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High-precision calculation of the geometric quantities of two-electron atoms based on the Hylleraas configuration-interaction basis

Li Guang Jiao,[*] Li Rong Zan, and Lin Zhu
College of Physics, Jilin University, Changchun 130012, People's Republic of China

Yong Zhi Zhang
College of Physical Science and Technology, Heilongjiang University, Harbin 150080, People's Republic of China

Yew Kam Ho
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan

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The expectation values of radial geometric quantities $\langle r_< \rangle$, $\langle r_> \rangle$, $\langle r \rangle$, and $\langle r_{12} \rangle$ and angular ones $\langle \theta_{12} \rangle$ and $\langle \cos\theta_{12} \rangle$ are investigated in detail for two-electron systems. Although these quantities can be calculated straightforwardly in the framework of Hartree-Fock or configuration-interaction methods, their computations based on explicitly correlated type wave functions are nontrivial tasks. In this work we employ the Hylleraas configuration-interaction basis functions to produce accurate system energies and wave functions for the He atom and He-like ions. Computational methods are developed to accurately and efficiently calculate the geometric quantities, especially for inner and outer electron radii, i.e., $\langle r_< \rangle$ and $\langle r_> \rangle$, and the average interelectronic angle $\langle \theta_{12} \rangle$. Compared to previous Hartree-Fock and multiconfiguration Hartree-Fock predictions and the configuration-interaction calculations based on Slater-type orbitals, our present work improve significantly the accuracy of all geometric quantities for He atom in the ground and singly excited states. The application of the present method to He-like ions with different nuclear charge reveals asymptotic power laws for both radial and angular quantities as they approach to the high-Z limit. Further extensions of the present work to other systems are discussed.

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I. INTRODUCTION

The investigation of radial and angular geometric quantities of multielectron atomic systems has attracted considerable interest in recent years due to their important roles in our understanding of the quantum correlation effect through different kinds of measurement and characterization of quantum many-body systems from a classical viewpoint [1–6]. The radial quantities $\langle r^n \rangle$ and $\langle r_{12}^n \rangle$ with both positive and negative integer power n have been extensively investigated in various studies of atomic properties, e.g., the calculation of relativistic and higher-order quantum electrodynamic energy corrections in few-electron atomic systems [7–10], the approximation of multipole polarizabilities for atomic systems [11–13], the asymptotic expansion of binding energy for Rydberg atoms consisting of high-excitation electrons moving in the field of a polarizable core [14,15], and the information-theoretic measure of Fisher information for atomic systems in conjugate coordinate and momentum spaces [16,17]. The angular one $\langle \cos\theta_{12} \rangle$, which is also referred to as $\langle \hat{r}_1 \cdot \hat{r}_2 \rangle$, together with $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ $(=\langle r_1 r_2 \cos\theta_{12} \rangle)$, also has its own application in the contribution of high-order relativistic effects [7–10], categorizing and classifying the doubly excited resonances into different series [18,19], and extracting orientational information about the electrons in position space [20].

In a series work Koga and co-workers [21–40] further investigated the average inner and outer electron radii, i.e., $\langle r_< \rangle$ and $\langle r_> \rangle$ where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$, the average interelectronic angle $\langle \theta_{12} \rangle$, and their corresponding density distributions in atomic systems. Based on the Hartree-Fock (HF) and multiconfiguration Hartree-Fock (MCHF) methods, a variety of radial and angular properties for various elements in the Periodic Table have been worked out systematically. Investigations of the radial properties have concentrated on the average electron radius, inner and outer electron radii, and their corresponding radial densities in many-electron atoms [21–26], the electron-pair radial sum and difference moments in atoms [27,28], and the properties of electron conditional radial densities [29,30]. Those for the angular properties are related to the uncorrelated and correlated interelectronic angle, its cosine value, and their density distributions for multielectron atoms in both position and momentum spaces [31–35], the angular quantities of equivalent and subshell-pair electrons in HF theory with *LS* couplings [36–38], and the lower and upper bounds to the average interelectronic angle and its cosine for various atoms [39,40].

Besides the plentiful work of Koga and co-workers, the usefulness of the geometric quantities $r_<$, $r_>$, $\cos\theta_{12}$, and θ_{12} has been realized by many authors concerning different

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[*] lgjiao@jlu.edu.cn

aspects of application in atomic systems. The pioneering work of Schwartz [41] was the first to suggest that the inclusion of coordinates $r_<$ and $r_>$ in the basis set has built in the ability to easily deal with the interelectronic Coulomb potential at the singularity $r_< = r_>$. The subsequent development of so-called modified configuration-interaction and radially uncoupled configuration-interaction (CI) methods by Goldman [42–45] showed the superiority of such types of basis functions in improving the convergence with respect to both radial and angular expansions, compared to conventional CI methods based on Slater or natural orbitals. The usefulness of geometric quantities in investigating the doubly excited resonance states of two-electron systems has also been largely revealed. Bylicki and Nicolaides [46,47] calculated the expectation value of $\langle r_> \rangle$ to estimate the general size of a resonance and also to distinguish the different series of resonance states. Bürgers and Rost [48] used the quantities of $\langle r_< \rangle$, $\langle r_> \rangle$, and $\langle \theta_{12} \rangle$ (they use, however, the approximation of $\langle \theta_{12} \rangle \approx \arccos\langle \cos\theta_{12} \rangle$) to construct the Lewis structures for resonance states and then describe the interference phenomena between different resonance series. The angular quantity $\langle \cos\theta_{12} \rangle$ has been used for a long time to categorize the resonance series and furthermore determine their approximate good quantum numbers through the formula $\langle \cos\theta_{12} \rangle \xrightarrow{n\to\infty} -\frac{K}{N}$ [18,19]. The expectation values of $\langle \theta_{12} \rangle$ and $\arccos\langle \cos\theta_{12} \rangle$ were calculated by Themelis [49] for Wannier-ridge resonance states and by Ordóñez-Lasso *et al.* [50] and Jiao and Ho [51] in studies of the geometric structure of resonances in a plasma screening environment.

We restrict the present work to the bound states of a two-electron He atom and He-like ions for which extremely accurate system energies, wave functions, and abundant physical quantities are available in the literature [7]. The geometric quantities including $\langle r^n \rangle$, $\langle r_{12}^n \rangle$, $\langle \cos\theta_{12} \rangle$, and $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle$ have also been reported within high accuracy by many authors. However, for those $\langle r_< \rangle$, $\langle r_> \rangle$, $\langle \theta_{12} \rangle$, and their corresponding density distributions, the calculations are quite limited. Besides the series work of Koga employing HF and MCHF methods, our recent CI calculations [52] based on Slater-type orbitals (STOs) have largely improved the accuracy of these quantities, especially for the ground and low-lying excited states. However, the CI results are far less satisfying due to the fact that the coupled system wave functions do not fulfill the two-electron coalescence Kato cusp condition [53] and moreover the convergence of energy and almost all quantities is inevitably slow with respect to both radial and angular expansions [43]. It is well known that the explicitly correlated type wave functions, such as Hylleraas, Kinoshita, and Pekeris wave functions [7,54–56], Hylleraas with logarithm functions [57,58], exponential correlated wave functions [9,59,60], explicitly correlated Gaussians [61], and Hylleraas Gaussian [62], Hylleraas *B*-spline [63], and Hylleraas configuration-interaction (HyCI) wave functions [64–68], which are also known as the superposition of correlated configurations (SCC) method [69–78], are applicable to perform high-precision calculations for few-electron atomic systems. However, as we will show in the following, their application to those geometric quantities mentioned above are nevertheless nontrivial.

In this work we adopt the HyCI (or SCC) type wave functions [64–78] to produce explicitly correlated type system wave functions and calculate the radial and angular geometric quantities. Such a type of basis sets can be easily constructed from the conventional CI ones [51,52] and at the same time show special advantages compared to the original Hylleraas one, e.g., requires less computational effort, is probably more appropriate for describing multiply excited and autoionizing resonance states, and is more easily extended to three- and four-electron systems.

The paper is organized as follows. Section II describes the details of the theoretical method including the construction of HyCI basis functions, the optimization of basis sets by orthogonalization, and the computational methodology in calculating radial and angular quantities. Section III presents our calculated results and discusses the ground and singly excited states of the He atom and the ground state of He-like ions. Benchmark expectation values of geometric quantities for various states are shown in detail. Section IV summarizes the present work and discusses further the application of our method to other systems and topics of interest. Atomic units are used throughout this paper unless otherwise stated.

