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General coalescence conditions for the exact wave functions. II. Higher-order relations for many-particle systems

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We derived the necessary conditions that must be satisfied by the non-relativistic time-independent exact wave functions for many-particle systems at a two-particle coalescence (or cusp) point. Some simple conditions are known to be Kato's cusp condition (CC) and Rassolov and Chipman's CC. In a previous study, we derived an infinite number of necessary conditions that two-particle wave functions must satisfy at a coalescence point. In the present study, we extend these conditions to many-particle systems. They are called general coalescence conditions (GCCs), and Kato's CC and Rassolov and Chipman's CC are included as special conditions. GCCs can be applied not only to Coulombic systems but also to any system in which the interaction between two particles is represented in a power series of inter-particle distances. We confirmed the correctness of our derivation of the GCCs by applying the exact wave function of a harmonium in electron-electron and electron-nucleus coalescence situations. In addition, we applied the free complement (FC) wave functions of a helium atom to the GCCs to examine the accuracy of the FC wave function in the context of a coalescence situation. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4879266>]

I. INTRODUCTION

The behavior of particles can be described by a wave function which is the solution of the Schrödinger equation (SE): $(\hat{H} - E)\psi = 0$. If we can solve the SE exactly, then it will be perfectly possible to understand and predict the behavior of particles from a chemistry perspective. We studied the "structure" of the exact wave function¹ and used it as a free complement (FC) wave function.²⁻⁵ It is guaranteed that the total energy of the FC wave function converges to the exact solution of the SE.²⁻⁵ The converging speed of the FC wave function itself is much slower in coalescence (or cusp) points than in other regions.⁶

A coalescence point is a singular point where two charged particles come very near each other and where the Coulomb potential \hat{V} in the Hamiltonian diverges to plus or minus infinity. However, the local energy defined by the sum of the potential and kinetic terms, i.e., $E_L \equiv \hat{V} + \hat{K}\psi/\psi$, becomes a constant everywhere, even at the singular points, if the wave function ψ is the exact solution of the SE. This occurs because the kinetic term $\hat{K}\psi/\psi$ exactly cancels the divergence of the Coulomb potential.

The divergence of the local energy does not occur if the wave function satisfies a coalescence condition (CC). The coalescence condition is derived as follows: the SE of N -particle system can be written using the relative coordinate and the center of mass coordinate of particle 1 and 2, namely $\mathbf{r}_{12} \equiv \mathbf{r}_2 - \mathbf{r}_1$ and $\mathbf{G} \equiv (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$ where m_i is the mass of particle i , respectively, instead of the coordinates of \mathbf{r}_1 and \mathbf{r}_2 . If we integrate out the angular coordinates (θ_{12} and ϕ_{12}) of \mathbf{r}_{12} from the SE with a weighting factor Y_{LM}^* (the complex

conjugate of the spherical harmonics), only the radial coordinate (r_{12}) remains. The integrated SE can be expressed in a power series with respect to the r_{12} coordinate when r_{12} is very small as

$$\int d\theta_{12}d\phi_{12}Y_{LM}^*(\theta_{12}, \phi_{12})(\hat{H} - E)\psi = c_{-1}r_{12}^{-1} + c_0 + c_1r_{12} + c_2r_{12}^2 + \dots, \quad (1)$$

where the L and M are arbitrary integers ($L = 0, 1, 2, \dots$ and $-L \leq M \leq L$) and the c_n s are the expansion coefficients depending on the coordinates of \mathbf{G} , $\mathbf{3}$, $\mathbf{4}$, \dots , \mathbf{N} , L and M , and E . If the ψ is the exact, the left hand side (lhs) of Eq. (1) is zero. This is realized only when

$$c_n = 0 \quad (-1 \leq n < \infty). \quad (2)$$

These equations are equivalent to what we call "primitive general coalescence conditions (pGCCs)," and will play important roles in this study, as shown later.

The first equation, $c_{-1} = 0$, is equivalent to the Pack and Byers-Brown's form⁷ of Kato's CC,⁸

$$(L + 1)f_{LM}^{(1)} = \zeta f_{LM}^{(0)}, \quad (3)$$

where $f_{lm}^{(k)}$ is the k th derivative of the lm -component of the wave function defined by

$$f_{lm}^{(k)} \equiv \frac{1}{(k + l)!} \lim_{r_{12} \rightarrow 0} \frac{\partial^{k+l}}{\partial r_{12}^{k+l}} \int d\theta_{12}d\phi_{12}Y_{lm}^*(\theta_{12}, \phi_{12})\psi. \quad (4)$$

$\zeta \equiv Z_1Z_2\mu_{12}$, μ_{12} is the reduced mass of coalescence particles 1 and 2, and Z_i is the charge of particle i . Other necessary conditions at the coalescence point have been examined in some situations.⁹⁻¹⁴

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Recently, the cusp-condition-constrained wave functions have been proposed and used in quantum chemistry; examples include the R12 method,^{15–18} the F12 method,^{18,19} the Quantum Monte Carlo method,²⁰ and Gaussian functions with a linear r term.²¹ The local energies calculated with these wave functions, at least, do not diverge at the coalescence point. However, this is not enough since the local energy must be equal to the total energy E at the coalescence point. Therefore, other necessary conditions must exist for exact wave functions.

The next equations, $c_0 = 0$ and $c_1 = 0$ in Eq. (2), were solved simultaneously, and Rassolov and Chipman's (RC's) CC,⁹

$$f_{00}^{(3)} = \frac{2\xi}{3} f_{00}^{(2)} - \frac{\xi^3}{6} f_{00}^{(0)}, \quad (5)$$

was derived. Generally, the coefficients c_n ($0 \leq n$) include an unknown term E and the coordinates of \mathbf{G} , $\mathbf{3}$, $\mathbf{4}$, \dots , \mathbf{N} , but Rassolov and Chipman eliminated them and derived the RC's CC (5) without any unknown terms. This condition states the relation between the third, second, and zeroth order derivatives of wavefunctions.

There must be other necessary conditions that are derived from the equations $c_n = 0$ for $n = 2, 3, \dots$ (see Eq. (2)). Based on this idea, we studied the necessary conditions that the exact wave function of two-particle systems must satisfy at the coalescence point and derived an infinite number of general coalescence conditions (GCCs) for two-particle systems in a previous paper.²²

In the previous and present studies, the potential between coalescence particles 1 and 2 assumes a general form, $\hat{V}_{12} \equiv \sum_{a=-1}^A C^{(a)} r_{12}^a$ (see Sec. II for details). The GCC equations for two-particle systems are²²

$$\begin{aligned} & \frac{2\mu_{12} \sum_{a=-1}^A C^{(a)} f_{LM}^{(n-a-1)} - (n+1)(n+2+2L) f_{LM}^{(n+1)}}{2\mu_{12} \sum_{a=-1}^A C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)}} \\ &= \frac{f_{LM}^{(n-1)}}{f_{LM}^{(n)}} (n = 0, 1, 2, \dots). \end{aligned} \quad (6)$$

In general, Eq. (6) states the relations between the $(n-1)$ th, n th, $(n+1)$ th, $(n+2)$ th, $(n-a)$ th, and $(n-a-1)$ th derivatives of the wave function ($a = -1, 0, \dots, A$). Equation (6) includes every reported CC. For example, for a Coulombic system ($A = -1$ and $C^{(-1)} = Z_1 Z_2$), when $n = 0$ the equations reduce to Kato's CC (3), and when $n = 1$ they reduce to RC's CC (5). The GCCs (6) are valid only for two-particle systems.

In the present paper, we derive the general coalescence conditions for many-particle systems. The paper is organized as follows. In Sec. II, we define some quantities in the Schrödinger equation. In Sec. III A, we derive the "primitive general coalescence conditions" (pGCCs). These include an unknown term E . We explain how to eliminate the known terms and then derive the GCCs in Sec. III B. In Sec. IV, the GCCs of a Coulombic system are provided as examples, and in Sec. V, we confirm the correctness of the GCC derivation by applying the exact wave function of a harmonium;^{23,24} in

addition, we apply the free complement (FC) wave functions of a helium atom.²⁵ A summary is provided in Sec. VI.

