General coalescence conditions for the exact wave functions: Higher-order relations for two-particle systems

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General coalescence conditions for the exact wave functions: Higher-order relations for two-particle systems

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We derived the necessary conditions that the non-relativistic time-independent exact wave functions for two-particle systems must satisfy at a coalescence (or cusp) point. Some of such necessary conditions are already known to be Kato's cusp condition (CC) and Rassolov and Chipman's CC. In the present study, we extended and generalized those conditions, calling them generalized coalescence conditions (GCCs). Kato's CC and Rassolov and Chipman's CC were shown to be specific cases included in the GCCs. The GCCs can be applied not only to Coulombic systems but also to any systems where the interaction between two particles is represented in a power series of the inter-particle distance. We confirmed the correctness of our derivation of these GCCs by applying the free complement wave functions of a hydrogen atom in ground and excited states, a harmonic oscillator, and a system with an interacting potential of $V = r$. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4816281]

I. INTRODUCTION

The coalescence region, where two charged particles come very close to each other, is a special region in molecular quantum mechanics because it is a singular point of the Coulombic potential ($\hat{V} \equiv \sum_{i,j} Z_i Z_j / r_{ij}$) in the Hamiltonian $\hat{H}$ of the Schrödinger equation (SE):

$$\left(\hat{H} - E \right) \psi = 0. \tag{1}$$

Even so, the local energy defined by $E_L \equiv \hat{V} + \hat{K}\psi/\psi$, where $\hat{K}$ is the kinetic operator, must be a constant given by the energy E in Eq. (1) for the exact wave function ψ. In other words, the kinetic local energy $\hat{K}\psi/\psi$ exactly cancels the divergence of the Coulomb potential $\hat{V}$, resulting in the exact energy E. When a wave function, although approximate, satisfies a special cusp condition (CC) called "Kato's cusp condition,"[1] the local energy does not diverge even at the singular points, although it is not necessarily equal to the exact energy E.

There are two types of Kato's CCs: one is the electron-electron (e-e) CC,

$$\left. \frac{\partial \bar{\psi}}{\partial r_{12}} \right|_{r_{12}=0+} = \frac{1}{2} \left. \bar{\psi} \right|_{r_{12}=0+}, \tag{2}$$

where particles 1 and 2 are both electrons; and the other is the nucleus-electron (n-e) CC,

$$\left. \frac{\partial \bar{\psi}}{\partial r_{12}} \right|_{r_{12}=0+} = -Z_1 \left. \bar{\psi} \right|_{r_{12}=0+}, \tag{3}$$

where particles 1 and 2 are a nucleus and an electron, respectively, r_{ij} is the distance between particles i and j, Z_i is the charge on particle i, and $\bar{\psi}$ represents the wave function spherically averaged over a small sphere centered at the point

$r_{12} = 0$. The Born-Oppenheimer (BO) approximation is assumed in Eq. (3).

Pack and Byers-Brown (PB) unified Kato's e-e and n-e CCs and provided the following expression:[2]

$$(l+1)f_{lm}^{(1)} = \zeta f_{lm}^{(0)} \quad \text{(for } l = 0, 1, 2, \cdots \text{ and } m = -l, \cdots, l\text{)}, \tag{4}$$

where

$$f_{lm}^{(k)} \equiv \frac{1}{(k+l)!} \lim_{r \to 0+} \frac{\partial^{k+l}}{\partial r^{k+l}} \iint d\Omega\, Y_{lm}^*(\theta, \phi)\, \psi, \tag{5}$$

$\zeta \equiv Z_1 Z_2 \mu_{12}$, μ_{12} is the reduced mass of particles 1 and 2, and (r, θ, ϕ) are the polar coordinates of the vector $\mathbf{r}_{12}$. Y_{lm}^* is the complex conjugate of the spherical harmonics, and $\iint d\Omega = \iint \sin\theta\, d\theta\, d\phi$ represents the integration over the angles. $f_{lm}^{(k)}$ is the kth order coefficient of the radial part of the Y_{lm} component of the wave function. PB's CC does not assume the BO approximation, but the BO wave function also satisfies the condition: If particles 1 and 2 are the nucleus and electron and μ_{12} is set to unity instead of the true reduced mass, then Eq. (4) holds for the BO wave function without any modification. Kato's CCs are a special case of PB's CC when $l = m = 0$ and the BO approximation is assumed for the n-e case.

