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Fock's expansion, Kato's cusp conditions, and the exponential ansatz

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We have examined the recent solution of the Fock expansion through $O(r^2)$ for the ground state of the helium atom and have verified that it correctly treats the discontinuity in the local energy characteristic of the triple-collision point. We have also developed an exponential representation of the Fock expansion that satisfies Kato's cusp conditions for two-particle collisions even when the expansion is truncated at a finite order.

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I. INTRODUCTION

Eigenfunctions of Hamiltonians for atomic and molecular systems exhibit singular behavior at those points in configuration space where two or more charged particles come together and the resulting potential becomes infinite. At two-particle coalescences, derivatives of the wave function Ψ with respect to Cartesian coordinates have a discontinuity characterized by the famous Kato cusp conditions [1], and the inclusion of functions with such cusps in trial wave functions has been shown to improve dramatically the rates of convergence of Rayleigh-Ritz variational calculations [2]. There are also singularities involving more than two particles, such as the triple-collision singularity in the helium atom, when both electrons simultaneously approach the nucleus. A formal expansion in powers of the hyperradius r and its logarithm $\ln r$ about this singular point was proposed by Fock [3] over 35 years ago for helium atom S-state wave functions. Subsequently, much effort has been devoted to understanding this expansion [4]. The $O(r^0)$, $O(r^1)$, and $O(r^2 \ln r)$ terms in Fock's expansion are easy to obtain analytically, but it is only recently that the $O(r^2)$ term in the expansion has been obtained in closed form by Maslen and co-workers, through the extensive use of computer algebra [5]. We have examined their result, and have verified that the inclusion of this term in the expansion yields a continuous local energy, whereas the local energy is finite but discontinuous at $r=0$ if the term is omitted. Although the conventional Fock expansion truncated at $O(r^N)$ fails to obey the two-particle cusp conditions, we have discovered an exponential representation of the Fock expansion that not only preserves the correct three-particle singularity, but also exactly obeys the two-particle Kato cusp conditions even when the expansion is truncated at finite order.

II. NONANALYTICITIES IN ELECTRONIC WAVE FUNCTIONS

A. Two-particle cusps

A brief review of two-particle cusps in electronic wave functions is appropriate. Two-particle cusps arise because the Coulomb interaction between charged particles diverges as they approach each other. As a result, there must exist a compensating divergence in the kinetic energy such that the sum of kinetic and potential energies is finite; this divergence is manifested as a cusp in the electronic wave function at zero interparticle separation.

The true wave function must satisfy a set of "cusp conditions" which prescribe the proper derivative discontinuity at the collision points. Kato [1] first rigorously derived these conditions as a general property of Coulombic systems, arriving at the conclusion that in the limit that two particles of masses m_i and m_j and charges q_i and q_j approach each other and all other interparticle distances remain larger than zero,

$$\left.\frac{\partial\hat{\Psi}}{\partial r_{ij}}\right|_{r_{ij}=0} = \mu_{ij} q_i q_j \Psi(r_{ij}=0) \ , \tag{1}$$

where $\mu_{ij}=m_i m_j/(m_i+m_j)$ is the reduced mass of the two-particle subsystem and $\hat{\Psi}$ is the average of Ψ over an infinitesimally small sphere centered at $r_{ij}=0$. Pack and Byers-Brown [6] generalized Kato's result by solving the multiparticle Schrödinger equation in the neighborhood of a two-particle coalescence. Near such a collision, the problem reduces to one similar to that for a hydrogenic atom. Writing the wave function near such a collision as

$$\Psi=\sum_{l=0}^{\infty}\sum_{m=-l}^{l} r^l f_{lm}(r) Y_l^m(\theta,\phi) , \tag{2}$$

where $r=r_{ij}$, $\theta=\theta_{ij}$, $\phi=\phi_{ij}$ for the collision point $\mathbf{r}_{ij}=0$, and the $Y_l^m(\theta,\phi)$ are the usual spherical harmonics, they find

$$f_{lm}(r)=f_{lm}^{(0)}\left[1+\frac{q_i q_j \mu_{ij}}{l+1} r+O(r^2)\right] , \tag{3}$$

with $f_{lm}^{(0)}$ being the first term in the expansion $f_{lm}(r)=\sum_{k=0}^{\infty} f_{lm}^{(k)} r^k$.

Equations (2) and (3) are perhaps best understood if we consider the solution ψ_4 of the hydrogenic ion ($q_1=-Z$, $q_2=1$, $\mu_{12}=\mu$), which can be written as

$$\Psi_{\mathrm{H}}\sim r^l\left[1-\frac{\mu Z r}{l+1}+O(r^2)\right] Y_l^m(\theta,\phi) , \tag{4}$$

implying that

$$\frac{\partial\Psi_{\mathrm{H}}}{\partial r}\sim[l r^{l-1}-\mu Z r^l+O(r^{l+1})] Y_l^m(\theta,\phi) . \tag{5}$$

For S states, $\partial\Psi_{\mathrm{H}}/\partial r=-Z\Psi(0)$, without the need to spherically average (although a spherical average of Y_0^0 does not alter this). For P states, $\partial\Psi_{\mathrm{H}}/\partial r\sim Y_1^m(\theta,\phi)$, which is nonzero, but which averages to zero around the sphere, in accordance with Kato's cusp condition. For states with $l>1$, $\partial\Psi_{\mathrm{H}}/\partial r\sim l r^{l-1}$, which vanishes as $r\to 0$, as does the wave function. In all cases, the hydrogenic wave function has the general form of Eq. (3), with the proper derivative discontinuity as specified by Eq. (1).

