Compact representation of helium wave functions in perimetric and hyperspherical coordinates

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Variational calculations of the ground-state energy of helium are performed using a basis set representation that includes an explicit treatment of the Fock expansion in hyperspherical coordinates. The construction of basis functions that have the correct cusp behavior at three-particle coalescence points and the evaluation of integrals containing these functions is discussed. The basis set in hyperspherical coordinates is added to a basis set consisting of products of Laguerre polynomials in perimetric coordinates. It is demonstrated that the use of Fock basis functions provides a substantial improvement in the convergence rate of the basis set expansion.

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I. INTRODUCTION

A two-electron atomic system is an excellent testing ground for new quantum theories since it is the simplest system with enough complexity to contain the main features of a many-body theory. This complexity arises from the electron-electron Coulomb energy which depends on the interelectronic distance $r_{12}=|\vec{r}_1-\vec{r}_2|$. Furthermore, the scaled Hamiltonian for infinite nuclear mass and charge Z, given in atomic units by

$$H=-\frac{1}{2}(\nabla_1^2+\nabla_2^2)-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{Zr_{12}}, \tag{1}$$

does not depend on any experimental constants whose values change with improvements in measurement techniques. Therefore, it provides a standard for theoretical calibration. After the wave function belonging to this Hamiltonian has been obtained, it is possible to compute perturbative corrections to the nonrelativistic energy. It has been established [1] that relativistic and QED corrections to the energy levels of an atomic or molecular system require highly accurate nonrelativistic wave functions. Rayleigh-Ritz variational calculations provide a wave function with relative error approximately proportional to the square root of the relative error in the energy. Therefore, if nonrelativistic variational wave functions are to be used for perturbative applications, and if the energies are used to estimate the quality of the wave functions, then it is necessary to calculate the nonrelativistic energies to far greater accuracy than would otherwise be needed.

The success of variational calculations depends upon the rate of convergence of the basis set expansion used to construct the trial wave function. The convergence rate is controlled by the analytic structure of the exact wave function [2–7]. For problems in atomic or molecular physics, the main consideration when constructing trial wave functions is the cusp behavior at two particle coalescences. This behavior is described by the Kato condition [2]

$$\left(\frac{\partial\hat{\Psi}}{\partial \boldsymbol{r}_{ij}}\right)_{r_{ij}=0}=\mu_{ij}q_iq_j\Psi(\boldsymbol{r}_{ij}=0), \tag{2}$$

where μ_{ij} is the reduced mass of particles i and j, q_i and q_j are the charges of the two particles, and the caret over the wave function denotes a spherical average. A lesser but still very important consideration is the cusp behavior at three-particle coalescences. This behavior is believed to be properly described by the Fock expansion [8–13]

$$\Psi(r,\alpha,\theta)=\sum_{k=0}^{\infty}\sum_{l=0}^{[k/2]}\psi_{k,l}(\alpha,\theta)r^k(\ln r)^l, \tag{3}$$

where use of the hyperspherical coordinates r,α, and θ [defined in Eqs. (18)–(20) below] reveals the presence of a logarithmic singularity as the hyperradius tends to zero. This region is only a tiny part of the full configuration space and is often neglected when constructing trial wave functions. In such cases, the convergence rate can be very slow, particularly if the basis functions that must approximate the neighborhood of the singularity are inflexible. A primary objective of this work is to handle the logarithmic singularity directly so that the remainder of the basis set is free to concentrate on regions of configuration space that are further away from the nucleus. If successful, this strategy should provide an improved convergence rate for the basis set expansion, or equivalently, a more compact representation of the helium wave function.

Many different basis sets have been applied to the helium Hamiltonian (1) with varying degrees of success. It is not the intent of this work to provide a complete account of the many contributions that have been reported in the literature for this problem. However, we would like to benchmark the present method, so it is useful to provide a brief review of some of the current standards. One very successful method is to use a Hylleraas-type basis set [14] which effectively handles the electron correlation through use of r_{12} as a coordinate. A related method introduced by Drake [15,16] uses "doubled" basis sets in which two different exponential scale factors are used for each combination of $\boldsymbol{r}_1^i\boldsymbol{r}_2^j\boldsymbol{r}_{12}^k$. This method, originally designed for states of high angular momentum [15], has been successfully applied to S-states by Drake [16] and also by Kleindienst, Lüchow, and Merckens [17]. These basis sets build in the two-particle cusps due to the linear terms in $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, and $\boldsymbol{r}_{12}$, but generally have difficulty handling the three-particle cusp characterized by the logarithmic terms of the Fock expansion. Nevertheless, these

basis sets tend to be very flexible, particularly the doubled basis sets, so that the three-particle cusp may be adequately approximated if enough functions are used. Another method, introduced by Frankowski and Pekeris [18,19], uses the basis functions

$$\phi_{n,l,m,j}(s,t,u)=s^n t^l u^m (\ln s)^j \exp(-s/2)\times\begin{cases}\cosh(ct)\\ \sinh(ct)\end{cases} \tag{4}$$

in the Hylleraas coordinates

$$s=r_1+r_2,\quad t=r_2-r_1,\quad u=r_{12},$$

subject to the constraints

$$l,m\geqslant 0,$$

and

$$\begin{cases}(n+l+m)\geqslant 2j\geqslant 0 & \text{if } n\geqslant 0,\\ (n+l+m)\geqslant 2j+2\geqslant 0 & \text{if } n<0.\end{cases}$$

This basis set provides the correct cusp structure at all two-particle coalescences due to linear terms in r_1, r_2, and r_{12} and the correct singularity structure at the three-particle coalescence since the logarithmic terms of the Fock expansion are expandable in powers of $s, \ln(s)$, and (t/s). For the ground state, the nonlinear variational parameter c is zero, and it is required that l be even in order to ensure that the basis set has the proper symmetry under exchange of particles $\boldsymbol{r}_1 \leftrightarrow \boldsymbol{r}_2$, or equivalently, $t\leftrightarrow -t$. For excited states, c is used to build in the correlation that occurs when one electron is close to the nucleus with the other electron far away. The choice of $\cosh(ct)$ or $\sinh(ct)$ is made to give the basis function the proper symmetry under exchange of particles. Hence for singlet states $\cosh(ct)$ is used when the index l is even and $\sinh(ct)$ is used with odd values of l. For triplet states the situation is reversed. The Frankowski-Pekeris method described above has been used by Baker, Freund, Hill, and Morgan [20] to calculate very accurate wave functions for the low-lying S-states of helium using only several hundred basis functions. The basis set was very successful in application to high-energy double photoionization [21] where a proper description of electron correlation near the nucleus is essential. It can, however, be difficult to use in some cases because of possible computational linear dependence problems as the size of the basis set increases.