Rassolov and Chipman (RC) extended Kato's CCs to a higher order:[3]

$$f_{00}^{(3)} = \frac{2\zeta}{3} f_{00}^{(2)} - \frac{\zeta^3}{6} f_{00}^{(0)}. \tag{6}$$

This equation states the relation between the third and second derivatives of the wave function. Tew derived similar equations and examined different kinds of wave functions.[4]

Several authors investigated the various aspects of these Coulombic CCs, such as for Gaussian functions with linear r term,[5] unnatural-parity state,[6] combination with the boundary

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conditions,[7,8] three particle coalescence,[9,10] and the density on nucleus,[11] etc.

Loos and Gill studied the spherium "atom,"[12,13] in which two electrons move on the surface of the sphere of radius R. It is an interesting system because "Kato value" for this system is not 1/2 but 1.[12,13] However, we do not deal with this system in the present paper since the potential in this "atom" is completely different from those in ordinary atoms and molecules.

Silanes, Ugalde, and Boyd (SUB) derived Kato's CCs for non-Coulombic interactions;[14] they considered the potential to be not only Coulombic, but also any one written in general as

$$\hat{V} \equiv \sum_{i=1}^{N-1} \sum_{j>i}^{N} \sum_{a=-1}^{A} C_{ij}^{(a)} r_{ij}^{a}, \tag{7}$$

where N is the number of particles of the system, A is a finite integer, and $C_{ij}^{(a)}$ are linear combination coefficients. Various types of potentials were represented; for example, setting $C_{ij}^{(a)} = Z_i Z_j$ and $A = -1$ provides the Coulombic potential, and setting $C_{ij}^{(-1)} = C_{ij}^{(0)} = C_{ij}^{(1)} = 0, C_{ij}^{(2)} = \frac{1}{2}\omega_{ij}$ and $A = 2$ provides the harmonic potential ($\hat{V} = \frac{1}{2}\sum_{i>j}^{N-1,N} \omega_{ij} r_{ij}^2$). SUB's CCs treat these potentials; however, they are limited to the relations between the zeroth and first derivatives of the wave function. Note that it is more appropriate to call these a "coalescence condition" instead of a "cusp condition" because there is no "cusp" in the exact wave function of the harmonic oscillator, for example.

In our current study for solving the Schrödinger equation,[15–17] we use the local Schrödinger equation (LSE) as the necessary conditions to calculate the variables included in the potentially exact wave function.[18] This is an integration-free method and can be a general methodology for atoms and molecules. In this method, the correct treatment of the coalescence region is very important, and further studies into the coalescence region are needed.

In this paper, we derive the relations among the higher-order derivatives of wave functions for two-particle systems at the coalescence point with a general form of the potential. This paper is organized as follows: In Sec. II A, we derive "primitive generalized coalescence conditions" (pGCCs), which are necessary conditions for the exact wave function but include unknown terms. These unknown terms are eliminated to yield the generalized coalescent conditions (GCCs) in Sec. II B. In Sec. III, we confirm the correctness of the GCCs by applying the exact wave functions to them. Conclusions are presented in Sec. IV. Throughout this paper, we mainly focus on two-particle systems. The GCCs for many-particle systems will appear in a forthcoming paper.

II. DERIVATION OF GENERAL COALESCENCE CONDITIONS

A. Derivation of the primitive generalized coalescence condition

We first derive the pGCCs prior to deriving the GCCs. Let us consider a system of two charged particles with the Hamiltonian,

$$\hat{H} \equiv -\sum_{i=1}^{2} \frac{1}{2m_i} \nabla_i^2 + \hat{V}, \tag{8}$$

where m_i is the mass of the particle i, and $\hat{V}$ is the potential of the general type given by Eq. (7) with $N = 2$. Particles 1 and 2 are not necessarily of the same type. Next, we focus our attention on the solution of the SE where r_{12} is very small ($r_{12} < \varepsilon$). Using the relative coordinate, $\mathbf{r}_{12} \equiv \mathbf{r}_2 - \mathbf{r}_1$, and the center of mass coordinate, $\mathbf{G} \equiv (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/m_{12}$, with $m_{12} \equiv m_1 + m_2$, the SE can be written as

$$\left(-\frac{1}{2\mu_{12}} \nabla_{r_{12}}^2 + \sum_{a=-1}^{A} C_{12}^{(a)} r_{12}^a + \hat{O} \right) \psi = 0. \tag{9}$$