II. THEORETICAL METHOD

A. HyCI basis functions

The Hamiltonian of the two-electron system with infinite nuclear mass in the nonrelativistic framework is given by

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

where Z is the positive nuclear charge. The HyCI basis functions employed in this work to expand the system wave functions are constructed from the usual CI basis sets. They are expressed in terms of the product of STOs with the r_{12} coordinate included explicitly

$$\Psi(\vec{r}_1, \vec{r}_2) = (1 - \hat{P}_{12}) \sum_{k=0}^{k_{\max}} \sum_{l_{a,b}=0}^{l_{\max}} \sum_{i,j} C_{a_i,b_j} r_{12}^k \phi_{a_i}(r_1) \phi_{b_j}(r_2) \times Y_{l_a,l_b}^{LM}(\hat{r}_1, \hat{r}_2) S^{S,M_S}(\sigma_1, \sigma_2), \tag{2}$$

where $\phi(r)$ is the radial part of the one-electron STO

$$\phi_{a_i}(r) = r^{n_{a_i}-1} e^{-\xi_{a_i} r}, \tag{3}$$

in which ξ is the nonlinear variational parameter to be optimized for a specific state. Here $Y_{l_a,l_b}^{LM}(\hat{r}_1, \hat{r}_2)$ and $S^{S,M_S}(\sigma_1, \sigma_2)$ are the two-electron coupled angular momentum and total spin wave functions, respectively, and i and j represent different STOs with the same angular momentum l. The nonnegative integer k refers to the power of the interelectronic distance. The restriction of $k_{\max} = 0$ reduces the HyCI basis functions to the conventional STO CI ones used in our previous work [51,52].

In the HyCI calculations, the maximum value of k is generally set to 1 (or 2 if the electron correlation contribution is large, e.g., in the ground state of atomic systems), which doubles (or triples) the total number of basis functions in the STO CI basis set. For one-electron STOs, both quantum numbers n and l are truncated to finite values as large as possible, accessing an approximately *full* CI calculation even without the r_{12}^k terms. Then the additional r_{12} terms take into account the Kato cusp condition at two-electron coalescence and furthermore cover partially the higher-lying angular momentum couplings. Note that the HyCI basis set constructed in this manner differs from the original Hylleraas ones, which only explicitly include the lowest-order angular momentum couplings (e.g., *s*-*p* coupling for *P*-type states and *s*-*d* and *p*-*p* couplings for *D*-type states), and all higher-order angular momentum couplings are taken into account through the expansion of r_{12}^k terms, where k takes in principle all even and odd integers [79]. An advantage of the restriction of $k_{\max} = 1$ (or 2) is attributed to the fact that in calculating the radial integrals of the overlap and Hamiltonian matrix elements computational effort can be reduced.

In constructing the two-electron HyCI (and STO CI) basis set, we use two groups of STOs for the one-electron orbital, with each group sharing the same parameter ξ, i.e., only two parameters need to be optimized in the Rayleigh-Ritz variational procedure. This would again significantly reduce the computational effort in calculating the radial integrals $I_{***varLambda}(a, b, c, \alpha, \beta)$ for various matrix elements (for details, see Ref. [7]). The HyCI basis set constructed in this way is labeled $(n_1, n_2)k_{\max}$, where n_1 is the maximum principal quantum number of STOs in the first group with all possible values of angular momenta $l < n_1$ and so forth for n_2. However, it is known that the Hylleraas-like basis functions are designed specifically for the description of ground or lower-lying excited states and their extension to higher-lying Rydberg states is not easy. Two techniques have been introduced by Drake and co-workers to successfully deal with such a problem [80,81]. The first one uses directly the multiple distance scales required for an accurate representation of the wave functions in the entire radial space by writing the Hylleraas basis functions in doubled or even tripled basis sets. These sets with different parameters produce a flexible description of the system wave function in close-, middle-, and far-range coordinate sectors. The second technique includes the product of screened hydrogenic wave functions as a single basis due to the fact that it is already a good approximation of the high-lying Rydberg states. The combination of these two techniques implemented by Drake and co-workers has produced very accurate system energies and wave functions for two-electron systems in both low- and high-lying states with a variety of total angular momenta.

To maintain the simplicity and efficiency of our HyCI basis and recalling that basis functions with relatively large values of n_1 and n_2 can cover a wide range of coordinate sectors, here we adopt only the second one to improve our basis set, i.e., incorporating a product of screened hydrogenic wave functions for the He-like ion with nuclear charge Z,

$$\Psi_0(\vec{r}_1, \vec{r}_2) = (1 - \hat{P}_{12}) C_0 \phi^{Z}_{n_1,l_1}(r_1) \phi^{Z-1}_{n_2,l_2}(r_2) \times Y^{LM}_{l_1,l_2}(\hat{r}_1, \hat{r}_2) S(\sigma_1, \sigma_2), \tag{4}$$

into the HyCI basis set in Eq. (2), with

$$\phi^{Z}_{n,l}(r) = N^{\alpha}_{n,l} (2\alpha r)^l e^{-\alpha r} L^{2l+1}_{n-l-1}(2\alpha r), \tag{5}$$

where $N_{n,l}$ is the normalization coefficient, $L^m_n(r)$ is the associated Laguerre polynomial, and $\alpha = Z/n$. The dimension of the new basis set is simply increased by 1.

B. Canonical orthogonalization

With continuously increasing the number of basis functions and also including the hydrogenic wave functions, the linearly dependent problem inherent in the explicitly correlated HyCI basis functions becomes more and more serious and it would inevitably lead to the solution of the generalized eigenvalue problem being very unstable. Application of higher-precision arithmetics (e.g., the arbitrary precision package developed by Bailey [82]) in numerical computations would solve such a problem; however, the user must put forth considerably more computational effort.

In our previous work [83] we successfully applied Löwdin's canonical orthogonalization method [84] to the variational calculations of atomic systems based on STO CI wave functions. It was shown that such a method is powerful in reconstructing the nonorthogonal basis functions as orthogonal ones while removing the redundant parts of the basis set in the most optimal way. This method can be employed here to refine the HyCI basis sets used in this work (for details, readers are referred to Refs. [83,84]). The minimum value of the eigenvalues for the overlap matrix measures the linear independence inherent in the original basis set and in this manner we can truncate the eigenvalues used in the construction of the transformation matrix. By setting a small quantity, all eigenvalues smaller than it are discarded. The transformed standard eigenvalue problem is then solved accurately. In our following calculations, quadruple-precision arithmetic is used and the small quantity is set to $\sim 10^{-30}$. It is generally found that the reduction would never exceed 15% in our most extensive calculations with the basis sets $k_{\max} = 2$.

C. Radial quantities

Once the eigenvalue for a specific state is obtained from the multiparameter variational procedure, we can calculate various radial quantities. The calculations of expectation values of the electron-nucleus distance $\langle r^n \rangle$ and electron-electron one $\langle r_{12}^n \rangle$ are quite straightforward. However, the calculations of expectation values of smaller and larger components of the electron-nucleus distance, i.e., $\langle r_<^n \rangle$ and $\langle r_>^n \rangle$, for arbitrary angular momentum states are much more involved. We start from the Hylleraas-type integrals developed by Drake [7] employing a transformation of the full six-dimensional volume element into the product of a three-dimensional angular integral and a three-dimensional radial integral over r_1, r_2, and r_{12}. This yields the basic integral

$$\left\langle Y^{LM*}_{l_1,l_2} Y^{LM}_{l_1',l_2'} f(a, b, c; \alpha, \beta) \right\rangle_{\vec{r}_1, \vec{r}_2} = \sum_q C_q I_q(a, b, c; \alpha, \beta), \tag{6}$$

where

$$C_q = \frac{(2q+1)}{2} (-1)^{L+q} [(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2} \begin{pmatrix} l_1' & l_1 & q \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2' & l_2 & q \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l_1 & l_2 \\ q & l_2' & l_1' \end{Bmatrix} \tag{7}$$

and

$$I_q(a,b,c;\alpha,\beta) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} dr_{12} \times f(a,b,c;\alpha,\beta) P_q(\cos\theta_{12}), \tag{8}$$

with

$$f(a,b,c;\alpha,\beta) = r_1^a r_2^b r_{12}^c e^{-\alpha r_1} e^{-\beta r_2}. \tag{9}$$

The calculations of $\langle r^n \rangle$ and $\langle r_{12}^n \rangle$ can be performed directly by using the efficient recursion relations developed by Drake [7]. For $\langle r_<^n \rangle$ and $\langle r_>^n \rangle$, the above procedure does not work and we must seek an alternative way to calculate the radial integral I_q.