Another successful method [22–25] is to use a Laguerre basis in perimetric coordinates. This basis set is analytically equivalent to Hylleraas-type basis sets. Therefore, it builds in the two-particle cusps but fails to effectively model the three-particle cusp characterized by the logarithmic terms of the Fock expansion. The method, however, is very efficient since the matrix element integrals can be evaluated analytically. Also, since Laguerre polynomials are numerically stable and since the relevant matrices are sparse, many functions can be included in the basis set. In fact, Bürgers *et al.* [25] have used better than ten thousand such functions in order to obtain a benchmark nonrelativistic ground-state energy.

Large numbers of basis functions are now routinely being used together with advances in computing power to produce remarkable new benchmarks for the ground-state energy of helium [26–30]. Schwartz has likened this effort to the competition between mathematicians to compute ever more digits of the number π [30]. Some of the recent calculations, most notably those of Korobov [27], have achieved their success using simple expansions that seem to ignore the analytic structure of the wave function. Like the Laguerre basis in perimetric coordinates [25], the latest benchmarks [26–30] require several thousands of basis functions. In the present work, we desire to utilize the insights provided by our current understanding of the analytic properties of the wave function, and find a basis which will cut down on the number of functions needed to get good convergence. In doing so, we remove the flexibility provided by other methods and confirm the importance of the logarithmic singularity.

The present approach uses the Laguerre basis in perimetric coordinates as a primary basis in order to build in the correct two-particle cusps. A small number of functions which exactly incorporate the first few terms of the Fock expansion are then added to the primary Laguerre basis. The computational linear dependence problem that plagues some methods is not an issue here since the Laguerre functions are close to orthogonal and the number of Fock functions is small. Furthermore, we expect that the number of Laguerre functions will be considerably reduced as a consequence of dealing with the three-particle cusp directly. In the following sections, we will show how these "Fock functions" can be derived and also how the matrix element integrals containing the Fock functions can be evaluated to 30 digits via Gaussian quadrature in three dimensions. We use the new basis set to variationally solve the Schrödinger equation for the Hamiltonian (1). The optimized nonlinear parameters are given for the new basis sets, and the variational energies are compared with well-known values obtained using the standard basis sets described above.

II. COORDINATES AND NOTATION

The Hamiltonian (1) contains six independent coordinates. The most common set of six coordinates consists of the electronic spherical polar coordinates r_1, θ_1, ϕ_1, and $\boldsymbol{r}_2$, θ_2, ϕ_2. The kinetic-energy operator in these coordinates is given by

$$-\frac{1}{2}(\nabla_1^2+\nabla_2^2)=-\frac{1}{2}\sum_{n=1}^{2}\left(\frac{\partial^2}{\partial r_n^2}+\frac{2}{r_n}\frac{\partial}{\partial r_n}+\frac{\Lambda_n}{r_n^2}\right), \tag{5}$$

where

$$\Lambda_n=\frac{1}{\sin\theta_n}\frac{\partial}{\partial\theta_n}\left(\sin\theta_n\frac{\partial}{\partial\theta_n}\right)+\frac{1}{\sin^2\theta_n}\frac{\partial^2}{\partial\varphi_n^2}. \tag{6}$$

In order to take account of the effects of electron-electron correlation, it is convenient to use coordinate systems that

explicitly contain the interelectronic distance $\boldsymbol{r}_{12}$. The most common set is r_1, r_2, r_{12}, α, β, and γ, where α, β, and γ are the three Euler angles which specify the rotation from the space-fixed axes to the body-fixed axes. For $\boldsymbol{S}$ states, the Euler angles are ignorable and the kinetic-energy operator is given by

$$-\frac{1}{2}(\nabla_1^2+\nabla_2^2)=-\frac{1}{2}\left(\frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{2}{r_2}\frac{\partial}{\partial r_2}+\frac{4}{r_{12}}\frac{\partial}{\partial r_{12}}+\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+2\frac{\partial^2}{\partial r_{12}^2}+\frac{r_1^2-r_2^2+r_{12}^2}{r_1 r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}+\frac{r_2^2-r_1^2+r_{12}^2}{r_2 r_{12}}\frac{\partial^2}{\partial r_2\partial r_{12}}\right), \tag{7}$$

with the volume element

$$d\tau=8\pi^2(r_1 r_2 r_{12})dr_1 dr_2 dr_{12}. \tag{8}$$

The coordinates r_1, r_2, and r_{12} are easily transformed to the perimetric coordinates [22]

$$q_1=-r_1+r_2+r_{12}, \tag{9}$$

$$q_2=r_1-r_2+r_{12}, \tag{10}$$

$$q_{12}=r_1+r_2-r_{12}, \tag{11}$$

with each coordinate having domain $[0,\infty]$ as a consequence of the triangle condition for r_1, r_2, and r_{12}. The kinetic energy in perimetric coordinates is

$$-\frac{1}{2}(\nabla_1^2+\nabla_2^2)=(r_1 r_2 r_{12})^{-1}\left\{\frac{\partial}{\partial q_{12}}(Q_1+Q_2)\frac{\partial}{\partial q_{12}}+\frac{\partial}{\partial q_2}P_1\frac{\partial}{\partial q_2}+\frac{\partial}{\partial q_1}P_2\frac{\partial}{\partial q_1}-\frac{\partial}{\partial q_{12}}Q_1\frac{\partial}{\partial q_2}-\frac{\partial}{\partial q_2}Q_1\frac{\partial}{\partial q_{12}}-\frac{\partial}{\partial q_{12}}Q_2\frac{\partial}{\partial q_1}-\frac{\partial}{\partial q_1}Q_2\frac{\partial}{\partial q_{12}}\right\}, \tag{12}$$

where

$$P_1=2Q_1+Q_{12}+2q_1q_2q_{12}, \tag{13}$$

$$P_2=2Q_2+Q_{12}+2q_1q_2q_{12}, \tag{14}$$

and

$$Q_1=q_{12}^2q_2+q_{12}q_2^2, \tag{15}$$

$$Q_2=q_{12}^2q_1+q_{12}q_1^2, \tag{16}$$

$$Q_{12}=q_1^2q_2+q_1q_2^2. \tag{17}$$

The conventional hyperspherical coordinates r, α, and θ are obtained from r_1, r_2, and r_{12} via the definitions

$$r=\sqrt{r_1^2+r_2^2}, \tag{18}$$

$$\alpha=2\tan^{-1}\left(\frac{r_2}{r_1}\right), \tag{19}$$

$$\theta=\cos^{-1}\left(\frac{r_1^2+r_2^2-r_{12}^2}{2r_1r_2}\right). \tag{20}$$

The kinetic-energy operator in hyperspherical coordinates is given by

$$-\frac{1}{2}(\nabla_1^2+\nabla_2^2)=-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2}+\frac{5}{r}\frac{\partial}{\partial r}\right)-\frac{2}{r^2}\mathcal{L}, \tag{21}$$

where

$$\mathcal{L}=\frac{\partial^2}{\partial\alpha^2}+2\cot(\alpha)\frac{\partial}{\partial\alpha}+\csc^2(\alpha)\left[\frac{\partial^2}{\partial\theta^2}+\cot(\theta)\frac{\partial}{\partial\theta}\right]. \tag{22}$$

