Potential-harmonic expansion for atomic wave functions

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(Received 18 June 1991)

One way to reduce the large degeneracy of the hyperspherical-harmonic basis for solving few- and many-body bound-state problems is to introduce an optimal basis truncation called the potential-harmonic (PH) basis. In this paper we introduce various potential-harmonic truncation schemes and assess their accuracies in predicting the energies of the helium and H^- ground states and the excited $2\,^1S$ level of the helium atom. We first find that the part of the PH basis that accounts for one-body correlations gives a better ground-state energy for He than Hartree-Fock (2.8790 a.u. versus 2.8617 for Hartree-Fock and 2.9037 exact). When an orthogonal complement is introduced to the basis to account for e-e correlations, we find that the error in the binding energy is 0.00025 a.u., and 0.00015 a.u. for ground-state and excited helium, and 0.00035 a.u. for H^-. Furthermore, the PH truncation is about 99.9% accurate in accounting for contributions coming from large values of the global angular momentum. This PH scheme is also much more accurate than previous versions based on the Faddeev equations. The present results indicate that the PH truncation can render the hyperspherical-harmonic method useful for systems with $N > 3$.

PACS number(s): 31.15.+q

I. INTRODUCTION

The hyperspherical-harmonic (HH) method [1] is an elegant tool for reducing the partial differential equations describing a many-body system to coupled ordinary differential equations. Unfortunately, the method suffers from two serious deficiencies: (1) The convergence of the HH expansion is rather slow when potentials are singular (e.g., $1/r$ ad $r \to 0$) or nonanalytic, because of the mismatch between the analytic structure of the exact wave function and that of the basis set [2]. (2) The size of the basis set grows exponentially with the number of particles. Both of these deficiencies seriously hinder the technique's usefulness in solving the Schrödinger equation for atomic, molecular, and nuclear systems.

Recently Haftel and Mandwlzweig [3] have successfully attacked the convergence problem in three-body atomic systems by incorporating Jastrow correlation functions along with the HH expansion. Still, the problem of basis-set degeneracy remains for $N > 3$. The main purpose of this paper is to propose an approach to this problem based on the potential-harmonic (PH) approach [4] and to assess the success of this method compared to previous techniques also based on potential harmonics.

The basic idea of potential harmonics is to limit the HH basis to those harmonics that appear in the expansion of the interparticle potential. In the simplest form, only one harmonic appears for each value of the global angular momentum K. Since for an N-body system the corresponding number of harmonics in the full basis set is

$\sim K^{3N-5}$, this technique leads to a drastic reduction in computation. The simplification not only reduces the number of coupled equations to be solved, but it also dramatically reduces the number of matrix elements to be calculated, which can be huge if, as for nuclear potentials, they must be computed for each value of the hyperradius r. The very important question remains: How accurate is the PG method?

Erens, Visschers, and van Wageningen [5] demonstrated in a model triton problem that the simplest PH approach [sometimes called the optimal subset (OS) approach] led to only a 0.001% error in the energy. In a careful comparison between OS and full-basis-set (FS) calculations for the ground and excited Helium atoms, Haftel and Mandelzweig [6] found the OS method accurate to 0.2% and 2% for the ground and $2\,^1S$ excited states, respectively. Given the high standards of accuracy in variational atomic calculations, this type of accuracy is not satisfactory for simple atomic and molecular bound states. Neither does it bode well for extension to many-body ($N > 3$) systems.

Since these early calculations, the PH method has been considerably refined. Fabre and coworkers [7–9] have developed PH methods, based on the Faddeev equations, that can be summed over all K by means of a two-dimensional integrodifferential equation. The basis set in this case is capable of including all two-body correlations in the wave function. At the same time, in the three-body problem, a maximum of three equations occur (less if there are identical particles) for each K. Like reductions

occur for many-body problems. While this method has been extensively employed in nuclear bound-state problems [8,9] (e.g., ^{3}H, ^{4}He, ^{16}O), its accuracy is unclear because the results are compared with other methods where the accuracy is also quite approximate. In this paper we assess the accuracy of the total energies of the helium atom and H$^-$ ion predicted by PH methods. Here both very accurate variational [10] and full-set [11] calculations exist for comparison.

Section II of this paper summarizes the mathematical development of the PH approach. Starting with the Schrödinger equation for two independent electrons (as in the helium atom), we show that the summed potential harmonics, relevant for nucleus-electron interactions, give an exact solution of this problem. The equations are then modified to take into account the e-e repulsion. To this point the PH method take into account one-body correlations—but not two-body correlations—and is similar in spirit to the Hartree-Fock approach. We calculate the helium ground-state energy as functions of the maximum global angular momentum for this PH expansion both with and without the e-e repulsion, and also extrapolate our results to infinite maximum global angular momentum. We find that the extrapolation is very accurate (to eight significant figures), and that the PH expansion gives a better ground-state energy than the Hartree-Fock method [12].