The work of Perkins [85] expanded the arbitrary powers of the interelectronic coordinate r_{12}^ν into powers of $r_<$ and $r_>$,

$$r_{12}^\nu = \sum_{q=0}^{L_1} P_q(\cos\theta_{12}) \sum_{k=0}^{L_2} C_{\nu,q,k} r_<^{q+2k} r_>^{\nu-q-2k}, \tag{10}$$

where $L_1 = \frac{1}{2}\nu$ and $L_2 = \frac{1}{2}\nu - q$ for even values of ν, and $L_1 = \infty$ and $L_2 = \frac{1}{2}(\nu+1)$ for odd values of ν. The coefficient $C_{\nu,q,k}$ is given by

$$C_{\nu,q,k} = \frac{(2q+1)}{(\nu+2)} \frac{(\nu+2)!}{(2k+1)!(\nu-2k+1)!} \prod_{t=0}^{\min\{(q-1),[(\nu+1)/2]\}} \times \frac{(2k+2t-\nu)}{(2k+2q-2t+1)}. \tag{11}$$

Utilization of Eq. (10) in the calculations of the basic six-dimensional integral gives a compact form that does not need the transformation of the volume element. This was performed in the work of Yan and Drake [86]. Equation (6) now becomes

$$\big\langle Y_{l_1,l_2}^{LM*} Y_{l'_1,l'_2}^{LM} f(a,b,c;\alpha,\beta) \big\rangle_{\vec{r}_1,\vec{r}_2} = \sum_{q,k} C_{c,q,k} G_q I_R(a,b,c;\alpha,\beta;q,k), \tag{12}$$

where

$$G_q = \frac{2}{2q+1} C_q \tag{13}$$

and the radial integral reads

$$I_R(a,b,c;\alpha,\beta;q,k) = \int_0^\infty dr_1 \int_0^\infty dr_2 r_1^{a+2} r_2^{b+2} r_<^{q+2k} r_>^{c-q-2k} e^{-\alpha r_1} e^{-\beta r_2}. \tag{14}$$

Separating the integral domain of r_2 into $(0, r_1)$ and (r_1, ∞) and using the expression of the hypergeometric function ${}_2F_1$, one finally gets

$$I_R(a,b,c;\alpha,\beta;q,k) = \frac{s!}{(\alpha+\beta)^{s+1}} \left[\frac{1}{A'+1} {}_2F_1\left(1, s+1, A'+2; \frac{\alpha}{\alpha+\beta}\right) + \frac{1}{B+1} {}_2F_1\left(1, s+1, B+2; \frac{\beta}{\alpha+\beta}\right) \right], \tag{15}$$

where

$$A' = a+2+q+2k, \quad B = b+2+q+2k, \tag{16}$$

and

$$s = a+b+c+5. \tag{17}$$

When calculating $\langle r_<^n \rangle$, one just needs to make the substitutions $A'+n \to A'$, $B+n \to B$, and $s+n \to s$ in Eq. (15), while in calculating $\langle r_>^n \rangle$, one only needs $s+n \to s$. It is worth mentioning here that at $n = 1$ the relation [21]

$$2\langle r \rangle = \langle r_< \rangle + \langle r_> \rangle \tag{18}$$

exists, which is useful to verify the calculations based on the above two methods.

D. Angular quantities

The angular quantities investigated here are the expectation values of the interelectronic angle $\langle \theta_{12} \rangle$ and its cosine $\langle \cos\theta_{12} \rangle$. Before calculating them, it is useful to present a general expression for the expectation value of an arbitrary angular function $f(\theta_{12})$. The work of Koga *et al.* [31–35] employed the interelectronic angle density introduced by Banyard and Ellis [87,88] together with the multipole expansion technique based on Legendre polynomials to calculate the angular quantities. For the study of expectation values in this work, it appears simplest to directly apply the multipole expansion to the angular function, i.e.,

$$f(\theta_{12}) = \sum_{k=0}^\infty c_k P_k(\cos\theta_{12}) \tag{19}$$

[the k used here should not be confused with that in Eq. (2) for the power of r_{12}], where the expansion coefficients can be obtained by virtue of the orthonormality of the Legendre polynomials

$$c_k = \frac{2k+1}{2} \int_0^\pi d\theta_{12} \sin\theta_{12} P_k(\cos\theta_{12}) f(\theta_{12}). \tag{20}$$

Once the values of c_k can be calculated exactly, the expectation value of the angular function $\langle f(\theta_{12}) \rangle$ is

$$\langle f(\theta_{12}) \rangle = \sum_{k=0}^\infty c_k q_k, \tag{21}$$

where

$$q_k = \langle P_k(\cos\theta_{12}) \rangle. \tag{22}$$

The expression for the expectation values of the nth power of the interelectronic angle $\langle \theta_{12}^n \rangle$ is given by

$$\langle \theta_{12}^n \rangle = \frac{1}{2} \sum_{k=0}^\infty (2k+1) I_{n,k} q_k, \tag{23}$$

where

$$I_{n,k} = \int_0^\pi d\theta_{12} \sin\theta_{12} P_k(\cos\theta_{12}) \theta_{12}^n = \int_{-1}^1 dx\, P_k(x) \arccos^n(x), \tag{24}$$

in which $x = \cos\theta_{12}$. For the angular quantity $\langle\theta_{12}\rangle$ investigated here, the integral $I_{1,k}$ can be performed analytically [89]:

$$I_{1,k} = \begin{cases} \pi\,\delta_{m,0}, & k = 2m \\ \pi\sum_{i=0}^{m}(-1)^{m-i}\frac{(2m+2i+1)!!}{(2i+2)!(2m-2i)!!}\left[\frac{(2i+1)!!}{(2i+2)!!}-1\right], & k = 2m+1. \end{cases} \tag{25}$$

The calculations of $q_k = \langle P_k(\cos\theta_{12})\rangle$ in the framework of Hartree-Fock or configuration-interaction methods based on products of one-electron orbitals (e.g., STOs) are available everywhere. However, their computation for explicitly correlated type system wave functions, e.g., the usual Hylleraas or present HyCI types, are much more involved.

With the help of the addition theorem

$$P_k(\cos\theta_{12}) = \frac{4\pi}{2k+1}\sum_{q=-k}^{k} Y^*_{kq}(\hat{r}_1)Y_{kq}(\hat{r}_2) \tag{26}$$

and recalling the definition of vector coupled product of tensor operators

$$T^q_{k_1,k_2,k}(\hat{r}_1,\hat{r}_2) = \sum_{q_1,q_2}\langle k_1k_2q_1q_2|kq\rangle T^{q_1}_{k_1}(\hat{r}_1)T^{q_2}_{k_2}(\hat{r}_2), \tag{27}$$

it can be easily verified that

$$P_k(\cos\theta_{12}) = (-1)^k\frac{4\pi}{\sqrt{2k+1}}T^0_{k,k,0}. \tag{28}$$

The complete integral of a general vector coupled product of tensor operators based on Hylleraas-like basis functions has been explicitly given by Drake [90] and it can be used here, however, with some changes.[1] Here we present the final expressions to calculate q_k in the Hylleraas-like basis functions

$$q_k = \langle P_k(\cos\theta_{12})\rangle = \sum_q C_q I_q[a,b,c;\alpha,\beta;P_k(\cos\theta_{12})], \tag{29}$$

where

$$I_q[a,b,c;\alpha,\beta;P_k(\cos\theta_{12})] = \sum_K(2K+1)\begin{pmatrix} q & k & K \\ 0 & 0 & 0\end{pmatrix}^2 I_K(a,b,c;\alpha,\beta) \tag{30}$$

and C_q and $I_K(a,b,c;\alpha,\beta)$ are given by Eqs. (7) and (8), respectively.

For the product type of basis functions, it has been shown that the infinite summation in Eq. (23) becomes a finite one due to the limiting number of angular momentum quantum numbers l coupled in the system wave functions [31,52]. However, for the explicitly correlated type basis functions where r_{12}^{ν} terms are included in the system wave functions, the number of angular momentum couplings is infinite with infinitely high values of l_a and l_b, as one can see from Eq. (10), although the basic angular momentum couplings in the present HyCI and original Hylleraas wave functions are finite. Consequently, the summation in Eq. (23) is intrinsically infinite. To make the computation feasible, we truncate the summation over q to a maximum number $q_{\max}$ where the magnitude of $q_kI_{n,k}$ is small enough, and the contributions of higher terms from $q_{\max}$ to ∞ are estimated by using a fitted formula.

The calculation of $\langle\cos\theta_{12}\rangle$ is quite straightforward,

$$\langle\cos\theta_{12}\rangle = \langle P_1(\cos\theta_{12})\rangle = q_1, \tag{31}$$

and it is useful in estimating the value of $\langle\theta_{12}\rangle$ in its first-order approximation. As was shown by Koga [35], by retaining the first two terms of the multipole expansion one gets

$$\langle\theta_{12}\rangle \approx \frac{\pi}{2} - \frac{3\pi}{8}\langle\cos\theta_{12}\rangle. \tag{32}$$

III. RESULTS AND DISCUSSION

A. He ground state

In this work the HyCI basis sets $(n_1, n_2)k_{\max}$ described in Sec. II A are used to calculate the ground state of the He atom. The nonrelativistic system energy and both radial and angular quantities with increasingly large basis sets are displayed in Table I. The product of hydrogenic orbitals shown in Eq. (4) are included in the basis sets and correspondingly the total number of basis functions is simply labeled as $N_{\text{total}} = N + 1$. Also shown in Table I are the HF and MCHF predictions by Koga *et al.* [21,31,33,35], B-spline CI results by Lin and Ho [91], and our previous CI calculations based on STOs [51,52]. Those calculations with explicitly correlated basis functions, e.g., the exponential-correlated basis set by Thakkar and Smith [59] and Frolov [92] and the Hylleraas basis sets by Drake [7] and Montgomery [93], are also included for comparison when they are available. However, calculations on quantities $\langle r_<\rangle$, $\langle r_>\rangle$, and $\langle\theta_{12}\rangle$ have not been performed with any type of explicitly correlated basis functions.