Another set of hyperspherical angles that turned out to be very useful in the present context was first introduced by Pluvinage [31]. These angles are defined by

$$\xi=\tan^{-1}\left[\frac{|\vec{r}_1+\vec{r}_2|(-r_1+r_2)+r_{12}(r_1+r_2)}{|\vec{r}_1+\vec{r}_2|(r_1+r_2)+r_{12}(r_1-r_2)}\right], \tag{23}$$

$$\eta=\tan^{-1}\left[\frac{|\vec{r}_1+\vec{r}_2|(r_1-r_2)+r_{12}(r_1+r_2)}{|\vec{r}_1+\vec{r}_2|(r_1+r_2)+r_{12}(-r_1+r_2)}\right]. \tag{24}$$

The angular kinetic-energy operator in Pluvinage coordinates is

$$\mathcal{L}=w(\xi,\eta)^{-1}\left\{\frac{\partial}{\partial\xi}\left[\sin(2\xi)\frac{\partial}{\partial\xi}\right]+\frac{\partial}{\partial\eta}\left[\sin(2\eta)\frac{\partial}{\partial\eta}\right]\right\}, \tag{25}$$

where

$$w(\xi,\eta)=[\sin(2\xi)+\sin(2\eta)]. \tag{26}$$

Using the Jacobian

$$\frac{\partial(r_1,r_2,r_{12})}{\partial(r,\xi,\eta)}=\frac{r^2}{\sqrt{2}}\cos\left(\frac{\xi+\eta}{2}\right), \tag{27}$$

together with Eqs. (8) and (26), gives the volume element

$$d\tau=\pi^2r^5w(\xi,\eta)drd\xi d\eta. \tag{28}$$

III. FOCK EXPANSION

In order to construct basis functions that incorporate the Fock expansion, it is necessary to know the angular coefficients $\psi_{k,l}$ in Eq. (3). The standard method for obtaining these coefficients is to put the Fock expansion into the

Schrödinger equation to get the recursion relation

$$\left[-\mathcal{L}-\frac{1}{4}k(k+4)\right]|\psi_{k,\ell}\rangle=(\ell+1)(k+2)|\psi_{k,\ell+1}\rangle+(\ell+1)\times(\ell+2)|\psi_{k,\ell+2}\rangle+\frac{1}{2}\left(\frac{r}{r_1}+\frac{r}{r_2}-\frac{r}{Zr_{12}}\right)|\psi_{k-1,\ell}\rangle+\frac{1}{2}E|\psi_{k-2,\ell}\rangle. \tag{29}$$

The inhomogeneous problem (29) was solved numerically by Feagin, Macek, and Starace [32]. It has also been solved independently by Hill [33] using hyperangles expressed in Pluvinage coordinates (23) and (24). The operator $\mathcal{L}$ in Pluvinage coordinates (25) is self-adjoint for ξ and η in the interval $[0,\pi/2]$ with the volume element (28). The eigenvalues of $\mathcal{L}$ are given by $-n(n+2)$ with n a non-negative integer, and the eigenvectors are given by [33,34]

$$\phi_{n,m}(\xi,\eta)=2^m m!\sqrt{\frac{(2m+1)(n+1)(n-m)!}{\pi(n+m+1)!}}[\cos(\eta-\xi)]^m P_m\left[\frac{\cos(\eta+\xi)}{\cos(\eta-\xi)}\right]C_{n-m}^{m+1}[\sin(\eta-\xi)], \tag{30}$$

where P_m and C_n^m are the Legendre and Gegenbauer polynomials, respectively. The operator on the left-hand side of Eq. (29) is singular if $k=2n$. Therefore, the right-hand side of Eq. (29) must be orthogonal to all of the eigenvectors belonging to this n if solutions are to exist. If solutions do exist, they will contain linear combinations of homogeneous solutions for each value of ℓ. Apart from the $\ell=0$ case, the constants in these linear combinations can be uniquely determined if the right-hand side of Eq. (29) is made orthogonal to the eigenvectors for $\ell-1$. The first few terms of the Fock expansion have been worked out analytically [8,12,33]. The result in Pluvinage coordinates is $\psi_{00}=1$ and

$$\psi_{10}=\frac{\sqrt{2}}{2Z}\sin\left(\frac{\eta+\xi}{2}\right)-\sqrt{2}\cos\left(\frac{\eta-\xi}{2}\right), \tag{31}$$

$$\psi_{20}=\frac{1}{6}\left(2-E+\frac{1}{2Z^2}\right)-\frac{2}{3Z}(\sin\xi+\sin\eta)+\sin(\eta+\xi)\times\left(\frac{\pi-\xi-\eta}{3\pi Z}\right)+\frac{1}{2}\cos(\eta-\xi)\left(1+\frac{1}{3Z}\right)+\frac{1}{3\pi Z}\sin(\eta-\xi)[F_{2d}(\xi)-F_{2d}(\eta)]+\cos(\eta+\xi)\left\{C-\frac{1}{2Z}\ln 2-\frac{1}{3Z}\ln\left[\cos\left(\frac{\xi}{2}-\frac{\pi}{4}\right)\cos\left(\frac{\eta}{2}-\frac{\pi}{4}\right)\right]\right\}, \tag{32}$$

$$\psi_{21}=\frac{1}{3Z}\left(\frac{2}{\pi}-1\right)\cos(\eta+\xi), \tag{33}$$

where C is the coefficient of the homogeneous solution at second order. The function $F_{2d}(\phi)$ and its derivative are defined by [33]

$$F_{2d}(\phi)=\frac{i}{2}\{\mathrm{Li}_2[1+\exp(2i\phi)]-\mathrm{Li}_2[1+\exp(i\pi+2i\phi)]\}+\pi\ln[1+\exp(i\phi)]-\frac{i\pi^2}{8}, \tag{34}$$

$$\frac{dF_{2d}(\phi)}{d\phi}=\frac{-2\phi+\pi[1-\cos(\phi)]}{\sin(2\phi)}, \tag{35}$$

where Li_2 is the dilogarithm function [35]. The first-order poles in Eq. (35) indicate that the function $F_{2d}(\phi)$ has logarithmic branch-point singularities at $\phi=n\pi/2$ for $n\neq 0$ and $n\neq 1$. Although these singularities are outside the physical range $0\leqslant\phi\leqslant\pi/2$, they will nevertheless have an important impact on the convergence rate of the basis set expansion used to obtain the higher-order terms of the Fock expansion and ultimately on the effectiveness of the numerical methods used to compute the matrix element integrals. To obtain the higher-order terms of the Fock expansion, the inhomogeneous problem (29) was solved numerically [33] using the Schwinger-Levine variational principle

$$\lambda=\max_{|\tilde{\chi}\rangle}\frac{|\langle\Psi|\tilde{\chi}\rangle|^2}{\langle\tilde{\chi}|A|\tilde{\chi}\rangle}. \tag{36}$$

