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Rates of convergence of the partial-wave expansion beyond the Kato cusp condition

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The rates of convergence for the partial-wave expansion with odd-power r_{12} terms for the ground-state energy of the helium atom are derived. For both the second-order $1/Z$ expansion and the Rayleigh-Ritz variational method, the energy increments of the partial-wave expansion converge as $O(L^{-N-7})$, where N is the highest odd-power r_{12} function. The derivations require assumptions of the regularities for the ground-state helium wave function, which have not been established. Numerical results are presented for supporting the theoretical rates of convergence.

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I. INTRODUCTION

The eigenvalue for an electronic Hamiltonian

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{1}$$

is typically evaluated by expressing Eq. (1) into a discrete representation, truncating at a finite dimension, then solving the matrix eigenvalue problem. Since the exact solutions are not available for general systems, the knowledge of the rate of convergence with respect to a basis is helpful.

The helium atom is a prototype of electron correlation. Under certain assumptions of the analytical structure of the ground-state wave function [1,2], it can be shown for a partial-wave expansion (PWE) in terms of the Legendre polynomial,

$$\psi(r_1,r_2,\theta_{12}) = \sum_{l=0}^{L} \chi_l(r_1,r_2)P_l(\cos\theta_{12}), \tag{2}$$

that the error of energy, $E(L) - E_{\text{exact}}$, and the increments, $E(L) - E(L-1)$, converge as L^{-3} and L^{-4}, respectively [1–6]. By adding a single term containing the interelectron distance r_{12}, the rate of convergence can be improved to L^{-8} for the energy increments [7,8]. A similar basis-set convergence has also been observed for the correlation energies of many-electron systems [9–16].

Very fast rates of convergence for the helium atom can be obtained from the Hylleraas-type expansions [17–24]. The Hylleraas-type wave functions consist of basis functions containing general odd-power r_{12} terms. The aim of the present work is to analyze the rate of convergence with odd-power r_{12} terms beyond the linear order.

In this article we shall first discuss the rate of convergence of the second-order energy in the $1/Z$ expansion, then the Rayleigh-Ritz variational method. In addition, a preliminary investigation of the rate of convergence for the Gaussian geminals approaches is presented in the Supplemental Material [25].

II. ANALYSIS OF RATE OF CONVERGENCE IN THE 1/Z EXPANSION

A. Ansatz for the PWE with odd-power r_{12} functions

For simplicity, we first discuss the rate of convergence for the second-order energy in the $1/Z$ expansion [26]. Consider a nonrelativistic electronic Hamiltonian of a two-electron atom,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}; \tag{3}$$

the $1/Z$ expansion is defined by introducing a scale transformation $r \to r/Z$ and choosing a partition of the Hamiltonian as

$$\hat{H}_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} \quad \text{and} \quad \hat{H}' = \frac{1}{r_{12}}. \tag{4}$$

The energy can then be written as

$$E = Z^2E_0 + ZE_1 + E_2 + Z^{-1}E_3 + \cdots. \tag{5}$$

The ground-state helium atom is inside the radius of convergence [27,28]. The first- and second-order energies are exactly solvable as -1 and $5/8$, respectively [29]. The Hylleraas functional provides an upper bound of the second-order energy for the ground state [26]:

$$\langle\tilde{\psi}|\hat{H}_0 - E_0|\tilde{\psi}\rangle + 2\,\langle\tilde{\psi}|\hat{H}' - E_1|\Phi\rangle \geqslant E_2, \tag{6}$$

where $\Phi = e^{-r_1-r_2}/\pi$ is the ground-state eigenfunction of $\hat{H}_0$. In the present study we omit the spin function. $\tilde{\psi}$ is a trial wave function.

In a typical calculation, the trial wave function is optimized to be stationary for certain parameters. The ground state of the helium atom can be described by $\{r_1,r_2,r_{12}\}$ or $\{r_1,r_2,\theta_{12}\}$ coordinates [17,30]. Since we are interested in the angular correlation, the following ansatz may be considered:

$$\tilde{\psi} = \sum_{n=1,3,5,\ldots}^{N} r_{12}^n\tilde{\Phi}_n(r_1,r_2) + \tilde{\chi}(r_1,r_2,\theta_{12}), \tag{7}$$

$$\tilde{\chi}(r_1,r_2,\theta_{12}) = \sum_{l=0}^{L} \tilde{\chi}_l(r_1,r_2)P_l(\cos\theta_{12}). \tag{8}$$

The energy of the PWE from $\tilde{\psi}$, $\tilde{E}_2(L)$, is defined as the infimum of the Hylleraas functional (6) for all physical accessible trial wave functions $\tilde{\Phi}_n$ and $\tilde{\chi}_l$. However, the

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explicit expressions of the optimized $\tilde{\Phi}_n$ and $\tilde{\chi}_l$ are difficult to obtain. Inspired by Hill [1], we introduce a reference function $\psi^{(a)}$:

$$\psi^{(a)}(r_1,r_2,r_{12}) := \sum_{n=1,3,5,\ldots}^{N} r_{12}^n \Phi_n(r_1,r_2) + \chi(r_1,r_2,\theta_{12}), \quad (9)$$

$$\chi(r_1,r_2,\theta_{12}) = \sum_{l=0}^{L} \chi_l(r_1,r_2) P_l(\cos\theta_{12}), \quad (10)$$

$$\Phi_n(r_1,r_2) = \frac{1}{n!}\left[\sum_{m=0}^{N-n+1} \frac{(-|r_1-r_2|)^m}{m!} \left.\frac{\partial^{n+m}\psi}{\partial r_{12}^{n+m}}\right|_{r_{12}=|r_1-r_2|}\right], \quad (11)$$

$$\chi_l(r_1,r_2) = \frac{2l+1}{2}\int_0^{\pi}\left[\psi(r_1,r_2,r_{12}) - \sum_{n=1,3,5,\ldots}^{N} r_{12}^n \Phi_n(r_1,r_2)\right] \times P_l(\cos\theta_{12}) \sin\theta_{12} d\theta_{12}. \quad (12)$$

Here ψ is the exact first-order wave function. Φ_n is chosen according to the series expansion of r_{12} around $|r_1 - r_2|$. Since the analytic structure of the first-order wave function is not established, we only assume the existence of the partial derivatives in Eq. (11).

We then define the energy of the PWE from $\psi^{(a)}$ as

$$E_2(L) := \langle\psi^{(a)}|\hat{H}_0 - E_0|\psi^{(a)}\rangle + 2\langle\psi^{(a)}|\hat{H}' - E_1|\Phi\rangle. \quad (13)$$

By definition, $E_2(L) \geqslant \tilde{E}_2(L)$. Nevertheless the relaxation from $E_2(L)$ to $\tilde{E}_2(L)$ is beyond the scope of the present study. For the Rayleigh-Ritz variational calculation without odd-power r_{12} function, it is known to be a higher-order effect [1]. In Appendix A, we also discuss an alternative definition of $E_2(L)$.

As we shall see later in Eq. (59), if we decrease the upper limit of summation in Eq. (11), the large-L rate of convergence of $E_2(L)$ will be slower. If we increase the upper limit of summation in Eq. (11), the large-L rate of convergence of $E_2(L)$ will remain the same. In this sense, the ansatz (9) is optimal.

B. Expression of the second-order energy with PWE

The Hylleraas functional (6) includes kinetic operators acting on r_{12} term, which is not convenient for analyzing the PWE. To obtain a more transparent expression, we exchange $\hat{H}_0$ and r_{12}^n. Equation (13) then becomes

$$\begin{aligned} E_2(L) &= \sum_{n,m}\langle\Phi_n r_{12}^n| - m(m+1)r_{12}^{m-2} + \hat{U}_m + r_{12}^m(\hat{H}_0 - E_0)|\Phi_m\rangle \\ &\quad + 2\sum_m\langle\chi| - m(m+1)r_{12}^{m-2} + \hat{U}_m + r_{12}^m(\hat{H}_0 - E_0)|\Phi_m\rangle \\ &\quad + \langle\chi|\hat{H}_0 - E_0|\chi\rangle \\ &\quad + 2\sum_m\langle\Phi_m r_{12}^m|\hat{H}' - E_1|\Phi\rangle + 2\langle\chi|\hat{H}' - E_1|\Phi\rangle. \end{aligned} \quad (14)$$

Here a generalized operator $\hat{U}_m$ is introduced as

$$\left[\hat{H}_0 - E_0, r_{12}^m\right] = -m(m+1)r_{12}^{m-2} + \hat{U}_m. \quad (15)$$

A straightforward calculation shows $\hat{U}_m = -mr_{12}^{m-2}(\mathbf{r}_1 - \mathbf{r}_2)\cdot(\boldsymbol{\nabla}_1 - \boldsymbol{\nabla}_2)$. The bold face indicates a vector. In our conventions $\hat{U}_1$ is two times the original definition [7].

As suggested by Kutzelnigg and Morgan [8], it is simpler to analyze the rate of convergence by utilizing the first-order equation

$$(\hat{H}_0 - E_0)|\psi\rangle = -(\hat{H}' - E_1)|\Phi\rangle. \quad (16)$$

Inserting Eq. (9) into Eq. (16) yields

$$\begin{aligned} \langle\chi|\hat{H}_0 - E_0|\chi\rangle &= -\sum_m\langle\chi| - m(m+1)r_{12}^{m-2} + \hat{U}_m \\ &\quad + r_{12}^m(\hat{H}_0 - E_0)|\Phi_n\rangle - \langle\chi|\hat{H}' - E_1|\Phi\rangle. \end{aligned} \quad (17)$$

With the help of Eq. (17), Eq. (14) can be written as

$$E_2(L) = A_2 + G_2(L), \quad (18)$$

$$\begin{aligned} A_2 &:= \sum_{n,m}\langle\Phi_n r_{12}^n| - m(m+1)r_{12}^{m-2} + \hat{U}_m \\ &\quad + r_{12}^m(\hat{H}_0 - E_0)|\Phi_m\rangle + 2\sum_m\langle\Phi_m r_{12}^m|\hat{H}' - E_1|\Phi\rangle, \end{aligned} \quad (19)$$

$$\begin{aligned} G_2(L) &:= \sum_m\langle\chi| - m(m+1)r_{12}^{m-2} + \hat{U}_m \\ &\quad + r_{12}^m(\hat{H}_0 - E_0)|\Phi_m\rangle + \langle\chi|\hat{H}' - E_1|\Phi\rangle. \end{aligned} \quad (20)$$

The rate of convergence of PWE is determined by $G_2(L)$.

C. A note on the rate of convergence without odd-power r_{12} function

The simplest case is $N = 0$ in Eq. (9). It has been suggested that at the large-L limit the ground-state wave function approaches [3]

$$\psi(r_1,r_2,r_{12}) \to \tfrac{1}{2}r_{12}\Phi(r_1,r_2). \quad (21)$$

The original derivation was based on the perturbative term $H' = 1/r_{12} = \sum_{l=0}^{\infty} r_<^l/r_>^{l+1} P_l(\cos\theta_{12})$ which highly peaks at $\mathbf{r}_1 = \mathbf{r}_2$ when $L \to \infty$. Here $r_< := \min(r_1,r_2)$ and $r_> := \max(r_1,r_2)$. In this region, Eq. (16) becomes

$$\frac{1}{4}(\boldsymbol{\nabla}_1 - \boldsymbol{\nabla}_2)^2\psi = \frac{1}{r_{12}}\Phi. \quad (22)$$

The asymptotic behavior (21) was obtained by solving Eq. (22). Nevertheless it was assumed that the three-particle-coalescence singularity ($r_1 = r_2 = r_{12} = 0$) is not effective [31].

In Appendix B, we provide an alternative derivation for the rate of convergence and the large-L behavior of ψ. The main purpose of Appendix B is to make the discussion of the rate of convergence with the odd-power r_{12} function more convenient.

D. Analysis of the rate of convergence with the odd-power r_{12} function

1. Effects of $r_< - r_>$, r_{12}^2, and $\hat{U}_1$ terms for the large-L rate of convergence

In the following discussion, the generalized-Laplace expansion [32,33],

$$r_{12}^{\nu} = \sum_{l=0}^{L_1} R_{\nu l}(r_1,r_2)\, P_l(\cos\theta_{12}), \quad (23)$$

$$R_{\nu l}(r_1,r_2) = \sum_{k=0}^{L_2} C_{\nu l k} r_<^{l+2k} r_>^{\nu-l-2k}, \quad (24)$$

$$C_{\nu l k} = \frac{(-\nu/2)_l}{(1/2)_l}\,\frac{(l-\nu/2)_k(-1/2-\nu/2)_k}{(l+3/2)_k\qquad k!}, \quad (25)$$

will be used to convert the r_{12}^{ν} term into the Legendre polynomial, $P_l(\cos\theta_{12})$. Here ν is an integer. $L_1 = \infty$ or $\nu/2$ for an odd or even ν, respectively. $L_2 = \lfloor(\nu+1)/2\rfloor$, where $\lfloor\cdots\rfloor$ is the floor function, defined as the largest integer no greater than its argument. x_n is the Pochhammer symbol, defined as $x_0 = 1$ and $x_n := x(x+1)\cdots(x+n-1),\ n \geqslant 1$.

To analyze the rate of convergence with the odd-power r_{12} terms, we shall derive three Lemmas.

Lemma 1. For a sufficiently large l, the term $r_< - r_>$ accelerates the rate of convergence by $(l+a)^{-1}$, where a is a coefficient independent of l. More specifically, if a function can be written as $r_<^{l+n} r_>^{-l} f(r_>)$, where $f(r_>)$ is a function of $r_>$ and n is a non-negative integer, the following relation holds:

$$\int_0^{\infty}\int_0^{r_>} (r_< - r_>)\, r_<^{l+n} r_>^{-l} f(r_>)\, r_<^2 r_>^2 dr_< dr_> = [\,C(l+a)^{-1} + O((l+a)^{-2})]\int_0^{\infty}\int_0^{r_>} r_<^{l+n} r_>^{-l} f(r_>)\, r_<^2 r_>^2 dr_< dr_>, \quad (26)$$

where C is a coefficient independent of l. We assume all integrals involving $f(r_>)$ exist.