The two MCHF calculations performed by Koga *et al.* [21,33,35] show quite similar results for all quantities listed in the table and they are undoubtedly much better than the HF ones [21,31]. Our previous CI results [52] improve all predictions to higher accuracy; however, compared to the present HyCI calculations, it is clearly seen that the inclusion of r_{12} terms would significantly improve the binding energy as well as all radial and angular quantities investigated here. Those work based on explicitly correlated type basis functions, such as the Hylleraas basis by Drake [7] and Montgomery [93], exponential-correlated basis by Thakkar and Smith [59] and Frolov [92], and the complicated Hylleraas-like basis including logarithm functions by Nakashima and Nakatsuji [94], have obtained highly accurate results on the system energy, $\langle r\rangle$, $\langle r_{12}\rangle$, and $\langle\cos\theta_{12}\rangle$, and our HyCI results are comparable to their predictions. Only Nakashima and Nakatsuji [94] have calculated the expectation value of $\langle r_>\rangle$ (however, they labeled it as $\langle r_1\rangle$, which in our opinion should be $\langle r_>\rangle$) and only the last digit is somewhat different from ours. It is expected,

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[1] Equation (19) in Ref. [90] may contain errors and one should multiply the right-hand side of the equation by an additional coefficient $(-1)^k(2k+1)^{1/2}$.

TABLE I. Comparison of the nonrelativistic system energy and expectation values of various radial and angular quantities for the He atom in its ground state between calculations by the present HyCI basis sets and other theoretical methods. See the text for more details.

$(n_1, n_2)k_{\max}$	N_{total}	E	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
(4,4)1	140+1	−2.903724371700	0.602359458647	1.256585039210	0.929472248928	1.422070165287	−0.0642026144503	94.355494428
(5,4)1	190+1	−2.903724376012	0.602359429005	1.256585142224	0.929472285614	1.422070237599	−0.0642026143490	94.355491447
(5,5)1	250+1	−2.903724376814	0.602359421044	1.256585164037	0.929472292541	1.422070250995	−0.0642026142500	94.355490269
(6,5)1	322+1	−2.903724376966	0.602359419839	1.256585168344	0.929472294092	1.422070254046	−0.0642026142307	94.355490235
(6,6)1	406+1	−2.903724377019	0.602359419059	1.256585170310	0.929472294685	1.422070255195	−0.0642026142212	94.355490026
(7,6)1	504+1	−2.903724377030	0.602359418895	1.256585170740	0.929472294818	1.422070255456	−0.0642026142201	94.355490030
(7,7)1	616+1	−2.903724377033	0.602359418809	1.256585170899	0.929472294854	1.422070255527	−0.0642026142195	94.355490051
(8,7)1	744+1	−2.903724377034	0.602359418792	1.256585170941	0.929472294866	1.422070255551	−0.0642026142193	94.355490046
(7,6)2	756+1	−2.903724377034	0.602359418798	1.256585170936	0.929472294867	1.422070255552	−0.0642026142193	94.355490040
(7,7)2	924+1	−2.903724377034	0.602359418777	1.256585170969	0.929472294873	1.422070255565	−0.0642026142192	94.355490042
Nakashima and Nakatsuji [94]		−2.9037243770341		1.25658517095		1.42207025553		
Frolov [92]		−2.9037243770341			0.9294722948736	1.4220702555658	−0.06420261421919	
Drake [7]		−2.9037243770341			0.929472294874	1.422070255566		
Montgomery [93]		−2.9037243770			0.929472295	1.422070256	−0.064202614	
Thakkar and Smith [59]		−2.903724363			0.929472196	1.42207008	−0.064202621	
Koga (HF) [21,31]		−2.86168	0.622000	1.232547	0.927273	1.36212	−0.0	90
Koga and Matsuyama (MCHF) [21,33]		−2.90360	0.602438	1.256535	0.929487		−0.064266	94.360
Koga *et al.* (MCHF) [35]			0.602440	1.25654	0.92949	1.42216		94.3598
Lin and Ho (B-spline CI) [91]		−2.90358	0.60237	1.25666	0.92952		−0.06427	
Jiao and Ho (STO CI) [51]		−2.903683	0.60236	1.25658	0.92950	1.42213	−0.06422	
(11,11)0 [52]	1078	−2.90368937	0.60236076	1.25658543	0.92947309	1.42208270	−0.0642183	94.356551
(12,12)0 [52]	1378	−2.90369721	0.60236045	1.25658552	0.92947299	1.42208010	−0.0642147	94.356327
(13,13)0 [52]	1729	−2.90370286	0.60236024	1.25658556	0.92947290	1.42207820	−0.0642122	94.356147

TABLE II. Contribution of different k terms to the interelectronic angle $\langle\theta_{12}\rangle$ based on the (7,7)2 HyCI basis set.

k	q_k	$I_{1,k}$	$(2k+1)q_kI_{1,k}$	$\langle\theta_{12}\rangle$
1	-6.42026×10^{-2}	-2.50000×10^{-1}	4.81520×10^{-2}	94.333676460
3	-2.05126×10^{-3}	-1.56250×10^{-2}	2.24356×10^{-4}	94.353868542
5	-3.45255×10^{-4}	-3.90625×10^{-3}	1.48352×10^{-5}	94.355203706
7	-1.00999×10^{-4}	-1.52588×10^{-3}	2.31169×10^{-6}	94.355411759
9	-3.94528×10^{-5}	-7.47681×10^{-4}	5.60464×10^{-7}	94.355462201
11	-1.84297×10^{-5}	-4.20570×10^{-4}	1.78273×10^{-7}	94.355478245
13	-9.72239×10^{-6}	-2.59638×10^{-4}	6.81561×10^{-8}	94.355484379
15	-5.60135×10^{-6}	-1.71402×10^{-4}	2.97625×10^{-8}	94.355487058
17	-3.44995×10^{-6}	-1.19029×10^{-4}	1.43725×10^{-8}	94.355488351
19	-2.23909×10^{-6}	-8.59983×10^{-5}	7.50978×10^{-9}	94.355489027
21	-1.51578×10^{-6}	-6.41434×10^{-5}	4.18078×10^{-9}	94.355489403
23	-1.06232×10^{-6}	-4.91098×10^{-5}	2.45200×10^{-9}	94.355489624
25	-7.66428×10^{-7}	-3.84306×10^{-5}	1.50217×10^{-9}	94.355489759
27	-5.66741×10^{-7}	-3.06366×10^{-5}	9.54966×10^{-10}	94.355489845
29	-4.28049×10^{-7}	-2.48157×10^{-5}	6.26717×10^{-10}	94.355489902
∞	0	0	0	94.355490042

but still startling, that the quantities $\langle r_<\rangle$ and $\langle r_>\rangle$ calculated by the smallest HyCI basis set (4,4)1 with the number of basis functions $140 + 1$ show much better accuracy than the most extensive STO CI predictions [52] with basis set (13,13)0, where a total number of 1729 basis functions are used. The accuracy of $\langle r_<\rangle$ and $\langle r_>\rangle$ can be estimated indirectly through the equality of Eq. (18), where the benchmark value of $\langle r\rangle$ has been produced by several authors. It is therefore expected that the results with (7,7)2 basis set are the most accurate ones in the present calculations. With continuously increasing the number of HyCI basis functions, it can be generally concluded that all radial geometric quantities can be calculated within the same order of accuracy as the energy by employing explicitly correlated type basis functions.

The calculation of expectation values of angular quantities is more difficult than radial ones, as mentioned earlier. The HF theory gives explicitly zero values of $\langle P_k(\cos\theta_{12})\rangle$ for arbitrary positive values of k and consequently a value of 90° for $\langle\theta_{12}\rangle$, as we can see from Eq. (23) [21,31]. All electron correlation effects contribute to the deviation of $\langle\theta_{12}\rangle$ from 90° through both radial and higher-order angular couplings. The best MCHF prediction of Koga *et al.* [35] gives an angle of 94.3598° for $\langle\theta_{12}\rangle$, while our previous STO CI calculation with the largest basis set [52] gives a smaller result of 94.356147°. For the present calculations based on HyCI functions, the expectation value of this angle decreases continuously to a lower value, although its convergence is somewhat slower than the radial quantities as well as $\langle\cos\theta_{12}\rangle$. In Table II we show the contributions of different k terms calculated based on the (7,7)2 HyCI basis set. The value of q_1 simply reproduces $\langle\cos\theta_{12}\rangle$. The summation over k is truncated to the integer where $q_kI_{1,k}$ is less than 10^{-11} (such a criterion is used in all the following calculations). All even terms vanish, so they are not included in the table. In Fig. 1 we show the fitting formula in a power form of $y = ax^b$ for values of $(2k+1)q_kI_{1,k}$ with respect to the variable k. It is observed that numerical values are in better agreement with the power law at larger values of k, and hence only the last several points are used to produce the fitting formula. The best result of $\langle\theta_{12}\rangle$ in the present HyCI calculations is around 94.355490042° (the last digit may contain a rounding error). Such a value extends greatly the accuracy of predictions by the MCHF and STO CI methods. The approximation of $\langle\theta_{12}\rangle \approx \arccos\langle\cos\theta_{12}\rangle$ gives an angle of 93.681070668° and the first-order approximation in Eq. (32) gets 94.333676459°; both are smaller than the exact value. Recalling the fact that the HF limit of $\langle\theta_{12}\rangle$ for two-electron atoms equals exactly 90°, it can be generally concluded in the nonrelativistic framework that all radial and angular correlation effects in the He atom result in the remaining 4.355490042°.