The general result of Pack and Byers-Brown is achieved by requiring those terms that diverge in the limit $r_{ij}\to 0$ to cancel. For S states of a two-electron atom, such a process can be done trivially by writing the (nonrelativistic, infinite nuclear mass) Hamiltonian of the atom in interparticle coordinates (r_1, r_2, and r_{12}):

$$\begin{aligned} H=-\frac{1}{2}\Bigg[&\frac{\partial^2}{\partial r_1^2}+\frac{\partial^2}{\partial r_2^2}+2\frac{\partial^2}{\partial r_{12}^2}+\frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{2}{r_2}\frac{\partial}{\partial r_2}\\ &+\frac{4}{r_{12}}\frac{\partial}{\partial r_{12}}+\left[\frac{r_1^2-r_2^2+r_{12}^2}{r_1 r_{12}}\right]\frac{\partial^2}{\partial r_1 r_{12}}\\ &+\left[\frac{r_2^2-r_1^2+r_{12}^2}{r_2 r_{12}}\right]\frac{\partial^2}{\partial r_2 r_{12}}\Bigg]\\ &+\left[\frac{-Z}{r_1}+\frac{-Z}{r_2}+\frac{1}{r_{12}}\right] . \end{aligned} \tag{6}$$

The second derivatives of Ψ are all bounded, as in hydrogen, so in the limit of a two-particle collision, there are two terms in the Schrödinger equation that diverge. By requiring them to cancel, we arrive at a set of cusp conditions for a singlet S state of a two-electron atom, which are valid without the need for spherically averaging. One condition describes the collision of one electron and the nucleus, and the other, the collision of two (opposite-spin) electrons [7]:

$$\begin{aligned} &\left.\frac{\partial\hat{\Psi}}{\partial r_i}\right|_{r_i=0}=-Z\Psi(r_i=0), \quad \text{electron and nucleus}\\ &\left.\frac{\partial\hat{\Psi}}{\partial r_{ij}}\right|_{r_{ij}=0}=\tfrac{1}{2}\Psi(r_{ij}=0), \quad \text{electron}(\uparrow)\text{ and electron}(\downarrow) . \end{aligned} \tag{7}$$

The study of singular points requires a local measure of the quality of a wave function. It is useful to define the local energy E_{loc} of an N-electron wave function Ψ at a point $\mathbf{r}$ in the $3N$-dimensional configuration space of the electrons as

$$E_{\mathrm{loc}}(\mathbf{r})\equiv\frac{H\Psi(\mathbf{r})}{\Psi(\mathbf{r})} . \tag{8}$$

For the true ground-state wave function (and for any eigenstate of the Hamiltonian), throughout the entire configuration space this quantity has a constant value E, the energy of the eigenstate. Deviations from constant local energy E signify an error in the trial wave function in that region of configuration space. Nonanalytic deviations from a constant local energy are characteristic of electronic wave functions which do not treat two- and/or multiparticle collisions properly. For two-particle collisions, a trial wave function that fails to obey the cusp conditions [Eqs. (7)] will suffer a diverging local energy when the two particles approach each other. Of course, this diverging local energy is not fatal, since the region of configuration space where the cusp dominates is very small; on the contrary, very accurate energies can be attained with single-particle orbitals. But the misrepresentation of the cusp hampers the rapid convergence of variational calculations using smooth basis functions, and thus can become a bottleneck in sufficiently large calculations.

B. Three-particle nonanalyticity

In 1935, Bartlett, Gibbons, and Dunn [8] realized that a power series in r_1, r_2, and r_{12} was incapable of satisfying the Schrödinger equation for the ground state of the helium atom because of a singularity associated with the coalescence of all three particles, and in 1937 Bartlett [9], building on the work of Gronwall [10], suggested that a generalized power series including logarithmic terms might solve the Schrödinger equation. In 1954 Fock [3] independently constructed a formal expansion of the helium atom ground state involving logarithmic terms which treated the three-particle singularity, and which he proved was capable of solving the Schrödinger equation.

Before introducing the Fock expansion, we first discuss the symptoms of this three-particle singularity in terms of the local energy. Specifically, we describe the behavior of

the local energy for a simple trial wave function which contains the prescribed two-particle cusps but which has no extra nonanalytic terms to represent the three-particle singularity at the nucleus.

Consider the two terms in the Hamiltonian [Eq. (6)] involving mixed partial derivatives of Ψ. The terms multiplying these derivatives are independent of length; they are simply twice the cosines of the angles θ_1 and θ_2, respectively, as shown in Fig. 1. Hence these terms are well defined in the limit that the triangle formed by the three particles is shrunk uniformly toward the nucleus, and the Hamiltonian depends on the shape of the triangle even as the size of the triangle is taken to zero.

To show that this shape dependence will produce a singularity in the local energy at the triple collision, we must show that the mixed partial derivatives which multiply the cosines are nonzero in the limit under consideration. Consider a simple trial wave function that has the proper two-particle cusps but which does not treat the three-particle singularity. One can easily verify that the following wave function satisfies Eqs. (7):

$$\Psi(r_1,r_2,r_{12})=\exp[-Z(r_1+r_2)+\tfrac{1}{2}r_{12}]\ . \tag{9}$$

Evaluating the mixed partial derivatives in the limit in question, we find

$$\left.\frac{\partial^2\Psi}{\partial r_1 r_{12}}\right|_{r_1=r_{12}=0}=\left.\frac{\partial^2\Psi}{\partial r_2 r_{12}}\right|_{r_2=r_{12}=0}=-\tfrac{1}{2}Z\Psi(0)\ , \tag{10}$$

where $\Psi(0)\equiv\Psi(r_1=r_2=r_{12}=0)$ is nonzero (and positive) for the ground state of the system [11]. For the wave function (9), $E_{\rm loc}=-(Z^2+\frac{1}{4})+(Z/2)\cos\theta_1+(Z/2)\cos\theta_2$, so the local energy is clearly not well defined in the triple-collision limit, but depends upon the shape of the triangle through the angles θ_1 and θ_2. Therefore, for this trial wave function which treats two-particle collisions but does nothing about the triple collision, there exists a *finite discontinuity* in the local energy at the origin. The variation in the cosine terms yields a full variation in the local energy of magnitude Z. While Eq. (10) is not intended as a rigorous proof (particularly with regard to taking the limits in question for arbitrary analytic functions of r_1, r_2, and r_{12}), it is evident that most trial wave functions that are analytic in the interparticle coordinates and satisfy the two-particle cusp conditions will similarly exhibit a discontinuity in the local energy of magnitude Z.