II. BASIC FORMULATION

We consider the non-relativistic time-independent Schrödinger equation of an N -particle system, $(\hat{H} - E)\psi = 0$. The Hamiltonian can be written as

$$\hat{H} \equiv - \sum_{i=1}^N \frac{1}{2m_i} \nabla_i^2 + \hat{V}, \quad (7)$$

where m_i is the mass of particle i , and \hat{V} is the potential written generally as

$$\hat{V} \equiv \sum_{i=1}^{N-1} \sum_{j>i}^N \sum_{a=-1}^{A_{ij}} C_{ij}^{(a)} r_{ij}^a, \quad (8)$$

with integer A_{ij} . Equation (8) can express any potential that is written in a power series of the inter-particle distance r_{ij} ; for example, the Coulomb, harmonic, and $V = r$ potentials. A combination of different kinds of potentials in a system is allowed; e.g., Sec. VI shows an example in which the potentials of a harmonium consist of the Coulomb and harmonic potentials. Note that there is no "cusp" in the exact wave function of the harmonic oscillator, which is why we use the term "coalescence condition" instead of "cusp condition."

We investigate the situation in which particles 1 and 2 come near each other ($r_{12} \rightarrow 0$) and coalesce, while any other particles i ($i \geq 3$) are well separated from the coalescence region and all the other particles, and fixed at given positions. Using the relative coordinate, \mathbf{r}_{12} , and the center of mass coordinate, \mathbf{G} , the SE can be written as

$$\left[-\frac{1}{2\mu_{12}} \nabla_{\mathbf{r}_{12}}^2 + V_{12} + W(1, 2 : 3, 4, \dots, N) + \hat{O} - E \right] \psi = 0, \quad (9)$$

where V_{12} is the potential acting between particles 1 and 2 and is written as

$$V_{12} \equiv \sum_{a=-1}^{A_{12}} C_{12}^{(a)} r_{12}^a, \quad (10)$$

W is the remaining part of the potentials acting on particles 1 and 2 and is written as

$$W(1, 2 : 3, 4, \dots, N) \equiv \sum_{i=3}^N \left(\sum_{a=-1}^{A_{1i}} C_{1i}^{(a)} r_{1i}^a + \sum_{a=-1}^{A_{2i}} C_{2i}^{(a)} r_{2i}^a \right). \quad (11)$$

E is the solution of the SE so generally unknown and the fourth term is the remaining part of the Hamiltonian and is written as

$$\hat{O} \equiv -\frac{1}{2m_{12}} \nabla_{\mathbf{G}}^2 - \sum_{i=3}^N \frac{1}{2m_i} \nabla_i^2 + \sum_{i=3}^N \sum_{j>i}^N \sum_{a=-1}^{A_{ij}} C_{ij}^{(a)} r_{ij}^a. \quad (12)$$

The \hat{O} includes all the variables except for \mathbf{r}_{12} . The total energy E is generally unknown. The W and the second and third

terms of \hat{O} vanish in two-particle systems ($N = 2$), leading to rather simple GCCs.²²

Since r_{ii} ($i = 3, 4, \dots, N, I = 1$ and 2) are related by the cosine theorem to r_{12} by $r_{Ii} = \sqrt{r_{G1}^2 + r_{Gi}^2 + 2\mathbf{r}_{G1}\mathbf{r}_{Gi}}$, with $\mathbf{r}_{G1} = -\mathbf{r}_{12} m_2/m_{12}$, $\mathbf{r}_{G2} = \mathbf{r}_{12} m_1/m_{12}$, and $m_{12} \equiv m_1 + m_2$, the r_{Ii} in Eq. (11) can be expressed using r_{12} . The W , therefore, can be expressed with the radial and angular parts of \mathbf{r}_{12} , as

$$W = \sum_{q=0}^{\infty} r_{12}^q \sum_{q'=-q}^q \left(\sum_{q''=0}^{\infty} R_{qq'}^{(q'')} r_{12}^{q''} \right) Y_{qq'}(\theta_{12}, \phi_{12}), \quad (13)$$

where $R_{qq'}^{(q'')}$ is the expansion coefficient depending on the coordinates of \mathbf{G} , $\mathbf{3}$, $\mathbf{4}$, \dots , \mathbf{N} , and θ_{12} and ϕ_{12} represent angles pointing to the $\mathbf{r}_{12} \equiv \mathbf{r}_2 - \mathbf{r}_1$ direction. Now we can assume that \mathbf{G} , where particles 1 and 2 coalesce, is fixed since the center of mass of the whole system is fixed, and, as previously assumed, the coordinates of $\mathbf{3}$, $\mathbf{4}$, \dots , \mathbf{N} are fixed; therefore, the center of mass coordinate of the remaining particles (i.e., $\mathbf{1}$ and $\mathbf{2}$) should be fixed. Consequently, $R_{qq'}^{(q'')}$ is a constant. If W is given in the form of Eq. (11), $R_{qq'}^{(q'')}$ is determined by

$$R_{qq'}^{(q'')} \equiv \lim_{r_{12} \rightarrow 0} \frac{1}{(q + q'')} \left(\frac{\partial}{\partial r_{12}} \right)^{q+q''} \int Y_{qq'}^*(\theta_{12}, \phi_{12}) W d\Omega. \quad (14)$$

Some examples of $R_{qq'}^{(q'')}$ s are provided in Appendix B.

The most general bounded solution of Eq. (9) can be expanded around $r_{12} = 0$ as

$$\psi \equiv \sum_{l=0}^{\infty} r_{12}^l \sum_{m=-l}^l \left(\sum_{k=0}^{\infty} f_{lm}^{(k)} r_{12}^k \right) Y_{lm}(\theta_{12}, \phi_{12}), \quad (15)$$

where $f_{lm}^{(k)}$ is the expansion coefficient depending on the coordinate of \mathbf{G} , $\mathbf{3}$, $\mathbf{4}$, \dots , \mathbf{N} . The $f_{lm}^{(k)}$ is associated with the wave functions by Eq. (4). There is no possibility that the wave function exists in the logarithmic form.²⁶

Consequently, the SE can be expressed using the relative and the center of mass coordinates.

III. DERIVATION OF THE GENERAL COALESCENCE CONDITION

A. Primitive general coalescence condition

Using the quantities defined in Sec. II, we can derive primitive general coalescence conditions (pGCCs), i.e., the explicit expressions for Eq. (2). The derivations are given in Appendix A. The final expressions of pGCCs are written as

$$\begin{aligned} & -(n+2)(n+3+2L)f_{LM}^{(n+2)} + 2\mu \sum_{a=-1}^A C^{(a)} f_{LM}^{(n-a)} \\ & + 2\mu \sum_{q=0}^{n+L} \sum_{q''=0}^{n+L-q} \sum_{l=0}^{n+L-q-q''} \sum_{q'=-q}^q \\ & \times R_{qq'}^{(q'')} I_{qq'l, M-q'}^{LM} f_{l, M-q'}^{(n+L-q-q''-l)} + 2\mu \hat{O} f_{LM}^{(n)} \\ & = 2\mu E f_{LM}^{(n)} \quad (-1 \leq n < \infty). \end{aligned} \quad (16)$$

In Eq. (16), the $f_{lm}^{(k)}$ s and $R_{qq'}^{(q'')}$ s are associated to the wave function and potentials in the SE, respectively (see Eqs. (4) and (14)). The I is a constant defined by Eq. (A3). The pGCCs are series of necessary conditions which must be satisfied by the exact wave function at the coalescence point, otherwise the SE does not hold true. However, the pGCCs for $n \geq 0$ are not useful since they contain the unknown term E . (The ‘‘primitive’’ included in pGCCs implies the presence of an unknown term). The way of eliminating it from pGCCs is mentioned in Sec. III B.

In the special case of $n = -1$, the unknown term vanishes and Eq. (16) is simplified to

$$-(1+L)f_{LM}^{(1)} + \mu \sum_{a=-1}^A C^{(a)} f_{LM}^{(-1-a)} = 0. \quad (17)$$

This equation represents Kato's CCs (Eq. (3)) when the potential is Coulombic ($A = -1$, $C^{(-1)} = Z_1 Z_2$).