The first and second terms in the bracket of Eq. (9) are the kinetic operator and the potential acting between particles 1 and 2, respectively. The third term is the remaining part of the SE,

$$\hat{O} \equiv -\frac{1}{2m_{12}} \nabla_{\mathbf{G}}^2 - E, \tag{10}$$

which includes the exact energy of the system, E. Since E is generally unknown, $\hat{O}$ is also unknown. Now we can assume that $\mathbf{G}$ is fixed since the center of mass of the whole system is fixed, which allows us to neglect the first term in the rhs of Eq. (10). Therefore, $\hat{O}$ is an unknown constant, i.e., $\hat{O} = -E$.

For simplicity in the following discussion, we remove the subscript "12" from C_{12}, μ_{12}, and r_{12} if it is not specifically mentioned.

After some manipulation using these quantities, we obtain the pGCCs represented as follows for $n = -1, 0, 1, 2, \ldots$ (see the Appendix for detailed derivations):

$$2\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)}$$

$$= -2\mu \hat{O} f_{LM}^{(n)}, \tag{11}$$

where $f_{LM}^{(n)}$ are associated with the wave function by Eq. (5) with arbitrary quantum numbers L and M ($L = 0, 1, 2, \ldots$ and $-|L| \le M \le |L|$). n means the number of differentiations of the Y_{lm} component of the wave function at a coalescence point. Note that we defined $f_{LM}^{(n)} \equiv 0$ when $n \le -1$ for all L and M (see the Appendix). The system of Eq. (11) is a series of necessary conditions which the exact wave function must satisfy at the coalescence region. The "primitive" included in pGCC implies the presence of an unknown term $\hat{O}$.

When $n = -1$ only, Eq. (11) is simplified to

$$\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(-1-a)} - (1+L) f_{LM}^{(1)} = 0. \tag{12}$$

In the case that particles 1 and 2 are both electrons ($\mu = \frac{1}{2}$) and their interactions are Coulombic ($A = -1, C^{(-1)} = Z_1 Z_2 = 1$), Eq. (12) reads

$$\frac{1}{2} f_{LM}^{(0)} - (1+L) f_{LM}^{(1)} = 0, \tag{13}$$

which is Kato's e-e CC when $L = M = 0$. In the case that particles 1 and 2 are the nucleus and electron, respectively, with Coulombic interaction ($\mu = 1$, $C^{(-1)} = -Z_1$), Eq. (12) also represents Kato's n-e CC. Furthermore, the "cusp condition for p-wave function" is also derived from Eq. (13) if we set $L = 1$. Similarly, that of the d-, f-, g-, ... wave function is derived corresponding to $L = 2, 3, 4, \ldots$, respectively.

B. Derivation of the general coalescence condition

One may think that Eq. (11) does not provide useful information because it contains the unknown term $\hat{O}$. In order to eliminate this term, we divide both sides of Eq. (11) for $n = n - 1$ by the equation for $n = n$. This gives us

$$\frac{2\mu \sum\limits_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a-1)} - (n+1)(n+2+2L) f_{LM}^{(n+1)}}{2\mu \sum\limits_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)}}$$

$$= \frac{f_{LM}^{(n-1)}}{f_{LM}^{(n)}} (n = 0, 1, 2, \ldots), \tag{14}$$

which does not include any unknown terms. This manipulation is possible when $f_{LM}^{(n)} \neq 0$.