We graphically demonstrate this discontinuity by calculating the local energy around a circle in configuration space surrounding the nucleus and shrinking that circle to zero. Consider a geometry in which one electron sits fixed near the origin at a distance $R/2$, while the other electron travels around a circle of radius R, as shown in Fig. 2. In Fig. 3, we plot the error in the local energy ($\Delta E_{\rm loc}\equiv E_{\rm loc}-E$) as a function of the angle θ for various radii R of an optimized trial wave function [12] which possesses the required two-particle cusps but which contains no extra nonanalytic terms. As can be seen, $\Delta E_{\rm loc}$ varies over a range of Z ($=2$) as the radius of the circle is shrunk to zero. Hence $\Delta E_{\rm loc}$ is not well defined at the triple-collision limit, but can be anywhere in that range.

It is clear that the finite discontinuity associated with the triple-collision point is not as severe as the diverging local energy associated with two-particle collisions (for trial wave functions lacking the proper cusps). Furthermore, since the triple-collision point is an isolated singularity which occurs in a region of configuration space whose contribution to the total integrated energy is severely depressed by a factor of r^5 in the Jacobian in hyperspherical coordinates, the failure to include the proper terms does not necessarily prevent one from calculating highly accurate energies for the helium atom ground state [13,14]. But just as a proper description of two-particle cusps has been shown to improve dramatically convergence in variational calculations by not requiring smooth basis functions to fit singular functions, it has been demonstrated that the inclusion of variational degrees of freedom reminiscent of terms in the Fock expansion also significantly enhances convergence [15,16]. We have been motivated by a desire to construct more accurate wave functions by representing the singular behavior of those functions exactly, and more generally, to understand to what extent singularities dictate the overall behavior of electronic wave functions.

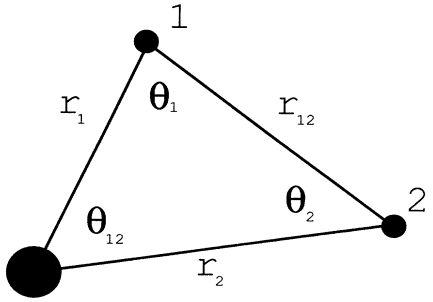

FIG. 1. Interparticle coordinates and associated angles for helium atom [nucleus and two electrons (1,2)].

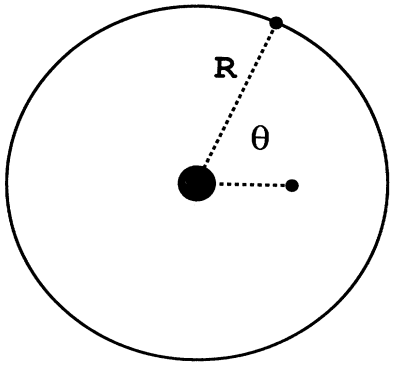

FIG. 2. Geometry for plots of local energy, to show discontinuity as $R\rightarrow 0$. Inner electron is at a distance $R/2$ from the nucleus.

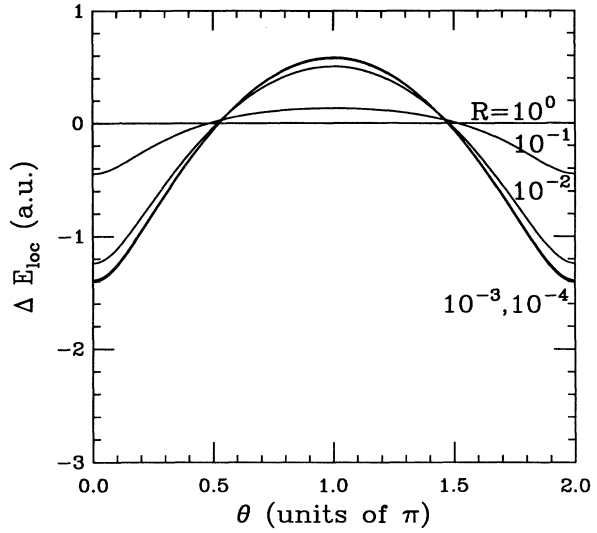

FIG. 3. Error in the local energy $\Delta E_{\rm loc}$ of a trial wave function as a function of θ for various radii R, for the geometry specified in Fig. 2. The curves are labeled by the value of R (in a.u.) for that plot. The wave function used here is an optimized variational wave function containing two-particle cusps but including no extra nonanalytic terms to treat the three-particle singularity. The variation of magnitude Z ($=2$) around the circle as the radius $R\rightarrow 0$ is symptomatic of a wave function which satisfies the cusp conditions but does not successfully treat the triple collision.

III. FOCK'S EXPANSION

A. Introduction

Because in the limit of the three-particle collision all the interparticle coordinates vanish, it is useful to transform to a set of hyperspherical coordinates, in which the desired limit involves only a single vanishing coordinate. In this coordinate system, which differs slightly from Fock's original hyperspherical system,

$$r=\left[r_1^2+r_2^2\right]^{1/2},$$
$$\alpha=2\tan^{-1}(r_2/r_1), \tag{11}$$
$$\theta=\cos^{-1}\left[\frac{r_1^2+r_2^2-r_{12}^2}{2r_1r_2}\right]=\theta_{12}=\mathbf{r}_1\cdot\mathbf{r}_2/r_1r_2 .$$

This transformation reflects a separation of the six-dimensional configuration space of the two electrons into a one-dimensional *hyperradial* part (r) and a five-dimensional *hyperangular* piece, of which α and θ comprise two coordinates [the other three consisting of "external coordinates" (Euler angles) describing the orientation of the triangle, in which the wave function is constant for an S state]. This system is useful for a study of the triple-collision point since the limit in question is simply $r\rightarrow 0$. The overall size of the triangle is described by the hyperradius r, and its shape by the hyperangles.

Fock's ansatz for an S state of the helium atom makes use of the separation into hyperradial and hyperangular pieces. His expansion (modified to reflect the altered hyperspherical coordinate) about $r=0$ is

$$\Psi(r,\alpha,\theta)=\sum_{k=0}^{\infty}\sum_{p=0}^{[k/2]} r^k(\ln r)^p\psi_{k,p}(\alpha,\theta) , \tag{12}$$

where the upper limit $[k/2]$ on the second summation denotes the largest integer which does not exceed $k/2$. Substituting the expansion into the Schrödinger equation yields a partial differential recurrence relation for the hyperangular functions $\psi_{k,p}(\alpha,\theta)$:

$$\begin{aligned}[\Lambda^2-k(k+4)]\psi_{k,p}=&\,2(k+2)(p+1)\psi_{k,p+1}\\&+(p+1)(p+2)\psi_{k,p+2}\\&-2V\psi_{k-1,p}+2E\psi_{k-2,p} ,\end{aligned} \tag{13}$$

where Λ^2 is the generalized angular momentum operator. Fock proved that it is possible in principle to find all the $\psi_{k,p}(\alpha,\theta)$ to achieve a full solution, although actual progress in solving for terms in the series has been painfully slow.