B. Elimination of the unknown terms

In the two-particle case, the unknown term E can be eliminated by dividing Eq. (16) for $n = n - 1$ by the equation for $n = n$; this yields Eq. (6).²² In many-particle cases, if we eliminate the unknown term in the same way, $f_{lm}^{(n)}$ appears in the denominator. However, we cannot tell, in general, in which case the denominator becomes zero since the $f_{lm}^{(n)}$ is a function of the coordinates of $\mathbf{3}$, $\mathbf{4}$, \dots , \mathbf{N} . Instead, we can eliminate the unknown term E in an inductive way as follows. First, we confirm that Eq. (17) holds even for many-particle systems with arbitrary L and M ($L = 0, 1, 2, \dots$ and $-L \leq M \leq L$), and it is a zeroth-order GCC. Note that Eq. (17) is linear with respect to $\{f_{lm}^{(n)}\}$ and it does not include the unknown term E . Next, we assume that the n th-order GCC for arbitrary n is given in the linear form with respect to $\{f_{lm}^{(n)}\}$ as

$$\sum_{s=0}^S \sum_{t=0}^T \sum_{u=-t}^t a_{tu}^{(s)} f_{tu}^{(s)} = 0, \quad (18)$$

where $\{a_{tu}^{(s)}\}$ are the linear combination coefficients or operators acting on $f_{lm}^{(n)}$, and that all the terms are known (or given). We further assume without loss of generality that one of the coefficients, which we call ‘‘leading’’ coefficient, is unity, because we can always divide Eq. (18) by the leading coefficient. The definition of the ‘‘leading’’ term is arbitrary. We employ here a useful definition by choosing the coefficient with the maximum s value. If there are many such terms, then the coefficient with the maximum t value should be chosen.

Operating $2\mu E$ from the left in Eq. (18), we obtain

$$\sum_{s=0}^S \sum_{t=0}^T \sum_{u=-t}^t a_{tu}^{(s)} (2\mu E f_{tu}^{(s)}) = 0. \quad (19)$$

We can obtain all the $2\mu E f_{tu}^{(s)}$ terms in Eq. (19) from Eq. (16) by substituting (n, L, M) in Eq. (16) for (s, t, u) . Then, we

obtain

$$\begin{aligned} & \sum_{s=0}^S \sum_{t=0}^T \sum_{u=-t}^t a_{tu}^{(s)} (2\mu E f_{tu}^{(s)}) \\ &= \sum_{s=0}^S \sum_{t=0}^T \sum_{u=-t}^t a_{tu}^{(s)} \left[- (s+2)(s+3+2t) f_{tu}^{(s+2)} \right. \\ & \quad + 2\mu \sum_{a=-1}^A C^{(a)} f_{tu}^{(s-a)} + 2\mu \sum_{q=0}^{s+t} \sum_{q''=0}^{s+t-q} \sum_{l=0}^{s+t-q-q''} \sum_{q'=-q}^q \\ & \quad \left. \times R_{qq'}^{(q'')} I_{qq'l, u-q''}^{tu} f_{l, u-q'}^{(s+t-q-q''-l)} + 2\mu \hat{O} f_{tu}^{(s)} \right] = 0. \quad (20) \end{aligned}$$

The equality to zero comes from Eq. (19). Equation (20) is a new linear relation among $\{f_{lm}^{(n)}\}$, which is regarded as the $(n+1)$ th-order GCC. Actually, we can rewrite Eq. (20) to be in the same form as Eq. (18). Note that Eq. (20) always differs from Eq. (18), because the maximum superscript of f_{tu} included in Eq. (20) is $S+2$, whereas that of Eq. (18) is S . By performing the same manipulation of Eq. (18) to the form of Eq. (20) repeatedly, we can generate new GCCs inductively. Consequently, we can obtain an infinite number of GCCs without unknown terms.

IV. GCCS OF MANY-PARTICLES FOR COULOMBIC SYSTEMS

In this section, we apply the recursion process described above to the Coulombic system ($A_{ij} = -1$, $C_{ij}^{(-1)} = Z_i Z_j$ for all i and j) to obtain a new coalescence condition, as we have high interest in the Coulombic system. We omit the superscript (q'') from $R_{qq'}$ for simplicity in this section because only $R_{qq'}^{(0)} (\equiv R_{qq'})$ is nonzero in the Coulombic system, as explained in Appendix B.

First, let us start from Kato's CC (zeroth-order GCC), which corresponds to the case of $n = -1$ and $L = M = 0$ in Eq. (17),

$$f_{00}^{(1)} - \zeta f_{00}^{(0)} = 0, \quad (21)$$

with $\zeta \equiv Z_1 Z_2 \mu_{12}$. This corresponds to Eq. (18) with $S = 1$, $T = 0$, $a_{00}^{(1)} = 1$, and $a_{00}^{(0)} = -\zeta$, and it involves $\{f_{LM}^{(n)}\}$ with $(n, L, M) = (0, 0, 0)$ and $(1, 0, 0)$. The pGCC (Eq. (16)) for $(n, L, M) = (0, 0, 0)$ reads

$$2\zeta f_{00}^{(1)} - 6f_{00}^{(2)} + \frac{\mu R_{00}}{\sqrt{\pi}} f_{00}^{(0)} + 2\mu \hat{O} f_{00}^{(0)} = 2\mu E f_{00}^{(0)}, \quad (22)$$

and that for $(n, L, M) = (1, 0, 0)$ reads

$$2\zeta f_{00}^{(2)} - 12f_{00}^{(3)} + \frac{\mu R_{00}}{\sqrt{\pi}} f_{00}^{(1)} + 2\mu \hat{O} f_{00}^{(1)} = 2\mu E f_{00}^{(1)}. \quad (23)$$

Taking the sum of Eq. (23) $-\zeta \times$ Eq. (22) and using Eq. (21) yields a new relation,

$$f_{00}^{(3)} - \frac{2\zeta}{3} f_{00}^{(2)} + \frac{\zeta^2}{6} f_{00}^{(1)} = 0, \quad (24)$$

which corresponds to Eq. (20) at the first recurrence. The "leading term" is $f_{00}^{(3)}$. Equation (24) is equivalent to the RC's CC (Eq. (5)). We call Eq. (24) the first-order GCC for the $L = 0$ component.

Next, we start from Eq. (24) and perform a recursion process to increase the maximum superscript of f by two. Then, we obtain

$$\begin{aligned} & f_{00}^{(5)} - \frac{23}{45} \zeta f_{00}^{(4)} + \frac{\zeta^2}{9} f_{00}^{(3)} - \frac{\zeta^3}{90} f_{00}^{(2)} \\ & - \frac{\mu}{30\sqrt{\pi}} \sum_{M=-1}^1 (-1)^M R_{1M} f_{1,-M}^{(1)} + \frac{\zeta \mu}{45\sqrt{\pi}} \\ & \times \sum_{M=-1}^1 (-1)^M R_{1M} f_{1,-M}^{(0)} = 0, \quad (25) \end{aligned}$$

which is what we call the second-order GCC for $L = 0$. The fifth and sixth terms are the coupling terms between the p-component of the wave function and the p-component of the geometry of non-coalescence particles. Thus, the second- and higher-order GCCs depend on the geometry information for non-coalescence particles, while the zeroth- and first-order GCCs do not. Next, we can perform the same process from Eq. (25) and obtain the third-order GCC. In the third- and higher-order GCCs, a term of $\hat{O} f_{lm}^{(n)}$ appears. This term contains the derivatives of the wave function with respect to the non-coalescence particles.