For a Coulombic system and $n = 0$, Eq. (14) reduces to the PB form of Kato's CC (Eq. (4)). When $n = 1$ and $L = M = 0$, Eq. (14) reads

$$\frac{\zeta f_{00}^{(1)} - 3 f_{00}^{(2)}}{\zeta f_{00}^{(2)} - 6 f_{00}^{(3)}} = \frac{f_{00}^{(0)}}{f_{00}^{(1)}}. \tag{15}$$

If a wave function satisfies Kato's CC, i.e., $f_{00}^{(0)} / f_{00}^{(1)} = 1/\zeta$, coupling it with Eq. (15) provides RC's CC (Eq. (6)). Thus, Eq. (14) includes all the CCs ever reported. Using the n value, then Kato's CCs are zeroth-order CCs, RC's CCs are first-order CCs, and Eq. (14) represents nth order CCs. We name Eq. (14) the GCC for two-particle systems. Any wave functions of two-particle systems must satisfy Eq. (14); otherwise the wave function never satisfies the SE. Strictly speaking, RC's CC and the first-order GCC are different equations because RC's CC holds true when a wave function satisfies Kato's CC; however, we would regard the first-order GCC as RC's CC since they are essentially the same.

It may be considered that more-than-third differentiations of the wave function are physically meaningless, since the Hamiltonian includes up to the second differentiation and the derivatives do not influence the local energy at the coalescence region. However, the third- and higher-order derivatives of the wave function are associated with the zeroth, first, and second derivatives by Eq. (14). Consequently, such higher-order derivatives indirectly influence the local energy at the coalescence region.

The GCCs are the infinite numbers of necessary conditions for the wave functions to be the exact solution of SE. Now, is it possible to determine all of the $f_{LM}^{(n)}$s only from the GCCs? The first- and higher-order GCCs for Coulombic systems are four-step recurrence relations among $f_{LM}^{(n)}$s ($n = n$

-1, n, $n + 1$, and $n + 2$). So we need at least three starting values to determine all $f_{LM}^{(n)}$s. If the normalization of the wave function is not considered, we can assume the leading term to be unity, $f_{LM}^{(0)} = 1$, without loss of generality. Then, the next coefficient is given as $f_{LM}^{(1)} = \frac{\zeta}{L+1} f_{LM}^{(0)}$ by the zeroth-order GCC. If one of the second- and higher-order coefficients is obtained by some other necessary conditions, for example, by the LSE method,[18] all the $f_{LM}^{(n)}$s are automatically determined by the GCC equations.

It should be noted that when the denominator of Eq. (14) is zero, i.e., $f_{LM}^{(n)} = 0$, we employ Eq. (11) as the nth order GCC equation, which then reads

$$2\mu \sum\limits_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)} = 0. \tag{16}$$

III. NUMERICAL EXAMINATION OF THE GCC WITH THE FREE COMPLEMENT WAVE FUNCTIONS

In this section, we wish to numerically check the correctness of the GCC. A straightforward numerical check would be to apply the GCC to the exact wave functions; however, they are generally not known except for very simple systems. Therefore, here we employ the free complement (FC) wave functions obtained in our laboratory.[15–20] The FC method was proposed by one of the authors to solve the SE in an analytical expansion form, and it is guaranteed to be exact at convergence.[15–17] The exactness of the FC wave functions for small systems was examined and they were shown to have high accuracy.[19,20] We previously showed that the FC wave functions of the helium atom and hydrogen molecule satisfy the zeroth-order CC.[21,22] It is well known that the conventional Gaussian type wave function never satisfies the zeroth-order CC (Kato's CC), while the FC wave function does satisfy the zeroth-order CC even when we use Gaussian type functions as the complement functions.[22] The FC wave function employed in the present study is briefly explained in Subsection III A, and more details are provided in the references.[15–20,23] The purpose of Secs. III A–III D is to confirm the correctness of the GCC and to examine whether the GCCs indicate the quality of the wave function under consideration.

A. FC wave functions

Let us first introduce the iterative complement (IC) wave function, which is guaranteed to become exact at convergence.[15–17,24] This theory was first formulated in a second quantized form and was originally named the iterative configuration (complement) interaction (ICI) method.[24] The IC wave function in its simplest form (simplest IC) is given in its recurrence form as[15–17,24]

$$\psi_{IC}^n \equiv [1 + C^n g(\hat{H} - E^{n-1})] \psi_{IC}^{n-1}, \tag{17}$$

where g is the scaling operator that was introduced to circumvent the singularity problem caused by the diverging

Coulomb potential.[15–17] The parameters C^n are determined variationally or by the local requirement of the SE (LSE method),[18] and E^n is given by $E^n = \langle \psi_{IC}^n | H | \psi_{IC}^n \rangle$. The initial wave function ψ_{IC}^0 is arbitrary if it has an overlap with the exact wave function under consideration.