The maximum is achieved when

$$|\tilde{\chi}\rangle=\frac{c}{A}|\Psi\rangle, \tag{37}$$

where c is an arbitrary constant. In the present case, $A=-\mathcal{L}-\frac{1}{4}k(k+4)$ and Ψ is equal to the right-hand side of Eq. (29). For each combination of k and ℓ, a trial function of the form

$$\tilde{\chi}(\xi,\eta)=\sum_{m=0}^{N}\sum_{n=0}^{N}c_{m,n}T_m(x)T_n(y) \tag{38}$$

was used [33], where T_m are Chebyshev polynomials of the first kind with x and y related to the Pluvinage angles by

$$\xi=\frac{\pi}{4}(x+1), \tag{39}$$

$$\eta=\frac{\pi}{4}(y+1). \tag{40}$$

Rapid convergence of the trial function (38) is necessary in order to devise an efficient quadrature scheme for matrix element evaluation (see Sec. V). The convergence rate for Chebyshev expansions may be analyzed [36,37] by considering the expansion of an arbitrary analytic function

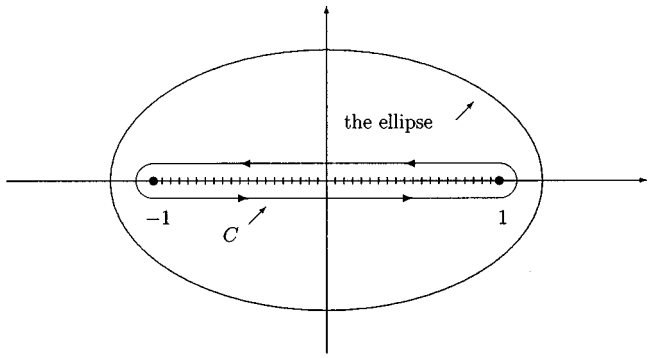

FIG. 1. The integration contour C and the ellipse of analyticity for evaluating the coefficients of a Chebyshev expansion [37] of the Fock expansion. The singularities that limit the size of the ellipse occur at ± 3 and yield coefficients c_n that decrease like R^{-n} with $R=3+2\sqrt{2}$.

$$f(x)=\sum_{n=0}^{\infty} c_n T_n(x)(1-x^2)^{-1/4}, \tag{41}$$

where

$$c_n=\frac{2}{\pi}\int_{-1}^{1} f(x)T_n(x)(1-x^2)^{-1/4}dx \tag{42}$$

for $n>0$. The coefficients c_n can be evaluated by using contour integration in the complex z plane. The result is [34]

$$c_n=\frac{2^{-n}}{i\pi}\int_C f(z)(1-z^2)^{1/4}(z-1)_2^{-n-1} \times F_1\left(n+1,n+\frac{1}{2};2n+1;\frac{2}{1-z}\right)dz. \tag{43}$$

The contour is shown in Fig. 1. The large-n behavior of c_n is dominated by R^{-n}, where R is the largest value such that $(1-z^2)^{1/4}f(z)$ is analytic within the ellipse [36,37]

$$\mathrm{Re}(z)=\tfrac{1}{2}(R+R^{-1})\cos(\theta), \tag{44}$$

$$\mathrm{Im}(z)=\tfrac{1}{2}(R-R^{-1})\sin(\theta), \tag{45}$$

with $0\leq\theta<2\pi$. For $R>1$, the series (41) converges to $f(z)$ for all z inside the ellipse (see Fig. 1) in analogy with the circular region of convergence of Taylor-series expansions. As shown above, the nearest singularities of the Fock expansion appear to occur in the ψ_{20} term at $-\pi/2$ and π. The inverse transformations of Eqs. (39) and (40) map these singularities to ± 3. Therefore, the coefficients c_n decrease like R^{-n} with $R=|z+\sqrt{z^2-1}|=3+2\sqrt{2}\approx 5.828$. This estimate is confirmed by the observed convergence behavior and is useful when analyzing matrix element evaluation in Sec. V.

IV. BASIS SET

From the considerations of the preceding section, we have at our disposal all the terms of the Fock expansion through any desired order. We note, however, that we cannot simply add the terms of the Fock expansion directly to our basis set since they do not falloff properly at large distances. We can get around the problem by building in the exponential decay at large distances and then removing the exponential effects at small distances. The resulting function is

$$\phi_K(r,\xi,\eta)=\sum_{k=0}^{K}\sum_{l=0}^{[k/2]} g_{K-k}(r,\xi,\eta)\psi_{k,l}(\xi,\eta)r^k(\ln r)^l, \tag{46}$$

where

$$g_k(r,\xi,\eta)=\sum_{m=0}^{k}\frac{1}{m!}[rf(\xi,\eta)]^m\exp[-rf(\xi,\eta)]. \tag{47}$$

The contribution from the function $f(\xi,\eta)$, which is needed to provide the proper falloff at large distance, is removed at small r so that ϕ_K reproduces the Fock expansion through order K. We note that the unknown energy E and the unknown coefficients c_m of the homogeneous solutions are contained within the single function ϕ_K. We could in principle treat these unknown parameters as nonlinear variational parameters and attempt to optimize them. A better approach is to use the expansion

$$\psi_{k,l}(\xi,\eta)=\sum_{m=0}^{M}\sum_{n=0}^{N} c_m E^n \psi_{k,l,m,n}(\xi,\eta), \tag{48}$$

in order to break up ϕ_K into separate basis functions, and then use the diagonalization to determine the values of the unknown parameters. This procedure uniquely defines the Fock functions which we denote $\phi_{m,n}^{(K)}$. For example, for $K=7$, which is the largest value of K considered in this work, we obtain the basis functions

$$\begin{aligned}\phi_{0,0}^{(7)}=c_0(&g_7\psi_{0000}+g_6\psi_{1000}r+g_5\psi_{2000}r^2+g_5\psi_{2100}r^2\ln r\\&+g_4\psi_{3000}r^3+g_4\psi_{3100}r^3\ln r+g_3\psi_{4000}r^4\\&+g_3\psi_{4100}r^4\ln r+g_3\psi_{4200}r^4\ln^2 r+g_2\psi_{5000}r^5\\&+g_2\psi_{5100}r^5\ln r+g_2\psi_{5200}r^5\ln^2 r+g_1\psi_{6000}r^6\\&+g_1\psi_{6100}r^6\ln r+g_1\psi_{6200}r^6\ln^2 r+g_1\psi_{6300}r^6\ln^3 r\\&+g_0\psi_{7000}r^7+g_0\psi_{7100}r^7\ln r+g_0\psi_{7200}r^7\ln^2 r\\&+g_0\psi_{7300}r^7\ln^3 r),\end{aligned} \tag{49}$$