It is also possible to start from the zeroth-order GCC with arbitrary L and M and to generate another series of GCCs. As an example, here we show a new GCC series starting from $L = 1$ and $M = 0$. First, in this case Eq. (17) becomes

$$f_{10}^{(1)} - \frac{\zeta}{2} f_{10}^{(0)} = 0, \quad (26)$$

which is the zeroth-order GCC. The first- and second-order GCCs are written as

$$f_{10}^{(3)} - \frac{7\zeta}{18} f_{10}^{(2)} + \frac{\zeta^3}{36} f_{10}^{(0)} - \frac{\mu \zeta}{36\sqrt{\pi}} R_{10} f_{00}^{(0)} = 0 \quad (27)$$

and

$$\begin{aligned} & f_{10}^{(5)} - \frac{29}{90} \zeta f_{10}^{(4)} + \left(\frac{7}{360} \zeta^2 - \frac{\mu R_{00}}{40\sqrt{\pi}} \right) f_{10}^{(3)} + \left(\frac{\zeta^3}{144} + \frac{7\mu \zeta}{720} R_{00} \right) f_{10}^{(2)} - \left(\frac{\zeta^5}{1440} + \frac{\mu \zeta^3}{1440\sqrt{\pi}} R_{00} \right) f_{10}^{(0)} \\ & - \frac{\mu}{40\sqrt{\pi}} R_{10} f_{00}^{(3)} + \frac{\mu \zeta}{180\sqrt{\pi}} R_{10} f_{00}^{(2)} + \left(\frac{\mu \zeta^3}{1440\sqrt{\pi}} R_{10} + \frac{\mu^2 \zeta}{1440\pi} R_{10} R_{00} \right) f_{00}^{(0)} - \frac{\mu}{20} \hat{O} f_{10}^{(3)} + \frac{7\mu \zeta}{360} \hat{O} f_{10}^{(2)} \\ & - \frac{\mu \zeta^3}{720} \hat{O} f_{10}^{(0)} + \frac{\mu^2 \zeta}{720\sqrt{\pi}} R_{10} \hat{O} f_{00}^{(0)} + \frac{7\sqrt{5}\mu \zeta}{3600\sqrt{\pi}} \sum_{M=-1}^1 (-1)^M \sqrt{4-|M|} R_{1M} f_{2M}^{(0)} \\ & - \frac{\sqrt{5}\mu}{200\sqrt{\pi}} \sum_{M=-1}^1 (-1)^M \sqrt{4-|M|} R_{1M} f_{2M}^{(1)} - \frac{\sqrt{5}\mu \zeta}{1800\sqrt{\pi}} \sum_{M=-1}^1 \sqrt{4-|M|} R_{2M} f_{1M}^{(0)} = 0, \quad (28) \end{aligned}$$

respectively. These are the GCCs for $L = 1$.

Finally, let us investigate the GCCs for a triplet pair of electrons ($\zeta = \frac{1}{2}$). In this case, the spatial part of the wave function must be anti-symmetric under permutations of electrons, which means that only odd l values survive the expansion of Eq. (15). Therefore, $f_{LM}^{(n)}$ with only odd L values are nonzero from the definition of Eq. (4), so that the GCC equations starting from $L = 0$ are nonsense, i.e., the lhs of Eq. (21) is always zero and also is the higher order.

The zeroth-order GCC for a triplet pair of electrons becomes

$$f_{10}^{(1)} - \frac{1}{4}f_{10}^{(0)} = 0 \quad (29)$$

(see Eq. (26)). Coupling this with Eq. (27) gives

$$f_{10}^{(3)} - \frac{7}{36}f_{10}^{(2)} + \frac{1}{288}f_{10}^{(0)} = 0, \quad (30)$$

which is equivalent to RC's CC for the triplet pair of electrons.⁹

Thus, the present GCCs for a many-particle system automatically include Kato's and RC's CCs as the zeroth- and first-order GCCs, respectively. It is possible to derive higher-order GCC equations for any L and M values.

V. EXAMINATION OF GCCS FOR HARMONIUM AND HELIUM ATOMS

In this section, we apply the exact wave functions of a harmonium to the GCCs to check the correctness of the GCCs' derivation. Also, we apply the FC wave function of a helium atom to examine how accurately the FC wave function is calculated. The harmonium is a special system because it consists of three particles and the exact wave function is written in closed form.^{23,24} The FC method is proposed by one of the authors for obtaining the exact wave function of any system.²⁻⁵ The FC wave function of a helium atom used here is not written in closed form, but its energy has more than 42 digits of accuracy.²⁵

A. Nucleus-electron coalescence of a harmonium

First, we check the nucleus-electron (n-e) coalescence of a harmonium, numbering the nucleus as 1, the coalescence electron as 2, and the other electron as 3, and we assume the Born-Oppenheimer approximation as shown in Fig. 1. We define the variables $r_{12} = r_2$, $r_{13} = r_3$, $\theta_{12} = \theta_2$, and $\phi_{12} = \phi_2$. One of the Hamiltonians whose solution is written in closed form is²⁴

$$\hat{H} = -\frac{1}{2}(\nabla_2^2 + \nabla_3^2) + \frac{1}{8}(r_2^2 + r_3^2) + \frac{1}{r_{23}}, \quad (31)$$

and its eigenfunction is

$$\psi = N_{norm} \exp(-\frac{1}{4}r_2^2) \exp(-\frac{1}{4}r_3^2) (1 + \frac{1}{2}r_{23}), \quad (32)$$

where N_{norm} is the normalization constant. Now we investigate the situation that electron 2 comes close to nucleus 1. The parameters in Eq. (9) are $V_{12} = \frac{1}{8}r_2^2$ and $W = \frac{1}{8}r_3^2 + \frac{1}{r_{23}}$. We assume that electron 3 is fixed at $(r_3, \theta_3, \phi_3) = (G, 0, 0)$.

Then, W is written as

$$W = \frac{1}{8}G^2 + \sum_{q=0}^{\infty} \sqrt{\frac{4\pi}{2q+1}} \sum_{q'=-q}^q (-1)^{q'} \frac{(q-|q'|)!}{(q+|q'|)!} \times Y_{qq'}(\theta_2, \phi_2) \frac{r_2^q}{G^{q+1}}, \quad (33)$$

where we used the Perkins expansion to express $1/r_{23}$ with \mathbf{r}_2 (see Eq. (B2) in Appendix B).²⁷

Comparing Eq. (33) with Eq. (13), we get

$$R_{qq'}^{(q'')} = 0 \text{ (for } q'' \neq 0), \quad (34)$$

$$R_{qq'}^{(0)} = \sqrt{\frac{4\pi}{2q+1}} \left[\frac{1}{8}G^2 \delta_{q,0} + (-1)^{q'} \frac{1}{G^{q+1}} \frac{(q-|q'|)!}{(q+|q'|)!} \right].$$

It is also possible to directly calculate these terms from Eq. (14).

Using these quantities in Eq. (16), we obtain the pGCCs for the $(L, M) = (0, 0)$ component as

$$\left\{ \begin{array}{l} f_{00}^{(1)} = 0 \quad (n = -1) \\ \frac{8+G^3}{4G} f_{00}^{(0)} - 6f_{00}^{(2)} + 2\hat{O} f_{00}^{(0)} = 2E f_{00}^{(0)} \quad (n = 0) \\ \frac{8+G^3}{4G} f_{00}^{(1)} - 12f_{00}^{(3)} + 2\hat{O} f_{00}^{(1)} = 2E f_{00}^{(1)} \quad (n = 1) \\ \frac{1}{4} f_{00}^{(0)} + \frac{3G^3+24}{12G} f_{00}^{(2)} - 20f_{00}^{(4)} + \frac{2\sqrt{3}}{3G^2} f_{10}^{(0)} + 2\hat{O} f_{00}^{(2)} = 2E f_{00}^{(2)} \quad (n = 2), \\ \frac{1}{4} f_{00}^{(1)} + \frac{3G^3+24}{12G} f_{00}^{(3)} - 30f_{00}^{(5)} + \frac{2\sqrt{3}}{3G^2} f_{10}^{(1)} + 2\hat{O} f_{00}^{(3)} = 2E f_{00}^{(3)} \quad (n = 3) \\ \vdots \end{array} \right. \quad (35)$$

and for the $(L, M) = (1, 0)$ component as

$$\left\{ \begin{array}{l} f_{10}^{(1)} = 0 \quad (n = -1) \\ \frac{2\sqrt{3}}{3G^2} f_{00}^{(0)} + \frac{24 + 3G^3}{12G} f_{10}^{(0)} - 10f_{10}^{(2)} + 2\hat{O} f_{10}^{(0)} = 2E f_{10}^{(0)} \quad (n = 0) \\ \frac{2\sqrt{3}}{3G^2} f_{00}^{(1)} + \frac{24 + 3G^3}{12G} f_{10}^{(1)} - 18f_{10}^{(3)} + 2\hat{O} f_{10}^{(1)} = 2E f_{10}^{(1)} \quad (n = 1) \\ \frac{2\sqrt{3}}{3G^2} f_{00}^{(2)} + \frac{48 + 15G^3}{60G^3} f_{10}^{(0)} + \frac{15G^3 + 120}{60G} f_{10}^{(2)} - 28f_{10}^{(4)} + \frac{4}{\sqrt{15}G^2} f_{20}^{(0)} + 2\hat{O} f_{10}^{(2)} = 2E f_{10}^{(2)} \quad (n = 2) \\ \frac{2\sqrt{3}}{3G^2} f_{00}^{(3)} + \frac{48 + 15G^3}{60G^3} f_{10}^{(1)} + \frac{15G^3 + 120}{60G} f_{10}^{(3)} - 40f_{10}^{(5)} + \frac{4}{\sqrt{15}G^2} f_{20}^{(1)} + 2\hat{O} f_{10}^{(3)} = 2E f_{10}^{(3)} \quad (n = 3) \\ \vdots \end{array} \right. \quad (36)$$