B. He excited states

The radial and angular quantities for $1snl$ ($n \leqslant 6$) singly excited states of the He atom within S, P, and D symmetries are shown in Tables III and IV for singlet and triplet states, respectively. The HyCI basis sets (7,7)1 are used in S- and

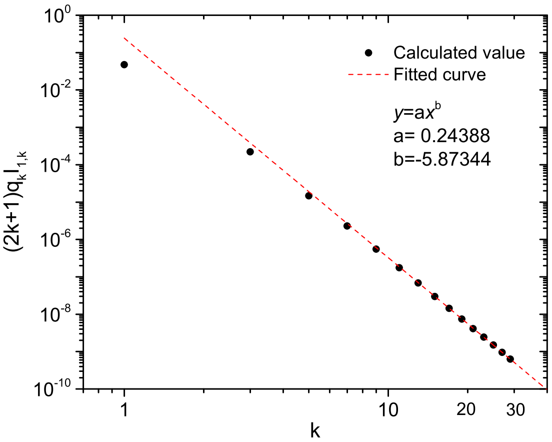

FIG. 1. Contribution of different k terms to the interelectronic angle $\langle\theta_{12}\rangle$ based on the HyCI basis set (7,7)2. Scatters are calculated values and the line is the fitted curve with the power-law formula $y = ax^b$.

TABLE III. Comparison of various radial and angular quantities for the singlet singly excited state of the He atom obtained in this work with other theoretical calculations. The reference “MCHF” represents the predictions of Koga *et al.* [35], “STO CI” our previous work in [52], “EC” the exponential correlated basis calculations of Thakkar and Smith [98] for the $1s2s\,^1S$ state only, “Hylleraas” the Hylleraas basis results of Cann *et al.* [96,97] for $\langle \cos\theta_{12} \rangle$ only, and “HyCI” the present work based on HyCI-type basis sets.

nl	Ref.	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
$2s$	MCHF	0.749162	5.19730	2.97323	5.27004		90.9925
$2s$	STO CI	0.7491610	5.1969758	2.973068	5.2697038	−0.0146588	90.992173
$2s$	EC			2.9730385	5.2696574	−0.014658852	
$2s$	HyCI	0.7491627115	5.1969595573	2.9730611344	5.2696962023	−0.01465704336	90.992052292
$3s$	MCHF	0.749948	12.2741	6.51202	12.3052		90.2922
$3s$	STO CI	0.7499482	12.273526	6.511737	12.304644	−0.0043174	90.292109
$3s$	Hylleraas					−0.0043170	
$3s$	HyCI	0.7499487440	12.273406163	6.5116774533	12.304523683	−0.00431703674	90.292081211
$4s$	MCHF	0.750001	22.3544	11.5522	22.3715		90.1214
$4s$	STO CI	0.7500011	22.353503	11.551752	22.370564	−0.0017956	90.121474
$4s$	Hylleraas					−0.0017954	
$4s$	HyCI	0.7500012748	22.353375180	11.551688227	22.370435325	−0.00179547145	90.121464529
$5s$	MCHF	0.750005	35.4352	18.0926	35.4460		90.0615
$5s$	STO CI	0.7500054	35.434154	18.092080	35.444892	−0.0009087	90.061471
$5s$	Hylleraas					−0.00090869	
$5s$	HyCI	0.7500055129	35.433951622	18.091978567	35.444689504	−0.00090864255	90.061467405
$6s$	MCHF	0.750005	51.5165	26.1332	51.5239		90.0352
$6s$	STO CI	0.7500045	51.515038	26.132521	51.522410	−0.0005212	90.035256
$6s$	Hylleraas					−0.00052103	
$6s$	HyCI	0.7500046156	51.514700802	26.132352709	51.522072394	−0.00052113859	90.035252943
$2p$	MCHF	0.747950	5.07394	2.91095	5.13886		90.3294
$2p$	STO CI	0.7479510	5.0735106	2.910731	5.138424	−0.0047758	90.327452
$2p$	HyCI	0.7479521972	5.0734164877	2.9106843424	5.1383283721	−0.00477313392	90.327266051
$3p$	MCHF	0.749325	12.6119	6.68061	12.6402		90.0846
$3p$	STO CI	0.7493300	12.609907	6.679618	12.638161	−0.0011778	90.080947
$3p$	Hylleraas					−0.0011768	
$3p$	HyCI	0.7493304184	12.609764246	6.6795473322	12.638017448	−0.00117686994	90.080885490
$4p$	MCHF	0.749708	23.1497	11.9497	23.1655		90.0317
$4p$	STO CI	0.7497103	23.146010	11.947860	23.161811	−0.0004688	90.032248
$4p$	Hylleraas					−0.00046828	
$4p$	HyCI	0.7497103902	23.145857727	11.947784058	23.161657905	−0.00046839447	90.032221286
$5p$	MCHF	0.749848	36.6899	18.7199	36.7000		90.0152
$5p$	STO CI	0.7498501	36.682284	18.716067	36.692368	−0.0002339	90.016099
$5p$	Hylleraas					−0.00023372	
$5p$	HyCI	0.7498501559	36.682081238	18.715965697	36.692165708	−0.00023376128	90.016087480
$6p$	MCHF	0.749911	53.2313	26.9906	53.2383		90.0085
$6p$	STO CI	0.7499127	53.218669	26.984291	53.225661	−0.0001334	90.009182
$6p$	Hylleraas					−0.00013345	
$6p$	HyCI	0.7499128003	53.218364797	26.984138799	53.225356606	−0.00013347733	90.009188061
$3d$	MCHF	0.750063	10.4817	5.61588	10.5136		90.2488
$3d$	STO CI	0.7500639	10.481398	5.615731	10.513322	−0.0036799	90.248711
$3d$	Hylleraas					−0.0035986	
$3d$	HyCI	0.7500639491	10.481391795	5.6157278720	10.513314851	−0.00367988372	90.248708767
$4d$	MCHF	0.750026	20.9754	10.8627	20.9928		90.1056
$4d$	STO CI	0.7500273	20.974926	10.862477	20.992299	−0.0015549	90.105107
$4d$	Hylleraas					−0.0015162	
$4d$	HyCI	0.7500273759	20.974921227	10.862474301	20.992294348	−0.00155491917	90.105106879
$5d$	MCHF	0.750013	34.4693	17.6097	34.4802		90.0541
$5d$	STO CI	0.7500141	34.468553	17.609284	34.479448	−0.0007966	90.053853

TABLE III. *(Continued.)*

nl	Ref.	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
$5d$	Hylleraas					−0.00077521	
$5d$	HyCI	0.7500141078	34.468551042	17.609282575	34.479445855	−0.00079665692	90.053854951
$6d$	MCHF	0.750008	50.9631	25.8566	50.9705		90.0313
$6d$	STO CI	0.7500082	50.962222	25.856115	50.969684	−0.0004611	90.031172
$6d$	Hylleraas					−0.00044856	
$6d$	HyCI	0.7500081926	50.962215577	25.856111885	50.969677761	−0.00046117976	90.031177509

TABLE IV. Comparison of various radial and angular quantities for the triplet singly excited state of the He atom obtained in this work with other theoretical calculations. The reference “MCHF” represents the predictions of Koga *et al.* [35], “STO CI” is our previous work in [52], “EC” and “EC2” are the exponential correlated basis calculations of Thakkar and Smith [98] and Frolov [92], respectively, for the $1s2s\,^3S$ state only, “Hylleraas” is the Hylleraas basis result of Cann *et al.* [96,97] for $\langle \cos\theta_{12} \rangle$ only, and “HyCI” is the present work based on HyCI-type basis sets.