Examination of the recurrence relation (13) reveals that only the first four terms of the series, $\psi_{0,0}+\psi_{1,0}r+\psi_{2,1}r^2\ln r+\psi_{2,0}r^2$, are needed to correct the singular behavior at the origin. $\psi_{0,0}$, $\psi_{1,0}$ and $\psi_{2,1}$ were all known by the late 1950s [3,17], but $\psi_{2,0}$ resisted solution until very recently [5]. The recurrence relation for $\psi_{2,0}$ is associated with terms of $O(r^0)$ in the local energy, which explains why failure to include the proper $\psi_{2,0}$ leads to a finite discontinuity in $E_{\rm loc}$. It also explains why higher-order terms do not contribute to the local energy at the origin, since they come in as higher powers of r, which vanish as $r\rightarrow 0$.

The Fock expansion should provide a formal solution to the two-electron Schrödinger equation, but by itself says nothing about satisfying the boundary condition of normalizability. There are, however, in addition to the infinite set of hyperangular functions $\psi_{k,p}$, an infinite set of harmonic polynomials $Y_{k,l}$ which can be added in arbitrary amounts to Ψ without changing the local energy at any point in space. The coefficients for these harmonic polynomials, $a_{k,l}$, are not determined by the Schrödinger equation but by the boundary conditions of the normalizability of the wave function. To second order in r, there are two such harmonic polynomials ($Y_{2,0}$ and $Y_{2,1}$), and hence two arbitrary coefficients ($a_{2,0}$ and $a_{2,1}$). $a_{2,0}$ is identically zero for the ground state of helium by the required exchange symmetry of the spatial part of the wave function, but $Y_{2,1}$ is allowed by symmetry; hence $a_{2,1}$ cannot be deduced from the local behavior of the Schrödinger equation near the nucleus. We note, however, that in work to be described elsewhere [18], we have been able to compare the exact result [5] for $\psi_{2,0}$ quoted below with highly precise variational calculations to determine an accurate estimate of $a_{2,1}$.

The work of Maslen, Abbott, Gottschalk, and McIsaac [5] is impressive both in its accomplishments and its innovative use of symbolic algebra. The central part of their work for this project was the successful reduction of $\psi_{2,0}$ to a finite set of terms. This result is still quite complicated, involving some special functions. We present

here an expression equivalent to the result of Gottschalk and Maslen [19] for the single S state (labeled *nsms* ^1S on p. 2796 of their paper); we have only reordered certain terms and substituted for their general Coulombic parameters $(\mu_1,\mu_2,\mu_{12},\mu_A,\mu_S)$ the values of those parameters for a two-electron atom. The result is written in terms of r_1, r_2, and r_{12}, but is equivalent to $\psi_{0,0}+\psi_{1,0}r+\psi_{2,1}r^2\ln r+\psi_{2,0}r^2+a_{2,1}Y_{2,1}$:

$$\Psi(r_1,r_2,r_{12})=1-Z(r_1+r_2)+\tfrac{1}{2}r_{12}-\left[\frac{\pi-2}{3\pi}\right]ZY_{2,1}\ln r-\frac{Z}{3}Y_{2,1}\ln\left[\frac{r_1+r_2+r_{12}}{r}\right]$$
$$+\frac{Z}{12}Y_{2,0}\left[2\ln(r_1-r_2+r_{12})-\left[s_1-\frac{1}{\pi}s_2\right]\right]$$
$$+\frac{Z}{6\pi}r_{12}(2r^2-r_{12}^2)^{1/2}[2\sin^{-1}(y\Omega)+\pi]$$
$$-\frac{E}{6}r^2+\frac{4Z^2+1}{12}r_{12}^2-\frac{2Z}{3}r_{12}(r_1+r_2)+\frac{Z(3Z+1)}{3}r_1r_2+a_{2,1}Y_{2,1}\quad(r_1>r_2) \tag{14}$$

where

$$s_1=\ln[r_{12}(2r^2-r_{12}^2)^{1/2}+r_1^2-r_2^2]\,,$$

$$s_2=\alpha\ln\left[\frac{1+\Omega}{1-\Omega}\right]-\beta\{\ln[r_{12}(2r^2-r_{12}^2)^{1/2}+r_1^2-r_2^2]-\ln[r_{12}(2r^2-r_{12}^2)^{1/2}-r_1^2+r_2^2]\}$$
$$+2\left[L\left[\frac{\alpha-\beta}{2}\right]-L\left[\frac{\alpha+\beta}{2}\right]+L\left[\frac{\pi-\alpha+\beta}{2}\right]-L\left[\frac{\pi-\alpha-\beta}{2}\right]\right]\,,$$

$$L(x)=-\int_0^x\ln|\cos t|\,dt\quad\text{(the Lobachevsky function)}\,,$$

$$Y_{2,0}=r_1^2-r_2^2\,,$$

$$Y_{2,1}=r_1^2+r_2^2-r_{12}^2=r_{12}\sin\alpha\cos\theta\,,$$

$$r=(r_1^2+r_2^2)^{1/2}\,,$$

$$y=\sin(\alpha)=\frac{2r_1r_2}{r_1^2+r_2^2}\,,$$

$$\Omega=\cos\theta\,,$$

$$\beta=\sin^{-1}(y\Omega)\,.$$

B. Fock's expansion to $O(r^2)$

We have examined the Fock expansion to $O(r^2)$ [Eq. (14), henceforth referred to as $\Psi^{(2)}$] and have verified that it eliminates the discontinuity in the local energy at the origin which is symptomatic of trial functions which lack the correct analytic structure at the triple-collision singularity. Figure 4 consists of a series of plots similar to those in Fig. 3 ($\Delta E_{\rm loc}$ vs θ around a circle of radius R), this time for $\Psi^{(2)}$. As a triangle is shrunk toward the origin, the error in the local energy vanishes, demonstrating that the second-order Fock expansion does indeed represent the three-particle singularity exactly.