Proof. Equation (26) can be verified by a direct calculation. After integrating over $r_<$, we obtain

$$\begin{aligned}
&\int_0^{\infty}\int_0^{r_>} (r_< - r_>)\, r_<^{l+n} r_>^{-l} f(r_>)\, r_<^2 r_>^2 dr_< dr_> \\
&= -\frac{1}{(l+n+4)(l+n+3)}\int_0^{\infty} r_>^{n+6} f(r_>) dr_> = -\frac{1}{(l+a+n-a+4)(l+a+n-a+3)}\int_0^{\infty} r_>^{n+6} f(r_>) dr_> \\
&= -\frac{1}{(l+a)^2}\frac{1}{\left(1+\frac{n-a+4}{l+a}\right)\left(1+\frac{n-a+3}{l+a}\right)}\int_0^{\infty} r_>^{n+6} f(r_>) dr_> = -[(l+a)^{-2} + O((l+a)^{-3})]\int_0^{\infty} r_>^{n+6} f(r_>) dr_>, \\
&\qquad l > \max(-a, n-2a+4),
\end{aligned} \quad (27)$$

$$\begin{aligned}
&\int_0^{\infty}\int_0^{r_>} r_<^{l+n} r_>^{-l} f(r_>)\, r_<^2 r_>^2 dr_< dr_> = \frac{1}{l+n+3}\int_0^{\infty} r_>^{n+5} f(r_>) dr_> = [(l+a)^{-1} + O((l+a)^{-2})]\int_0^{\infty} r_>^{n+5} f(r_>) dr_>, \\
&\qquad l > \max(-a, n-2a+3).
\end{aligned} \quad (28)$$

In the third line of Eq. (27), we have used the expansion of the geometric series. The condition $l > \max(-a, n-2a+4)$ is determined by the convergence radius of the geometric series. A similar procedure was used in deriving Eq. (28). By comparing Eqs. (27) and (28), we can establish Eq. (26),

$$\begin{aligned}
&\frac{\int_0^{\infty}\int_0^{r_>} (r_< - r_>)\, r_<^{l+n} r_>^{-l} f(r_>)\, r_<^2 r_>^2 dr_< dr_>}{\int_0^{\infty}\int_0^{r_>} r_<^{l+n} r_>^{-l} f(r_>)\, r_<^2 r_>^2 dr_< dr_>} \\
&= -\frac{(l+a)^{-2}[1 + O((l+a)^{-1})]}{(l+a)^{-1}[1 + O((l+a)^{-1})]}\frac{\int_0^{\infty} r_>^{n+6} f(r_>) dr_>}{\int_0^{\infty} r_>^{n+5} f(r_>) dr_>} \\
&= -(l+a)^{-1}[1 + O((l+a)^{-1})][1 - O((l+a)^{-1}) + O((l+a)^{-2}) + \cdots]\frac{\int_0^{\infty} r_>^{n+6} f(r_>) dr_>}{\int_0^{\infty} r_>^{n+5} f(r_>) dr_>} \\
&= -[(l+a)^{-1} + O((l+a)^{-2})]\frac{\int_0^{\infty} r_>^{n+6} f(r_>) dr_>}{\int_0^{\infty} r_>^{n+5} f(r_>) dr_>}, \quad l > \max(-a, n-2a+4),
\end{aligned} \quad (29)$$

where $C = -\int_0^{\infty} r_>^{n+6} f(r_>) dr_> / \int_0^{\infty} r_>^{n+5} f(r_>) dr_>$. In the third line we used the expansion of geometric series for the term $1 + O((l+a)^{-1})$ in the denominator. ∎

Lemma 2. For a sufficiently large l, the term r_{12}^2 accelerates the rate of convergence by $(l+a)^{-2}$, where a is a coefficient independent of l. More specifically, the following relation holds:

$$\begin{aligned}
&\int_0^{\infty}\int_0^{\infty}\int_0^{\pi} r_{12}^{\nu+2}\, f(r_1,r_2) P_l(\cos\theta_{12}) \sin\theta_{12} r_1^2 r_2^2 d\theta_{12} dr_1 dr_2 \\
&= [\,C(l+a)^{-2} + O((l+a)^{-3})]\int_0^{\infty}\int_0^{\infty}\int_0^{\pi} r_{12}^{\nu}\, f(r_1,r_2)\, P_l(\cos\theta_{12}) \sin\theta_{12} r_1^2 r_2^2 d\theta_{12} dr_1 dr_2.
\end{aligned} \quad (30)$$

Here ν is an odd integer. C is coefficient independent of l. $f(r_1,r_2)$ is a symmetric function with respect to r_1 and r_2. It has the first-order partial derivative of $r_<$ with the following bound properties:

$$\left|\frac{\partial f(r_<,r_>)}{\partial r_<}\right| \leqslant \tilde{f}(r_>), \quad r_< \in (0,r_>), \tag{31}$$

where $\tilde{f}(r_>)$ is a function of $r_>$. We assume all integrals involving $f(r_1,r_2)$ and $\tilde{f}(r_>)$ exist. The condition (31) has been proposed by Goddard [2] to refine the proof of Hill [1]. This lemma characterizes the effect of increasing power of r_{12} in ansatz (9). In addition, the values of $a,C,$ and f are, in general, different in each lemma.

Proof. After applying the generalized-Laplace expansion for $r_{12}^{\nu+2}$ and integrating over θ_{12}, the left-hand side (LHS) of Eq. (30) becomes

$$2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>} R_{\nu+2,l}(r_<,r_>)\, f(r_<,r_>)r_<^2 r_>^2 dr_< dr_>. \tag{32}$$

We expand $f(r_<,r_>)$ with a Lagrange form of the remainder,

$$f(r_<,r_>) = f(r_>,r_>) + (r_< - r_>)\left.\frac{\partial f(r_<,r_>)}{\partial r_<}\right|_{r_<=\sigma}, \tag{33}$$

where $\sigma \in (r_<,r_>)$. Inserting Eq. (33) into Eq. (32), we obtain

$$\begin{aligned}&2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>} R_{\nu+2,l}(r_<,r_>)\, f(r_>,r_>)r_<^2 r_>^2 dr_< dr_>\\ &\quad+2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(r_<-r_>)R_{\nu+2,l}(r_<,r_>)\left.\frac{\partial f(r_<,r_>)}{\partial r_<}\right|_{r_<=\sigma} r_<^2 r_>^2 dr_< dr_>.\end{aligned} \tag{34}$$

By the properties (31), the second term in Eq. (34) has bounds

$$\begin{aligned}&2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(-1)^\nu(r_<-r_>)R_{\nu+2,l}(r_<,r_>)\tilde{f}(r_>)r_<^2 r_>^2 dr_< dr_>\\ &\quad\leqslant 2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(r_<-r_>)R_{\nu+2,l}(r_<,r_>)\left.\frac{\partial f(r_<,r_>)}{\partial r_<}\right|_{r_<=\sigma} r_<^2 r_>^2 dr_< dr_>\\ &\quad\leqslant -2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(-1)^\nu(r_<-r_>)R_{\nu+2,l}(r_<,r_>)\tilde{f}(r_>)r_<^2 r_>^2 dr_< dr_>.\end{aligned} \tag{35}$$

The upper and lower bounds in Eq. (35) are determined by the following properties of the $R_{\nu,l}$ function [31, Eq. (21)]:

$$R_{\nu,l}(r_<,r_>) = \frac{\left(-\frac{1}{2}\nu\right)_l}{\left(\frac{1}{2}\right)_l}\frac{r_<^l(r_>^2-r_<^2)^{\nu+2}}{r_>^{l+\nu+4}}\,{}_2F_1\left[l+\frac{1}{2}\nu+2,\frac{1}{2}\nu+\frac{3}{2};l+\frac{3}{2};\frac{r_<^2}{r_>^2}\right], \tag{36}$$

where ${}_2F_1$ is the hypergeometric function. Therefore $(-1)^\nu R_{\nu,l}(r_<,r_>) \geqslant 0$ for $l \geqslant \lfloor \nu/2 \rfloor$.

According to Lemma 1, the upper and lower bounds of Eq. (35) converge faster than the first term in Eq. (34). Therefore, the leading term of the large-L convergence is the first one in Eq. (34).

The expression $R_{\nu+2,l}(r_<,r_>)$ can be related to $R_{\nu,l}(r_<,r_>)$ by expanding $r_{12}^2 r_{12}^\nu$ in terms of the Legendre polynomial,

$$\begin{aligned}r_{12}^2 r_{12}^\nu &= (r_<^2+r_>^2-2r_<r_>\cos\theta_{12})\sum_{l=0}^{\infty}\sum_{k=0}^{(\nu+1)/2} C_{\nu lk} r_<^{l+2k} r_>^{\nu-l-2k} P_l(\cos\theta_{12})\\ &= \sum_{l=0}^{\infty}\sum_{k=0}^{(\nu+1)/2}\left[\left(C_{\nu lk}-\frac{2l+2}{2l+3}C_{\nu,l+1,k}\right)r_<^{l+2k+2}r_>^{\nu-l-2k}+\left(C_{\nu lk}-\frac{2l}{2l-1}C_{\nu,l-1,k}\right)r_<^{l+2k}r_>^{\nu-l-2k+2}\right]P_l(\cos\theta_{12}).\end{aligned} \tag{37}$$

In the first and second lines we have used the generalized-Laplace expansion [32,33], Eq. (23), and the recursive relation of the Legendre polynomial,

$$\cos\theta_{12}P_l(\cos\theta_{12}) = [l P_{l-1}(\cos\theta_{12}) + (l+1)P_{l+1}(\cos\theta_{12})]/(2l+1). \tag{38}$$

Therefore $R_{\nu+2,l}(r_<,r_>)$ is the expression inside the square brackets in Eq. (37),

$$R_{\nu+2,l}(r_<,r_>) = \left(C_{\nu lk}-\frac{2l+2}{2l+3}C_{\nu,l+1,k}\right)r_<^{l+2k+2}r_>^{\nu-l-2k}+\left(C_{\nu lk}-\frac{2l}{2l-1}C_{\nu,l-1,k}\right)r_<^{l+2k}r_>^{\nu-l-2k+2}. \tag{39}$$

With the help of the explicit expression (25), the relation between $C_{\nu l+1k}$ and $C_{\nu lk}$ is

$$C_{\nu,l+1,k} = \frac{(l+3/2)(l+k-\nu/2)}{(l+1/2)(l+k+3/2)}\,C_{\nu lk}. \tag{40}$$

Inserting Eqs. (39) and (40) into the first term in Eq. (34), then integrating over $r_<$, we obtain

$$\begin{aligned}&\int_0^\infty\int_0^\infty\int_0^\pi r_{12}^{\nu+2}\,f(r_1,r_2)P_l(\cos\theta_{12})\sin\theta_{12}r_1^2r_2^2d\theta_{12}dr_1dr_2\\ &\quad= 2(l+1/2)^{-1}[\,C'(l+a)^{-3}+O((l+a)^{-4})]\sum_{k=0}^{(\nu+1)/2}C_{\nu lk}\int_0^\infty r_>^{\nu+7}f(r_>,r_>)dr_>,\end{aligned} \tag{41}$$

for a sufficiently large l. Here $C' = -\frac{\nu^2}{4} - \frac{5}{2}\upsilon - \frac{17}{4}$. Similarly, the right-hand side (RHS) of Eq. (30) can be written as

$$\begin{aligned}&\int_0^\infty\int_0^\infty\int_0^\pi r_{12}^{\nu}f(r_1,r_2)P_l(\cos\theta_{12})\sin\theta_{12}r_1^2r_2^2d\theta_{12}dr_1dr_2\\ &\quad= 2(l+1/2)^{-1}[\,(l+a)^{-1}+O((l+a)^{-2})]\sum_{k=0}^{(\nu+1)/2}C_{\nu lk}\int_0^\infty r_>^{\nu+5}f(r_>,r_>)dr_>.\end{aligned} \tag{42}$$

By comparing Eqs. (41) and (42), we have established Eq. (30). The procedure of obtaining the coefficient C is similar with Eq. (29). ■

Lemma 3. For a sufficiently large l, the operator $\hat{U}_1$ accelerates the rate of convergence by $(l+a)^{-2}$, where a is a coefficient independent of l. More specifically, the following relation holds:

$$\begin{aligned}&\int_0^\infty\int_0^\infty\int_0^\pi \hat{U}_1 f(r_1,r_2)P_l(\cos\theta_{12})\,\sin\theta_{12}r_1^2r_2^2d\theta_{12}dr_1dr_2\\ &\quad= [\,C(l+a)^{-2}+O((l+a)^{-3})]\int_0^\infty\int_0^\infty\int_0^\pi r_{12}^{-1}\,f(r_1,r_2)\,P_l(\cos\theta_{12})\,\sin\theta_{12}r_1^2r_2^2d\theta_{12}dr_1dr_2.\end{aligned} \tag{43}$$

Here $f(r_1,r_2)$ is a symmetric function with respect to r_1 and r_2. It is assumed to be first-order differentiable. The first-order derivatives of $f(r_1,r_2)$ are not necessarily symmetric. We can define the symmetric and antisymmetric parts of the first-order derivatives as

$$f_\pm^{(1)}(r_1,r_2) := \frac{1}{2}\left[\frac{\partial f(r_1,r_2)}{\partial r_1} \pm \frac{\partial f(r_1,r_2)}{\partial r_2}\right], \tag{44}$$

and assume the following bound properties:

$$\left|\frac{\partial f_+^{(1)}(r_<,r_>)}{\partial r_<}\right| \leqslant \tilde{f}_+(r_>),\quad r_<\in(0,r_>), \tag{45}$$

$$\left|\frac{\partial^2 f_-^{(1)}(r_<,r_>)}{\partial r_<^2}\right| \leqslant \tilde{f}_-(r_>),\quad r_<\in(0,r_>). \tag{46}$$

This lemma characterizes the regularity of the operator $\hat{U}_1$.