nl	Ref.	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
$2s$	MCHF	0.729461	4.37148	2.55047	4.44755		91.0714
$2s$	STO CI	0.7294609	4.3714647	2.550463	4.447536	−0.0158392	91.071488
$2s$	EC			2.5504623	4.4475345	−0.015839224	
$2s$	EC2			2.55046267687	4.44753521696	−0.015839217088	
$2s$	HyCI	0.7294609429	4.3714644108	2.5504626769	4.4475352170	−0.01583921709	91.071485484
$3s$	MCHF	0.745171	10.9668	5.85599	10.9988		90.2870
$3s$	STO CI	0.7451705	10.966770	5.855970	10.998777	−0.0042451	90.286997
$3s$	Hylleraas					−0.0042451	
$3s$	HyCI	0.7451704868	10.966769109	5.8559697979	10.998775343	−0.00424508599	90.286996041
$4s$	MCHF	0.748150	20.5743	10.6612	20.5917		90.1137
$4s$	STO CI	0.7481501	20.574261	10.661206	20.591666	−0.0016869	90.114032
$4s$	Hylleraas					−0.0016870	
$4s$	HyCI	0.7481500950	20.574260557	10.661205326	20.591665042	−0.00168693400	90.114031179
$5s$	MCHF	0.749102	33.1837	16.9664	33.1946		90.0560
$5s$	STO CI	0.7491024	33.183594	16.966348	33.194499	−0.0008314	90.056195
$5s$	Hylleraas					−0.00083132	
$5s$	HyCI	0.7491023679	33.183592975	16.966347672	33.194498447	−0.00083136526	90.056194377
$6s$	MCHF	0.749498	48.7935	24.7715	48.8010		90.0316
$6s$	STO CI	0.7494981	48.793417	24.771458	48.800883	−0.0004686	90.031675
$6s$	Hylleraas					−0.00046860	
$6s$	HyCI	0.7494980626	48.793419058	24.771458560	48.800884586	−0.00046862501	90.031674844
$2p$	MCHF	0.752957	4.59531	2.67413	4.70028		92.4780
$2p$	STO CI	0.7529521	4.5949727	2.673962	4.699957	−0.0367194	92.479403
$2p$	HyCI	0.7529521689	4.5949711414	2.6739616552	4.6999550075	−0.03671932603	92.479401620
$3p$	MCHF	0.750680	11.8929	6.32179	11.9326		90.7037
$3p$	STO CI	0.7506798	11.891578	6.321129	11.931205	−0.0104204	90.703469
$3p$	Hylleraas					−0.010420	
$3p$	HyCI	0.7506797880	11.891576301	6.3211280446	11.931203148	−0.01042038644	90.703468559
$4p$	MCHF	0.750259	22.1892	11.4697	22.2097		90.2902
$4p$	STO CI	0.7502588	22.187141	11.468700	22.207621	−0.0042930	90.289802
$4p$	Hylleraas					−0.0042928	
$4p$	HyCI	0.7502588517	22.187142035	11.468700443	22.207622662	−0.00429301633	90.289801424
$5p$	MCHF	0.750126	35.4872	18.1187	35.4996		90.1466
$5p$	STO CI	0.7501259	35.482420	18.116273	35.494866	−0.0021678	90.146335
$5p$	Hylleraas					−0.0021677	
$5p$	HyCI	0.7501259181	35.482422989	18.116274453	35.494869447	−0.00216781908	90.146336252

TABLE IV. *(Continued.)*

nl	Ref.	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
$6p$	MCHF	0.750071	51.7830	26.2665	51.7913		90.0842
$6p$	STO CI	0.7500708	51.777619	26.263845	51.785965	−0.0012434	90.083931
$6p$	Hylleraas					−0.0012434	
$6p$	HyCI	0.7500707571	51.777613653	26.263842205	51.785959760	−0.00124339176	90.083932914
$3d$	MCHF	0.750084	10.4760	5.61304	10.5079		90.2432
$3d$	STO CI	0.7500851	10.475743	5.612914	10.507632	−0.0036067	90.243604
$3d$	Hylleraas					−0.0035498	
$3d$	HyCI	0.7500850641	10.475742254	5.6129136593	10.507631324	−0.00360673888	90.243604213
$4d$	MCHF	0.750038	20.9666	10.8583	20.9840		90.1020
$4d$	STO CI	0.7500392	20.966144	10.858092	20.983497	−0.0015122	90.102125
$4d$	Hylleraas					−0.0014867	
$4d$	HyCI	0.7500392040	20.966145781	10.858092493	20.983498596	−0.00151217291	90.102125592
$5d$	MCHF	0.750020	34.4578	17.6039	34.4687		90.0524
$5d$	STO CI	0.7500208	34.457159	17.603590	34.468042	−0.0007718	90.052125
$5d$	Hylleraas					−0.00075876	
$5d$	HyCI	0.7500208306	34.457163048	17.603591939	34.468045948	−0.00077185417	90.052125641
$6d$	MCHF	0.750012	50.9491	25.8496	50.9566		90.0303
$6d$	STO CI	0.7500123	50.948365	25.849189	50.955820	−0.0004459	90.030109
$6d$	Hylleraas					−0.00043866	
$6d$	HyCI	0.7500122882	50.948370592	25.849191440	50.955825385	−0.00044589124	90.030111745

P-state calculations, which produce a total of $616 + 1$, $896 + 1$, $504 + 1$, and $896 + 1$ basis functions for ^1S, ^1P, ^3S, and ^3P states, respectively. Basis sets (7,6)1 are used for $^{1,3}D$ states, where the total numbers of terms in the expansion of system wave functions are $852 + 1$ and $780 + 1$. The notation $+1$ simply refers to the additional single product of hydrogenic orbitals as in the ground state calculations. The system energies calculated for all states investigated here are compared to the benchmark values obtained by Drake [7] and Nakashima *et al.* [95]. The relative errors are generally lying between 10^{-13} and 10^{-10}, with higher-lying states less accurate than the lower-lying ones. The accuracy of the system wave functions for these excited states can then be estimated accordingly. It is expected that all radial and angular quantities displayed in Tables III and IV are accurate to the listed significant digits, except that the last one may contain a rounding error.

The MCHF calculations of Koga *et al.* [35] and our previous STO CI results [52] are included in the tables for comparison, together with the values of $\langle \cos\theta_{12} \rangle$ calculated by Cann *et al.* [96,97] using the Hylleraas basis functions for $1snl$ ($n \geqslant 3$) states. The exponential correlated basis calculations performed by Thakkar and Smith [98] and Frolov [92] about $\langle r \rangle$, $\langle r_{12} \rangle$, and $\langle \cos\theta_{12} \rangle$ are also available, however for He $1s2s\ ^{1,3}S$ states only. Compared to the MCHF, STO CI, and previous Hylleraas results, the present work based on HyCI basis functions improves significantly all the quantities investigated here. The differences between the HyCI and our previous STO CI results diminishes as the atom is increasingly excited. Indeed, for high-lying singly excited states with $n > 6$ the STO CI results are good enough to give a quantitative estimate of the variation trend for both radial and angular quantities. In our previous work [52] we left the unresolved problem that the predictions of $\langle \cos\theta_{12} \rangle$ for $^{1,3}D$ states by Cann *et al.* [96,97] using Hylleraas basis functions are systematically smaller than our STO CI results. The present HyCI calculations fully support the STO CI ones, keeping in mind that the computational procedures between these two types of basis functions are quite different.

With continuously increasing excitation of the He atom, the geometric quantities approach their Rydberg limits monotonically,

$$\begin{aligned}
\langle r_< \rangle &\to 3/4, \\
\langle r_> \rangle &\to [3n^2 - l(l+1)]/2, \\
\langle r \rangle &\equiv [\langle r_< \rangle + \langle r_> \rangle]/2, \\
\langle r_{12} \rangle &\to \sqrt{\langle r_< \rangle^2 + \langle r_> \rangle^2}, \\
\langle \cos\theta_{12} \rangle &\to 0, \\
\langle \theta_{12} \rangle &\to \pi/2,
\end{aligned} \tag{33}$$

with the exception for $1sns\ ^1S$ states, where $\langle r_< \rangle$ first increases and exceeds the asymptotic limit, reaches a maximum at $1s5s$ state, and then decreases to the asymptotic value 3/4.

Another interesting phenomenon is the relationship between radial quantities $\langle r_> \rangle$ and $\langle r_{12} \rangle$, which has been shown by Matsuyama and Koga [24] following a nearly linear law. We plot in Fig. 2 the variations of $\langle r_{12} \rangle$ along with $\langle r_> \rangle$ for all excited states investigated here. The fitting formulas are $\langle r_{12} \rangle \approx 0.999\langle r_> \rangle + 0.050$ and $\langle r_{12} \rangle \approx 0.999\langle r_> \rangle + 0.061$ for singlet and triplet states, respectively, which show a relationship of $\langle r_{12} \rangle \approx \langle r_> \rangle$ between singlet and triplet excited states which is similar to the MCHF predictions by Matsuyama and Koga [24], which are $\langle r_{12} \rangle \approx 0.998450\langle r_> \rangle + 0.057663$ and $\langle r_{12} \rangle \approx 0.997940\langle r_> \rangle + 0.071538$ for singlet and triplet states, respectively. Recalling that the sampling data used in the fitting procedure are different from each other, the good linearity between these two radial quantities can be well established. The relationships between $\langle r_{12} \rangle$ and the

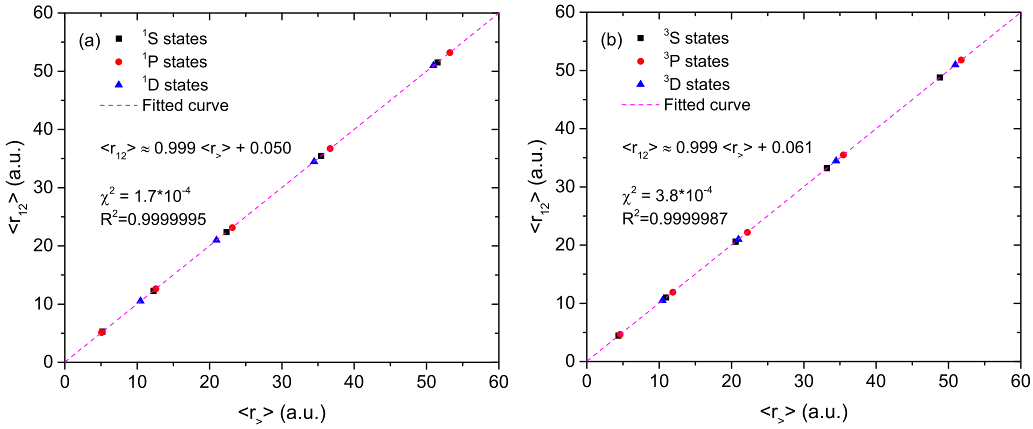

FIG. 2. Linear fitting of the radial quantities $\langle r_{12}\rangle$ with respect to $\langle r_>\rangle$ for $1snl$ singly excited states of the He atom with $n \leqslant 6$. Scatters are calculated values and the line is the fitted curve with a linear formula $y = ax + b$. The reduced χ^2 refers to the goodness of the overall fit. (a) Singlet excited states and (b) triplet excited states.

maximum location of the outer radial density for the He atom [25] and those between $\langle r_>^{-1}\rangle$ and the interelectronic repulsion energy for complex atoms [22] have been discussed by the corresponding authors and they will not be addressed here.

