^2+1)^{-3/2}}{360\rho}\Big\{ &-6i\left[(5\rho^4-10\rho^2+1)\mathrm{Li}_2\left(-e^{2i\arctan\rho}\right) + \rho(\rho^4-10\rho^2+5)\mathrm{Li}_2\left(e^{2i\arctan\rho}\right)\right] \\ &+20\rho(3\rho^2+\rho-2)\ln\left(\frac{2}{1+\rho^2}\right) + 8\ln(1+\rho^2) + \arctan(\rho)\Big[12(5\rho^4-10\rho^2+1)\ln\left(\frac{2i}{\rho+i}\right) \\ &+12\rho(\rho^4-10\rho^2+5)\ln\left(\frac{2\rho}{\rho+i}\right) - \rho(7\rho^4-77\rho^3-46\rho^2+114\rho+3) + 6(1-i)(\rho-i)^5\arctan(\rho) + 9\Big] \\ &-\rho(7\rho^3-11\rho^2-81\rho-31) - 8(1+\ln 2)\Big\}, \end{aligned} \tag{A5}$$

where $\mathrm{Li}_2(z)$ is the dilogarithm function and $i = \sqrt{-1}$. The problem is that the particular solution (A5) is singular and complex in the vicinity of the point $\rho = 0$; in particular,

$$g_0^{(P_1)}(\rho) \underset{\rho\to 0}{=} \frac{1}{720\rho}\left[i\pi^2 - 16(1+\ln 2)\right] - \frac{1}{72}\left[i\pi^2 + 8(1-\ln 2)\right] - \frac{\rho}{1440}(23i\pi^2 - 608 - 128\ln 2) + O(\rho^2). \tag{A6}$$

It is more convenient to use the real and finite particular solution [marked by s superscript (P_2)] that can be obtained by the transformation

$$g_0^{(P_2)}(\rho) = g_0^{(P_1)}(\rho) + \frac{i\pi^2}{72}v_{3,0}(\rho) + \frac{16(1+\ln 2) - i\pi^2}{720}u_{3,0}(\rho). \tag{A7}$$

The power-series expansion for the latter particular solution reads

$$g_0^{(P_2)}(\rho) \underset{\rho\to 0}{=} \frac{1}{9}(1-\ln 2) + \frac{\rho}{6}(1-\ln 2) + \frac{\rho^2}{18}(6\ln 2 - 5) + O(\rho^3). \tag{A8}$$

The physical solution of Eq. (A2) with $l = 0$ can be calculated in the form [19]

$$g_0(\rho) = g_0^{(P_2)}(\rho) + c_0 v_{3,0}(\rho). \tag{A9}$$

To find the coefficient c_0, we apply the coupling equation (61) of Ref. [19], which for this case becomes

$$\mathcal{F}_{0,0} = \frac{32}{\pi}\int_0^1 g_0(\rho)\frac{\rho^2}{(\rho^2+1)^3}d\rho, \tag{A10}$$

where $\mathcal{F}_{n,l}$ represents the unnormalized HH expansion coefficient for the subcomponent

$$\psi_{3,0}^{(2d)}(\alpha,\theta) = \sum_{l=0}^{\infty}\mathcal{F}_{n,l}Y_{nl}(\alpha,\theta). \tag{A11}$$

It was shown (see Appendix D of Ref. [19]) that for the AFC $\psi_{k,p}^{(j)}$ with $k = 3$, the following relation is valid:

$$\mathcal{F}_{n,l} = \frac{\mathcal{H}_{n,l}}{(n-3)(n+7)}, \tag{A12}$$

where

$$\mathcal{H}_{n,l} = N_{nl}^2 \int h_{3,0}^{(2d)}(\alpha,\theta) Y_{nl}(\alpha,\theta) d\Omega \tag{A13}$$

represents the coefficient of the HH expansion on the rhs $h_{3,0}^{(2d)}$ defined by Eqs. (82) and (A1). The normalization coefficient N_{nl} and the volume element $d\Omega$ are defined in Ref. [19]. Thus, inserting Eq. (A13) into the rhs of Eq. (A12) with $n = l = 0$, one obtains

$$\mathcal{F}_{0,0} = -\frac{2N_{00}^2\pi^2}{21}\int_0^\pi h_0(\rho)\sin^2\alpha d\alpha = -\frac{32[2\sqrt{2} + \ln(6-4\sqrt{2}) - 5]}{945\pi}. \tag{A14}$$

Equating the right-hand sides of Eqs. (A10) and (A14) and using Eq. (A9), one finds the required coefficient in the form

$$c_0 = -\left(\int_0^1 v_{3,0}(\rho)\frac{\rho^2}{(\rho^2+1)^3}d\rho\right)^{-1}\left[\frac{2\sqrt{2} + \ln(6-4\sqrt{2}) - 5}{945} + \int_0^1 g_0^{(P_2)}(\rho)\frac{\rho^2}{(\rho^2+1)^3}d\rho\right] \simeq -0.0316978107237. \tag{A15}$$