Proof. From Eq. (44), we have

$$\frac{\partial f(r_1,r_2)}{\partial r_1} = f_+^{(1)}(r_1,r_2) + f_-^{(1)}(r_1,r_2), \tag{47}$$

$$\frac{\partial f(r_1,r_2)}{\partial r_2} = f_+^{(1)}(r_1,r_2) - f_-^{(1)}(r_1,r_2). \tag{48}$$

Inserting Eqs. (47) and (48) into the LHS of Eq. (43), with the help of the Laplace expansion (23), and the recursive relation of the Legendre polynomial (38), we obtain

$$\begin{aligned}&\int_0^\infty\int_0^\infty\int_0^\pi \hat{U}_1 f(r_1,r_2)P_l(\cos\theta_{12})\,\sin\theta_{12}r_1^2r_2^2d\theta_{12}dr_1dr_2\\ &= -2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}\left[(r_<+r_>)\left(\frac{r_<^l}{r_>^{l+1}} - \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} - \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^l}\right)f_+^{(1)}(r_<,r_>)\right.\\ &\quad\left. + (r_<-r_>)\left(\frac{r_<^l}{r_>^{l+1}} + \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} + \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^l}\right)f_-^{(1)}(r_<,r_>)\right]r_<^2r_>^2dr_<dr_>.\end{aligned} \tag{49}$$

Applying the Taylor expansion for $f_{\pm}^{(1)}(r_<,r_>)$ with Lagrange forms of the remainders,

$$f_{+}^{(1)}(r_<,r_>) = f_{+}^{(1)}(r_>,r_>) + (r_< - r_>)\frac{\partial f_{+}^{(1)}(r_<,r_>)}{\partial r_<}\bigg|_{r_<=\sigma_+}, \quad \sigma_+ \in (r_<,r_>), \tag{50}$$

$$f_{-}^{(1)}(r_<,r_>) = f_{-}^{(1)}(r_>,r_>) + (r_< - r_>)\frac{\partial f_{-}^{(1)}(r_<,r_>)}{\partial r_<}\bigg|_{r_<=r_>} + \frac{(r_< - r_>)^2}{2}\frac{\partial^2 f_{-}^{(1)}(r_<,r_>)}{\partial r_<^2}\bigg|_{r_<=\sigma_-}, \quad \sigma_- \in (r_<,r_>), \tag{51}$$

and noticing $f_{-}^{(1)}(r_>,r_>) = 0$, we obtain the leading term of Eq. (49) as

$$-2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}\left[(r_< + r_>)\left(\frac{r_<^l}{r_>^{l+1}} - \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} - \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^{l}}\right)f_{+}^{(1)}(r_>,r_>)\right.$$
$$\left. + (r_< - r_>)^2\left(\frac{r_<^l}{r_>^{l+1}} + \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} + \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^{l}}\right)\frac{\partial f_{-}^{(1)}(r_<,r_>)}{\partial r_<}\bigg|_{r_<=r_>}\right]r_<^2 r_>^2\, dr_< dr_>. \tag{52}$$

Here we have used the bound properties (45) and (46) and Lemma 1 to isolate the leading term. Namely by observing for $l \geqslant 1$

$$2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(r_< + r_>)(r_< - r_>)\frac{(2l-1)\left[(l+1)r_< - (l+2)r_>\right](r_< - r_>) + 2r_>^2}{(2l-1)(2l+3)}\frac{r_<^{l-1}}{r_>^{l+2}}\tilde{f}_{+}(r_>)r_<^2 r_>^2\, dr_< dr_>$$
$$\leqslant -2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(r_< + r_>)(r_< - r_>)\left(\frac{r_<^l}{r_>^{l+1}} - \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} - \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^{l}}\right)\frac{\partial f_{+}^{(1)}(r_<,r_>)}{\partial r_<}\bigg|_{r_<=\sigma_+} r_<^2 r_>^2\, dr_< dr_>$$
$$\leqslant -2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}(r_< + r_>)(r_< - r_>)\frac{(2l-1)\left[(l+1)r_< - (l+2)r_>\right](r_< - r_>) + 2r_>^2}{(2l-1)(2l+3)}\frac{r_<^{l-1}}{r_>^{l+2}}\tilde{f}_{+}(r_>)r_<^2 r_>^2\, dr_< dr_> \tag{53}$$

and

$$2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}\frac{(r_< - r_>)^3}{2}\left(\frac{r_<^l}{r_>^{l+1}} + \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} + \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^{l}}\right)\tilde{f}_{-}(r_>)r_<^2 r_>^2\, dr_< dr_>$$
$$\leqslant -2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}\frac{(r_< - r_>)^3}{2}\left(\frac{r_<^l}{r_>^{l+1}} + \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} + \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^{l}}\right)\frac{\partial^2 f_{-}^{(2)}(r_<,r_>)}{\partial r_<^2}\bigg|_{r_<=\sigma_-} r_<^2 r_>^2\, dr_< dr_>$$
$$\leqslant -2(l+1/2)^{-1}\int_0^\infty\int_0^{r_>}\frac{(r_< - r_>)^3}{2}\left(\frac{r_<^l}{r_>^{l+1}} + \frac{l+1}{2l+3}\frac{r_<^{l+1}}{r_>^{l+2}} + \frac{l}{2l-1}\frac{r_<^{l-1}}{r_>^{l}}\right)\tilde{f}_{-}(r_>)r_<^2 r_>^2\, dr_< dr_>, \tag{54}$$

the upper and lower bounds in Eqs. (53) and (54) converge faster than Eq. (52).

Similar to Lemma 1, the term $(r_< + r_>)$ will not affect the inverse-power law of the rate of convergence. By repeatedly using Lemma 1, the term $(r_< - r_>)^2$ will accelerate the rate of convergence by $(l+a)^{-2}$. Thus Eq. (52) and the LHS of Eq. (43) is $O((l+a)^{-3})$. Similarly the integral in the RHS of Eq. (43) converges as $O((l+a)^{-1})$. Therefore we have established Eq. (43). ■

2. Large-L behavior for the first-order wave function under ansatz (9)

With the help of these lemmas, we shall now analyze the rate of convergence in Eq. (20). The following derivations will be based on three assumptions of the analytic structure of the exact first-order wave function ψ: (i) ψ has continuous partial derivatives, $\partial^n\psi/\partial r_{12}^n$, $n = 0,1,2,\ldots,N+2$ and

$$\int_{|r_1-r_2|}^{r_1+r_2}\left|\frac{\partial^{N+3}\psi}{\partial r_{12}^{N+3}}\right|^2 dr_{12} < \infty, \tag{55}$$

$$\int_0^\infty r_1^2 dr_1\int_0^\infty r_2^2 dr_2\, r_>^5\int_{|r_1-r_2|}^{r_1+r_2}\left|\frac{\partial^{N+3}\psi}{\partial r_{12}^{N+3}}\right|^2 dr_{12} < \infty; \tag{56}$$

(ii) ψ has the mixed partial derivatives of $\partial^{i+j+k+1}\psi/\partial r_<^{i+k}\partial r_{12}^{j+1}$ for $i+j \leqslant N+2$, $k = 0,1,2$ with the following bound properties:

$$\left|\frac{\partial^{i+j+k+1}\psi}{\partial r_<^{i+k}\partial r_{12}^{j+1}}\right| \leqslant \tilde{A}(r_>), \quad i+j = N+2,$$
$$k = 0,1,2, \quad r_< \in (0,r_>), \tag{57}$$

where $\tilde{A}(r_>)$ is a function of $r_>$; (iii) all integrals in the derivation exist.

The rate of convergence may be derived from weaker or alternative assumptions of the exact first-order wave function, such as Eq. (62). However, investigating this possibility is beyond the scope of the present study. It is also possible that neither the assumptions of the first-order wave function nor the derived rates of convergence are strictly valid. Under a reasonable range of numerical accuracy, the derived rates of convergence are approximately valid.

Similar to Eq. (B14), we first apply Hill's theorem II [1] at $2J-1=N+3$ with the help of assumption (i),

$$\begin{aligned}\psi_l(r_1,r_2) &:= \frac{2l+1}{2}\int_0^\pi \psi(r_1,r_2,r_{12})P_l(\cos\theta_{12})\sin\theta_{12}d\theta_{12}\\ &= \sum_{n=0}^{N+3}\left.\frac{\partial^n\psi}{\partial r_{12}^n}\right|_{r_{12}=|r_1-r_2|}\xi_{nl}(r_1,r_2)+\Omega_{\lfloor(N+4)/2\rfloor,l}(r_1,r_2)\\ &= \sum_{n=0}^{N+3}\sum_{m=0}^{n}\frac{1}{n!}\binom{n}{m}(-|r_1-r_2|)^m R_{n-m,l}\left.\frac{\partial^n\psi}{\partial r_{12}^n}\right|_{r_{12}=|r_1-r_2|}+\Omega_{\lfloor(N+4)/2\rfloor,l}(r_1,r_2)\\ &= \sum_{n=0}^{N+3}\frac{R_{nl}}{n!}\left[\sum_{m=0}^{N-n+3}\frac{(-|r_1-r_2|)^m}{m!}\left.\frac{\partial^{n+m}\psi}{\partial r_{12}^{n+m}}\right|_{r_{12}=|r_1-r_2|}\right]+\Omega_{\lfloor(N+4)/2\rfloor,l}(r_1,r_2),\end{aligned}\tag{58}$$

where $\xi(r_1,r_2)$ and $\Omega_{JI}(r_1,r_2)$ are defined in Eqs. (89)–(B6).

By comparing expansion (58) and ansatz (9), we identify

$$\begin{aligned}\chi_l = &\sum_{n=1,3,5,\dots}^{N+2}\frac{R_{nl}}{n!}\left[\frac{(-|r_1-r_2|)^{N-n+2}}{(N-n+2)!}\left.\frac{\partial^{N+2}\psi}{\partial r_{12}^{N+2}}\right|_{r_{12}=|r_1-r_2|}\right]+\sum_{n=1,3,5,\dots}^{N+3}\frac{R_{nl}}{n!}\left[\frac{(-|r_1-r_2|)^{N-n+3}}{(N-n+3)!}\left.\frac{\partial^{N+3}\psi}{\partial r_{12}^{N+3}}\right|_{r_{12}=|r_1-r_2|}\right]\\ &+\Omega_{\lfloor(N+4)/2\rfloor,l},\quad l\geqslant\left\lfloor\frac{N+3}{2}\right\rfloor,\end{aligned}\tag{59}$$

since N is an odd number in ansatz (9) and the terms with even power of r_{12} have finite PWE.

Furthermore, we can use assumption (ii) to perform a series expansion for Φ_n and χ_l in analogy with Eqs. (B31), (B50), and (B51). Namely by expanding $\partial^{n+m}\psi/\partial r_{12}^{n+m}$ in Φ_n (11) and $\partial^{N+2}\psi/\partial r_{12}^{N+2}$ and $\partial^{N+3}\psi/\partial r_{12}^{N+3}$ in χ_l (59) for variables $r_<$ and r_{12} at $r_<=r_>$ and $r_{12}=0$, Eqs. (11) and (59) become

$$\Phi_n = \frac{1}{n!}\left[\sum_{m=0}^{N-n+2}\frac{(r_<-r_>)^m}{m!}\left.\frac{\partial^{m+n}\psi}{\partial r_<^m\partial r_{12}^n}\right|_{\substack{r_<=r_>,\\ r_{12}=0}}+\frac{(r_<-r_>)^{N-n+3}}{(N-n+3)!}\left.\frac{\partial^{N+3}\psi}{\partial r_<^{N-n+3}\partial r_{12}^n}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}}\right]\tag{60}$$

$$\begin{aligned}\chi_l = &\frac{R_{N+2,l}}{(N+2)!}\left[\left.\frac{\partial^{N+2}\psi}{\partial r_{12}^{N+2}}\right|_{\substack{r_<=r_>,\\ r_{12}=0}}+(r_<-r_>)\left.\frac{\partial^{N+3}\psi}{\partial r_<\partial r_{12}^{N+2}}\right|_{\substack{r_<=\sigma',\\ r_{12}=\tau'}}\right]\\ &+\frac{R_{N+3,l}}{(N+3)!}\left[\left.\frac{\partial^{N+3}\psi}{\partial r_{12}^{N+3}}\right|_{\substack{r_<=r_>,\\ r_{12}=0}}+(r_<-r_>)\left.\frac{\partial^{N+4}\psi}{\partial r_<\partial r_{12}^{N+3}}\right|_{\substack{r_<=\sigma'',\\ r_{12}=\tau''}}\right]+\Omega_{\lfloor(N+4)/2\rfloor,l},\end{aligned}\tag{61}$$

where $\sigma,\sigma',\sigma''\in(r_<,r_>)$ and $\tau,\tau',\tau''\in(r_>-r_<,r_>+r_<)$.

Since Eqs. (60) and (61) only contain information at the coalescence region, they are somehow more transparent than ansatz (9). Equation (61) indicates that χ is $O(r_{12}^{N+2})$.

In addition, assumption (ii) is mainly used to connect to the original ansatz in the $R12$ approach [7], i.e., $\Phi_1=\Phi/2$. As we shall see, both $n=1$ in Eq. (60) and $\Phi_1=\Phi/2$ can suppress the contribution of $\langle\chi|-m(m+1)r_{12}^{m-2}|\Phi_m\rangle+\langle\chi|r_{12}^{-1}|\Phi_m\rangle$ in Eq. (20) when $m=1$. Therefore we do not have a contribution of $O(L^{-6})$, if the $N\geqslant 1$ geminal function is used in ansatz (9). Numerical results [7] suggest that the $O(L^{-6})$ rate of convergence does not appear in the $R12$ calculations. Therefore assumption (ii) is numerically supported for $n=1$.

As we shall discuss later, a similar cancellation of $O(L^{-6})$ does not appear in $n>1$ terms from ansatz (9). For $n>1$, the assumption (ii) may be weakened to

$$\left|\frac{\partial^{N+i+2}\psi}{\partial r_<^i\partial r_{12}^{N+2}}\right|\leqslant\tilde{A}(r_>),\quad i=1,2,3,\quad r_<\in(0,r_>).\tag{62}$$

The expressions of Φ_n and χ_l will be rather complicated. They do not necessarily coincide with Eqs. (60) and (61). Investigating the weaker assumptions and further evaluating the prefactors of the rates of convergence are beyond the scope of the present study.

3. *Termwise large-L rates of convergence for the PWE with odd-power r_{12} functions*

Now we turn to analyze the rate of convergence in Eq. (20). In the beginning of the development of the $R12$ method [7], Φ_1 was chosen as $\Phi/2$ according to the large-L behavior of the first-order wave function, Eq. (21). It leads to a highly remarkable consequence. Namely, in Eq. (20) $\langle\chi|-m(m+1)r_{12}^{m-2}|\Phi_m\rangle$ will be canceled with $\langle\chi|r_{12}^{-1}|\Phi_m\rangle$ when $m=1$ [7,8]. Under our assumptions of the first-order wave function, $\Phi_1=\Phi/2$ includes Eq. (60) when $n=1$.