The pGCCs for $(n, L, M) = (-1, 0, 0)$ and $(-1, 1, 0)$ read $f_{00}^{(1)} = 0$ and $f_{10}^{(1)} = 0$, respectively, which do not include the unknown terms. These are the zeroth-order GCCs for the $(L, M) = (0, 0)$ and $(1, 0)$ components, respectively. Substituting them for the pGCCs for $(n, L, M) = (1, 0, 0)$ and $(1, 1, 0)$ leads to $f_{00}^{(3)} = 0$ and $f_{10}^{(3)} = 0$, which are the first-order GCCs. Similarly, we can obtain pGCCs for other sets of L s, and use them successively to yield

$$f_{L0}^{(k)} = 0 \quad (k : \text{odd}, L = 0, 1, 2, \dots). \quad (37)$$

These equations do not include any unknown terms and do not depend on the position of the non-coalescence electron. Equation (37) is the $[(k - 1)/2]$ th-order GCCs of the $(L, 0)$ components for the n-e coalescence of harmonium. In brief, these equations state that the odd derivatives of the wave function are zero at the coalescence point. Unfortunately, we could not derive any useful information about the even derivatives of the wave function.

Next, we verified whether or not the exact wave function, Eq. (32), satisfies these GCCs. The wave function can be written using the \mathbf{r}_2 and \mathbf{r}_3 coordinates as

$$\psi = N_{norm} \exp\left(-\frac{1}{4}r_2^2\right) \exp\left(-\frac{1}{4}r_3^2\right) \left\{ 1 + \frac{1}{2} \sum_{q=0}^{\infty} \left[\frac{4\pi}{2q+1} \sum_{q'=-q}^q (-1)^q Y_{q,-q'}(\theta_3, \phi_3) Y_{qq'}(\theta_2, \phi_2) \left(C_{1q0} \frac{r_2^q}{r_3^{q+1}} + C_{1q1} \frac{r_2^{q+2}}{r_3^{q+3}} \right) \right] \right\}, \quad (38)$$

where we used the Perkins expansion to express r_{23} with \mathbf{r}_2 and \mathbf{r}_3 (see Eq. (B2) in Appendix B). Substituting Eq. (38) for Eq. (4) for odd k gives Eq. (37). Thus, we could verify that the exact wave function of the harmonium satisfies the n-e GCCs.

B. Electron-electron coalescence of a harmonium

In this subsection, we discuss the e-e coalescence of a harmonium: electrons 1 and 2 coalesce with each other at the origin $\mathbf{g} = (0, 0, 0)$, $r_{13} = r_1$, $r_{12} = r_2$, and $\mu = 1/2$ (see Fig. 2). We assume that nucleus 3 is fixed at $(r_3, \theta_3, \phi_3) = (G, 0, 0)$. The parameters in the Hamiltonian becomes $V_{12} = 1/r_{12}$ and $W = \frac{1}{8}(r_1^2 + r_2^2) = \frac{1}{4}G^2 + \frac{1}{16}r_{12}^2$. Comparing these with Eqs. (10) and (13) gives $A_{12} = -1$, $C^{(-1)} = 1$, $R_{00}^{(0)} = G^2\sqrt{\pi}/2$, $R_{00}^{(2)} = \sqrt{\pi}/8$, and $R_{qq'}^{(q'')} = 0$ (otherwise). Using these parameters in Eq. (17), we get the pGCCs for the $(L, M) = (0, 0)$ component as

$$\left\{ \begin{array}{l} f_{00}^{(1)} - \frac{1}{2}f_{00}^{(0)} = 0 \quad (n = -1) \\ \frac{1}{4}G^2 f_{00}^{(0)} - 6f_{00}^{(2)} + f_{00}^{(1)} + \hat{O} f_{00}^{(0)} = E f_{00}^{(0)} \quad (n = 0) \\ \frac{1}{4}G^2 f_{00}^{(1)} - 12f_{00}^{(3)} + f_{00}^{(2)} + \hat{O} f_{00}^{(1)} = E f_{00}^{(1)} \quad (n = 1) \\ \frac{1}{4}G^2 f_{00}^{(2)} + \frac{1}{16}f_{00}^{(0)} - 20f_{00}^{(4)} + f_{00}^{(3)} + \hat{O} f_{00}^{(2)} = E f_{00}^{(2)} \quad (n = 2) \\ \vdots \\ \frac{1}{4}G^2 f_{00}^{(n)} + \frac{1}{16}f_{00}^{(n-2)} - (n+2)(n+3)f_{00}^{(n+2)} + f_{00}^{(n+1)} + \hat{O} f_{00}^{(n)} = E f_{00}^{(n)} \quad (n = n) \end{array} \right. \quad (39)$$

The GCCs are provided after eliminating the unknown terms along with the way, as mentioned in Sec. IV. For example, the zeroth- to third-order GCCs are

$$f_{00}^{(1)} - \frac{1}{2}f_{00}^{(0)} = 0, \quad (40)$$

$$f_{00}^{(3)} - \frac{1}{3}f_{00}^{(2)} - \left(\frac{1}{48}G^2 - \frac{1}{24}\right)f_{00}^{(1)} + \frac{1}{96}G^2f_{00}^{(0)} = 0, \quad (41)$$

$$f_{00}^{(5)} - \frac{23}{90}f_{00}^{(4)} + \left(-\frac{1}{60}G^2 + \frac{1}{36}\right)f_{00}^{(3)} + \left(\frac{1}{180}G^2 - \frac{1}{720}\right)f_{00}^{(2)} \\ + \left(\frac{1}{5760}G^4 - \frac{1}{1440}G^2 - \frac{1}{480}\right)f_{00}^{(1)} + \left(-\frac{1}{11520}G^4 + \frac{1}{1440}\right)f_{00}^{(0)} = 0, \quad (42)$$

and

$$f_{00}^{(7)} - \frac{22}{105}f_{00}^{(6)} + \left(\frac{7}{360} - \frac{3}{224}G^2\right)f_{00}^{(5)} + \left(-\frac{1}{1008} + \frac{23}{6720}G^2\right)f_{00}^{(4)} \\ + \left(-\frac{1}{2688}G^2 + \frac{1}{8960}G^4 - \frac{31}{20160}\right)f_{00}^{(3)} + \left(\frac{1}{53760}G^2 + \frac{1}{2520} - \frac{1}{26880}G^4\right)f_{00}^{(2)} \\ + \left(\frac{1}{215040}G^4 - \frac{1}{23040} - \frac{1}{1290240}G^6 + \frac{1}{35840}G^2\right)f_{00}^{(1)} \\ + \left(-\frac{1}{107520}G^2 + \frac{1}{2580480}G^6 + \frac{1}{645120}\right)f_{00}^{(0)} = 0, \quad (43)$$

respectively.

The exact wave function of the harmonium can be written using the \mathbf{r}_{12} coordinate as

$$\psi = N_{norm} \exp\left(-\frac{1}{2}G^2\right) \exp\left(-\frac{1}{8}r_{12}^2\right) \left(1 + \frac{1}{2}r_{12}\right). \quad (44)$$

The $f_{lm}^{(k)}$ values are calculated from Eq. (4) to be

$$f_{00}^{(0)} = 4\pi N_{norm} \exp\left(-\frac{1}{2}G^2\right),$$

$$f_{00}^{(k)} = f_{00}^{(0)} \left(\frac{-1}{8}\right)^{(k/2)} \frac{1}{(k/2)!} \quad (\text{for } k = 2, 4, 6, \dots), \quad (45)$$

$$f_{00}^{(k)} = f_{00}^{(0)} \frac{1}{2} \left(\frac{-1}{8}\right)^{(k-1)/2} \frac{1}{[(k-1)/2]!} \quad (\text{for } k = 1, 3, 5, \dots).$$

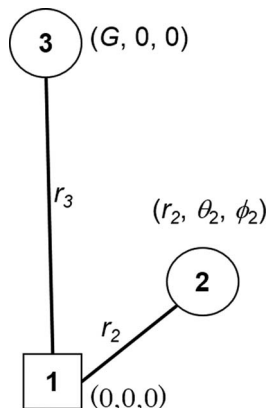


FIG. 1. Nucleus-electron coalescence of a harmonium. Bold lines indicate the harmonic potentials.