It is seen from the complicated representation (A5) that it is very difficult to derive the exact value of c_0 using Eq. (A15). However, there is no problem with calculating its numerical value. Thus, substitution of the results of this Appendix into Eq. (86) yields the following numerical value for the component $\psi_{3,0}^{(2d)}$ at the ENC:

$$\psi_{3,0}^{(2d)}\left(0,\frac{\pi}{2}\right) = g_0^{(P_2)}(0) + c_0 v_{3,0}(0) = \frac{1-\ln 2}{9} + c_0 = 0.002396946991882. \tag{A16}$$

It is easy to verify that the numerical value of the exact representation (87) obtained in Sec. III coincides with the numerical result (A16), as expected. This enables us, among other things, to establish the exact value of the coefficient

$$c_0 = \frac{\pi(16-3\pi) - 48G - 8 + 32\ln 2}{288}. \tag{A17}$$

[1] T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics, Commun. Pure Appl. Math. **10**, 151 (1957).

[2] R. T. Pack and W. Byers Brown, Cusp conditions for molecular wavefunctions, J. Chem. Phys. **45**, 556 (1966).

[3] J. A. Chapman and D. P. Chong, Cusp constraints for the atomic wavefunctions, Can. J. Chem. **48**, 2722 (1970).

[4] D. Prendergast, M. Nolan, C. Filippi, S. Fahy, and J. C. Greer, Impact of electron-electron cusp on configuration interaction energies, J. Chem. Phys. **115**, 1626 (2001).

[5] E. Z. Liverts, M. Ya. Amusia, R. Krivec, and V. B. Mandelzweig, Boundary solutions of the two-electron Schrödinger equation at two-particle coalescences of the atomic system, Phys. Rev. A **73**, 012514 (2006).

[6] Y. I. Kurokawa, H. Nakashima, and H. Nakatsuji, General coalescence conditions for the exact wave functions: Higher-order relations for two-particle systems, J. Chem. Phys. **139**, 044114 (2013).

[7] E. Z. Liverts, Two-particle atomic coalescences, Phys. Rev. A **89**, 032506 (2014).

[8] E. Z. Liverts, M. Ya. Amusia, E. G. Drukarev, R. Krivec, and V. B. Mandelzweig, Shape variation of the two-electron photoionization spectrum with photon energy growth, Phys. Rev. A **71**, 012715 (2005).

[9] V. A. Fock, On the Schrödinger Equation of the Helium Atom, Izv. Akad. Nauk SSSR, Ser. Fiz. **18**, 161 (1954); [Det K. Norske Vidensk. Selsk. Forh. **31**, 138 (1958)].

[10] J. H. Bartlett, The Helium Wave Equation, Phys. Rev. **51**, 661 (1937).

[11] J. D. Morgan, III, Convergence properties of Fock's expansion for *S*-state eigenfunctions of the helium atom, Theor. Chim. Acta. **69**, 181 (1986).

[12] J. Leray, in *Trends and Applications of Pure Mathematics to Mechanics*, edited by P. G. Ciarlet and M. Roseau, Lecture Notes in Physics Vol. 195 (Springer, Berlin, 1984), p. 235; J. Leray, *Methods of Functional Analysis of Elliptic Operators* (Universita di Napoli, Naples, 1982).

[13] Ph. Pluvinage, Premiers termes du développement de Fock pour les états *S* de *HeI* et de sa séquence isoélectronique, J. Phys. (Paris) **43**, 439 (1982).

[14] J. M. Feagin, J. Macek, and A. F. Starace, Use of the Fock expansion for ^1S-state wave functions of two-electron atoms and ions, Phys. Rev. A **32**, 3219 (1985).

[15] P. C. Abbott and E. N. Maslen, Coordinate systems and analytic expansions for three-body atomic wavefunctions: I. Partial summation for the Fock expansion in hyperspherical coordinates, J. Phys. A **20**, 2043 (1987).

[16] J. E. Gottschalk, P. C. Abbott and E. N. Maslen, Coordinate systems and analytic expansions for three-body atomic wavefunctions: II. Closed form wavefunction to second order in *r*, J. Phys. A **20**, 2077 (1987).

[17] J. E. Gottschalk and E. N. Maslen, Coordinate systems and analytic expansions for three-body atomic wavefunctions: III. Derivative continuity via solution to Laplace's equation, J. Phys. A **20**, 2781 (1987).

[18] R. C. Forrey, Compact representation of helium wave functions in perimetric and hyperspherical coordinates, Phys. Rev. A **69**, 022504 (2004).

[19] E. Z. Liverts and N. Barnea, Angular Fock coefficients: Refinement and further development, Phys. Rev. A **92**, 042512 (2015).

[20] E. Z. Liverts, Analytic calculation of the edge components of the angular Fock coefficients, Phys. Rev. A **94**, 022504 (2016).

[21] P. C. Abbott, Analytic solutions to the few-body Schrödinger equation using hyperspherical coordinates, Ph.D. thesis, University of Western Australia, 1986.