We can use a weaker condition (60) than $\Phi_1=\Phi/2$ to show that the term $\langle\chi|-m(m+1)r_{12}^{m-2}|\Phi_m\rangle+\langle\chi|r_{12}^{-1}|\Phi_m\rangle$, $m=1$, contributes to the rate of convergence higher than the leading order. First we notice when $n = 1$ Eq. (60) becomes

$$\Phi_1 = \frac{1}{2}\sum_{m=0}^{N+1}\frac{(r_< - r_>)^m}{m!}\frac{\partial^m \Phi}{\partial r_<^m}\bigg|_{r_<=r_>} + O((r_< - r_>)^{N+2}) \tag{63}$$

thus

$$\begin{aligned}\langle\chi| - 2r_{12}^{-1}|\Phi_1\rangle + \langle\chi|r_{12}^{-1}|\Phi\rangle \\ = -16\pi^2(l+1/2)^{-1} \\ \times\int_0^\infty\int_0^{r_>}\chi_l\,R_{-1,l}\,(2\Phi_1 - \Phi)\,r_<^2 r_>^2 dr_< dr_>.\end{aligned} \tag{64}$$

Equation (64) converges as $O(L^{-2N-7})$ for the increments, i.e., $E_2(L) - E_2(L-1)$. Hereafter the rate of convergence means the incremental rate. The $O(L^{-2N-7})$ rate of convergence can be seen from Eq. (61), that the leading term of χ_l is $\partial^{N+2}\psi/\partial r_{12}^{N+2}R_{N+2,l}$. In analogy with Eq. (B54), $2\Phi_1 - \Phi$ is of order $O((r_< - r_>)^{N+2})$. By Lemmas 1 and 2, we obtain $O(L^{-2N-7})$ rate of convergence for Eq. (64). By the Cauchy-Schwartz inequality, the remainder $\Omega_{\lfloor(N+4)/2\rfloor}$ converges as $o(L^{-2N-7})$. The derivation is similar to Eq. (B42).

Therefore, in Eq. (20), $\langle\chi| - m(m+1)r_{12}^{m-2}|\Phi_m\rangle$ will be canceled by $\Phi_1 = \Phi/2$ [7] or suppressed to $O(L^{-2N-7})$, for $m = 1$. For $m \geqslant 3$, by repeatedly using Lemma 2, we see that its increment converges as $O(L^{-N-m-4})$. The contribution from the remainder $\Omega_{\lfloor(N+4)/2\rfloor}$ converges as $o(L^{-N-m-4})$. The rate of convergence for $\sum_m\langle\chi| - m(m+1)r_{12}^{m-2}|\Phi_m\rangle$ is determined by the slowest converged component, $m = 3$. Therefore it converges as $O(L^{-N-7})$.

$\langle\chi|\hat{U}_m|\Phi_m\rangle$ converges as $O(L^{-N-m-6})$ according to Lemmas 2 and 3. The contribution from the remainder $\Omega\lfloor(N+4)/2\rfloor$ converges as $o(L^{-N-m-6})$. Here the minimum value of m with nonzero contribution is 1. Therefore the rate of convergence is $O(L^{-N-7})$.

$\langle\chi|r_{12}^m(\hat{H}_0 - E_0)|\Phi_m\rangle$ either disappears by $\Phi_1 = \Phi/2$ or is suppressed to $O(L^{-3N-8})$ by Eq. (61), for $m = 1$. For $m \geqslant 3$, it converges as $O(L^{-N-m-6})$. The remainder $\Omega_{\lfloor(N+4)/2\rfloor}$ converges as $o(L^{-N-m-6})$. Since the slowest component is determined by $m = 3$, it converges as $O(L^{-N-9})$.

$\langle\chi|\hat{H}'|\Phi\rangle$ is canceled by $\Phi_1 = \Phi/2$ or suppressed to $O(L^{-2N-7})$ by Eq. (61). The last term, $-\langle\chi|E_1|\Phi\rangle$, only contributes to the s-type increment of the PWE. Therefore the total rate of convergence of Eq. (20) is $O(L^{-N-7})$. The fast convergence of ansatz (9) is intuitive. Since all odd-power r_{12} functions have infinite PWE, unitizing such terms will yield a compact representation of the ground state.

III. NUMERICAL RESULTS FOR THE 1/Z EXPANSION

Here we present some numerical results for the second-order $1/Z$-expansion energy under the ansatz (7). Our wave function is a modification of the basis F in Schwartz's article [20],

$$\begin{aligned}\tilde{\psi} = &\sum_{\lambda\mu\nu\xi} a_{\lambda\mu\nu\xi}s^\lambda(t/s)^\mu(u/s)^\nu(\ln s)^\xi e^{-\alpha s} \\ &+ \sum_{\lambda\mu\xi l} b_{\lambda\mu\xi l}s^\lambda(t/s)^\mu(\ln s)^\xi e^{-\alpha s}P_l(\cos\theta_{12});\end{aligned} \tag{65}$$

here the coordinates $s := r_1 + r_2, t := r_2 - r_1$, and $u := r_{12}$. The indices λ, μ, ν, and ξ are non-negative integers. The order of basis function is defined by $0 \leqslant \lambda + \mu + \nu \leqslant \omega$. In each order, $\xi = 0,1$. Since we shall variationally optimize the wave function and energy, the superscript $\sim$ is used according to the notations in Eqs. (7) and (8). The wave function (65) corresponds to

$$\tilde{\Phi}_\nu = \sum_{\lambda\mu\xi} a_{\lambda\mu\nu\xi}\, s^{\lambda-\mu-\nu}\, t^\mu\,(\ln s)^\xi e^{-\alpha s}, \tag{66}$$

$$\tilde{\chi}_l = \sum_{\lambda\mu\xi} b_{\lambda\mu\xi l}\, s^{\lambda-\mu}\, t^\mu\,(\ln s)^\xi e^{-\alpha s}, \tag{67}$$

in the ansatz (7). We fix $\tilde{\Phi}_1 = \Phi/2 = e^{-s}/2\pi$ according to the cusp condition, Eq. (21) [8]. Similar relations to Eq. (21) for the higher-order derivatives at two-particle-coalescence points have been obtained [34,35]. It is highly interesting to investigate the computational approaches employing such conditions [34,35]. Nevertheless this possibility is beyond the scope of the present study. We use Eq. (66) to represent them.

Besides describing the three-particle-coalescence singularity [36–39] from the logarithmic function in Eqs. (65)–(67), a practical reason to adopt this basis is that setting $\alpha = 1$ will give fairly good variational energies. We simply would like to avoid the optimization for the exponents.

The numerical results are presented in Table I and Fig. 1. Detailed data are given in the Supplemental Material [25]. The L^{-8}, L^{-10}, and L^{-12} rates of convergence are observed.

In addition, we notice that at higher accuracies the radial saturation becomes increasingly difficult. Since it is insufficient to conclude the asymptotic behavior from numerical study, we stop the calculation slightly beyond the finite nuclear effect. The finite nuclei correction of the ^{4}He ground state is about 5.7×10^{-9} a.u. [40]. It is possible that the present rates of convergence break down at higher accuracies due to certain nondifferentiability of the exact first-order wave function.

IV. ANALYSIS OF RATE OF CONVERGENCE IN THE RAYLEIGH-RITZ VARIATIONAL CALCULATIONS

A. Ansatz for the PWE with odd-power r_{12} functions

Similar with the $1/Z$ expansion, we consider the following ansatz:

$$\begin{aligned}\tilde{\psi}(r_1,r_2,r_{12}) = \tilde{\Phi}_0(r_1,r_2) + \sum_{n=1,3,5,\ldots}^{N} r_{12}^n\tilde{\Phi}_n(r_1,r_2) \\ + \tilde{\chi}(r_1,r_2,\theta_{12}),\end{aligned} \tag{68}$$

$$\tilde{\chi}(r_1,r_2,\theta_{12}) := \sum_{l=0}^{L}\tilde{\chi}_l(r_1,r_2)P_l(\cos\theta_{12}). \tag{69}$$

The general scheme of evaluating the rate of convergence for a Rayleigh-Ritz variational calculation was established [1]. We first briefly restate the formulation of Hill [1]. Consider a trial vector $|\tilde{\psi}\rangle$ in a variational calculation, $|\tilde{\psi}\rangle = \sum_{i=1}^N c_i|\phi_i\rangle$, where c_i and $|\phi_i\rangle$ are the linear parameter and basis vector, respectively. c_i is optimized to yield a stationary energy. Define $G_{ij}^{(N)}$ as the inverse of the Gram matrix $\sum_{k=1}^N\langle\phi_i|\phi_k\rangle G_{kj}^{(N)} = \sum_{k=1}^N G_{ik}^{(N)}\langle\phi_k|\phi_j\rangle = \delta_{ij}$. Let $\hat{P}_N$ be a projection operator for

TABLE I. Rates of convergence of the PWE increments for the second-order-$1/Z$ expansion energy of the ground-state helium atom. $\omega = 30$ is used. The atomic units are adopted.

	$\lvert\tilde{E}_2(L) - \tilde{E}_2(L-1)\rvert$		
L	$r_{12}\tilde{\Phi}_1 + \tilde{\chi}$	$r_{12}\tilde{\Phi}_1 + r_{12}^3\tilde{\Phi}_3 + \tilde{\chi}$	$r_{12}\tilde{\Phi}_1 + r_{12}^3\tilde{\Phi}_3 + r_{12}^5\tilde{\Phi}_5 + \tilde{\chi}$
0[a]	1.179×10^{-1}	1.543×10^{-1}	1.570×10^{-1}
1	3.921×10^{-2}	3.346×10^{-3}	6.370×10^{-4}
2	4.821×10^{-4}	1.260×10^{-5}	1.049×10^{-6}
3	3.444×10^{-5}	4.555×10^{-7}	2.840×10^{-8}
4	4.858×10^{-6}	4.255×10^{-8}	2.640×10^{-9}
5	1.012×10^{-6}	6.841×10^{-9}	4.592×10^{-10}
6	2.726×10^{-7}	1.561×10^{-9}	1.133×10^{-10}
7	8.830×10^{-8}	4.621×10^{-10}	3.614×10^{-11}
8	3.285×10^{-8}	1.338×10^{-10}	
9	1.361×10^{-8}		
10	6.155×10^{-9}		
11	2.989×10^{-9}		
ΔE[b]	3.729×10^{-9}	1.575×10^{-10}	2.793×10^{-11}

[a]The energy of $\lvert\tilde{E}_2(L)\rvert$, $L = 0$.
[b]Total energy at the largest L subtracts a reference value, $-0.157\,666\,429\,469\,150\,941\,056\,6$ a.u., obtained from a 3092-term expansion of the basis-F wave function with $\omega = 25$. The digits are expected to be converged by comparing with $\omega = 24$.

the trial vector, $\hat{P}_N := \sum_{i=1}^N \sum_{j=1}^N G_{ij}^{(N)} |\phi_i\rangle\langle\phi_j|$. To analyze the rate of convergence, the exact eigenvector $|\psi\rangle$ is decomposed into the reference vectors $|\psi^{(a)}\rangle$ and $|\psi^{(b)}\rangle$, which belong to the vectors in a finite dimensional space and the outside remainder. $|\psi^{(a)}\rangle$ is in the range of $\hat{P}_N$, namely $\hat{P}_N|\psi^{(a)}\rangle = |\psi^{(a)}\rangle$. By introducing the projection operators $\hat{P}^{(a)} := |\psi^{(a)}\rangle\langle\psi^{(a)}|\psi^{(a)}\rangle^{-1}\langle\psi^{(a)}|$, $\hat{P}_\perp^{(a)} := \hat{P}_N - \hat{P}^{(a)}$, and a generalized inverse $\hat{A}$, such that $[\hat{P}_\perp^{(a)}\hat{H}\hat{P}_\perp^{(a)} - \tilde{E}\hat{P}_\perp^{(a)}]\hat{A} = \hat{A}[\hat{P}_\perp^{(a)}\hat{H}\hat{P}_\perp^{(a)} - \tilde{E}\hat{P}_\perp^{(a)}] = \hat{P}_\perp^{(a)}$, the error of energy can be written as

$$\tilde{E} - E = \langle\psi^{(b)}|\hat{H}|\psi^{(b)}\rangle + R_1 + R_2 + R_3, \tag{70}$$

$$R_1 := [\langle\psi^{(a)}|\psi^{(a)}\rangle^{-1} - 1]\langle\psi^{(b)}|\hat{H}|\psi^{(b)}\rangle, \tag{71}$$

$$R_2 := -E\langle\psi^{(a)}|\psi^{(a)}\rangle^{-1}\langle\psi^{(b)}|\psi^{(b)}\rangle, \tag{72}$$

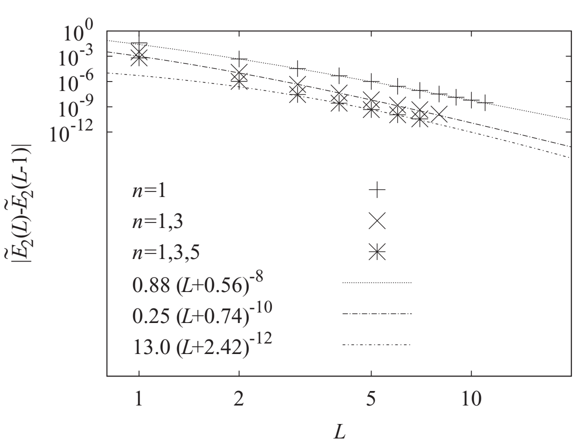

FIG. 1. $\lvert\tilde{E}_2(L) - \tilde{E}_2(L-1)\rvert$ vs L plot for the second-order $1/Z$ energy. The lines are obtained by numerical fittings from $L \geqslant \frac{N+3}{2}$ points. n indicates the odd-power r_{12} functions used in the ansatz (7). Atomic units are used in the figure.

$$R_3 := -\langle\psi^{(a)}|\psi^{(a)}\rangle^{-1}\langle\psi^{(b)}|(\hat{H}-E)\hat{P}_\perp^{(a)}\hat{A}\hat{P}_\perp^{(a)}(\hat{H}-E)|\psi^{(b)}\rangle, \tag{73}$$

where $\tilde{E}$ and E are the variational and exact eigenvalues, respectively. The exact wave function belongs to C^∞ class (any order differentiable) everywhere except for the coalescence points [41]. At these coalescence points, the existence of the first-order partial derivative with r_1, r_2, and r_{12} was proved [37,41–43]. We assume the existence of the partial derivatives in Eq. (76) for $n \geqslant 2$.