$$\begin{aligned}\phi_{1,0}^{(7)}=c_1(&g_5\psi_{2010}r^2+g_4\psi_{3010}r^3+g_3\psi_{4010}r^4+g_3\psi_{4110}r^4\ln r\\&+g_2\psi_{5010}r^5+g_2\psi_{5110}r^5\ln r+g_1\psi_{6010}r^6\\&+g_1\psi_{6110}r^6\ln r+g_1\psi_{6210}r^6\ln^2 r+g_0\psi_{7010}r^7\\&+g_0\psi_{7110}r^7\ln r+g_0\psi_{7210}r^7\ln^2 r),\end{aligned} \tag{50}$$

$$\begin{aligned}\phi_{2,0}^{(7)}=c_2(&g_3\psi_{4020}r^4+g_2\psi_{5020}r^5+g_1\psi_{6020}r^6+g_1\psi_{6120}r^6\ln r\\&+g_0\psi_{7020}r^7+g_0\psi_{7120}r^7\ln r),\end{aligned} \tag{51}$$

$$\phi_{3,0}^{(7)}=c_3(g_3\psi_{4030}r^4+g_2\psi_{5030}r^5+g_1\psi_{6030}r^6+g_1\psi_{6130}r^6\ln r+g_0\psi_{7030}r^7+g_0\psi_{7130}r^7\ln r), \tag{52}$$

$$\phi_{4,0}^{(7)}=c_4(g_1\psi_{6040}r^6+g_0\psi_{7040}r^7), \tag{53}$$

$$\phi_{5,0}^{(7)}=c_5(g_1\psi_{6050}r^6+g_0\psi_{7050}r^7), \tag{54}$$

$$\phi_{0,1}^{(7)}=c_0E(g_5\psi_{2001}r^2+g_4\psi_{3001}r^3+g_3\psi_{4001}r^4+g_3\psi_{4101}r^4\ln r+g_2\psi_{5001}r^5+g_2\psi_{5101}r^5\ln r+g_1\psi_{6001}r^6+g_1\psi_{6101}r^6\ln r+g_1\psi_{6201}r^6\ln^2 r+g_0\psi_{7001}r^7+g_0\psi_{7101}r^7\ln r+g_0\psi_{7201}r^7\ln^2 r), \tag{55}$$

$$\phi_{1,1}^{(7)}=c_1E(g_3\psi_{4011}r^4+g_2\psi_{5011}r^5+g_1\psi_{6011}r^6+g_1\psi_{6111}r^6\ln r+g_0\psi_{7011}r^7+g_0\psi_{7111}r^7\ln r), \tag{56}$$

$$\phi_{2,1}^{(7)}=c_2E(g_1\psi_{6021}r^6+g_0\psi_{7021}r^7), \tag{57}$$

$$\phi_{3,1}^{(7)}=c_3E(g_1\psi_{6031}r^6+g_0\psi_{7031}r^7), \tag{58}$$

$$\phi_{0,2}^{(7)}=c_0E^2(g_3\psi_{4002}r^4+g_3\psi_{4102}r^4\ln r+g_2\psi_{5002}r^5+g_2\psi_{5102}r^5\ln r+g_1\psi_{6002}r^6+g_1\psi_{6102}r^6\ln r+g_0\psi_{7002}r^7+g_0\psi_{7102}r^7\ln r), \tag{59}$$

$$\phi_{1,2}^{(7)}=c_1E^2(g_1\psi_{6012}r^6+g_1\psi_{6112}r^6\ln r+g_0\psi_{7012}r^7+g_0\psi_{7112}r^7\ln r), \tag{60}$$

$$\phi_{0,3}^{(7)}=c_0E^3(g_1\psi_{6003}r^6+g_1\psi_{6103}r^6\ln r+g_0\psi_{7003}r^7+g_0\psi_{7103}r^7\ln r). \tag{61}$$

The functional dependencies have been ignored in Eqs. (49)–(61) in order to save space. The $\psi_{k,l,m,n}$ are determined by the solution to Eq. (29). There are 13 basis functions for $K=6$ and $K=7$. Similar analysis yields 7 basis functions for $K=4$ and $K=5$, and 3 basis functions for $K=2$ and $K=3$. The basis set may be compacted further by combining $\phi_{m,n}^{(K)}$ with the same value of m. For $K=7$, this procedure yields the basis set

$$\tilde{\phi}_0^{(7)}=\phi_{0,0}^{(7)}+E\phi_{0,1}^{(7)}+E^2\phi_{0,2}^{(7)}+E^3\phi_{0,3}^{(7)}, \tag{62}$$

$$\tilde{\phi}_1^{(7)}=\phi_{1,0}^{(7)}+E\phi_{1,1}^{(7)}+E^2\phi_{1,2}^{(7)}, \tag{63}$$

$$\tilde{\phi}_2^{(7)}=\phi_{2,0}^{(7)}+E\phi_{2,1}^{(7)}, \tag{64}$$

$$\tilde{\phi}_3^{(7)}=\phi_{3,0}^{(7)}+E\phi_{3,1}^{(7)}, \tag{65}$$

$$\tilde{\phi}_4^{(7)}=\phi_{4,0}^{(7)}, \tag{66}$$

$$\tilde{\phi}_5^{(7)}=\phi_{5,0}^{(7)}. \tag{67}$$

In this procedure, the energy E may be input as an approximation or treated as a nonlinear variational parameter. The only remaining nonlinear variational parameters are contained in $f(\xi,\eta)$ which we choose to obey the condition

$$\exp(-b_1r_1-b_2r_2-b_{12}r_{12})=\exp[-rf(\xi,\eta)], \tag{68}$$

so that

$$f(\xi,\eta)=\frac{1}{\sqrt{2}}\cos\left(\frac{\xi}{2}\right)\cos\left(\frac{\eta}{2}\right)\left[(b_1+b_2)+(2b_{12}-b_1+b_2)\tan\left(\frac{\xi}{2}\right)+(2b_{12}+b_1-b_2)\tan\left(\frac{\eta}{2}\right)+(b_1+b_2)\tan\left(\frac{\xi}{2}\right)\tan\left(\frac{\eta}{2}\right)\right]. \tag{69}$$

We now add the Fock functions in hyperspherical coordinates to the primary basis set consisting of products of Laguerre polynomials in perimetric coordinates in order to obtain the compact representation of the full wave function. Using a mixed coordinate notation, we have

$$\Psi=\sum_{l,m,n}c_{l,m,n}U_{l,m,n}(q_1,q_2,q_{12})+\sum_{m,n}c_{m,n}\phi_{m,n}^{(K)}(r,\xi,\eta), \tag{70}$$

where

$$U_{l,m,n}(q_1,q_2,q_{12})=u_l(a_1;q_1)u_m(a_2;q_2)u_n(a_{12};q_{12}), \tag{71}$$

with the unnormalized Laguerre basis functions defined by

$$u_n(a;x)=\exp(-ax/2)L_n(ax). \tag{72}$$

The Laguerre length scales a_1, a_2, and a_{12} combine with the Fock length scales b_1, b_2, and b_{12} to total six nonlinear variational parameters. However, the dimensionality is reduced from six to four by recognizing that a_1 must be the same as a_2, and b_1 must be the same as b_2 since the electrons are indistinguishable. Further simplifications, such as assuming a hydrogenic exponential falloff for each electron, are helpful when fine tuning the optimizations.