C. He-like ions

In this section the variation of radial and angular quantities with respect to the nuclear charge Z is investigated. For H^-, where the convergence of the system energy is slowest in He-like ions due to the largest contribution of electron correlation effects, the HyCI basis sets (7,6)2, (7,7)2, and (8,7)2 are employed to gradually estimate the radial and angular quantities. The (7,6)2 and (7,7)2 sets have been applied to the He atom, as was shown in Sec. III A. For higher-charged ions, the basis set (7,6)2 is responsible for producing reasonably accurate system energies and wave functions. The relative errors of the calculated ground-state energies for He-like ions with $Z \leqslant 10$ are displayed in Fig. 3; the benchmark calculations are available in the literature [58]. The corresponding radial and angular quantities investigated in this work are compared with other theoretical calculations based on different methods or different types of basis function and the results are shown in Table V.

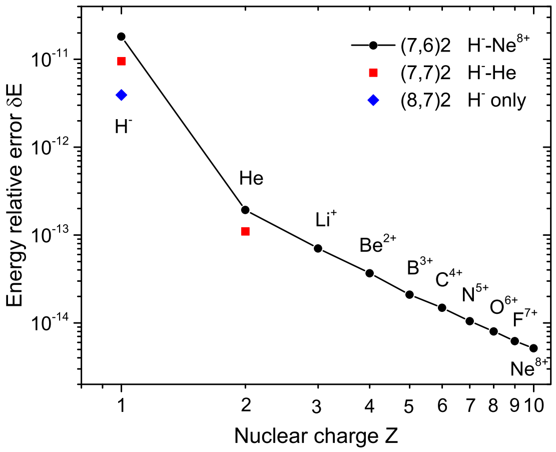

FIG. 3. Relative errors of the ground-state binding energies for He-like ions with $Z \leqslant 10$. The HyCI basis sets (76)2, (7,7)2, and (8,7)2 are used for H^-, (7,6)2, and (7,7)2 for He and (7,6)2 for higher-charged ions.

The MCHF calculations by Koga and Matsuyama [21,28,33] are available for only $\langle\cos\theta_{12}\rangle$ and $\langle\theta_{12}\rangle$. As a self-consistent theory partially considering the electron correlation effects, their results are good enough to predict the behavior of angular quantities when changing Z. The earlier exponential correlated basis results of Thakkar and Smith [59] show more improvement than the MCHF results on $\langle\cos\theta_{12}\rangle$, while the recent calculations of Frolov [10,92,99,100] employing a similar type of basis functions have established the most accurate predictions in the literature for $\langle r\rangle$, $\langle r_{12}\rangle$, and $\langle\cos\theta_{12}\rangle$, and their results are considered as benchmark values for comparison. The calculations of the Hylleraas basis including logarithm functions performed by Nakashima and Nakatsuji [94] obtained the most accurate system energies so far and they are also the only calculations of $\langle r_>\rangle$ based on explicitly correlated type basis functions (although the authors labeled them as $\langle r_1\rangle$). From the comparison it is seen that our HyCI results are in good agreement with other state-of-the-art explicitly correlated basis calculations for $\langle r\rangle$, $\langle r_{12}\rangle$, and $\langle\cos\theta_{12}\rangle$, give the complementary radial quantities $\langle r_<\rangle$ and $\langle r_>\rangle$ simultaneously, and improve significantly the interelectronic angle $\langle\theta_{12}\rangle$.

To investigate the variation trends of radial and angular quantities by changing the nuclear charge, it is useful to scale all radial variables with respect to Z [79]. The new Hamiltonian now becomes

$$H' = -\frac{1}{2}\nabla^2_{\rho_1} - \frac{1}{2}\nabla^2_{\rho_2} - \frac{1}{\rho_1} - \frac{1}{\rho_2} + \frac{1}{Z}\frac{1}{\rho_{12}}, \tag{34}$$

in which

$$\rho_i = Zr_i, \quad i =<,>,1,2,12. \tag{35}$$

At the limit of $Z \to \infty$, where all interelectronic correlation disappears, the (Z-scaled) wave function of two-electron systems becomes the product of two hydrogenic orbitals. For the ground state it reads

$$\Psi_0'(\vec{\rho}_1,\vec{\rho}_2) = C_0\phi_{1s}(\rho_1)\phi_{1s}(\rho_2)Y_{00}(\hat{\rho}_1)Y_{00}(\hat{\rho}_2). \tag{36}$$

TABLE V. Comparison of the nonrelativistic energy and various radial and angular quantities for He-like ions ($Z \leqslant 10$) in their ground state obtained in this work with other theoretical calculations. The reference "MCHF" represents the predictions of Koga and Matsuyama [21,28,33], "EC" and "EC2" are the exponential correlated basis calculations of Thakkar and Smith [59] and Frolov and Smith [10,92,99,100], respectively, "Hylleraas log" is the Hylleraas-like basis including logarithm functions by Nakashima and Nakatsuji [94], "Hylleraas" is the Hylleraas basis results of Drake [7], "$(n_1, n_2)k_{\max}$" is the present work based on HyCI-type basis functions, and "fitted" refers to the extrapolated values for the highly charged ion Ca^{18+} based on the fitting formula (see the text for more details).

Ions	Ref.	E	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
H^-	MCHF	−0.527713	1.427870	3.994040	2.710955		−0.105243	97.120
H^-	EC	−0.527750985			2.710175415	4.41268850	−0.10514789	
H^-	(7,6)2	−0.5277510165348	1.427714521	3.992642010	2.710178265	4.412694472	−0.105147693663	97.113720144
H^-	(7,7)2	−0.5277510165393	1.427714521	3.992642022	2.710178271	4.412694484	−0.105147693617	97.113720158
H^-	(8,7)2	−0.5277510165422	1.427714520	3.992642030	2.710178275	4.412694492	−0.105147693587	97.113720153
H^-	Hylleraas log	−0.527751016544377		3.99264203644		4.41269449799		
H^-	EC2	−0.527751016544377			2.7101782784444	4.4126944979917	−0.10514769356597	
H^-	Hylleraas	−0.527751016544377			2.710178278444	4.412694497992		
He	MCHF	−2.90360	0.602438	1.256535	0.929487		−0.064266	94.360
He	EC	−2.903724363			0.929472196	1.42207008	−0.064202621	
He	(7,7)2	−2.9037243770338	0.60235941877	1.25658517097	0.929472294873	1.422070255565	−0.0642026142192	94.355490042
He	Hylleraas log	−2.903724377034119		1.25658517095		1.42207025553		
He	EC2	−2.903724377034119			0.9294722948736	1.4220702555658	−0.06420261421919	
He	Hylleraas	−2.903724377034119			0.929472294874	1.422070255566		
Li^+	MCHF	−7.27975	0.380565	0.764986	0.572776		−0.043665	92.965
Li^+	EC	−7.27991327			0.572774165	0.862315292	−0.043632137	
Li^+	(7,6)2	−7.2799134126688	0.38051296593	0.76503533401	0.572774149970	0.862315375454	−0.0436322999334	92.963239422
Li^+	Hylleraas log	−7.279913412669305		0.76503533402		0.86231537545		
Li^+	EC2	−7.279913412669305			0.5727741499712	0.8623153754557	−0.04363229993338	
Li^+	Hylleraas	−7.279913412669305			0.572774149971	0.862315375456		
Be^{2+}	MCHF		0.278045	0.550522	0.414283		−0.032960	92.240
Be^{2+}	EC	−13.6555650			0.414283415	0.618756549	−0.032941229	
Be^{2+}	(7,6)2	−13.6555662384231	0.27800536213	0.55056129388	0.414283328006	0.618756314065	−0.0329409877490	92.238437900
Be^{2+}	Hylleraas log	−13.65556623842358		0.55056129388		0.61875631406		
Be^{2+}	EC2	−13.65556623842358			0.4142833280063	0.6187563140657	−0.03294098774898	
Be^{2+}	Hylleraas	−13.65556623842358			0.414283328006	0.618756314066		