The IC wave function at the nth order is a sum of complex analytical functions. In the FC method, we represent all the linearly independent analytical functions included in the IC wave function as $\{\phi_i\}$ and give an independent coefficient to each, namely,

$$\psi_{FC}^n \equiv \sum_{i=1}^{M_n} c_i \phi_i. \tag{18}$$

We refer to $\{\phi_i\}$ as the complement functions because they are elements of complete functions that describe the exact wave function when n is large. With the variation method, the solution is obtained by diagonalizing the secular equation composed of the Hamiltonian and overlap matrices, **H** and **S**. These matrices have elements $H_{ij} \equiv \langle \phi_i | H | \phi_j \rangle$. and $S_{ij} \equiv \langle \phi_i | \phi_j \rangle$, respectively.

We apply the FC method to the 1s and 2p states of a hydrogen atom, harmonic oscillator, and $V = r$ system. The initial wave functions of the FC wave functions employed in Secs. III C and III D are $\psi_{1s}^0 \equiv \exp(-1.1r)$ and $\psi_{2p}^0 \equiv \exp(-0.6r) Y_{10}(\theta, \phi)$ for the 1s and 2p states of a hydrogen atom, respectively; $\psi_{Harmonic}^0 \equiv \exp(-0.6r^2)$ for the harmonic oscillator; and $\psi_{V=r}^0 \equiv \exp(-3.5r)$ for the $V = r$ system. The g factor was used for the Coulombic system and is set to $g = 1 + r$. The exact energies of those systems are, in atomic units, E(H(1s)) = −0.5, E(H(2p)) = −0.125, E(harmonic) = 1.5, and E(V = r system) = −1.855 757 081 489 238 478 416... (the maximum negative solution of $Ai(2^{1/3}E) = 0$, where Ai is Airy's Ai function[25]). The calculated energies have accuracy of more than 20 digits (see Fig. 1). It should be noted that this is the first study that solves the SE of the V = r system with the FC method.
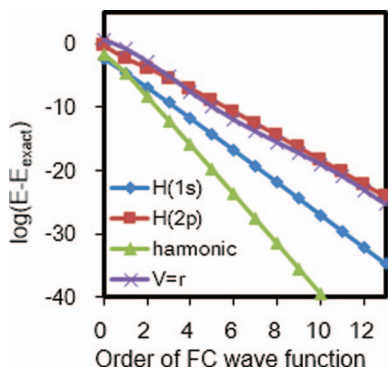

FIG. 1. The total energy (a.u.) of the FC wave function for the hydrogen atom in the 1s and 2p states, the harmonic oscillator, and the $V = r$ system. The differences from the exact values are shown on a logarithm scale. The exact values for these systems are, respectively, −0.5, −0.125, 1.5, and −1.855 757 081 489 238 478 416... (the maximum negative solution of $Ai(2^{1/3}E) = 0$), in a.u.

B. Coalescence values for two-particle systems

In order to examine how accurately the GCCs are satisfied by the wave function, we define the "nth order coalescence value" F for a two-particle system by

$$F_{LM}^{(n)} \equiv \frac{2\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a-1)} - (n+1)(n+2+2L) f_{LM}^{(n+1)}}{2\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)}} - \frac{f_{LM}^{(n-1)}}{f_{LM}^{(n)}}, \tag{19}$$

when $f_{LM}^{(n)}$ is nonzero, and by

$$F_{LM}^{(n)} \equiv 2\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)}, \tag{20}$$

when $f_{LM}^{(n)}$ is equal to zero. If the employed wave function satisfies the GCC, the coalescence value becomes zero; inversely, if the coalescence value becomes zero, then the wave function satisfies the GCC.