Unfortunately, as can be seen in Fig. 4, $\Psi^{(2)}$ describes the true wave function only very close to the nucleus, and has a large local energy error as r increases. Furthermore, higher-order terms in the expansion are even more complicated and difficult to solve for. (At any order in the expansion, there are some terms that can be solved for relatively easily, such as $\psi_{3,1}r^3\ln r$. We have put this term into a trial wave function and have seen that the re-

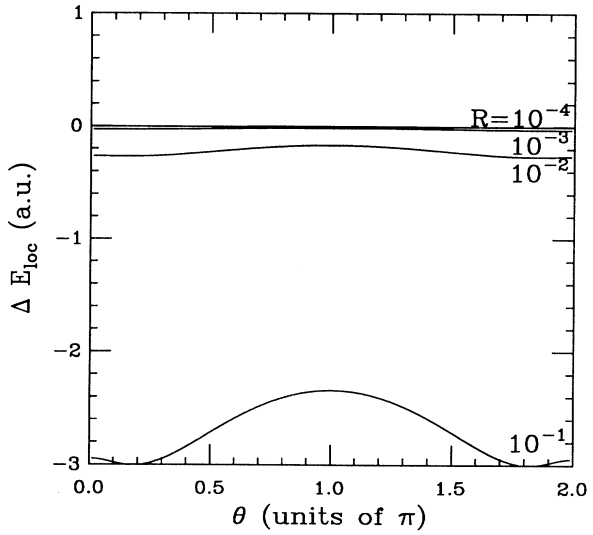

FIG. 4. Error in the local energy $\Delta E_{\rm loc}$ of the second-order Fock expansion [Eq. (14) in text] as a function of θ for various radii R, for the geometry specified in Fig. 2. The curves are labeled by the value of R (in a.u.) for that plot. The fact that the variation in $\Delta E_{\rm loc}$ around the circle vanishes as the radius $R\to 0$ indicates that the second-order Fock terms have successfully treated the three-particle singularity at the origin.

sulting function is better behaved at longer distances. But at every order, there will be terms at least as complicated as $\psi_{2,0}$. The third-order term $\psi_{3,0}$ has been reported [20], but we have opted not to include this term since it has not been completely reduced to closed form.) $\Psi^{(2)}$ itself diverges quadratically at long distances, so it obviously cannot represent the true wave function everywhere. Therefore the question arises as to how to incorporate this asymptotic result into a wave function valid over all of configuration space.

IV. EXPONENTIATION OF THE FOCK EXPANSION

The Fock expansion, if solved to infinite order in r, should have the correct two-particle cusps (for $r \neq 0$) as well as the exact three-particle singularity which it was originally constructed to treat. Unfortunately, if the expansion is known only to some finite order in r, the resulting approximate wave function will not have the proper cusps and will hence suffer a diverging local energy at two-particle coalescences. We demonstrate this by substituting into the Schrödinger equation a Fock-like expansion for Ψ: $\Psi=1+\psi_1+\psi_2+\cdots=\sum_{n=0}^{\infty}\psi_n$, where ψ_n consists of terms exclusively of $O(r^n)$ and $O(r^n \ln^p r)$, in the manner of the Fock expansion. Writing $\nabla^2=\nabla_1^2+\nabla_2^2$, the Schrödinger equation becomes

$$\sum_{n=0}^{\infty}(-\tfrac{1}{2}\nabla^2\psi_n+V\psi_n-E\psi_n)=0 , \tag{15}$$

which, upon equating terms order by order in r, yields

$$-\tfrac{1}{2}\nabla^2\psi_{n+2}+V\psi_{n+1}-E\psi_n=0 . \tag{16}$$

The error in the local energy for the Fock expansion truncated at order N is

$$\Delta E_{\rm loc}^{(N)}=\frac{\sum_{n=0}^{N}(-\tfrac{1}{2}\nabla^2\psi_n+V\psi_n-E\psi_n)}{\sum_{n=0}^{N}\psi_n} , \tag{17}$$

which from Eq. (16) reduces to

$$\Delta E_{\rm loc}^{(N)}=\frac{V\psi_N-E(\psi_{N-1}+\psi_N)}{\sum_{n=0}^{N}\psi_n} . \tag{18}$$

If we were dealing with a hydrogenic ion, for example, in its ground state with $\Psi(r)=e^{-Zr}$ and

$$\psi_n(r)=\frac{(-Z)^n}{n!}r^n , \tag{19}$$

then for a given truncation order N, $V\psi_N$ would be of $O(r^{N-1})$ and hence $\Delta E_{\rm loc}^{(N)}$ would be well behaved at $r=0$. For a multiparticle system, however, the right-hand side (rhs) of Eq. (18) is typically singular. For example, with

$$V=-Z(1/r_1+1/r_2)+1/r_{12} \tag{20}$$

and

$$\psi_1=-Z(r_1+r_2)+\tfrac{1}{2}r_{12} , \tag{21}$$

we have, for $N=1$

$$V\psi_1=Z^2\left[2+\frac{r_2}{r_1}+\frac{r_1}{r_2}\right]-Z\left[\left[\frac{1}{r_1}+\frac{1}{r_2}\right]\tfrac{1}{2}r_{12}+(r_1+r_2)\frac{1}{r_{12}}\right]+\tfrac{1}{2} , \tag{22}$$

which because of the cross terms is singular at any two-particle coalescence. This would also be true even if the r_{12}-dependent terms were absent from V and hence from ψ_1. The fundamental problem is that for any finite N, the Fock expansion through Nth-order of the product of two hydrogenic eigenfunctions $e^{-Zr_1}e^{-Zr_2}$ is not the same as the product of the Nth-order expansions of each function in powers of r_1 and r_2, although for any given pair of coordinates (r_1, r_2) the two would tend to each other as $N\to\infty$. In other words, the form of ψ_1 involving a weighted sum of interparticle distances does not naturally mesh with the product form of the true wave function.