V. MATRIX ELEMENT EVALUATION

The matrix elements containing only Laguerre functions in perimetric coordinates have been reported previously [23,24]. The matrix elements containing the Fock functions can be evaluated using Gaussian quadrature [38] in the three coordinates r, ξ, and η. We use Gauss-Legendre quadrature for the Pluvinage angular integrations

$$\int_{-1}^{1}f(z)dz=\sum_{k=1}^{N}w_kf(z_k)+E_N(f), \tag{73}$$

where the nodes z_k are the N zeros of the Legendre polynomial P_N and the weights w_k are given by

$$w_k = \frac{2[1-(z_k)^2]}{(N+1)^2[P_{N+1}(z_k)]^2}, \tag{74}$$

with the error E_N dependent on the singularities of f. We use Gauss-Laguerre quadrature for the hyperspherical radial integrations

$$\int_0^\infty z^\alpha \exp(-z) f(z) dz = \sum_{k=1}^{N} w_k f(z_k) + E_N(f), \tag{75}$$

where the nodes z_k are the N zeros of the Laguerre polynomial $L_N^{(\alpha)}$ and the weights w_k are given by

$$w_k = \frac{\Gamma(N+\alpha+1) z_k}{N![(N+1)L_{N+1}^{(\alpha)}(z_k)]^2}, \tag{76}$$

with the error E_N again dependent on the singularities of f. It was shown in Sec. III that the terms of the Chebyshev expansion decrease like $(3+2\sqrt{2})^{-n}$ where n is the order of the Chebyshev polynomial. Therefore, a twenty term Chebyshev expansion will provide double precision ($\sim 10^{-15}$) and a forty term Chebyshev expansion will provide quadruple precision ($\sim 10^{-30}$). Since the Gaussian quadrature rule exactly integrates a polynomial of order $2N-1$, we can achieve double precision for the angular integrals using $N=10$ and quadruple precision using $N=20$. These estimates for N should be doubled when computing inner products of basis functions. The singularities introduced into the angular integrations by the exponential factor $f(\xi,\eta)$ in Eq. (69) may be moved in the complex plane (see Fig. 1) beyond the nearest singularities of the Fock expansion by choosing appropriate values for the variational parameters b_1, b_2, and b_{12}.

The Gauss-Laguerre quadratures for the integrands which contain logarithms need to be modified in order to achieve the desired accuracy. The modification is obtained by differentiating the standard Gauss-Laguerre quadrature rule with respect to α on both sides of the equal sign. The modified Gauss-Laguerre rule is

$$\int_0^\infty [\ln(z)]^m z^\alpha \exp(-z) f(z) dz = \sum_{n=0}^{m} \left[\sum_{k=1}^{N} w_{m,n}^{(k)} \frac{\partial^n}{\partial z_k^n} f(z_k) + \frac{\partial^m}{\partial \alpha^m} E_N(f) \right], \tag{77}$$

where

$$w_{m,n}^{(k)} = w_{m-1,n-1}^{(k)} \frac{\partial z_k}{\partial \alpha} + \frac{d}{d\alpha} w_{m-1,n}^{(k)}, \tag{78}$$

with

$$w_{m,n}^{(k)} = \begin{cases} w_k & \text{for } m=n=0, \\ 0 & \text{for } n<0 \text{ or } m<n. \end{cases} \tag{79}$$

Since the weight functions all depend on α and z_k, we must use the total derivative operator

$$\frac{d}{d\alpha} = \frac{\partial}{\partial \alpha} + \frac{\partial z_k}{\partial \alpha} \frac{\partial}{\partial z_k}, \tag{80}$$

when operating on any of the weight functions. The derivatives of z_k with respect to α can be obtained by differentiating the node condition

$$L_n^{(\alpha)}(z_k) = 0 \tag{81}$$

to get

$$\frac{\partial z_k}{\partial \alpha} = -\left[\frac{\partial L_n^{(\alpha)}(z)/\partial \alpha}{\partial L_n^{(\alpha)}(z)/\partial z} \right]_{z=z_k}. \tag{82}$$

By construction, the Fock basis functions are truncated at order K. In the present work, $K=7$ was the highest value considered. Since the highest power of the logarithm of the hyperspherical radius is equal to $K/2$ for even K, and $(K-1)/2$ for odd K, the Fock functions will contain up to three powers of the logarithm, and the corresponding integrals will contain up to six powers of the logarithm. Because the modified Gauss-Laguerre quadrature (77) requires $m+1$ modified weights, the total number of modified weights for $K=7$ will be 27. A very convenient way to compute these weights was to symbolically differentiate the standard weights (76) with respect to α and z and define each derivative as a new function. The new derivative functions were then differentiated with respect to α and z to define further new functions. We proceed in this way until new functions of all the required combinations of the six derivatives with respect to α and z have been defined. Once all the differentiation has been completed, the nodes z_k and the value of α is substituted into the newly defined functions making them numerical arrays.

In order to use the quadrature rules outlined above, the matrix element integrands need to be separated into pieces which contain no logarithms, pieces which contain one power of the logarithm, pieces which contain two powers of the logarithm, and so on. For the Gram matrix elements this separation procedure is no problem, but for the Hamiltonian matrix elements the separation becomes more difficult due to the various derivatives involved. The difficulties with differentiating and separating the Fock function integrands may be reduced if a symbolic manipulation program is used. The Hamiltonian derivative operations and logarithmic separation procedures were performed by considering the function

$$U_K(r,\xi,\eta) = \exp[-rf(\xi,\eta)][U_K^{(0)}(r,\xi,\eta) + U_K^{(1)}(r,\xi,\eta) + U_K^{(2)}(r,\xi,\eta) + U_K^{(3)}(r,\xi,\eta)], \tag{83}$$