It is possible to verify that the exact wave function satisfies the GCCs if Eq. (45) is substituted for Eqs. (40)–(43).

We can obtain the GCCs for the $L = 1, 2, 3, \dots$ components similarly to the $L = 0$ case. However, they are automatically satisfied by the exact wave functions because Eq. (44) has no $L = 1, 2, 3, \dots$ components; thus, $f_{LM}^{(k)} = 0$ for $L = 1, 2, 3, \dots$.

Consequently, we could verify that the exact wave function of the harmonium satisfies both the n-e and e-e GCCs.

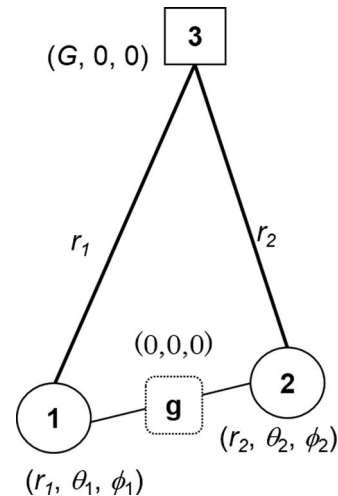


FIG. 2. Electron-electron coalescence of a harmonium. Bold lines indicate the harmonic potentials.

C. Nucleus-electron coalescence values of a helium atom

In this section, we apply the FC wave functions of a helium atom to the GCCs. The wave function has an accuracy of more than 42 digits in energy.²⁵

We fixed the positions of nucleus 1 and electron 3 at $(r_1, \theta_1, \phi_1) = (0, 0, 0)$ and $(r_3, \theta_3, \phi_3) = (1, 0, 0)$, respectively, and assumed that electron 2 approaches the nucleus, as shown in Fig. 3. The parameters are set as $\mu = 1$, $A = -1$, $C^{(-1)} = -2$, $R_{q0}^{(0)} = \sqrt{\frac{4\pi}{2q+1}}(2\delta_{q0} - 1)$, and $R_{qq'}^{(q'')} = 0$ (for $q' \neq 0$ or $q'' = 0$).

$$F_{00}^{(3)} \equiv f_{00}^{(7)} + \frac{88}{105} f_{00}^{(6)} + \frac{137}{1260} f_{00}^{(5)} - \frac{271}{1890} f_{00}^{(4)} - \frac{34}{945} f_{00}^{(3)} + \frac{43}{945} f_{00}^{(2)} - \frac{121}{1890} f_{00}^{(0)} - \frac{1}{28} \hat{O} f_{00}^{(5)} - \frac{23}{630} \hat{O} f_{00}^{(4)} + \frac{17}{945} \hat{O} f_{00}^{(2)} - \frac{4}{189} \hat{O} f_{00}^{(0)} - \frac{2\sqrt{3}}{105} f_{10}^{(3)} - \frac{2\sqrt{3}}{105} f_{10}^{(2)} - \frac{11\sqrt{3}}{3780} f_{10}^{(1)} - \frac{2\sqrt{3}}{405} f_{10}^{(0)} + \frac{\sqrt{3}}{1260} \hat{O} f_{10}^{(1)} + \frac{\sqrt{3}}{945} \hat{O} f_{10}^{(0)} - \frac{23\sqrt{3}}{3150} f_{20}^{(0)} - \frac{\sqrt{5}}{140} f_{20}^{(1)} = 0, \quad (49)$$

$$F_{10}^{(0)} \equiv f_{10}^{(1)} + f_{10}^{(0)}, \quad (50)$$

$$F_{10}^{(1)} \equiv f_{10}^{(3)} + \frac{7}{9} f_{10}^{(2)} - \frac{2}{9} f_{10}^{(0)} + \frac{\sqrt{3}}{27} f_{00}^{(0)}, \quad (51)$$

$$F_{10}^{(2)} \equiv f_{10}^{(5)} + \frac{29}{45} f_{10}^{(4)} + \frac{23}{180} f_{10}^{(3)} - \frac{1}{60} f_{10}^{(2)} + \frac{7}{450} f_{10}^{(0)} - \frac{1}{20} \hat{O} f_{10}^{(3)} - \frac{7}{180} \hat{O} f_{10}^{(2)} + \frac{1}{90} \hat{O} f_{10}^{(0)} - \frac{\sqrt{3}}{540} \hat{O} f_{00}^{(0)} - \frac{\sqrt{3}}{60} f_{00}^{(3)} - \frac{\sqrt{3}}{135} f_{00}^{(2)} - \frac{\sqrt{15}}{150} f_{20}^{(1)} - \frac{7\sqrt{15}}{1350} f_{20}^{(0)} - \frac{\sqrt{3}}{540} f_{00}^{(0)}, \quad (52)$$

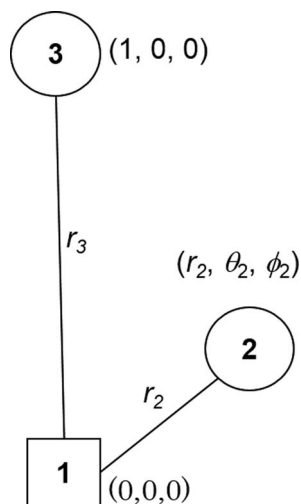


FIG. 3. Nucleus-electron coalescence of a helium atom.

We define the n th-order coalescence values, $F_{LM}^{(n)}$, to be the lhs of the n th-order GCCs. The low-order n-e coalescence values of the helium atom for the $(L, M) = (0,0)$ and $(L, M) = (1,0)$ components are as follows:

$$F_{00}^{(0)} \equiv f_{00}^{(1)} + 2f_{00}^{(0)}, \quad (46)$$

$$F_{00}^{(1)} \equiv f_{00}^{(3)} + \frac{4}{3} f_{00}^{(2)} - \frac{4}{3} f_{00}^{(0)}, \quad (47)$$

$$F_{00}^{(2)} \equiv f_{00}^{(5)} + \frac{46}{45} f_{00}^{(4)} - \frac{68}{135} f_{00}^{(2)} + \frac{16}{27} f_{00}^{(0)} - \frac{\sqrt{3}}{45} f_{10}^{(1)} - \frac{4\sqrt{3}}{135} f_{10}^{(0)}, \quad (48)$$

and so on. All of the F values should be zero if they are calculated with the exact wave function.

Fig. 4 shows the coalescence values of the FC wave functions of the helium atom in the ground state for the $L = 0$ and $L = 1$ components, where the x-axis represents the order of the FC wave function; i.e., the accuracy of the wave function and the y-axis represents $\ln |F_{LM}^{(n)}|$. It is observed that as the wave function becomes more accurate, the coalescence values of $n = 0, 1, 2$, and 3 for the $(L, M) = (0,0)$ component and those of $n = 0, 1$, and 2 for the $(L, M) = (1,0)$ component converge to zero. In other words, the FC wave function satisfies those GCCs. The convergence speed of the low-order coalescence values is faster than that of the high-order coalescence values.

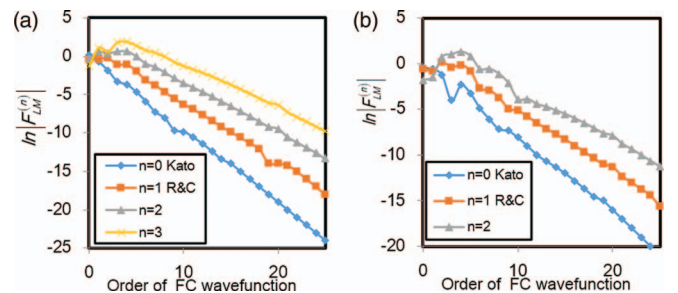


FIG. 4. Logarithmic plot of the nucleus-electron coalescence values of the FC wave functions of the helium atom in the ground state for the (a) $(L, M) = (0,0)$ and (b) $(L, M) = (1,0)$ components. “ n ” represents the order of the coalescence values. The x-axis represents the order of the FC wave function, i.e., the accuracy of the wave function.