Similar with the $1/Z$ expansion, we choose the reference functions $\psi^{(a)}$ and $\psi^{(b)}$ as

$$\psi^{(a)}(r_1,r_2,r_{12}) := \Phi_0(r_1,r_2) + \sum_{n=1,3,5,\ldots}^{N} r_{12}^n \Phi_n(r_1,r_2) + \sum_{l=0}^{L} \chi_l(r_1,r_2) P_l(\cos\theta_{12}), \tag{74}$$

$$\psi^{(b)}(r_1,r_2,r_{12}) := \sum_{l=L+1}^{\infty} \chi_l(r_1,r_2) P_l(\cos\theta_{12}), \tag{75}$$

$$\Phi_n(r_1,r_2) := \frac{1}{n!}\left[\sum_{m=0}^{N-n+1} \frac{(-|r_1-r_2|)^m}{m!} \left.\frac{\partial^{n+m}\psi}{\partial r_{12}^{n+m}}\right|_{r_{12}=|r_1-r_2|}\right], \tag{76}$$

$$\chi_l(r_1,r_2) := \frac{2l+1}{2}\int_0^\pi \Big[\psi(r_1,r_2,r_{12}) - \Phi_0(r_1,r_2) - \sum_{n=1,3,5,\ldots}^{N} r_{12}^n \Phi_n(r_1,r_2)\Big] P_l(\cos\theta_{12}) \sin\theta_{12} d\theta_{12}. \tag{77}$$

Here ψ is the exact ground-state helium wave function. The difference between the trial and reference functions is related to

$\hat{P}_{\perp}^{(a)}$. As discussed in the $1/Z$ expansion, we only focus on the rate of convergence from the reference functions. By choosing $\phi = \tilde{\psi} = \psi^{(a)}$, we have $\hat{P}_N = \hat{P}^{(a)}$, $\hat{P}_{\perp}^{(a)} = 0$, $|\tilde{\psi}^{(a)}\rangle := \hat{P}^{(a)}|\tilde{\psi}\rangle = |\psi^{(a)}\rangle$, and $|\tilde{\psi}_{\perp}^{(a)}\rangle := \hat{P}_{\perp}^{(a)}|\tilde{\psi}\rangle = 0$. Therefore the partition equations (3.15) and (3.16) in Ref. [1],

$$\hat{P}^{(a)}\hat{H}\hat{P}^{(a)}|\tilde{\psi}^{(a)}\rangle + \hat{P}^{(a)}\hat{H}\hat{P}_{\perp}^{(a)}|\tilde{\psi}_{\perp}^{(a)}\rangle = \tilde{E}\hat{P}^{(a)}|\tilde{\psi}^{(a)}\rangle, \quad (78)$$

$$\hat{P}_{\perp}^{(a)}\hat{H}\hat{P}^{(a)}|\tilde{\psi}^{(a)}\rangle + \hat{P}_{\perp}^{(a)}\hat{H}\hat{P}_{\perp}^{(a)}|\tilde{\psi}_{\perp}^{(a)}\rangle = \tilde{E}\hat{P}_{\perp}^{(a)}|\tilde{\psi}_{\perp}^{(a)}\rangle \quad (79)$$

become

$$\hat{P}^{(a)}\hat{H}\hat{P}^{(a)}|\tilde{\psi}\rangle = \tilde{E}\hat{P}^{(a)}|\tilde{\psi}\rangle, \quad (80)$$

$$0 = 0, \quad (81)$$

respectively. By a similar manipulation as in Ref. [1], the expressions of error of energy are the same as Eqs. (70)–(73), except $R_3 = 0$.

B. Termwise rates of convergence for the PWE with odd-power r_{12} functions

With the help of the quantity

$$\phi_l(r_1,r_2) := \frac{2l+1}{2}\int_0^{\pi} r_{12}^{-1}\Big[\psi(r_1,r_2,r_{12}) - \Phi_0(r_1,r_2) - \sum_n r_{12}^n\Phi_n(r_1,r_2)\Big]P_l(\cos\theta_{12})\sin\theta_{12}d\theta_{12}, \quad (82)$$

the term $\langle\psi^{(b)}|\hat{H}|\psi^{(b)}\rangle$ in Eq. (70) can be written as

$$\langle\psi^{(b)}|\hat{H}|\psi^{(b)}\rangle = W_1 + W_2 + W_3 + E\langle\psi^{(b)}|\psi^{(b)}\rangle, \quad (83)$$

$$W_1 = -8\pi^2\sum_{l=L+1}^{\infty}\frac{2}{2l+1}\times\int_0^{\infty}\int_0^{\infty}\chi_l(r_1,r_2)^*\phi_l(r_1,r_2)r_1^2r_2^2dr_1dr_2, \quad (84)$$

$$W_2 = 16\pi^2\sum_{l_1=L+1}^{\infty}\sum_{l_2=L+1}^{\infty}\sum_{l_3=0}^{\infty}\begin{pmatrix} l_1 & l_2 & l_3\\ 0 & 0 & 0\end{pmatrix}^2 \times\int_0^{\infty}\int_0^{\infty}\frac{r_<^{l_3}}{r_>^{l_3+1}}\chi_{l_1}(r_1,r_2)^*\chi_{l_2}(r_1,r_2)r_1^2r_2^2dr_1dr_2, \quad (85)$$

$$W_3 = -\langle\psi^{(b)}|\hat{H}\left|\Phi_0 + \sum_n r_{12}^n\Phi_n\right\rangle. \quad (86)$$

Here W_1 and W_2 have the same forms as in Hill's work [1], except the definitions of χ_l and ϕ_l. W_3 is a new term arising from the explicitly correlated functions. (:::) is a Wigner 3-j symbol. Since the expressions of the variational calculation are similar to the perturbative approach, we briefly state the results of the rates of convergence.

Similar to the $1/Z$ expansion, if all necessary analytic conditions hold, χ is $O(r_{12}^{N+2})$. To obtain the rate of convergence from the contribution of ϕ_l, we shall apply the Theorem 3 of Hill [1]. Let $\partial^j f(r_1,r_2,r_{12})/\partial r_{12}^j$ be a continuous function of r_{12} for $r_{12} \in [|r_1 - r_2|, r_1 + r_2]$, $0 \leqslant j \leqslant 2J$, and

$$\int_{|r_1-r_2|}^{r_1+r_2}\left|\frac{\partial^{2J+1}f}{\partial r_{12}^{2J+1}}\right|^2 dr_{12} < \infty, \quad (87)$$

$$\int_0^{\infty} r_1^2dr_1\int_0^{\infty} r_2^2dr_2\, r_>^{4J-1}\int_{|r_1-r_2|}^{r_1+r_2}\left|\frac{\partial^{2J+1}f}{\partial r_{12}^{2J+1}}\right|^2 dr_{12} < \infty; \quad (88)$$

the following expansion around $r_{12} = |r_1 - r_2|$ holds:

$$f(r_1,r_2,r_{12}) = \sum_l b_l(r_1,r_2)P_l(\cos\theta_{12}), \quad (89)$$

$$b_l(r_1,r_2) = \sum_{j=0}^{2J}\left.\frac{\partial^j f}{\partial r_{12}^j}\right|_{r_{12}=|r_1-r_2|}\eta_{jl}(r_1,r_2) + \tilde{\Omega}_{Jl}(r_1,r_2), \quad (90)$$

$$\eta_{jl}(r_1,r_2) = \frac{2l+1}{2}\int_0^{\pi}\frac{(r_{12}' - |r_1-r_2|)^j}{r_{12}'\,j!}\times P_l(\cos\theta_{12}')\sin\theta_{12}'d\theta_{12}', \quad (91)$$

$$\lim_{l\to\infty} l^{4J}\int_0^{\infty} r_1^2dr_1\int_0^{\infty} r_2^2dr_2|\tilde{\Omega}_{Jl}(r_1,r_2)|^2 = 0. \quad (92)$$

In Eq. (92), $r_{12}' := (r_1^2 + r_2^2 - 2r_1r_2\cos\theta_{12}')^{1/2}$ varies by θ_{12}'. $\tilde{\Omega}_{JI}(r_1,r_2)$ is the remainder.

We require $2J + 1 = N + 3$ for Hill's theorems 3 [1] and apply Lemma 2 of the present work. The incremental rate of convergence for W_1 and W_2 are $O(L^{-2N-6})$ and $O(L^{-2N-7})$, respectively.

W_3 has a similar structure with Eq. (20). It can be seen as the following:

$$\begin{aligned} W_3 &= -\langle\psi^{(b)}|\hat{H}|\Phi_0\rangle - \sum_n\langle\psi^{(b)}|\big[\hat{H},r_{12}^n\big] + r_{12}^n\hat{H}|\Phi_n\rangle \\ &= -\langle\psi^{(b)}|\hat{H}_0|\Phi_0\rangle - \langle\psi^{(b)}|r_{12}^{-1}|\Phi_0\rangle \\ &\quad - \sum_n\langle\psi^{(b)}| - n(n+1)r_{12}^{n-2} + \hat{U}_n + r_{12}^n\hat{H}|\Phi_n\rangle. \end{aligned} \quad (93)$$

Here $-\langle\psi^{(b)}|r_{12}^{-1}|\Phi_0\rangle + \langle\psi^{(b)}| - n(n+1)r_{12}^{n-2}|\Phi_n\rangle$ will be canceled by

$$\Phi_1 = \Phi_0/2 \quad (94)$$

or suppressed to $O(L^{-2N-7})$ according to Eq. (60). In the $1/Z$ expansion $\Phi_0 = \Phi = e^{-r_1-r_2}/\pi$. Here we do not have the explicit form of Φ_0. When $n \geqslant 1$ odd-power r_{12} functions are introduced in the reference function (74), the incremental rate of convergence is $O(L^{-N-7})$.

By similar analysis, we obtain the incremental rate of convergence for other terms $\delta_1 := \langle\psi^{(b)}|\hat{T}|\psi^{(b)}\rangle$, $\delta_2 := \langle\psi^{(b)}|\psi^{(b)}\rangle$, $R_1 = O(\delta_1\delta_2^{1/2})$, and $R_2 = O(\delta_2)$ as $O(L^{-N-7})$, $O(L^{-2N-8})$, $O(L^{-2N-7})$, and $O(L^{-2N-8})$, respectively. The quantities δ_1 and δ_2 are introduced in Eqs. (3.26) and (3.27), respectively in Ref. [1]. Therefore the incremental rate of convergence of the Rayleigh-Ritz variation under the ansatz (69) is $O(L^{-N-7})$, $n = 1,3,5,\ldots,N$.

TABLE II. Comparison between the numerical results and the Hill's formulas (96) and (97). The atomic units are adopted.

L	Numerical result[a]	Eq. (96)	Numerical result[b]	Eq. (97)[c]
5	1.1886×10^{-4}	1.2694×10^{-4}	8.7373×10^{-5}	8.7373×10^{-5}
10	1.9037×10^{-5}	1.9364×10^{-5}	6.3491×10^{-6}	6.3494×10^{-6}
20	2.7083×10^{-6}	2.7200×10^{-6}	4.2881×10^{-7}	4.2883×10^{-7}
50	1.8763×10^{-7}	1.8776×10^{-7}	1.1507×10^{-8}	1.1507×10^{-8}
100	2.4087×10^{-8}	2.4092×10^{-8}	7.3062×10^{-10}	7.3062×10^{-10}
200	3.0515×10^{-9}	3.0516×10^{-9}	4.6026×10^{-11}	4.6026×10^{-11}
300	9.0820×10^{-10}	9.0822×10^{-10}	9.1155×10^{-12}	9.1155×10^{-12}

[a]Obtained by Eq. (101) subtracting the reference value [21].
[b]Obtained by $|\tilde{E}(L)-\tilde{E}(L-1)|$.
[c]In absolute value.

V. NUMERICAL RESULTS FOR THE RAYLEIGH-RITZ VARIATIONAL CALCULATIONS

A. On the rate of convergence without odd-power r_{12} function

The Rayleigh-Ritz variation provided the best result for a given basis. It has some particularly important aspects for careful examination. For the simplest case, namely without odd-power r_{12} function, the theoretical rate of convergence was given as [1,2]

$$\tilde{\psi}(r_1,r_2,\theta_{12}) = \sum_{l=0}^{L} \tilde{\chi}_l(r_1,r_2)P_l(\cos\theta_{12}), \tag{95}$$

$$\Delta E := \frac{\langle\tilde{\psi}|\hat{H}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} - E_{\text{exact}} = C_1(L+1)^{-3} + C_2L^{-4} + O(L^{-5}), \tag{96}$$

$$\tilde{E}(L) - \tilde{E}(L-1) = -3C_1(L+1/2)^{-4} - 4C_2(L+1/2)^{-5} + O(L^{-6}), \tag{97}$$

$$C_1 = 2\pi^2\int_0^\infty |\psi(r,r,0)|^2 r^5 dr, \quad C_2 = \frac{12\pi}{5}\int_0^\infty |\psi(r,r,0)|^2 r^6 dr, \tag{98}$$

where ψ denotes the exact ground-state wave function. The derivation of Eqs. (96)–(98) relies on several assumptions of the analytic structure of the helium atom. For example, $\partial^j\psi(r_1,r_2,r_{12})/\partial r_{12}^j$ up to $j=5$ is continuous. On the other hand, the helium wave function presents a logarithmic behavior at the three-particle-coalescence point [36,38,39,44,45]. It raises the question of whether such a singularity will affect the rate of convergence.

The most accurate PWE was obtained using a spline basis [46]. Up to $L=80$, the error in energy was about 7.8×10^{-8} a.u. The agreement with other numerical studies [47–51] and Hill's formulas was excellent. Here we use an inverse scheme to reach higher accuracy. Namely, we first perform an explicitly correlated calculation, then do a PWE on top of this wave function.

Our basis for the explicitly correlated calculation is a small modification of the basis F in Schwartz's article [20],

$$\tilde{\psi} = \sum_{i=1}^{M_n} c_i\phi_i, \tag{99}$$

$$\phi = s^\lambda(t/s)^\mu(u/s)^\nu(\ln s)^\xi\, e^{-\alpha s}. \tag{100}$$

Since the bound-state eigenfunction of a nonrelativistic Coulombic Hamiltonian is bounded [41], we have removed the term $\ln s\, e^{-\alpha s}$ which diverges at the origin. Nevertheless the effects of excluding $\ln s e^{-\alpha s}$ and even $s\ln s e^{-\alpha}$ according to the differentiability of the exact wave function [37] are not significant in our calculations.