The functional form of the two-particle cusp conditions, which state that certain derivatives of the wave function are proportional to the wave function, suggests that the true wave function has some sort of exponential character. We first noticed that the first-order Fock expansion $\Psi^{(1)}=1-Z(r_1+r_2)+\frac{1}{2}r_{12}$ does not have the proper two-particle cusps away from $r=0$, whereas the exponential form of the function $\Phi^{(1)}=\exp[-Z(r_1+r_2)+\frac{1}{2}r_{12}]$ (subtracting the leading 1 since that term is generated upon exponentiation) does indeed satisfy the cusp conditions (7) everywhere in space [21]. We then hypothesized that an exponential form of the Fock expansion to second order would also have the correct cusps. So we considered the following wave function, which, upon expansion of the exponential, is seen to reproduce the Fock expansion to second order in r:

$$\Phi^{(2)}=\exp(\psi_{1,0}r+\psi_{2,1}r^2\ln r+\psi_{2,0}r^2+a_{2,1}Y_{2,1}-\tfrac{1}{2}\psi_{1,0}^2r^2) . \tag{23}$$

A straightforward algebraic evaluation of the cusp conditions (7) confirms that this exponentiated wave function has a local energy which is well behaved at two-particle collisions, despite the fact that the truncated second-order power series has a diverging local energy at those points. As illustrated in Fig. 5, the unexponentiated function $\Psi^{(2)}$ is seen to have a diverging local energy at a two-particle collision (at $x_2=0$ in the figure), whereas the local energy of the exponential function $\Phi^{(2)}$ is well behaved.

By using more formal methods, we can extend this statement concerning the exponentiated second-order Fock expansion, which we are able to evaluate explicitly, to arbitrarily high order: the "exponentiated Nth-order Fock expansion $\Phi^{(N)}$" [an exponential of the Fock expansion to $O(r^N)$ plus additional terms to ensure that the

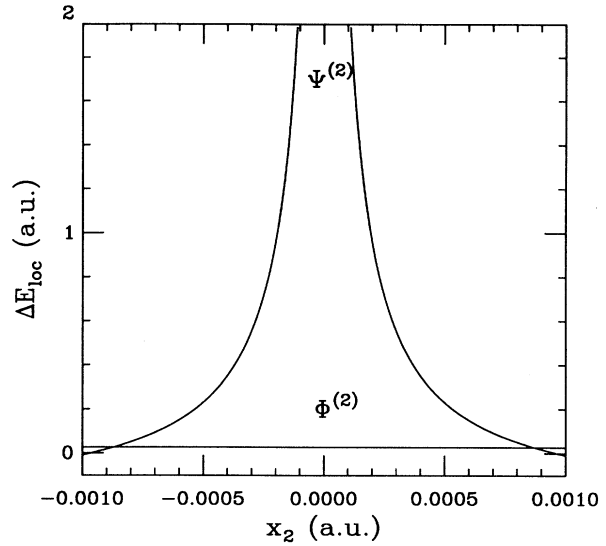

FIG. 5. Comparison of the local energy of the unexponentiated ($\Psi^{(2)}$) and the exponentiated ($\Phi^{(2)}$) second-order Fock expansions, in the neighborhood of a two-electron collision. One electron is fixed at $(x_1,y_1,z_1)=(0.0,0.005,0.0)$, while the second electron moves through it along the segment from $(x_2,y_2,z_2)=(-0.001,0.005,0.0)$ to $(+0.001,0.005,0.0)$. The collision is therefore situated at $x_2=0$. The unexponentiated function is seen to have a local energy which diverges at the collision, whereas the local energy of the exponentiated function is roughly constant throughout the region.

Fock expansion is reproduced through $O(r^N)$] has a local energy that is well behaved in the limit of two-particle collisions, even though the underlying Fock expansion has a diverging local energy at such points for finite order N.

We now prove this claim. Substitution of $\Psi=\exp(\phi)$ into the Schrödinger equation yields for ϕ the Ricatti equation

$$-\tfrac{1}{2}[(\nabla^2\phi)+(\nabla\phi)^2]+V-E=0\ . \tag{24}$$

Now expand $\phi=\sum_{i=1}^{\infty}\phi_n$, where ϕ_n is a function of $O(r^n,r^n\ln^p r)$, and which, in our approach, is a sum of the nth-order Fock term and appropriate products of lower-order Fock terms. Then, by substituting ϕ into the Schrödinger equation and equating terms order by order as before, we find

$$-\frac{1}{2}\left[\nabla^2\phi_n+\sum_{i=1}^{n-1}\nabla\phi_i\cdot\nabla\phi_{n-i}\right]+V\delta_{n,1}-E\delta_{n,2}=0\ . \tag{25}$$

The singular potential term V, being homogeneous of degree -1 in the hyperradius, now appears only at first order in this expansion. Hence the exponentiated first-order Fock expansion contains all of the required cusps. As a result, the error in the local energy for a wave function truncated at order $N\geq 2$ is

$$\Delta E_{\rm loc}^{(N)}=-\tfrac{1}{2}\sum_{n=N+1}^{2N}\sum_{i=n-N}^{N}\nabla\phi_i\cdot\nabla\phi_{n-i}-E\delta_{N,2}\ . \tag{26}$$

All the $\nabla\phi_n$ can be shown to be nonsingular (see the Appendix), so $\Delta E_{\rm loc}^{(N)}$ is likewise nonsingular, even at two-particle collisions. This argument is generalizable to the case of an arbitrary number of particles of arbitrary masses and charges interacting by Coulombic forces.

The exponentiated second-order function has all the singularities (two- and three-particle) required for a two-electron atom ground state. The fact that the truncated Fock expansion does not have the proper two-particle cusps while the full Fock expansion does implies that there is an intricate cancellation of terms out to infinite order; this cancellation is evident in the preceding discussion of the truncated Fock expansion. We suspect that much of the power series in the original Fock expansion is devoted to performing this delicate cancellation so as to generate a wave function of exponential character. As a result, further progress could perhaps be made in solving for terms in the Fock expansion by making an exponential ansatz such as the one we have made. Such an ansatz might raise new algebraic complications, but is worth further consideration.

V. INCORPORATING THE FOCK EXPANSION INTO TRIAL WAVE FUNCTIONS

The early work of Frankowski and Pekeris [15] and the more recent work of Freund, Huxtable, and Morgan [16] and others [22] demonstrate clearly that the inclusion of logarithmic terms in the basis improves significantly the rate of convergence of a Rayleigh-Ritz variational calculation. Furthermore, by comparing the coefficients of variational terms obtained by Baker and Morgan [22] and the coefficients of the corresponding terms in an appropriate expansion of the exact second-order result [Eq. (14)], we can show that the variational degrees of freedom are indeed mimicking the exact Fock wave function [18]. Therefore, including the Fock expansion, or some approximation to it, appears to be extremely useful for highly accurate calculations.