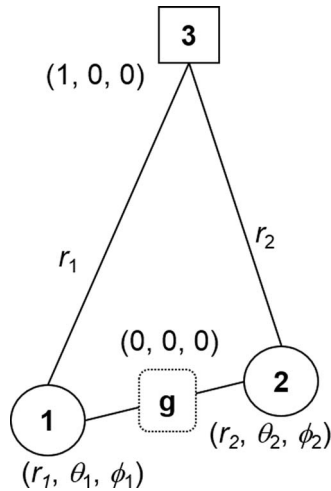


FIG. 5. Electron-electron coalescence of a helium atom.

D. Electron-electron coalescence values of a helium atom

Finally, in this subsection we check the e-e coalescence of the FC wave functions of a helium atom. We fixed the position of nucleus 3 at $(r_3, \theta_3, \phi_3) = (1, 0, 0)$, and assumed that electrons 1 and 2 come near each other and coalesce at $\mathbf{g} = (0, 0, 0)$, as shown in Fig. 5. The parameters are set at $\mu = 1/2$, $A = -1$, $C^{(-1)} = 1$, $R_{q_0}^{(0)} = -4\sqrt{\frac{\pi}{2q+1}}[(-1)^q + 1]/2^q$, and $R_{qq'}^{(q'')} = 0$ (for $q' \neq 0$ or $q'' = 0$).

We define the n th-order coalescence values, $F_{LM}^{(n)}$, to be the lhs of the n th-order GCCs, similar to the n-e case. Low-order e-e coalescence values of the helium atom for the $(L, M) = (0, 0)$ components are as follows:

$$F_{00}^{(0)} \equiv f_{00}^{(1)} - \frac{1}{2}f_{00}^{(0)}, \quad (53)$$

$$F_{00}^{(1)} \equiv f_{00}^{(3)} - \frac{1}{3}f_{00}^{(2)} + \frac{3}{8}f_{00}^{(1)} - \frac{1}{6}f_{00}^{(0)}, \quad (54)$$

$$F_{00}^{(2)} \equiv f_{00}^{(5)} - \frac{23}{90}f_{00}^{(4)} + \frac{53}{180}f_{00}^{(3)} - \frac{13}{144}f_{00}^{(2)} + \frac{1}{18}f_{00}^{(1)} - \frac{1}{45}f_{00}^{(0)}, \quad (55)$$

$$F_{00}^{(3)} \equiv f_{00}^{(7)} - \frac{22}{105}f_{00}^{(6)} + \frac{589}{2520}f_{00}^{(5)} - \frac{281}{5040}f_{00}^{(4)} + \frac{199}{5760}f_{00}^{(3)} - \frac{11}{1120}f_{00}^{(2)} + \frac{11}{2520}f_{00}^{(1)} - \frac{1}{630}f_{00}^{(0)} + \frac{\sqrt{5}}{280}f_{20}^{(1)} - \frac{23\sqrt{5}}{25200}f_{20}^{(0)}, \quad (56)$$

and so on. All of the F values should be zero if they are calculated with the exact wave function.

Figure 6 shows the coalescence values of the FC wave functions of the helium atom in the ground state for the $L = 0$ component. The wave functions in the singlet spin state have no $L = 1$ component. It is observed that the FC wave function satisfies the GCCs of order 0, 1, 2, and 3 as it becomes more accurate. The convergence speed of the low-order e-e coalescence values is faster than that of the high-order coalescence values. This tendency is similar to the n-e case.

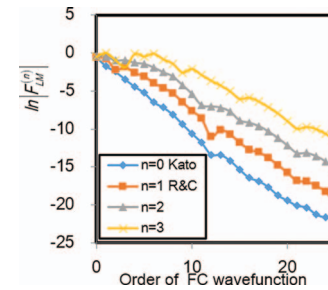


FIG. 6. Logarithmic plot of the electron-electron coalescence values of the FC wave functions of the helium atom in the ground state for the $(L, M) = (0, 0)$ component. “ n ” represents the order of the coalescence values. The x-axis represents the order of the FC wave function, i.e., the accuracy of the wave function.

VI. SUMMARY

In this study, we have formulated the general coalescence conditions for the exact wave functions focusing on the higher-order relations for many-particle systems. We first represented the Schrödinger equation with respect to the \mathbf{r}_{12} coordinate. Then, we derived the primitive general coalescence conditions (pGCCs) for many-particle systems. The pGCCs include an unknown term such as the total energy E of the system. We proposed an inductive way to eliminate the unknown term, allowing us to derive the general coalescence conditions (GCCs) for many-particle systems without any unknown terms. The GCC equations state the relations between the $\{f_{lm}^{(n)}\}$, which are the coefficients of power expansion of a wave function around the coalescence point. The zeroth- and first-order GCCs for the Coulombic system are the same as Kato’s and Rassolov and Chipman’s cusp conditions, respectively. The second- and higher-order GCCs are newly derived in the present study. The GCCs can be applied not only to Coulombic systems but also to any systems with potentials between the coalescence particles that are written as a power series of inter-particle distances. By applying the exact wave function of a harmonium to the nucleus-electron (n-e) and electron-electron (e-e) coalescence situations, we confirmed that our derivation of the GCCs is correct. Also, we observed that the Free Complement wave function of a helium atom satisfies better the n-e and e-e GCCs as the wave function becomes more and more accurate.

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APPENDIX A: DERIVATION OF THE PRIMITIVE GENERAL COALESCENCE CONDITION

In Appendix A, we derive the explicit expression for Eq. (2), i.e., pGCCs. Using the quantities defined in Sec. II, the SE can be written as

$$\left[-\nabla_r^2 + 2\mu \sum_{a=-1}^A C^{(a)} r^a + 2\mu \sum_{q=0}^{\infty} r^q \sum_{q'=-q}^q \left(\sum_{q''=0}^{\infty} R_{qq'}^{(q'')} r^{q''} \right) Y_{qq'}(\theta, \phi) + 2\mu \hat{O} - 2\mu E \right] \left[\sum_{l=0}^{\infty} r^l \sum_{m=-l}^l \sum_{k=0}^{\infty} f_{lm}^{(k)} r^k Y_{lm}(\theta, \phi) \right] = 0. \quad (\text{A1})$$

For simplicity in the following discussion, we remove the subscript “12” from A_{12} , C_{12} , μ_{12} , θ_{12} , ϕ_{12} , and r_{12} if it is not specifically mentioned. Note that $\nabla_r^2 \equiv \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \Lambda^2$ and Λ^2 operate only on the angular part as $\Lambda^2 Y_{lm}(\theta, \phi) = -l(l+1) Y_{lm}(\theta, \phi)$.

Operating $Y_{LM}^*(\theta, \phi) d\Omega$ with arbitrary non-negative integers L and M ($L = 0, 1, 2, \dots$ and $-L \leq M \leq L$) in Eq. (A1) from the left and integrating over the angles, we obtain the equation for the radial part as

$$\sum_{k=0}^{\infty} \left[-k(1+k+2L) f_{LM}^{(k)} r^{L+k-2} + 2\mu \sum_{a=-1}^A C^{(a)} f_{LM}^{(k)} r^{L+k+a} + 2\mu \sum_{q=0}^{\infty} \sum_{q'=-q}^q \sum_{q''=0}^{\infty} R_{qq'}^{(q'')} \sum_{l=0}^{\infty} f_{l, M-q'}^{(k)} I_{qq'l, M-q'}^{LM} r^{q+q''+l+k} + 2\mu r^{L+k} (\hat{O} - E) f_{LM}^{(k)} \right] = 0, \quad (\text{A2})$$

where I is defined by

$$I_{l_1 m_1 l_2 m_2}^{LM} \equiv \int_{\theta=0}^{\pi} \sin \theta d\theta \int_{\phi=-\pi}^{\pi} d\phi Y_{LM}^*(\theta, \phi) Y_{l_1 m_1}(\theta, \phi) Y_{l_2 m_2}(\theta, \phi) = (-1)^M \sqrt{\frac{(2l_1+1)(2l_2+1)(2L+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix}, \quad (\text{A3})$$

and $\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix}$ is Wigner's 3- j symbol.