C. Hydrogen atom

The hydrogen atom is the simplest Coulombic two-particle system ($\mu = 1$, $A = -1$, $C^{(-1)} = -1$), and the exact wave functions are known to be $\psi_{1s} = N_{00}e^{-r}$ and $\psi_{2p} = N_{1M}(1 - r/2)e^{-r/2}Y_{1M}(\theta, \phi)$ for the 1s and 2p states, respectively, where N_{LM} are the normalization factors. One can confirm that any order of the coalescence values of these wave functions are exactly zero, because the exact 1s wave function gives $f_{00}^{(n)} = \frac{2(-1)^n}{n!}$ and $f_{LM}^{(n)} = 0$ when $L \neq 0$, and the exact 2p wave function gives $f_{1M}^{(n)} = \frac{(-1)^{n+M}}{2\sqrt{6}} \frac{1}{(2n)!!}$ and $f_{LM}^{(n)} = 0$ when $L \neq 1$. Thus, the exact wave functions of these states satisfy the GCC equations at any order.

Next, we examine the GCC with the FC wave functions. Figure 2 shows the coalescence values of the FC wave functions for the hydrogen atom in the 1s ($L = 0$) and 2p ($L = 1$) states. Note that the 1s and 2p states have nonzero coalescence values only for the $L = 0$ and $L = 1$ components, respectively.
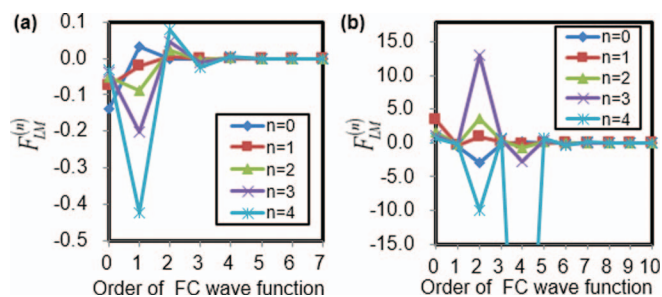

FIG. 2. Coalescence values of the FC wave functions of the hydrogen atom in the (a) 1s ($L = 0$) and (b) 2p ($L = 1$) states. "n" represents the order of the coalescence value. In the 2p state, the zeroth-order coalescence value of the zeroth-order FC wave function is minus infinity, and that of the fourth-order FC wave function is −58.8.

Any order of coalescence value of the low-order FC wave functions is far from zero in both the 1s and 2p states. However, as the wave function becomes exact, the coalescence values at any order converge to zero. For example, the error of the total energy and the coalescence values for $n = 0$–4 calculated with the first-order FC wave function are ca. 3.1×10^{-5} a.u., 3.3×10^{-2}, -2.0×10^{-2}, -8.8×10^{-2}, -2.0×10^{-1}, and -4.2×10^{-1}, respectively, whereas those of the sixth-order wave function greatly decrease to ca. 1.0×10^{-15} a.u., -6.8×10^{-8}, 1.2×10^{-6}, 7.1×10^{-6}, 2.8×10^{-5}, and 9.0×10^{-5}, respectively. It is observed that the convergence speed of the low-order (small n) coalescence values is faster than that of the high-order (large n) coalescence values, and the convergence speed of the total energy is faster than that of the zeroth-order coalescence values. Thus, even a good wave function in the variational sense is not good enough from the viewpoint of the GCCs. Generally speaking, in the variational method, the energy error is roughly the square of the wave function error. Similarly, the convergence speed of the first- and higher-order GCCs is much less than that of the variational energy. These tendencies apply not only to the hydrogen atom but also to other systems, as seen below.

It is very interesting that the converged FC wave functions automatically satisfy the GCC equations, even though the parameters in the FC wave functions are determined using completely different conditions, i.e., the variation principle. This is one of the numeric proofs showing that the FC wave function becomes exact at convergence.

D. Harmonic oscillator ($V = r^2/2$) and the linear potential ($V = r$) system

For the harmonic oscillator, we employ the potential $V = r^2/2$, which is expressed by $C^{(-1)} = C^{(0)} = C^{(1)} = 0$, $C^{(2)} = 1/2$, $\mu = 1$, and $A = 2$. In this case, the pGCC equations (Eq. (11)) become

$$f_{LM}^{(n-2)} - (n + 2)(n + 3 + 2L)f_{LM}^{(n+2)}$$
$$= -2\hat{O} f_{LM}^{(n)} \quad (n = -1, 0, 1, 2, \ldots). \quad (21)$$

Inserting $n = -1$ and $n = 1$ into Eq. (21) yields $f_{LM}^{(1)} = 0$ and $f_{LM}^{(3)} = \frac{2+L}{3} \hat{O} f_{LM}^{(1)} = 0$, because we previously defined $f_{lm}^{(p)} \equiv 0$ when $p \leq -1$. If we insert $n = 3, 5, 7, \ldots$ successively, we can easily derive that $f_{LM}^{(n)} = 0$ for odd n. Thus, the coalescence values for the harmonic oscillator should be given by Eq. (20) when n is odd; otherwise, Eq. (19) is employed.