Since we wish to incorporate the second-order Fock expansion into a trial function *exactly,* it is clear that, due to the complications of integrating the necessary functions, a standard basis set calculation such as those of Refs. [15] and [16] is not possible. Instead, we have sought to incorporate the exact second-order result into a variational Monte Carlo technique developed by one of us, and described elsewhere in the literature [23]. More details regarding this incorporation will be given below.

A useful diagnostic for trial wave functions is to plot, as a function of the hyperradius r, the error in the local energy for various hyperangular configurations, i.e., configurations with fixed α and θ. The solid curves in Fig. 6 show such a plot for the exponentiated second-order Fock expansion $\Phi^{(2)}$; we have selected two geometries with local energies which more or less bound the distribution of local energies at small r ($r\lesssim 0.2$). There are no variational parameters in this wave function; we have fixed the arbitrary coefficient a_{21} to the value that we determine from our comparison of the second-order terms in the exact wave function and those in a highly accurate variational wave function [18]. The

fact that $\Delta E_{\rm loc} \to 0$ as $r \to 0$ is again indication that the second-order Fock expansion is correctly representing the triple-collision singularity.

We note that $\Delta E_{\rm loc}$ for the exponentiated second-order function (solid curves in Fig. 6) grows rapidly as r is increased away from zero. From the analysis of Sec. IV [in particular, Eq. (26)], we can see that the error in the local energy for the exponentiated Fock expansion behaves at small r as $r^{N-1}\ln^p r$, where N is the order of truncation and p is the highest logarithmic power which is nonzero at $O(r^N)$. By including the exact Fock expansion to $O(r^2)$ we have driven $\Delta E_{\rm loc}$ to zero *at* the triple-collision point, but the error grows rapidly away from $r=0$ since $\Delta E_{\rm loc} \sim r \ln r$, implying that $\partial \Delta E_{\rm loc}/\partial r$ is infinite at $r=0$. Fortunately, this infinite derivative can be cured since the leading third-order term in the series, $\psi_{31} r^3 \ln r$, is known exactly [17]. By including this term as well in a trial wave function, the leading error in the local energy now scales as r. The dashed curves in Fig. 6 show $\Delta E_{\rm loc}$ for the incomplete third-order exponential function [incomplete since we have not included terms of $O(r^3)$]

$$\Phi^{(31)} = \Phi^{(2)} \exp(\psi_{3,1} r^3 \ln r - \psi_{1,0}\psi_{2,1} r^3 \ln r) , \tag{27}$$

for the same pair of hyperangular configurations. We see that the inclusion of the exact cubic logarithmic term results in a finite rather than infinite slope in the local energy error.

We note also that for both the second-order and incomplete third-order functions the local energy error is quite substantial at large r (and continues to deviate more at even larger r). Such deviations are not surprising, given that we have included only low-order terms in r. Even though we have remedied, through exponentiation, some of the problems associated with only having the first few terms of the series, exponentiation does not cure these problems fully. Nevertheless, the second- and third-order terms can be reigned in, to some extent, through appropriate cutoff functions at larger distances which mimic the effect of higher-order Fock terms that we have not included in our wave function.

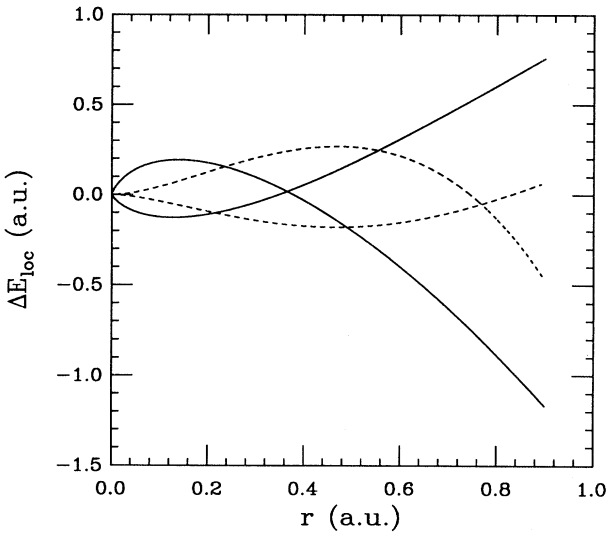

FIG. 6. Error in the local energy for the exponentiated second-order Fock wave function $\Phi^{(2)}$ (solid curves) and the incomplete exponentiated third-order function $\Phi^{(3,1)}$ (dashed curves) as a function of the hyperradius r for a fixed pair of hyperangular configurations: $(\alpha,\theta)=(2\tan^{-1}(\frac{1}{2}),0)$; $(\alpha,\theta)=(2\tan^{-1}(\frac{1}{2}),\pi)$. The second-order function has a local energy which grows with an infinite slope away from $r=0$, while the inclusion of the cubic logarithmic term $\psi_{3,1}\ln r$ reduces the infinite slope at the origin to a finite slope.

Consider the lowest-order logarithmic term $\psi_{2,1} r^2 \ln r$. In the infinite-order Fock expansion, this term would be appropriately canceled by higher-order terms, but in an approximate trial wave function, there is an unphysical behavior associated with the logarithm changing sign at $r=1$. This behavior can be effectively suppressed with a term that is proportional to r^3 for small r (hence leaving the second-order terms untouched), but which is proportional to $r^2 \ln r$ at larger distances and cancels $\psi_{2,1} r^2 \ln r$. This is the role of the term involving the exponential integral (Ei) function reported by Gottschalk, Abbott, and Maslen in Ref. [5]; we have achieved equivalent cutoffs using similar logarithmic functions, although we have not yet discovered an optimal logarithmic cutoff function. Further investigation reveals that more complicated polylogarithmic terms may be appropriate at higher orders [24].

In general, we have envisioned a matched asymptotic expansion smoothly interpolating between the small-r and large-r asymptotic wave functions, but such an expansion has not yet been constructed. More approximately, we can scale the quadratic terms in the exponential so that they behave linearly at large r. Such a linear exponential falloff is appropriate for atomic wave functions.