where

$$U_K^{(0)}(r,\xi,\eta) = \sum_{k=0}^{K} f_{k,0}(\xi,\eta) r^k, \tag{84}$$

$$U_K^{(1)}(r,\xi,\eta) = \sum_{k=2}^{K} f_{k,1}(\xi,\eta) r^k \ln r, \tag{85}$$

$$U_K^{(2)}(r,\xi,\eta)=\sum_{k=4}^{K} f_{k,2}(\xi,\eta)r^k\ln^2 r, \tag{86}$$

$$U_K^{(3)}(r,\xi,\eta)=\sum_{k=6}^{K} f_{k,3}(\xi,\eta)r^k\ln^3 r. \tag{87}$$

The angular f coefficients in Eqs. (84)–(87) are arbitrary functions that are to be determined by the Fock basis function of interest. The function U_K is separated in the above manner in order to allow the Gram and potential-energy matrix elements to be correctly separated at the outset. The kinetic-energy operator will mix up the logarithmic dependence, so a second separation procedure will be needed after the necessary derivatives have been completed. Using Pluvinage hyperspherical angles, we break the problem into four pieces: U_K, VU_K, RU_K, and LU_K, where V is the potential-energy operator, R is the radial kinetic-energy operator, and L is the angular kinetic-energy operator. The derivatives were performed by MAPLE and the separation was enacted by collecting the coefficients of the logarithms. We may now treat VU_K, RU_K, and LU_K simply as functions of r, ξ, and η that have a form similar to Eq. (83). After the differentiations were completed the exponential factor was removed since it will be put in by the Gauss-Laguerre quadrature rule. The angular f coefficients and their derivatives were given scalar variable names and saved for use in the next step. With the Hamiltonian operations already performed, the next step is to perform the differentiations required for the modified quadrature (77). If we let

$$z=rh(\xi,\eta), \tag{88}$$

then we can perform the necessary differentiations with respect to z. In analogy with the modified weight procedure, we define each derivative with respect to z to be a new function. After the differentiations have been completed, the nodes are substituted into the new functions to produce numerical arrays. The final step is to assemble the full integrands. The required integrands are of the type

$$I_1(z,\xi,\eta)=w(z,\xi,\eta)U_{l,m,n}(z,\xi,\eta)U_K(z,\xi,\eta), \tag{89}$$

$$I_2(z,\xi,\eta)=w(z,\xi,\eta)U_{l,m,n}(z,\xi,\eta)HU_K(z,\xi,\eta), \tag{90}$$

$$I_3(z,\xi,\eta)=w(z,\xi,\eta)U_K(z,\xi,\eta)U_K(z,\xi,\eta), \tag{91}$$

$$I_4(z,\xi,\eta)=w(z,\xi,\eta)U_K(z,\xi,\eta)HU_K(z,\xi,\eta). \tag{92}$$

In Eqs. (89) and (90) it is assumed that the perimetric coordinates are expressed in terms of the hyperspherical coordinates. The U_K and HU_K pieces in Eqs. (89)–(92) are available through order $K=7$ using the methods described above. In order to complete the requirements of the modified quadrature (77) it is necessary to also have available the derivatives of the physical weight function w and the Laguerre function $U_{l,m,n}$. For the integrands I_1 and I_2, these functions need to be differentiated with respect to z a total of three times due to the three powers of the logarithm. For the integrands I_3 and I_4, the physical weight function w needs to be differentiated with respect to z a total of six times due to the six powers of the logarithm. We again use MAPLE to separate the logarithmic terms and perform the differentiations with respect to z. We also used MAPLE to write out a FORTRAN code [34].

VI. RESULTS

The singlet and triplet eigenvalues may be computed with a single Laguerre basis set representation of the form given in Eq. (71). In this case, the number of functions is

$$n_L=\frac{1}{2}\sum_{l=0}^{l_{sum}}(l_{sum}-l+1)(l_{sum}-l+2)$$
$$=\frac{1}{6}l_{sum}^3+l_{sum}^2+\frac{11}{6}l_{sum}+1, \tag{93}$$

where l_{sum} equals the maximum sum of the three Laguerre indices. In the present work, we are mainly concerned with the singlet ground state. Therefore, it is convenient to partition the different symmetries. In this case, the number of Laguerre basis functions is

$$n_L=\left[\frac{1}{12}l_{sum}^3+\frac{5}{8}l_{sum}^2+\frac{17}{12}l_{sum}+\frac{7}{8}\right], \tag{94}$$

where the square brackets denote the nearest integer. The Fock functions were assembled and systematically added to the Laguerre basis in order to see the effect on the convergence rate. The total number of basis functions is n_L+n_F where n_F equals the number of Fock functions. Tables I and II show the error in the ground-state energy as a function of the optimized nonlinear variational parameters. Table I includes entries for $K=0,2,4,6$ corresponding to $n_F=0,3,7,13$ with l_{sum} in the range 10–15. In Table II, the Fock functions with the same homogeneous solution were added together in order to speed up the calculation [see Eqs. (62)–(67)]. This caused a significant decrease in the accuracy of the energy, presumably due to the decreased flexibility of the Fock functions. It is worth noting that the optimizations were performed by trial and error and are not perfect. The tables are included to provide a starting point for future refinements in the optimization.

Figure 2 shows the significant improvement in the rate of convergence that can be obtained by adding Fock functions to the basis set. The $K=0$ curve corresponds to an unmodified Laguerre basis set. It is easy to see that many more Laguerre functions are required for this basis set to match the accuracy obtained in the other curves, which are obtained by using Fock functions through Kth order. Eventually, the improvement pattern we see by going to higher orders in the Fock expansion begins to diminish. In fact, the $K=7$ curve which is not shown, shows an insignificant improvement over the $K=6$ curve. The reason that the improvement diminishes is that the cusp at the three-particle coalescence is handled well enough that other physical effects, such as radial "in-out" correlation, become more important. Figure 3 shows the optimized value of the nonlinear parameter a_{12} as

TABLE I. Optimized nonlinear parameters for basis sets that include $\phi_{m,n}^{(K)}$.

l_{sum}	K	n_F	a_1	a_{12}	b_1	b_{12}	Error
10	0	0	1.30	2.35			1.02×10^{-8}
10	2	3	1.20	2.40	1.00	0.00	8.14×10^{-10}
10	4	7	1.17	2.34	1.00	0.00	3.44×10^{-11}
10	6	13	1.10	2.20	1.01	0.00	8.52×10^{-12}
11	0	0	1.35	2.55			5.29×10^{-9}
11	2	3	1.20	2.40	1.00	0.00	4.46×10^{-10}
11	4	7	1.20	2.40	1.00	0.00	7.82×10^{-12}
11	6	13	1.10	2.20	1.00	0.00	1.82×10^{-12}
12	0	0	1.35	2.60			2.32×10^{-9}
12	2	3	1.25	2.50	1.00	0.00	1.74×10^{-10}
12	4	7	1.25	2.50	1.00	0.00	2.72×10^{-12}
12	6	13	1.10	2.20	1.00	0.00	4.75×10^{-13}
13	0	0	1.40	2.80			1.18×10^{-9}
13	2	3	1.30	2.60	1.00	0.00	6.31×10^{-11}
13	4	7	1.30	2.60	1.00	0.00	8.99×10^{-13}
13	6	13	1.19	2.39	1.07	0.04	9.13×10^{-14}
14	0	0	1.45	2.90			5.01×10^{-10}
14	2	3	1.30	2.60	1.00	0.00	3.64×10^{-11}
14	4	7	1.30	2.60	1.00	0.00	2.69×10^{-13}
14	6	13	1.20	2.40	1.00	0.01	9.50×10^{-15}
15	0	0	1.50	3.00			2.75×10^{-10}
15	4	7	1.30	2.60	1.00	0.00	8.88×10^{-14}
15	6	13	1.25	2.50	1.00	0.02	2.80×10^{-15}

a function of l_{sum} for different values of K. Because this parameter is approximately equal to twice the value of a_1, it determines the length scale of the Laguerre basis functions. When Fock functions are included in the basis set, the value of a_{12} decreases and the Laguerre functions are better able to represent electronic behavior that is further away from the nucleus.