The exact wave function of the harmonic oscillator in the ground state ($L = 0$) is known to be $\psi = N \exp\left(-\frac{1}{2}r^2\right)$. Figure 3 shows the coalescence values of the FC wave functions of the harmonic oscillator. As the wave function becomes exact, the coalescence values of any order converge to zero similarly to the hydrogen atom case.

A system with a linear potential of $V = r$ ($C^{(-1)} = C^{(0)} = 0$, $C^{(1)} = 1$, $\mu = 1$, and $A = 1$), namely, a constant force system, is unreal but we can derive its GCCs because the SE
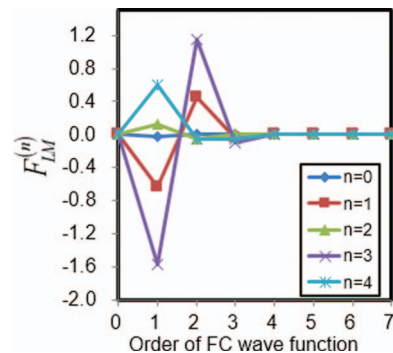

FIG. 3. Coalescence values of the FC wave function of the harmonic oscillator in the ground state ($L = 0$). "n" represents the order of the coalescence value.

of such a system exists. In this system, the pGCC equations become

$$2f_{LM}^{(n-1)} - (n + 2)(n + 3 + 2L)f_{LM}^{(n+2)}$$
$$= -2\hat{O} f_{LM}^{(n)} \quad (n = -1, 0, 1, 2, \ldots). \quad (22)$$

Inserting $n = -1$ gives $f_{LM}^{(1)} = 0$, which means that we should employ Eq. (20) as the first-order coalescence value $F_{LM}^{(1)}$, and Eq. (19) as the other order coalescence values.

The wave function of this system in the $L = 0$ state is expressed as

$$\psi \equiv r^{-1} Ai(ar + b). \quad (23)$$

The bounded discrete solution that gives the lowest energy is realized with $a \equiv 2^{1/3}$ and b as the largest negative solution of $Ai(ab) = 0$. Figure 4 shows the coalescence values of the FC wave functions in this state. As the wave function becomes exact, the coalescence values at any order converge to zero such as in the cases of the hydrogen atom and the harmonic oscillator.

In both systems, low-order coalescence values converge quickly to zero, while high-order ones converge slowly. In conclusion, the GCC equations for some two-particle systems are correctly derived, and the GCCs indicate the accuracy of the wave function.
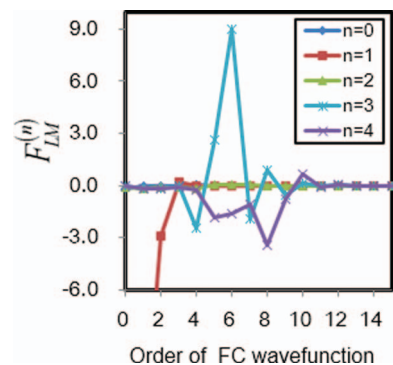

FIG. 4. Coalescence values of the FC wave function of the $V = r$ system in the ground state ($L = 0$). "n" represents the order of the coalescence value. The first-order coalescence values of the zeroth- and first-order FC wave function are -45.8 and -15.2, respectively.

IV. CONCLUSION

In this paper, we began by deriving the pGCCs that include an unknown term such as the total energy of the system. Then, by omitting these unknown terms, we derived the GCCs for two-particle systems. These GCCs are identified by three integers, n, L, and M. The order of the GCCs, represented by n, is related to the number of differentiations of the wave function. L and M represent the angular components of the wave function. The zeroth-order ($n = 0$) and first-order ($n = 1$) GCCs for the Coulombic system are just the Kato's and the 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 that have potentials written in a power expansion form, such as a harmonic oscillator and a $V = r$ system. By applying the FC wave functions for the hydrogen atom, harmonic oscillator, and $V = r$ system, we confirmed that our formulation of the GCCs is numerically correct. We observed that even a good wave function in the variational sense is not good from the viewpoint of the GCCs. Thus, the GCCs can be used to indicate the accuracy of a given wave function.