Other types of basis functions which contain $\ln(s+u)$ or $\ln u$ [22,23,52] also lead to very high accuracy. Such wave functions include different singularities at the truncated expansion. However, the evaluations of integrals are more complicated. Since the basis function (100) is complete at the untruncated limit [30], our variational calculation with wave function (100) may cover the effects of other logarithmic singularities.

We choose order $\omega=14$ and $M_n=743$ in Eq. (100). The error in the energy with respect to the reference value [37] is 1.50×10^{-16} a.u. We then use this wave function to compute the coefficients C_1 and C_2 defined in Eq. (98). The values are $C_1\approx 0.024\,741\,908$ and $C_2\approx 0.007\,747\,274\,7$. The digits are expected to become converged by comparing $\omega=13$ and $\omega=14$ calculations. The PWE is made on top of this optimized wave function. The energy is evaluated as

$$E(L) = \frac{\sum_{l,l'=0}^{L}\langle\tilde{\chi}_l P_l|\hat{T}+\hat{V}_{\text{en}}+\hat{V}_{\text{ee}}|P_{l'}\tilde{\chi}_{l'}\rangle}{\sum_{l,l'=0}^{L}\langle\tilde{\chi}_l P_l|P_{l'}\tilde{\chi}_{l'}\rangle} = \frac{\sum_{l=0}^{L}\frac{2}{2l+1}\langle\tilde{\chi}_l|\hat{T}+\hat{V}_{\text{en}}|\tilde{\chi}_l\rangle + 2\sum_{l,l'=0}^{L}\sum_{l''=|l-l'|}^{l+l'}\begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0\end{pmatrix}^2\langle\tilde{\chi}_l|r_<^{l''}/r_>^{l''+1}|\tilde{\chi}_{l'}\rangle}{\sum_{l=0}^{L}\frac{2}{2l+1}\langle\tilde{\chi}_l|\tilde{\chi}_l\rangle}. \tag{101}$$

TABLE III. Rate of convergence of the PWE increments for the Rayleigh-Ritz variational energy of the ground-state helium atom. $\omega = 20$ is used. The atomic units are adopted.

	$\lvert\tilde{E}(L) - \tilde{E}(L-1)\rvert$		
L	$\tilde{\Phi}_0 + r_{12}\tilde{\Phi}_1 + \tilde{\chi}$	$\tilde{\Phi}_0 + r_{12}\tilde{\Phi}_1 + r_{12}^3\tilde{\Phi}_3 + \tilde{\chi}$	$\tilde{\Phi}_0 + r_{12}\tilde{\Phi}_1 + r_{12}^3\tilde{\Phi}_3 + r_{12}^5\tilde{\Phi}_5 + \tilde{\chi}$
0[a]	2.903 498	2.903 702	2.903 720
1	2.216×10^{-4}	2.200×10^{-5}	4.488×10^{-6}
2	4.119×10^{-6}	1.056×10^{-7}	7.465×10^{-9}
3	3.031×10^{-7}	2.676×10^{-9}	7.658×10^{-11}
4	4.265×10^{-8}	1.589×10^{-10}	2.100×10^{-12}
5	8.860×10^{-9}	1.612×10^{-11}	1.101×10^{-13}
6	2.399×10^{-9}	2.360×10^{-12}	1.021×10^{-14}
7	7.807×10^{-10}	4.499×10^{-13}	1.054×10^{-15}
8	2.959×10^{-10}	1.101×10^{-13}	
9	1.246×10^{-10}		
ΔE[b]	1.299×10^{-10}	4.516×10^{-14}	1.954×10^{-16}

[a]The energy of $\lvert\tilde{E}(L)\rvert$, $L = 0$.
[b]Total energy at the largest L subtracts the reference value [21].

A comparison between the numerical PWEs and the Hill's formulas is presented in Table II, where the agreement is excellent. Since at this level of accuracy the logarithm term typically affects the rate of convergence in the explicitly correlated approaches [20–22], this result may imply that such singularity does not affect the rate of convergence of PWE (95).

In addition, we also performed a numerical calculation for the $1/Z$ expansion up to $L = 10\,000$ in the Supplemental Material [25]. The results fully agree with Schwartz's formula [3–5].

B. Rate of convergence with odd-power r_{12} functions

The "inverse scheme" used to verify the L^{-4} rate of convergence is not that effective for the case with odd-power r_{12} functions. Because the radial wave function $\tilde{\Phi}_n$ needed to be saturated first, the basis F, Eq. (100), is constructed in a different sequence, i.e., organized by parameter ω. Therefore, we use a wave function similar to that used in the $1/Z$ expansion,

$$\tilde{\psi} = \sum_{\lambda\mu\nu\xi} a_{\lambda\mu\nu\xi} s^{\lambda}(t/s)^{\mu}(u/s)^{\nu}(\ln s)^{\xi} e^{-\alpha s} + \sum_{\lambda\mu\xi l} b_{\lambda\mu\xi l} s^{\lambda}(t/s)^{\mu}(\ln s)^{\xi} e^{-\alpha s} P_l(\cos\theta_{12}). \quad (102)$$

Here $\tilde{\Phi}_\nu = \sum_{\lambda\mu\xi} a_{\lambda\mu\nu\xi}\, s^{\lambda-\mu-\nu}\, t^{\mu}\, (\ln s)^{\xi} e^{-\alpha s}$ and $\tilde{\chi}_l = \sum_{\lambda\mu\xi} b_{\lambda\mu\xi l}\, s^{\lambda-\mu}\, t^{\mu}\, (\ln s)^{\xi} e^{-\alpha s}$ correspond to the ansatz (69).

We fix $\tilde{\Phi}_1 = \tilde{\Phi}_0/2$ according to Eq. (94). $\tilde{\Phi}_0$ is a general two-electron function, represented by $\sum_{\lambda\mu\xi} a_{\lambda\mu 0\xi}\, s^{\lambda-\mu}\, t^{\mu}\, (\ln s)^{\xi} e^{-\alpha s}$. Our choice is similar to the XSP ansatz [53].

In the coupled-cluster formulation, the XSP ansatz is [53, Eq. 18]

$$|\Psi_{\rm XSP}\rangle = \{e^{\tilde{\mathcal{R}}}\} e^{T} |0\rangle,$$

where $|0\rangle$ and $|\Psi_{\rm XSP}\rangle$ are the reference and the coupled-cluster state vectors, respectively. The operators T and $\tilde{\mathcal{R}}$ correspond to the conventional and the explicitly correlated excitations, respectively. The XSP ansatz contains a geminal function acting on a general reference state, than a Hartree-Fock state. The detailed definitions can be found in Ref. [53]. We have removed the terms that diverge at the origin.

The numerical results are presented in Table III and Fig. 2. Detailed data are given in the Supplemental Material [25]. The L^{-8}, L^{-10}, and L^{-12} rates of convergence are observed. We notice in the original CI-R12 approach, no simple inverse-power law for the rate of convergence was found [7]. That result [7] may be due to the limited incorporation of the cusp condition by its ansatz, namely $r_{12}e^{-\alpha(r_1+r_2)}$.

VI. SUMMARY

In the present study, we analyzed the rate of convergence of the PWE for the ground state of the helium atom with the presence of the odd-power r_{12} functions, r_{12}^n. Under certain assumptions of the analytic structure for the helium wave function, the rate of convergence is L^{-N-7} for both the second-order $1/Z$ expansion and the Rayleigh-Ritz variational approach. N

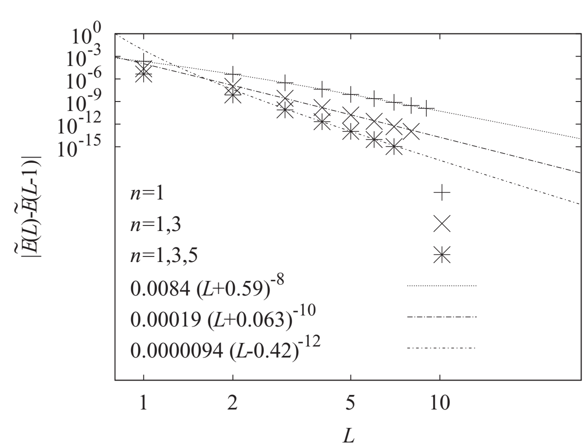

FIG. 2. $\lvert\tilde{E}(L) - \tilde{E}(L-1)\rvert$ vs L plot for the Rayleigh-Ritz variational energy. The lines are obtained by numerical fittings. $L \geqslant \frac{N+3}{2}$ points are used for the fittings. n indicates the odd-power r_{12} functions used in the ansatz (69). Atomic units are used in the figure.

is the highest power of the odd-power r_{12} functions. We also verified the theoretical results by numerical calculations.

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APPENDIX A: ABOUT THE ALTERNATIVE DEFINITION OF $E_2(L)$

Since the second-order perturbative energy is given by

$$E_2 = \langle \Phi | \hat{H}' - E_1 | \psi \rangle, \tag{A1}$$

the partial-wave energy may be defined as

$$\check{E}_2(L) := \langle \Phi | \hat{H}' - E_1 | \psi^{(a)} \rangle. \tag{A2}$$

If there is no odd-power r_{12} term in $\psi^{(a)}$, Eq. (A2) is essentially the same as the definition in Schwartz's work [4]. We shall show $\check{E}_2(L) = E_2(L)$ if $N = 0$ in ansatz (9). When $N \geqslant 1$, $\check{E}_2(L) \neq E_2(L)$.

Define $\psi^{(b)}$ as the remainder of $\psi^{(a)}$,

$$\psi^{(b)} := \psi - \psi^{(a)} \tag{A3}$$

$$= \sum_{l=L+1}^{\infty} \chi_l P_l(\cos\theta_{12}). \tag{A4}$$

Here Eq. (A4) comes from the definition of χ_l, (12). We left multiply $\langle \psi^{(a)} |$ on the first-order perturbative equation (16) then transpose it to obtain

$$\langle \psi^{(a)} | \hat{H}_0 - E_0 | \psi^{(a)} \rangle = -\langle \psi^{(a)} | \hat{H}_0 - E_0 | \psi^{(b)} \rangle - \langle \Phi | \hat{H}' - E_1 | \psi^{(a)} \rangle. \tag{A5}$$

Inserting Eq. (A5) into Eq. (13) yields

$$E_2(L) = -\langle \psi^{(b)} | \hat{H}_0 - E_0 | \psi^{(a)} \rangle + \langle \Phi | \hat{H}' - E_1 | \psi^{(a)} \rangle. \tag{A6}$$

Obviously, $E_2(L) = \check{E}_2(L)$ if and only if $\langle \psi^{(b)} | \hat{H}_0 - E_0 | \psi^{(a)} \rangle = 0$. This condition is valid for $N = 0$ in $\psi^{(a)}$, and generally not true for $N \geqslant 1$. Since the Hylleraas functional (6) provides an upper bound of the second-order energy, we choose $E_2(L)$ in our discussion.

APPENDIX B: AN ALTERNATIVE DERIVATION FOR THE FIRST-ORDER WAVE FUNCTION AND PWE ENERGIES WITHOUT r_{12} TERMS

1. Derivation for the $O(L^{-4})$ rate of convergence

a. Assumptions for the regularities of the first-order wave function

We first notice that Theorem 2 from Hill [1] (also see Lemma 6.12 from Goddard [2]) can expand a function into a Legendre series with a controllable remainder. Let $\partial^j f(r_1,r_2,r_{12})/\partial r_{12}^j$ be a continuous function of r_{12} for $r_{12} \in [|r_1 - r_2|, r_1 + r_2]$, $0 \leqslant j \leqslant 2J - 1$, and

$$\int_{|r_1-r_2|}^{r_1+r_2} \left| \frac{\partial^{2J} f}{\partial r_{12}^{2J}} \right|^2 dr_{12} < \infty, \tag{B1}$$

$$\int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2\, r_>^{4J-1} \int_{|r_1-r_2|}^{r_1+r_2} \left| \frac{\partial^{2J} f}{\partial r_{12}^{2J}} \right|^2 dr_{12} < \infty; \tag{B2}$$

the following expansion around $r_{12} = |r_1 - r_2|$ holds:

$$f(r_1,r_2,r_{12}) = \sum_l b_l(r_1,r_2) P_l(\cos\theta_{12}), \tag{B3}$$

$$b_l(r_1,r_2) = \sum_{j=0}^{2J-1} \left. \frac{\partial^j f}{\partial r_{12}^j} \right|_{r_{12}=|r_1-r_2|} \xi_{jl}(r_1,r_2) + \Omega_{Jl}(r_1,r_2), \tag{B4}$$

$$\xi_{jl}(r_1,r_2) = \frac{2l+1}{2} \int_0^{\pi} \frac{(r'_{12} - |r_1 - r_2|)^j}{j!} \times P_l(\cos\theta'_{12}) \sin\theta'_{12} d\theta'_{12}, \tag{B5}$$

$$\lim_{l\to\infty} l^{4J} \int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2 |\Omega_{Jl}(r_1,r_2)|^2 = 0. \tag{B6}$$

In Eq. (B5) $r'_{12} := (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta'_{12})^{1/2}$ varies by θ'_{12}. $\Omega_{Jl}(r_1,r_2)$ is the remainder.

Notice in the original paper [1], a normalized Legendre polynomial, $\Phi_l(\theta_{12}) := (l + 1/2)^{1/2} P_l(\cos\theta_{12})$, was used. Here we adopt the conventional Legendre polynomial, $P_l(\cos\theta_{12})$. As a result, our $\xi_{jl}(r_1,r_2)$ is $(l + 1/2)^{1/2}$ times Hill's definition [1, Eq. 4.36]. In the region $r_1 = r_2$, the expansion (B3) coincides with the generalized-Laplace expansion (23), i.e., $\xi_{jl}(r_1,r_2)|_{r_1=r_2} = R_{jl}/j!$.