TABLE V. *(Continued.)*

Ions	Ref.	E	$\langle r_< \rangle$	$\langle r_> \rangle$	$\langle r \rangle$	$\langle r_{12} \rangle$	$\langle \cos\theta_{12} \rangle$	$\langle \theta_{12} \rangle$
B^{3+}	EC	−22.0309704			0.3245556845	0.482435504	−0.026437366	
B^{3+}	MCHF		0.219022	0.430090	0.324556		−0.026450	91.798
B^{3+}	(7,6)2	−22.0309715802423	0.21899028496	0.43012120412	0.324555744543	0.482435849685	−0.0264374836422	91.797141082
B^{3+}	Hylleraas log	−22.03097158024278		0.43012120412		0.48243584968		
B^{3+}	EC2	−22.03097158024278			0.3245557445430	0.4824358496849	−0.02643748364215	
C^{4+}	MCHF						−0.022081	91.501
C^{4+}	EC	−32.4062454			0.2667938005	0.395316696	−0.022072207	
C^{4+}	(7,6)2	−32.4062466018980	0.18063870595	0.35294903111	0.266793868532	0.395316907599	−0.0220722806293	91.500766662
C^{4+}	Hylleraas log	−32.40624660189853		0.35294903111		0.39531690759		
C^{4+}	EC2	−32.40624660189853			0.2667938685321	0.3953169075993	−0.02207228062931	
N^{5+}	MCHF						−0.018948	91.288
N^{5+}	EC	−44.7814439			0.2264923355	0.334839523	−0.018941840	
N^{5+}	(7,6)2	−44.7814451487722	0.15371653167	0.29926826953	0.226492400601	0.334839661696	−0.0189418712904	91.288142105
N^{5+}	Hylleraas log	−44.78144514877270		0.29926826953		0.33483966169		
O^{6+}	MCHF						−0.016593	91.128
O^{6+}	EC	−59.1565938			0.196771716	0.290406322	−0.016587984	
O^{6+}	(7,6)2	−59.1565951227575	0.13377766684	0.25976587535	0.196771771095	0.290406415390	−0.0165880065012	91.128214481
O^{6+}	Hylleraas log	−59.15659512275792		0.25976587535		0.29040641538		
F^{7+}	MCHF						−0.014758	91.004
F^{7+}	EC	−75.5317108			0.173947752	0.256381467	−0.014753869	
F^{7+}	(7,6)2	−75.5317123639590	0.11841717094	0.22947840179	0.173947786367	0.256381544521	−0.0147539351509	91.003574390
F^{7+}	Hylleraas log	−75.53171236395949		0.22947840179		0.25638154452		
Ne^{8+}	MCHF						−0.013288	90.904
Ne^{8+}	EC	−93.9068024			0.1558690945	0.229491864	−0.013285282	
Ne^{8+}	(7,6)2	−93.9068065150371	0.10622060996	0.20551757051	0.155869090237	0.229491873880	−0.0132847478947	90.903713014
Ne^{8+}	Hylleraas log	−93.90680651503754		0.20551757051		0.22949187388		
Ca^{18+}	(7,6)2	−387.657233833154	0.05232549028	0.10054657610	0.076436033194	0.112003514202	−0.0066547433486	90.452866145
Ca^{18+}	fitted		0.052319	0.100515	0.076420	0.111972	−0.006668	90.452680

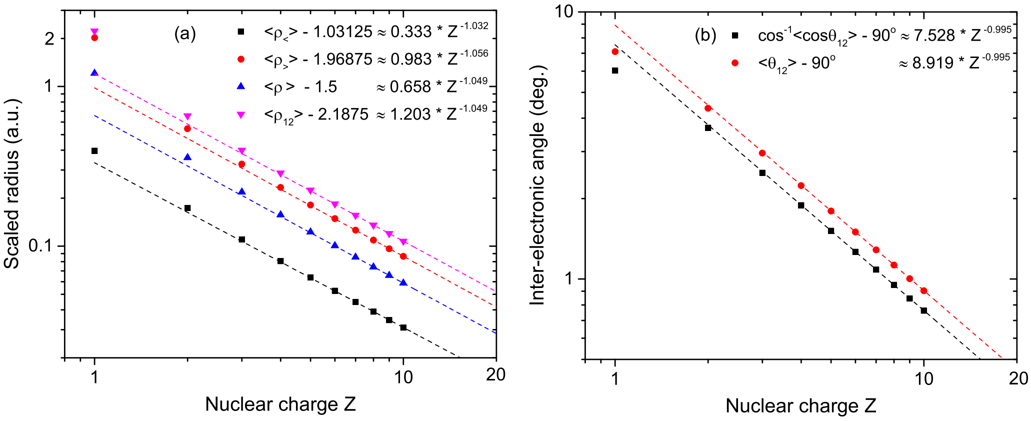

FIG. 4. Deviations of the Z-scaled radial and angular quantities investigated in this work with respect to their corresponding limits at $Z \to \infty$.

After a simple calculation, it can be obtained that, at $Z \to \infty$,

$$\begin{aligned}
\langle \rho_< \rangle &\to 1.031\,25,\\
\langle \rho_> \rangle &\to 1.968\,75,\\
\langle \rho \rangle &\to 1.5,\\
\langle \rho_{12} \rangle &\to 2.1875,\\
\langle \cos\theta_{12} \rangle &\to 0,\\
\langle \theta_{12} \rangle &\to \pi/2.
\end{aligned} \tag{37}$$

In Fig. 4 we show the deviations of various scaled radial and angular quantities with respect to their asymptotic values for He-like ions with $Z = 1$–10. The fitting processes are performed only on the last several points in each group of data. It is observed that all these quantities approach their corresponding limits in power laws, except that for the H^- ion they deviate far from the fitted curves. We can also see that the quantity $\langle \rho \rangle$ follows almost the same speed as $\langle \rho_{12} \rangle$ when they go to the limit, whereas $\langle \rho_< \rangle$ and $\langle \rho_> \rangle$ are faster and slower, respectively. As for angular quantities, both $\langle \theta_{12} \rangle$ and $\arccos\langle \cos\theta_{12} \rangle$ share almost the same speed. We finally test the fitting formulas by applying them to Ca^{18+}. Both the HyCI calculations based on the (7,6)2 basis set and those based on the extrapolated values are presented at the bottom of Table V. In most cases, almost four digits after the decimal points can be reproduced, which demonstrates the applicability of fitting formulas to highly charged ions.

IV. CONCLUSION

We have presented a comprehensive investigation of the radial ($\langle r_< \rangle$, $\langle r_> \rangle$, $\langle r \rangle$, and $\langle r_{12} \rangle$) and angular ($\langle \theta_{12} \rangle$ and $\langle \cos\theta_{12} \rangle$) geometric quantities for the He atom in both ground and singly excited states within S, P, and D symmetries. The explicitly correlated HyCI basis functions combined with a product of screened hydrogenic orbitals are used to expand the system wave functions. When the dimension of the basis set is increasingly large, Löwdin's canonical orthogonalization method is employed to overcome the possible linearly dependent problems which are inevitable when adopting a limited-precision arithmetic in numerical computations. With the r_{12} coordinate included explicitly in the system wave function, we have successfully developed computational methods to analytically calculate the arbitrary powers of the inner and outer radii, i.e., $\langle r_<^n \rangle$ and $\langle r_>^n \rangle$, as well as the arbitrary powers of the interelectronic angle $\langle \theta_{12}^n \rangle$. It was found that the summation in the multipole expansion of angular function is infinite in the calculation of the angular quantities. This is not surprising due to the fact that angular momentum couplings in explicitly correlated type basis functions are infinitely high. A truncation and power-law extrapolation technique was used in this work to calculate this quantity to high accuracy.

Compared with the HF and MCHF results of Koga *et al.* and our previous STO CI calculations, the present work based on HyCI basis sets improved significantly the accuracy of all geometric quantities for the He atom in both the ground and excited states, where $\langle r_< \rangle$, $\langle r_> \rangle$, and $\langle \theta_{12} \rangle$ are the most accurate predictions. For other quantities, such as $\langle r \rangle$, $\langle r_{12} \rangle$, and $\langle \cos\theta_{12} \rangle$, our results are in good agreement with state-of-the-art calculations based on different types of explicitly correlated basis functions. We have also applied the present methods to He-like ions, where the electron correlation effects are decreasing with increasing nuclear charge. A Z-scaled investigation of the two-electron systems shows that either the scaled radial or the angular quantities approach corresponding high-Z limits following power laws. This is useful in estimating the geometric structures of highly charged ions.

It is interesting to note that an extension of the present work to exotic systems, such as three-body atomic or molecular systems including muons, antiprotons, pions, or positrons, is promising, where extensive studies on their binding and structural properties are available in the literature [101–103]. Calculations of their geometric quantities are expected to be very useful. The critical phenomena in atomic systems have become increasingly interesting in recent years, e.g., the changes from bound to free states in two-electron systems with fractional charges [104] or in screened Yukawa atoms [105,106] and the transformation from a metastable bound state to a shape resonance [107] or from a Feshbach resonance to shape resonances [108,109] in a critical screening environment. Investigations of the variation of the geometric structure for these states may also shed some light on those vital problems.

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