APPENDIX: DETAILED DERIVATION OF THE PRIMITIVE GENERALIZED COALESCENCE CONDITION

We derive pGCCs (Eq. (11)) in this Appendix. The derivation follows those in Pack and Byers-Brown's and Rassolov and Chipman's papers.[2–4]

The most general bounded solution of Eq. (9) can be written in the form

$$\psi \equiv \sum_{l=0}^{\infty} \sum_{m=-l}^{l} r^l f_{lm}(r) Y_{lm}(\theta, \phi), \qquad (A1)$$

where the dependence of **G** is buried in $f_{lm}(r)$.

Substituting Eq. (A1) for Eq. (9), the SE reads

$$\left[-\nabla_r^2 + 2\mu \sum_{a=-1}^{A} C^{(a)} r^a + 2\mu \hat{O} \right]$$
$$\times \left[\sum_{l=0}^{\infty} \sum_{m=-l}^{l} r^l f_{lm}(r) Y_{lm}(\theta, \phi) \right] = 0. \qquad (A2)$$

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 ($-|L| \leq M \leq |L|$) on Eq. (A2) from the left and integrating over the angles, we get the equation for the radial part,

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{l} \left[-\frac{2}{r} \frac{\partial}{\partial r} - \frac{\partial^2}{\partial r^2} + 2\mu \frac{l(l+1)}{r^2} \right.$$
$$\left. + 2\mu \sum_{a=-1}^{A} C^{(a)} r^a + 2\mu \hat{O} \right] r^l f_{lm}(r) \delta_{lL} \delta_{mM} = 0. \quad (A3)$$

Equation (A3) is not an eigenvalue problem, but a second-order differential linear equation in terms of $f_{lm}(r)$ with the regular singular point at $r = 0$. There must exist at least one f_{lm} of the form

$$f_{lm}(r) \equiv \sum_{k=0}^{\infty} f_{lm}^{(k)} r^k, \qquad (A4)$$

with $f_{lm}^{(0)} \neq 0$, where each $f_{lm}^{(k)}$ is a function of positions of **G**, and are obtained by Eq. (5). For convenience, we define $f_{LM}^{(n)} \equiv 0$ when $n \leq -1$ for all L and M.

Substituting

$$\frac{\partial}{\partial r} f_{lm}(r) = \sum_{k=0}^{\infty} k f_{lm}^{(k)} r^{k-1},$$
$$\frac{\partial^2}{\partial r^2} f_{lm}(r) = \sum_{k=0}^{\infty} k(k-1) f_{lm}^{(k)} r^{k-2}, \qquad (A5)$$

Eqs. (5) and (A4) for (A3) leads to

$$\sum_{k=0}^{\infty} \left[2\mu \sum_{a=-1}^{A} C^{(a)} r^{k+a} - k(1 + k + 2L) r^{k-2} + 2\mu \hat{O} r^k \right] f_{LM}^{(k)}$$
$$= 0. \qquad (A6)$$

Now, terms in Eq. (A6) are ordered by k (or $f^{(k)}$). Let us reorder and collect terms with the same power of r in Eq. (A6). Then we get

$$\sum_{n=-1}^{\infty} \left[2\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)} \right.$$
$$\left. + 2\mu \hat{O} f_{LM}^{(n)} \right] r^n = 0. \qquad (A7)$$

Because the [] part in Eq. (A7) is independent of small r, the [] part must be zero for all n in order that Eq. (A1) satisfies the SE. Therefore, $\{f_{lm}^{(k)}\}$ must satisfy

$$2\mu \sum_{a=-1}^{A} C^{(a)} f_{LM}^{(n-a)} - (n+2)(n+3+2L) f_{LM}^{(n+2)}$$
$$= -2\mu \hat{O} f_{LM}^{(n)} \quad \text{for } n = -1, 0, 1, 2, \ldots, \qquad (A8)$$

with arbitrary n larger than -1. Equations (A8) are the pGCCs, which are the same as Eq. (11) in the main text.

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