We then make three assumptions to derive the L^{-4} rate of convergence: (i) the exact first-order wave function has continuous partial derivatives, $\partial^n \psi / \partial r_{12}^n$, $n = 0,1,2$, and

$$\int_{|r_1-r_2|}^{r_1+r_2} \left| \frac{\partial^3 \psi}{\partial r_{12}^3} \right|^2 dr_{12} < \infty, \tag{B7}$$

$$\int_0^{\infty} r_1^2 dr_1 \int_0^{\infty} r_2^2 dr_2\, r_>^5 \int_{|r_1-r_2|}^{r_1+r_2} \left| \frac{\partial^3 \psi}{\partial r_{12}^3} \right|^2 dr_{12} < \infty; \tag{B8}$$

(ii) the exact first-order wave function has mixed partial derivatives $\partial^{i+j+k+1}\psi / \partial r_<^{i+k} \partial r_{12}^{j+1}$ with the following bound properties:

$$\left| \frac{\partial^{i+j+k+1}\psi}{\partial r_<^{i+k} \partial r_{12}^{j+1}} \right| \leqslant \tilde{A}(r_>), \quad i + j = 1,\ k = 0,1,2,\ r_< \in (0, r_>), \tag{B9}$$

where $\tilde{A}(r_>)$ is a function of $r_>$; (iii) all integrals in the derivation exist. Assumption (i) corresponds to $J = 3/2$ in Eqs. (B1)–(B6). In assumption (ii), $i + j$ is the order of the Taylor expansion which corresponds to the remainders in Eq. (28). $k = 1,2$ corresponds to the first- and second-order differentiations in operators $\hat{U}_{1l}$ and $\hat{H}_0$ in Eqs. (B20) and (B24), respectively. The requirement of the differentiability of $r_<$ may be too strong. We can define the first-order wave function multiplies $r_<^2 r_>^2$ in the volume element, i.e., $\psi r_<^2 r_>^2$ as ψ in the assumption (ii). It will have extra differentiabilities. In addition, bound properties similar to Eq. (B9) have been proposed by Goddard [2] to refine the derivation of Hill [1].

Let the exact first-order wave function ψ be the function f in the theorem above, with the help of the low-order expressions of ξ_{jl} [1, Eqs. 5.88–5.90],

$$\xi_{0l} = \delta_{l0}, \tag{B10}$$

$$\xi_{1l} = -(r_> - r_<)\delta_{l0} + R_{1l}, \tag{B11}$$

$$\xi_{2l} = r_< r_>(\delta_{l0} - \delta_{l1}) - (r_> - r_<)\xi_{1l}; \tag{B12}$$

we have

$$\psi_l := \frac{2l+1}{2}\int_0^\pi \psi(r_1,r_2,r_{12})\, P_l(\cos\theta_{12})\sin\theta_{12} d\theta_{12} \tag{B13}$$

$$= \left[\frac{\partial\psi}{\partial r_{12}} - |r_1 - r_2|\frac{\partial^2\psi}{\partial r_{12}^2}\right]\Bigg|_{r_{12}=|r_1-r_2|} R_{1l} + \Omega_{3/2,l}, \quad l \geqslant 2. \tag{B14}$$

b. Termwise rates of convergence for the PWE

As shown in Appendix A, we can either start from the Hylleraas functional (13) or the expression of the second-order energy (A2) to analyze the rate of convergence. For convenience we use a similar procedure to that by Kutzelnigg and Morgan [8]. A few details which have been derived in their work [8] will be omitted. Namely we start from the partial-wave increment of the Hylleraas functional, $E_2(l)$,

$$E_2(L) = \sum_{l=0}^{L} E_2(l), \tag{B15}$$

$$E_2(l) := \langle\psi_l P_l|\hat{H}_0 - E_0|\psi_l P_l\rangle + 2\langle\psi_l P_l|\hat{H}' - E_1|\Phi\rangle. \tag{B16}$$

Rewrite Eq. (B14) as

$$\psi_l = \Phi_1 R_{1l} + \chi_l, \tag{B17}$$

$$\Phi_1 = \left[\frac{\partial\psi}{\partial r_{12}} - |r_1 - r_2|\frac{\partial^2\psi}{\partial r_{12}^2}\right]\Bigg|_{r_{12}=|r_1-r_2|}, \tag{B18}$$

$$\chi_l = \Omega_{3/2,l}. \tag{B19}$$

Notice the commutation relation (15) also holds for each PWE increment,

$$[\hat{H}_0 - E_0, R_{ml}] = -m(m+1)R_{m-2,l} + \hat{U}_{ml}; \tag{B20}$$

here $\hat{U}_{ml} := \frac{2l+1}{2}\int_0^\pi \hat{U}_m P_l(\cos\theta_{12})\sin\theta_{12} d\theta_{12}$. By combining Eqs. (B16)–(B20) and integrating out the angular variables, we obtain similar expressions with Eqs. (18)–(20),

$$E_2(l) = B(l) + D(l) + F(l) + B_\Omega(l) + D_\Omega(l) + F_\Omega(l), \quad l \geqslant 2, \tag{B21}$$

$$B(l) := 8\pi^2(l+1/2)^{-1}[-2\langle\Phi_1 R_{1l}|R_{-1l}\Phi_1\rangle + 2\langle\Phi_1 R_{1l}|R_{-1l}\Phi\rangle], \tag{B22}$$

$$D(l) := 8\pi^2(l+1/2)^{-1}\langle\Phi_1 R_{1l}|\hat{U}_{1l}|\Phi_1\rangle, \tag{B23}$$

$$F(l) := 8\pi^2(l+1/2)^{-1}\langle\Phi_1 R_{1l}|R_{1l}(\hat{H}_0 - E_0)|\Phi_1\rangle, \tag{B24}$$

$$B_\Omega(l) := 8\pi^2(l+1/2)^{-1}[-2\langle\Omega_{3/2,l}|R_{-1l}\Phi_1\rangle + 2\langle\Omega_{3/2,l}|R_{-1l}\Phi\rangle], \tag{B25}$$

$$D_\Omega(l) := 8\pi^2(l+1/2)^{-1}\langle\Omega_{3/2,l}|\hat{U}_{1l}|\Phi_1\rangle, \tag{B26}$$

$$F_\Omega(l) := 8\pi^2(l+1/2)^{-1}\langle\Omega_{3/2,l}|R_{1l}(\hat{H}_0 - E_0)|\Phi_1\rangle. \tag{B27}$$

The factor $8\pi^2$ comes from integrating over other angular variables. We first focus on the term $B(l)$. By assumption (ii), we expand $\partial\psi(r_<,r_>,r_{12})/\partial r_{12}$ around $r_< = r_>$ and $r_{12} = 0$ with the Lagrange remainders,

$$\frac{\partial\psi}{\partial r_{12}}\bigg|_{r_{12}=r_>-r_<} = \frac{\partial\psi}{\partial r_{12}}\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}} + (r_< - r_>)\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\bigg|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} + (r_> - r_<)\frac{\partial^2\psi}{\partial r_{12}^2}\bigg|_{\substack{r_<=\sigma,\\ r_{12}=\tau}}$$
$$= \frac{1}{2}\Phi(r_>,r_>) + (r_< - r_>)\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\bigg|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} + (r_> - r_<)\frac{\partial^2\psi}{\partial r_{12}^2}\bigg|_{\substack{r_<=\sigma,\\ r_{12}=\tau}}; \tag{B28}$$

Eq. (B18) then becomes

$$\Phi_1 = \Phi_{10} + \Phi_{11}, \tag{B29}$$

$$\Phi_{10} := \frac{1}{2}\Phi(r_>,r_>), \tag{B30}$$

$$\Phi_{11} := (r_< - r_>)\left[\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\bigg|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} - \frac{\partial^2\psi}{\partial r_{12}^2}\bigg|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} + \frac{\partial^2\psi}{\partial r_{12}^2}\bigg|_{r_{12}=r_>-r_<}\right], \tag{B31}$$

with $\sigma \in (0,r_>)$ and $\tau \in (r_> - r_<, r_> + r_<)$. Here we have used the cusp condition for the first-order wave function [8],

$$\frac{\partial\psi}{\partial r_{12}}\bigg|_{\substack{r_1=r_2\neq 0,\\ r_{12}=0}} = \frac{1}{2}\Phi\bigg|_{\substack{r_1=r_2\neq 0,\\ r_{12}=0}}. \tag{B32}$$

The cusp condition (B32) may not hold at the three-particle coalescence [28]. Nevertheless, a single point does not affect the values of integrals which are used for evaluating the electronic energy.

Inserting Eq. (B29) into Eq. (B22), we obtain

$$B(l) = B_1(l) + B_2(l) + B_3(l), \tag{B33}$$

$$B_1(l) := 8\pi^2(l+1/2)^{-1}[-2\langle\Phi_{10}R_{1l}|R_{-1l}\Phi_{10}\rangle + 2\langle\Phi_{10}R_{1l}|R_{-1l}\Phi\rangle], \tag{B34}$$

$$B_2(l) := 8\pi^2(l+1/2)^{-1}[-2\langle\Phi_{11}R_{1l}|R_{-1l}\Phi_{10}\rangle - 2\langle\Phi_{10}R_{1l}|R_{-1l}\Phi_{11}\rangle + 2\langle\Phi_{11}R_{1l}|R_{-1l}\Phi\rangle], \tag{B35}$$

$$B_3(l) := 8\pi^2(l+1/2)^{-1}[-2\langle\Phi_{11}R_{1l}|R_{-1l}\Phi_{11}\rangle]. \tag{B36}$$

For $B_1(l)$ we then have

$$\begin{aligned} B_1(l) &= -\frac{32\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} R_{1l}R_{-1l}\left[\frac{1}{2}\Phi(r_>,r_>)\Phi(r_>,r_>) - \Phi(r_>,r_>)\Phi(r_<,r_>)\right] r_<^2 r_>^2 dr_< dr_> \\ &= \frac{16\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} R_{1l}R_{-1l}\Phi(r_>,r_>)\Phi(r_>,r_>) r_<^2 r_>^2 dr_< dr_> \\ &\quad + \sum_{n=1}^{\infty}\frac{32\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} \frac{(r_< - r_>)^n}{n!} R_{1l}R_{-1l}\Phi(r_>,r_>)\left.\frac{\partial^n\Phi(r_<,r_>)}{\partial r_<^n}\right|_{r_<=r_>} r_<^2 r_>^2 dr_< dr_>. \end{aligned} \tag{B37}$$

In the second and third lines we used the Taylor expansion for $\Phi(r_<,r_>)$. As derived in Kutzelnigg and Morgan [8], the second line provides the origin of the $-45/256(L+1/2)^{-4}$ rate of convergence. Hereafter the rate of convergence means the incremental rate, $E_2(L) - E_2(L-1)$. There is no term at $O(L^{-5})$.

For $B_2(l)$ we have

$$B_2(l) = \sum_{n=1}^{\infty}\frac{64\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} \frac{(r_< - r_>)^{n+1}}{n!} R_{1l}R_{-1l}\left[\left.\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} - \left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} + \left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{r_{12}=r_>-r_<}\right]\left.\frac{\partial^n\Phi(r_<,r_>)}{\partial r_<^n}\right|_{r_<=r_>} \times r_<^2 r_>^2 dr_< dr_>. \tag{B38}$$

The first two terms in the square brackets of Eq. (B38) come from the Lagrange-type remainder. Therefore, we do not have explicit information to evaluate the rate of convergence. Nevertheless, we can use the bound properties (B9) to compute the rate of convergence for the upper and lower bounds. For the $n = 1$ term in Eq. (B38), the upper and lower bounds are

$$\begin{aligned} &-\frac{192\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} (r_< - r_>)^2 R_{1l}R_{-1l}\tilde{A}(r_>) r_<^2 r_>^2 dr_< dr_> \\ &\leqslant \frac{64\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} (r_< - r_>)^2 R_{1l}R_{-1l}\left[\left.\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} - \left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} + \left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{r_{12}=r_>-r_<}\right]\left.\frac{\partial\Phi}{\partial r_<}\right|_{r_<=r_>} r_<^2 r_>^2 dr_< dr_> \\ &\leqslant \frac{192\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} (r_< - r_>)^2 R_{1l}R_{-1l}\tilde{A}(r_>) r_<^2 r_>^2 dr_< dr_>. \end{aligned} \tag{B39}$$

Here we have used $|\partial\Phi/\partial r_<| = |-e^{-r_<-r_>}/\pi| < 1$. The upper and lower bounds in Eq. (B39) are determined by [2]

$$R_{1l}(r_<,r_>)R_{-1l}(r_<,r_>) = r_<^{2l} r_>^{-2l-2}\left(\frac{r_<^2}{2l+3} - \frac{r_>^2}{2l+1}\right) \leqslant 0, \tag{B40}$$

By Lemma 1 in the present work, we see the upper and lower bounds of Eqs. (B39) converge as $O(L^{-6})$. Again using Lemma 1, the upper and lower bounds of the terms $n > 1$ in Eq. (B38) converge in higher order than $O(L^{-6})$.

Similarly, the upper and lower bounds of $B_3(l)$ converge as $O(L^{-6})$.

$D(l)$ and $F(l)$ include the first- and second-order differentiation operators, $\hat{U}_{1l}$ and $\hat{H}_0$, respectively. These operators acting on $(r_< - r_>)$ in Φ_{11} will let Φ_{11} and Φ_{10} give the same order of the rate of convergence. By the presence of the Lagrange-type remainder in Φ_{11}, we could only use assumption (ii) to obtain the rate of convergence of the upper and lower bounds. The first- and second-order differentiation operators require $k = 1,2$ in assumption (ii). By assumption (ii), Lemmas 2 and 3, the upper and lower bounds of $D(l)$ and $F(l)$ converge as $O(L^{-6})$.