The most accurate result obtained in this work was $-2.903\,724\,377\,034\,116\,6$ a.u. for the ground-state energy of helium. This energy was computed using $l_{sum}=15$ and $K=6$, corresponding to a total of 457 basis functions ($n_L=444$ and $n_F=13$). This compares well to $-2.903\,724\,377\,034\,118\,4$ a.u. calculated by Baker *et al.* [20] using a Frankowski-Pekeris basis set containing 476 functions. The best standard is $-2.903\,724\,377\,034\,119\,5$ a.u. calculated by several groups [16,25–30] using substantially larger basis sets.

TABLE II. Optimized nonlinear parameters for basis sets that include $\tilde{\phi}_m^{(K)}=\Sigma_n E^n \phi_{m,n}^{(K)}$.

l_{sum}	K	n_F	a_1	a_{12}	b_1	b_{12}	Error
7	6	6	1.05	2.10	1.00	0.00	1.01×10^{-7}
8	6	6	1.05	2.10	1.00	0.00	8.72×10^{-9}
9	6	6	1.04	2.08	1.00	0.00	5.61×10^{-10}
10	6	6	1.13	2.13	1.00	0.00	1.11×10^{-10}

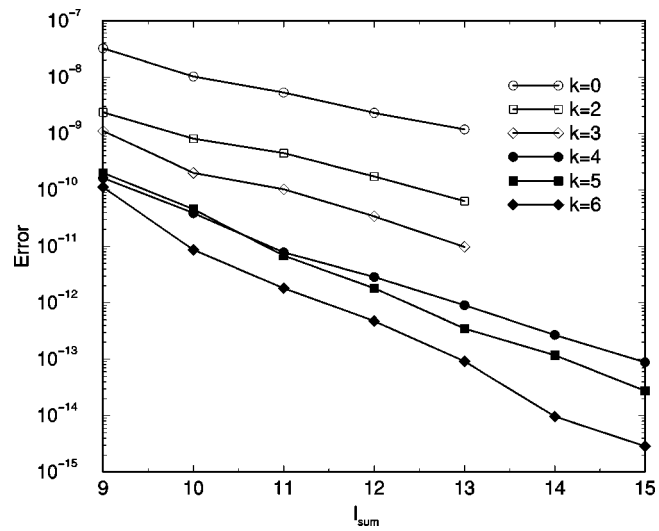

FIG. 2. Error in the ground-state energy as a function of l_{sum}. The $k=0$ curve corresponds to an unmodified Laguerre basis set. The $k>0$ curves include basis functions that reproduce the Fock expansion through kth order when the hyperradius tends to zero.

VII. CONCLUSIONS

The results of this work demonstrate that the convergence rate of a nearly orthogonal basis set, such as the triple product of Laguerre polynomials in perimetric coordinates, may be substantially improved through the addition of a few specially designed basis functions. These so-called Fock functions provide the exact analytic structure of the true wave function when two electrons coalesce near the nucleus. Because the terms that are logarithmic in the hyperradius have been explicitly treated by the methods described in this paper, the remaining portion of configuration space may be easily represented.

Several useful numerical methods have been developed or

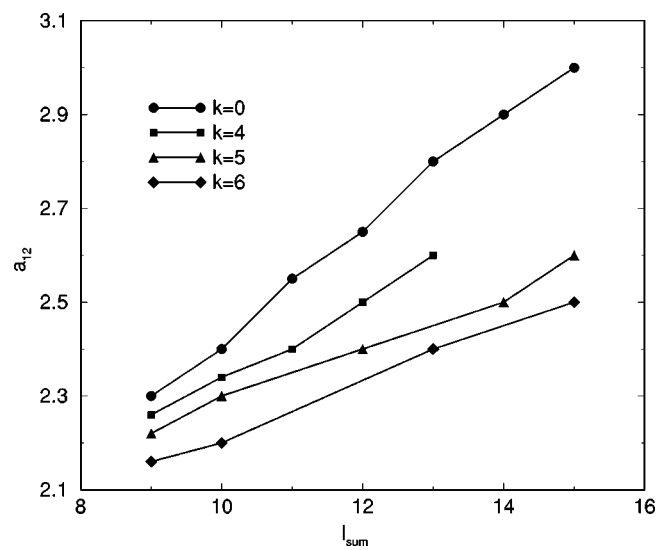

FIG. 3. Optimized value of the nonlinear parameter a_{12} as a function of l_{sum}. As more Fock functions are added to the basis set, the value of a_{12} decreases and the Laguerre functions are concentrated further away from the nucleus.

employed in this work. The modified Gauss-Laguerre quadrature allows an efficient and accurate numerical evaluation of integrals containing logarithms of the hyperradius. The use of Pluvinage hyperangles provides a convenient coordinate system for the numerical evaluation of integrals and an efficient method [33] for determining the angular coefficients of the Fock expansion.

The convergence rate of the basis set described here is similar to the Frankowski-Pekeris basis set used by Baker *et al.* [20]. The principle advantage of the present representation is that it does not struggle with numerical linear dependence problems due to the small number of Fock functions and the fact that the Laguerre basis is close to orthogonal. The major disadvantage of the present approach is the need to compute matrix element integrals numerically. Although the quadrature schemes described here are efficient and accurate, they are still quite slow compared to other basis set approaches that allow integrals of one or more of the coordinates to be evaluated analytically.

Finally, the present work allows the analytic behavior near the three-particle coalescence point to be treated without the need for invoking "flexibility" arguments. As Schwartz has recently pointed out [30], flexibility is a vague concept that lacks mathematical foundation. While flexible basis sets have certainly produced impressive benchmarks, they have created a situation where theoretical understanding of convergence rates "lags well behind the power of available computing machinery" [30]. It is hoped that the explicit treatment of singularities, such as presented here in regard to the Fock expansion, may provide a useful step toward the development of a rigorous theory of convergence rates for two-electron systems.

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