The terms in Eq. (A2) are ordered by k . Instead, let us reorder and collect terms with the same power of r . Then we get

$$\sum_{n=-1}^{\infty} \left[-(n+2)(n+3+2L) f_{LM}^{(n+2)} + 2\mu \sum_{a=-1}^A C^{(a)} f_{LM}^{(n-a)} + 2\mu (\hat{O} - E) f_{LM}^{(n)} + 2\mu \sum_{q=0}^{n+L} \sum_{q''=0}^{n+L-q} \sum_{l=0}^{n+L-q-q''} \sum_{q'=-q}^q R_{qq'}^{(q'')} I_{qq'l, M-q'}^{LM} f_{l, M-q'}^{(n+L-q-q''-l)} \right] r^n = 0. \quad (\text{A4})$$

Summations whose upper bound is smaller than the lower bound should be ignored in Eq. (A4). We define $f_{lm}^{(p)} \equiv 0$ when $p \leq -1$ for all l and m . The [] part in front of r^n in Eq. (A4) equals to c_n in Eq. (1). Because the [] part is independent of small r , it must be zero for all n so that the SE holds true at the coalescence point. Therefore, $\{f_{lm}^{(k)}\}$ must satisfy

$$-(n+2)(n+3+2L) f_{LM}^{(n+2)} + 2\mu \sum_{a=-1}^A C^{(a)} f_{LM}^{(n-a)} + 2\mu \sum_{q=0}^{n+L} \sum_{q''=0}^{n+L-q} \sum_{l=0}^{n+L-q-q''} \sum_{q'=-q}^q R_{qq'}^{(q'')} I_{qq'l, M-q'}^{LM} f_{l, M-q'}^{(n+L-q-q''-l)} + 2\mu \hat{O} f_{LM}^{(n)} = 2\mu E f_{LM}^{(n)}, \quad (\text{A5})$$

for arbitrary $n \geq -1$. We call Eq. (A5) “primitive general coalescence conditions(pGCCs).” This is the same as Eq. (16) in the main text.

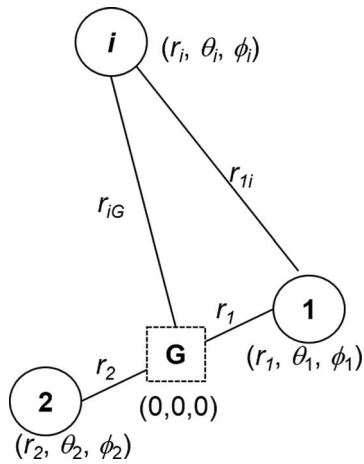
APPENDIX B: $R_{qq'}^{(q')}$ VALUES FOR THE COULOMBIC SYSTEM

We describe $R_{qq'}^{(q')}$ (see Eq. (13)) of the Coulombic system, in which all of the potentials between any two particles

are Coulombic, and we assume that particles 1 and 2 come near each other. We set the origin \mathbf{G} at their center of mass, as shown in Fig. 7.

In this system, W is written as

$$W(1, 2 : 3, 4, \dots, N) \equiv \sum_{i=3}^N \left(\frac{C_{1i}^{(-1)}}{r_{1i}} + \frac{C_{2i}^{(-1)}}{r_{2i}} \right), \quad (\text{B1})$$

FIG. 7. Coalescence of particles 1 and 2 at \mathbf{G} .

with $C_{1i}^{(-1)} = Z_1 Z_i$ and $C_{2i}^{(-1)} = Z_2 Z_i$. Now, $1/r_{1i}$ can be expressed using the Perkins expansion²⁷ as

$$r_{1i}^{\nu} = \sum_{q=0}^{\infty} P_q(\cos \theta_{1Gi}) \sum_{k=0}^{(v+1)/2} C_{\nu q k} s_{1i}^{q+2k} g_{1i}^{\nu-q-2k} \times (\nu = -1, 1, 3, \dots), \quad (\text{B2})$$

where $s_{1i} = \min(r_{G1}, r_{Gi}) = r_{G1}$, $g_{1i} = \max(r_{G1}, r_{Gi}) = r_{Gi}$ because $r_{G1} \ll r_{Gi}$ from the definition, and the $C_{\nu q k}$ are constants given by

$$C_{\nu q k} \equiv \frac{2q+1}{\nu+2} \binom{\nu+2}{2k+1} \prod_{j=0}^{\min[q-1, (\nu+1)/2]} \frac{2k+2j-\nu}{2k+2q-2j+1}. \quad (\text{B3})$$

From the addition theorem, the Legendre function in Eq. (B2) is decomposed into two spherical harmonics as

$$P_q(\cos \theta_{1Gi}) = \frac{4\pi}{2q+1} \sum_{q'=-q}^q (-1)^{q'} Y_{q,-q'}(\theta_i, \phi_i) Y_{qq'}(\theta_1, \phi_1). \quad (\text{B4})$$

Substituting these quantities for Eq. (B2) yields

$$\frac{1}{r_{1i}} = \sum_{q=0}^{\infty} \frac{4\pi}{2q+1} \sum_{q'=-q}^q (-1)^{q'} Y_{q,-q'}(\theta_i, \phi_i) \times Y_{qq'}(\theta_1, \phi_1) r_{G1}^q r_{Gi}^{-1-q}, \quad (\text{B5})$$

and then Eq. (B1) is written as

$$W = \sum_{q=0}^{\infty} \frac{4\pi}{2q+1} \sum_{q'=-q}^q (-1)^{q'} \left[\sum_{i=3}^N \frac{Z_i}{r_{Gi}^{1+q}} Y_{q,-q'}(\theta_i, \phi_i) \right] \times [Z_1 Y_{qq'}(\theta_1, \phi_1) r_{G1}^q + Z_2 Y_{qq'}(\theta_2, \phi_2) r_{G2}^q]. \quad (\text{B6})$$

Noting $\mathbf{r}_{G1} = -\mathbf{r}_{12} m_2 / m_{12}$, $\mathbf{r}_{G2} = \mathbf{r}_{12} m_1 / m_{12}$, $\theta_1 = \pi - \theta_2$, $\phi_1 = \pi + \phi_2$, $\theta_{12} = \theta_2$, $\phi_{12} = \phi_2$, and $Y_{qq'}(\pi - \theta, \pi + \phi)$

$= (-1)^q Y_{qq'}(\theta, \phi)$, W becomes

$$W = \sum_{q=0}^{\infty} \frac{4\pi}{2q+1} \sum_{q'=-q}^q (-1)^{q'} \left[\sum_{i=3}^N \frac{Z_i}{r_{Gi}^{1+q}} Y_{q,-q'}(\theta_i, \phi_i) \right] \times \frac{(-1)^q Z_1 m_2^q + Z_2 m_1^q}{m_{12}^q} r_{12}^q Y_{qq'}(\theta_{12}, \phi_{12}). \quad (\text{B7})$$

Comparing Eq. (B7) with Eq. (13), $R_{qq'}^{(q'')}$ is determined as

$$R_{qq'}^{(0)} = \frac{4\pi}{2q+1} (-1)^{q'} \left[\sum_{i=3}^N \frac{Z_i}{r_{Gi}^{1+q}} Y_{q,-q'}(\theta_i, \phi_i) \right] R_{(q)}, \quad (\text{B8})$$

$$R_{qq'}^{(q'')} = 0 \quad (\text{for } q'' \neq 0),$$

with $R_{(q)} \equiv [(-1)^q Z_1 m_2^q + Z_2 m_1^q] / m_{12}^q$. These are the $R_{qq'}^{(q'')}$ values for Coulombic systems.

The $[\]$ part in Eq. (B8) is a constant because it depends only on the position and charge of particle i . If particle 1 is a nucleus, particle 2 is an electron, and the Born-Oppenheimer approximation is employed, then $R_{(0)} = Z_1 - 1$ and $R_{(q)} = -1$ (for $q \neq 0$). If both particles 1 and 2 are electrons, then $R_{(q)} = -[(-1)^q + 1] / 2^q$.

If particle i ($i \geq 3$) comes near the coalescence region, i.e., three particles coalesce, the $R_{qq'}^{(q'')}$ values diverges because the r_{Gi} in Eq. (B8) becomes zero. Therefore, the coalescence conditions we derive in this article are valid only for two-particle coalescence situation.

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