The rate of convergence from the remainder $\Omega_{3/2,l}$, namely $B_\Omega(l)$, $D_\Omega(l)$, and $F_\Omega(l)$ can be estimated by the Cauchy-Schwartz inequality. Similar with the treatment of $B_2(l)$, we have

$$\begin{aligned} B_\Omega(l) &= \frac{32\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} \Omega_{3/2,l}R_{-1l}\Phi(r_>,r_>) r_<^2 r_>^2 dr_< dr_> \\ &\quad - \frac{64\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} \Omega_{3/2,l}R_{-1l}(r_< - r_>)\left[\left.\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} - \left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{\substack{r_<=\sigma,\\ r_{12}=\tau}} + \left.\frac{\partial^2\psi}{\partial r_{12}^2}\right|_{r_{12}=r_>-r_<}\right] r_<^2 r_>^2 dr_< dr_> \\ &\quad + \sum_{n=1}^{\infty}\frac{64\pi^2}{2l+1}\int_0^\infty\int_0^{r_>} \Omega_{3/2,l}R_{-1l}\frac{(r_< - r_>)^n}{n!}\left.\frac{\partial^n\Phi(r_<,r_>)}{\partial r_<^n}\right|_{r_<=r_>} r_<^2 r_>^2 dr_< dr_>. \end{aligned} \tag{B41}$$

By the Cauchy-Schwartz inequality, the first line of Eq. (B41) has the following bounds:

$$\frac{32\pi^2}{2l+1}\left|\int_0^\infty\int_0^{r_>}\Omega_{3/2,l}R_{-1l}\Phi(r_>,r_>)r_<^2r_>^2dr_<dr_>\right| \leqslant \frac{32\pi^2}{2l+1}\left[\int_0^\infty\int_0^{r_>}\Omega_{3/2,l}^2r_<^2r_>^2dr_<dr_>\right]^{1/2}\left[\int_0^\infty\int_0^{r_>}R_{-1l}^2\Phi(r_>,r_>)^2\right]^{1/2}=o(L^{-5}). \quad \text{(B42)}$$

The upper and lower bounds of other terms in Eq. (B41) converge as $o(L^{-6})$. By a similar procedure, the upper and lower bounds of $D_\Omega(l)$ and $F_\Omega(l)$ converge as $o(L^{-7})$.

2. Derivation for the $O(L^{-6})$ rate of convergence

a. Assumptions for the regularities of the first-order wave function

To obtain an explicit expression of $O(L^{-6})$, instead of estimating from the upper and lower bounds, we shall assume that (i) the exact first-order wave function has continuous partial derivatives with respect to r_{12}, $\partial^n\psi/\partial r_{12}^n$, $n=0,1,2,3$, and

$$\int_{|r_1-r_2|}^{r_1+r_2}\left|\frac{\partial^4\psi}{\partial r_{12}^4}\right|^2dr_{12}<\infty, \quad \text{(B43)}$$

$$\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\, r_>^5\int_{|r_1-r_2|}^{r_1+r_2}\left|\frac{\partial^4\psi}{\partial r_{12}^4}\right|^2dr_{12}<\infty; \quad \text{(B44)}$$

(ii) the exact first-order wave function has mixed partial derivatives $\partial^{i+j+k+1}\psi/\partial r_<^{i+k}\partial r_{12}^{j+1}$ for $i+j\leqslant 3, k=0,1,2$ with bound properties,

$$\left|\frac{\partial^{i+j+k+1}\psi}{\partial r_<^{i+k}\partial r_{12}^{j+1}}\right|\leqslant\tilde{A}(r_>),\qquad i+j=3,\quad k=0,1,2,\ r_<\in(0,r_>), \quad \text{(B45)}$$

where $\tilde{A}(r_>)$ is a function of $r_>$; (iii) all integrals in the derivation exist.

By assumption (i), we extend expansion (B14) into $J=2$,

$$\psi_l=\left[\frac{\partial\psi}{\partial r_{12}}-|r_1-r_2|\frac{\partial^2\psi}{\partial r_{12}^2}+\frac{|r_1-r_2|^2}{2}\frac{\partial^3\psi}{\partial r_{12}^3}\right]\Bigg|_{r_{12}=|r_1-r_2|}R_{1l}+\frac{1}{3!}\frac{\partial^3\psi}{\partial r_{12}^3}\bigg|_{r_{12}=|r_1-r_2|}R_{3l}+\Omega_{2,l},\qquad l\geqslant 2. \quad \text{(B46)}$$

In principle there are different choices of Φ_1 and χ_l as Eq. (B19); we use the following partition for convenience purpose:

$$\psi_l=\Phi_1R_{1l}+\chi_l, \quad \text{(B47)}$$

$$\Phi_1=\left[\frac{\partial\psi}{\partial r_{12}}-|r_1-r_2|\frac{\partial^2\psi}{\partial r_{12}^2}+\frac{|r_1-r_2|^2}{2}\frac{\partial^3\psi}{\partial r_{12}^3}\right]\Bigg|_{r_{12}=|r_1-r_2|}R_{1l}, \quad \text{(B48)}$$

$$\chi_l=\frac{1}{3!}\frac{\partial^3\psi}{\partial r_{12}^3}\bigg|_{r_{12}=|r_1-r_2|}R_{3l}+\Omega_{2,l}. \quad \text{(B49)}$$

By assumption (ii), we perform Taylor expansion for $\partial\psi/\partial r_{12}$, $\partial^2\psi/\partial r_{12}^2$, and $\partial^3\psi/\partial r_{12}^3$ in Eq. (B48) around $r_<=r_>$ and $r_{12}=0$. After a similar procedure as Eq. (B28), we obtain

$$\Phi_1=\frac{\partial\psi}{\partial r_{12}}\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}}+(r_<-r_>)\frac{\partial^2\psi}{\partial r_<\partial r_{12}}\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}}+\frac{(r_<-r_>)^2}{2}\frac{\partial^3\psi}{\partial r_<^2\partial r_{12}}\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}}+O((r_<-r_>)^3). \quad \text{(B50)}$$

Here $O((r_<-r_>)^3)$ contains the Lagrange-type remainders. We notice that the crossing terms, such as $-|r_1-r_2|\partial^2\psi/\partial r_{12}^2$, disappear. The absence of the crossing terms holds in general. We can consider the following expansion for a sufficient regular function:

$$\begin{aligned}\psi(r_<,r_>,r_{12})&=\sum_{m=0}^M\frac{(r_<-r_>)^m}{m!}\frac{\partial^m\psi}{\partial r_<^m}\bigg|_{r_<=r_>}+O((r_<-r_>)^{M+1})\\&=\sum_{m=0}^M\frac{(r_<-r_>)^m}{m!}\sum_{l=0}^\infty\left[\sum_{n=0}^N\frac{R_{nl}}{n!}\frac{\partial^{m+n}\psi}{\partial r_<^m\partial r_{12}^n}\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}}+\Omega_{\lfloor(N+1)/2\rfloor,l}\right]P_l(\cos\theta_{12})+O((r_<-r_>)^{M+1}).\end{aligned} \quad \text{(B51)}$$

The expansion for r_{12} is around $r_1=r_2$ in the second line of Eq. (B51). The crossing terms then disappear.

We can then use the cusp condition (B32) to replace Eq. (B50) as

$$\Phi_1=\frac{1}{2}\left[\Phi|_{r_<=r_>}+(r_<-r_>)\frac{\partial\Phi}{\partial r_<}\bigg|_{r_<=r_>}+\frac{(r_<-r_>)^2}{2}\frac{\partial^2\Phi}{\partial r_<^2}\bigg|_{r_<=r_>}+O((r_<-r_>)^3)\right]. \quad \text{(B52)}$$

Equation (B52) resembles the large-L behavior (21). The replacement of derivatives is tricky. At least we may demonstrate the legitimacy under integration. Without loss of generality, we consider

$$\begin{aligned}
&\int_0^\infty\int_0^{r_>} R_{-1l}R_{-1l}\,\frac{\partial^2}{\partial r_<^2}\left[\frac{\partial\psi}{\partial r_{12}}\frac{\partial\psi}{\partial r_{12}}\right]\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}} r_<^2r_>^2dr_<dr_>\\
&=\int_0^\infty\int_{r_<}^\infty R_{-1l}R_{-1l}\,\frac{\partial^2}{\partial r_<^2}\left[\frac{\partial\psi}{\partial r_{12}}\frac{\partial\psi}{\partial r_{12}}\right]\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}} r_<^2r_>^2dr_<dr_> = \frac{1}{2l-1}\int_0^\infty r_<^3\,\frac{\partial^2}{\partial r_<^2}\left[\frac{\partial\psi}{\partial r_{12}}\frac{\partial\psi}{\partial r_{12}}\right]\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}} dr_<\\
&=\frac{3\cdot 2}{2l-1}\int_0^\infty r_<\left[\frac{\partial\psi}{\partial r_{12}}\frac{\partial\psi}{\partial r_{12}}\right]\bigg|_{\substack{r_<=r_>,\\ r_{12}=0}} dr_< = \frac{3}{2(2l-1)}\int_0^\infty r_<\Phi(r_<,r_<)\Phi(r_<,r_<)dr_<\\
&=\int_0^\infty\int_0^{r_>} R_{-1l}R_{-1l}r_<^2r_>^2\,\frac{\partial^2}{\partial r_<^2}\left[\frac{\Phi(r_<,r_>)}{2}\frac{\Phi(r_<,r_>)}{2}\right]\bigg|_{r_<=r_>} dr_<dr_>;
\end{aligned}\tag{B53}$$

in the third line we have performed integration by parts. Since we can always group the same order of Taylor expansion of $\partial\psi/\partial r_{12}$ and $\partial\psi/\partial r_{12}$ in Eq. (B21) together, $\partial^{m+1}\psi/\partial r_<^m\partial r_{12}$ can be replaced by $\frac{1}{2}\partial^m\Phi/\partial r_<^m$.

b. Termwise rates of convergence for the PWE

Inserting Eqs. (B49) and (B52) into Eq. (B36), we can obtain the explicit expression of $O(L^{-6})$. The procedure is similar to that by Kutzelnigg and Morgan [8], except for the term $\langle\Phi_1|R_{1l}R_{1l}(\hat{H}_0-E_0)|\Phi_1\rangle$. Kutzelnigg and Morgan [8] used the result [3] $\Phi_1(r_<,r_>)=\Phi(r_<,r_>)/2=e^{-r_1-r_2}/(2\pi)$ and $(\hat{H}_0-E_0)e^{-r_1-r_2}/(2\pi)=0$. Since we only have the expression of Φ in Eq. (B52), we cannot perform this kind of derivation. Nevertheless as we can see

$$\begin{aligned}
&(\hat{H}_0-E_0)\frac{1}{2}\left[\Phi(r_>,r_>)+(r_<-r_>)\frac{\partial\Phi}{\partial r_<}\bigg|_{r_<=r_>}+\frac{(r_<-r_>)^2}{2}\,\frac{\partial^2\Phi}{\partial r_<^2}\bigg|_{r_<=r_>}+O((r_<-r_>)^3)\right]\\
&=\frac{1}{2}(\hat{H}_0-E_0)\left[\Phi(r_<,r_>)-\sum_{n=3}^\infty\frac{(r_<-r_>)^n}{n!}\frac{\partial^n\Phi}{\partial r_<^n}\bigg|_{r_<=r_>}+O((r_<-r_>)^3)\right]\\
&=\frac{1}{2}(\hat{H}_0-E_0)\left[-\sum_{n=3}^\infty\frac{(r_<-r_>)^n}{n!}\frac{\partial^n\Phi}{\partial r_<^n}\bigg|_{r_<=r_>}+O((r_<-r_>)^3)\right].
\end{aligned}\tag{B54}$$

In the third line, we used the fact that $\Phi(r_<,r_>)$ is the eigenfunction of $\hat{H}_0$. Since the Hamiltonian $\hat{H}_0=-\nabla_1^2/2-\nabla_2^2/2-1/r_1-1/r_2$, the rate of convergence of $\langle\Phi_1|R_{1l}R_{1l}(\hat{H}_0-E_0)|\Phi_1\rangle$ is proportional to $\langle\Phi_1|(r_<-r_>)R_{1l}R_{1l}|\Phi_1\rangle$. By Lemma 1 of the present work, its upper and lower bounds converge at $O(L^{-7})$. Since the $O((r_<-r_>)^3)$ term in Eq. (B50) contains the Lagrange-type remainders, we only have the results of the upper and lower bounds.

The remaining issue is that, while the previous studies stated the large-L behavior of the first-order wave function is [3,7,8],

$$\psi\to\frac{1}{2}r_{12}\Phi(r_<,r_>)=r_{12}\frac{e^{-r_<-r_>}}{2\pi},\quad L\to\infty,\tag{B55}$$

we have only obtained the expressions of $\Phi(r_<,r_>)$ and a few derivatives at $r_<=r_>$ in Eq. (B50). We may extend our assumptions of the analytic structure of the first-order wave function. Equation (B50) will approach Eq. (B55).

APPENDIX C: EVALUATION OF THE MAIN INTEGRAL IN THE NUMERICAL CALCULATIONS

In the numerical calculations, we frequently confront a main integral:

$$I(n_1,n_2,n_3,n_4,n_5,\alpha):=\int_0^\infty\int_0^{r_>} s^{n_1}t^{n_2}r_<^{n_3}r_>^{n_4}\,(\ln s)^{n_5}\,e^{-\alpha s}dr_<\,dr_>.\tag{C1}$$

It can be evaluated as follows:

$$\begin{aligned}
I&=\int_0^\infty\int_0^{\pi/2}2\rho^{n_1+n_2+n_3+n_4+1}(1+\sin^2\phi)^{n_1}\cos^{2n_2+1}\phi\,\sin^{2n_4+1}\phi\,[\ln((1+\sin^2\phi)\rho)]^{n_5}\,e^{-\alpha(1+\sin^2\phi)\rho}d\phi\,d\rho\\
&\qquad\qquad\qquad r_<\to\rho\sin^2\phi,\ r_>-r_<\to\rho\cos^2\phi\\
&=\frac{\partial^{n_5}}{\partial\upsilon^{n_5}}[\alpha^{-\nu}\Gamma(\nu)]|_{\nu=n_1+n_2+n_3+n_4+2}\int_0^1(1+\sin^2\phi)^{-n_2-n_3-n_4-2}\cos^{2n_2}\phi\,\sin^{2n_4}\phi\,d\sin^2\phi\\
&=\frac{\partial^{n_5}}{\partial\upsilon^{n_5}}[\alpha^{-\nu}\Gamma(\nu)]|_{\nu=n_1+n_2+n_3+n_4+2}B(n_2+1,n_3+1)\,{}_2F_1(n_2+n_3+n_4+2,n_3+1;n_2+n_3+n_4;-1),
\end{aligned}\tag{C2}$$

where $B(\ldots,\ldots)$ is the β function. Here we have restricted $t \geqslant 0$ as proposed by Hylleraas [54]. Therefore $r_1 = r_<$ and $r_2 = r_>$. Alternatively we can restrict n_2 to be an even number according to the symmetry of the helium ground state (we are indebted to a referee for pointing out this prescription). In the first line of Eq. (C2), the coordinate transformation from Frolov and Smith [55,56] was adopted. In the second and third lines, we have used the integral formula related to nth derivatives of the Γ function [57, Eq. 4.358.5] and the integral representation of the hypergeometric function [58, Eq. 15.3.1], respectively.

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