Even though we can construct accurate wave functions with very few variational degrees of freedom, the energies for these wave functions are still not as accurate as those calculated with large variational wave functions. Hence we have sought to supplement the exact Fock result with an appropriate trial function; specifically, we envision the exponentiated second-order Fock wave function as a complicated correlation term containing all the required singularities in the problem. While these calculations have yet to produce better total energies, we do not see this as a failure of the Fock expansion. Rather, we need to determine how the truncated exponential wave function is failing to reproduce the true wave function at larger distances, and find appropriate trial functions to remedy this.

VI. CONCLUSIONS

We have examined the recent solution of the $O(r^2)$ term of the Fock expansion and have verified empirically that it cures the finite discontinuity in the local energy that is symptomatic of wave functions which include two-particle but not three-particle nonanalytic terms. Given that the Fock expansion is a power series, however, we have realized that an approximate truncated Fock expansion does not have the proper two-particle cusps away from $r=0$. We have therefore constructed an alternate exponential representation of the truncated Fock ex-

pansion which does indeed have the correct cusps over all of space. This result suggests the extent to which the original Fock expansion is combining terms at all orders in the hyperradius in order to achieve an exponential wave function. We believe that this work will eventually help to yield significantly better energies than other trial functions with the same number of variational parameters, and could be important in other applications where an accurate representation of the wave function near the nucleus is of the utmost importance.

ACKNOWLEDGMENTS

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APPENDIX

Our proof that all higher terms ϕ_n, with $n \geq 2$, in the exponentiated Fock expansion are uniformly continuous and have uniformly continuous first derivatives on any compact set depends critically on the following well-known properties of harmonic functions.

Definition. A function $f: R^D \rightarrow R$ is said to be *harmonic* in a region $G \subseteq R^D$ if it obeys Laplace's equation:

$$-\nabla^2 f = 0 \quad \text{for all } \mathbf{r} \in G \ . \tag{A1}$$

Theorem 1. If a function f is harmonic in a region G, then on any compact subset of G, f is uniformly continuous and has uniformly continuous derivatives to all orders.

We also use an appropriate multidimensional generalization of a key theorem [25] of potential theory.

Theorem 2. Suppose $g(\mathbf{r})$ is bounded and integrable in a region G. Then

$$u(\mathbf{r}) = \int_G d^D\mathbf{r}' \frac{\Gamma(D/2)}{(D-2)2\pi^{D/2}} \frac{g(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{D-2}} \ , \tag{A2}$$

and its first derivatives with respect to Cartesian coordinates are everywhere uniformly continuous (the derivatives are obtained by differentiating under the integral sign), and $u(\mathbf{r})$ is a particular solution of Poisson's equation $-\nabla^2 f = g$.

Theorems 1 and 2 can be combined to yield the following.

Theorem 3. Under the hypotheses of Theorem 2 on g, *any* solution of

$$-\nabla^2 f = g \tag{A3}$$

obeys the continuity conditions of u in the conclusions of Theorem 2.

The proof of Theorem 3 is straightforward, since given any solution f,

$$-\nabla^2(f-u) = g - g = 0 \ , \tag{A4}$$

so on any region G, $f-u$ is harmonic. Then by Theorem 1, $f = (f-u)+u$ has the same continuity properties as u.

Now we commence our proof. The differential equation (25) obeyed by ϕ_n can be written as

$$-\nabla^2 \phi_n = \sum_{i=1}^{n-1} \nabla\phi_i \cdot \nabla\phi_{n-i} - 2V\delta_{n,1} + 2E\delta_{n,2} \ . \tag{A5}$$

Thus for $n = 0$,

$$-\nabla^2 \phi_0 = 0 \ , \tag{A6}$$

of which the solution homogeneous of degree 0 is simply

$$\phi_0 = \text{const} \ , \tag{A7}$$

so that

$$\nabla\phi_0 = \mathbf{0} \ . \tag{A8}$$

For $n = 1$, we have

$$-\nabla^2 \phi_1 = -2V = -2\left[-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right] \ . \tag{A9}$$

One particular solution of this equation is

$$\phi_1 = -Z(r_1 + r_2) + \tfrac{1}{2} r_{12} \ , \tag{A10}$$

whose six-dimensional gradient

$$\nabla\phi_1 = -Z(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) + \tfrac{1}{2}(\hat{\mathbf{r}}_{12}, \hat{\mathbf{r}}_{21}) \tag{A11}$$

is clearly bounded. All other solutions of the differential equation (A9) that are homogeneous of degree 1 differ from this particular solution by a harmonic function which is homogeneous of degree 1, i.e., a linear multinomial of the Cartesian coordinates. The requirement that for an S state ψ and hence ϕ be invariant under inversion constrains this linear multinomial to vanish.

The differential equation for ϕ_2 is

$$\begin{aligned} -\nabla^2 \phi_2 &= \nabla\phi_1 \cdot \nabla\phi_1 + 2E \\ &= 2Z^2 + \tfrac{1}{2} - Z((\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2)\cdot\hat{\mathbf{r}}_{12}) + 2E \ , \end{aligned} \tag{A12}$$

whose rhs is uniformly bounded but *not* continuous at $\mathbf{r}_1 = 0$ or $\mathbf{r}_2 = 0$. Except along these hyperplanes, however, it is piecewise continuous. Hence the theorems of potential theory are immediately applicable and we conclude that ϕ_2 and $\nabla\phi_2$ are uniformly continuous and hence uniformly bounded on any compact subset of any region G.

The proof for higher ϕ_n now proceeds by induction. For $n \geq 3$ the differential equation for ϕ_n is

$$-\nabla^2 \phi_n = \sum_{i=1}^{n-1} \nabla\phi_i \cdot \nabla\phi_{n-i} \ . \tag{A13}$$

Under the hypothesis that on any compact subset of G, $\nabla\phi_1, \ldots, \nabla\phi_{n-1}$, are all uniformly bounded (and hence integrable), the rhs of Eq. (A13) clearly obeys the hypothesis of the theorem of potential theory, so we conclude that ϕ_n and $\nabla\phi_n$ are uniformly continuous on any compact subset of G.

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