In Sec. III we introduce two-body (e-e) correlations by an addition to the PH basis relevant for e-e repulsion, with these basis functions orthogonalized with respect to the PH basis relevant for e—nucleus attraction. We show by numerical calculations that the PH approximation yields underbinding by about 0.01% for the He ground and excited 2 ^1S states and for the H$^-$ ground states. We then describe the relationship between the present PH method and the underlying PH method leading to the integrodifferential equation approach (IDEA) developed by Fabre de la Ripelle and coworkers [7]. Finally, we carry out parallel calculations using the PH basis underlying the IDEA technique (which are derived on the basis of the Faddeev equations). This version of the PH is much less accurate than the PH previously described.

Section IV contains concluding remarks. We conclude that the proposed PH expansion is the most accurate, giving the best results in our test cases involving helium and H$^-$. We also conclude that the PH method is a better starting point for the many-body problem then the Hartree-Fock method. Finally, the PH method is an efficient means to reduce the huge degeneracy of the HH basis for many-body problems and obtain accurate binding energies.

II. POTENTIAL-HARMONIC BASIS WITHOUT TWO-BODY CORRELATIONS

Our starting point is the Schrödinger equation for two independent electrons interacting with a nucleus of charge Z. As we shall show, the potential harmonic basis expansion is exact in this case. We will then show in the presence of e-e repulsion how the PH basis first takes care of single-electron correlations (similar to the Hartree-Fock method), and how an enlargement of the basis then takes into account all two-body correlations.

The Schrödinger equation for two independent electrons is (in atomic units $h = m = e = 1$)

$$\left[-\tfrac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left[\frac{1}{r_1} + \frac{1}{r_2} \right] - E \right] \psi(\mathbf{x}) = 0 \ , \qquad (1)$$

where $r_1 = |\mathbf{x}_1|$, $r_2 = |\mathbf{x}_2|$, Z is the nuclear charge, $\mathbf{x}$ denotes the six-dimensional position vector, and ∇_i^2 is the Laplacian for $\mathbf{x}_i$.

As is well known, the Schrödinger equation (1) is separable and the exact solution has the (anti)symmetrized product form

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) \pm \phi_2(\mathbf{x}_1)\phi_1(\mathbf{x}_2) \ , \qquad (2)$$

where the $+$ sign holds for electron spin singlet, and the $-$ sign holds for electron spin triplet. For total angular momentum zero, which we consider in this paper, $\mathbf{x}_1$ and $\mathbf{x}_2$ above can be replaced by the scalars r_1 and r_2. The exact solution is thus also expressible in the form of a summation

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = F_1(r_1, r) \pm F_2(r_2, r) \ , \qquad (3)$$

where r is the hyperradius $r = (r_1^2 + r_2^2)^{1/2}$. We now consider the expansion of (3) in the basis of potential harmonics.

We now introduce the hyperspherical coordinates, ω_1, ω_2, and ϕ such that ω_1 and ω_2 are the usual angular coordinates for $\mathbf{x}_1$ and $\mathbf{x}_2$, and

$$r_1 = r \cos\phi \ , \qquad (4a)$$

$$r_2 = r \sin\phi \ . \qquad (4b)$$

The kinetic energy operator, expressed in the hyperspherical coordinates, becomes

$$T = -\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} + \frac{5}{r}\frac{\partial}{\partial r} + \frac{L^2(\Omega)}{r^2} \right] \ , \qquad (5)$$

where Ω stands for the angular coordinates $(\omega_1, \omega_2, \phi)$, and $L^2(\Omega)$ is the grand orbital operator [4] for the angular coordinates. If we let

$$F(r_1, r) = \frac{U(r_1, r)}{r^{5/2}} \ , \qquad (6)$$

then

$$TF(r_1, r) = -\frac{1}{2r^{5/2}}\left[\frac{\partial^2}{\partial r^2} + \frac{\mathcal{L}^2(\Omega)}{r^2} \right] U(r_1, r) \ , \qquad (7)$$

where the eigenfunctions of $\mathcal{L}^2(\Omega) - Y_{[L]}(\Omega)$ —are the so-called hyperspherical-harmonic functions. These functions are characterized by the grand orbital quantum number L, and $r^L Y_{[L]}(\Omega)$ is the associated harmonic polynomial of degree L satisfying

$$[\mathcal{L}^2(\Omega) + (L + \tfrac{3}{2})(L + \tfrac{5}{2})] Y_{[L]}(\Omega) = 0 \ . \qquad (8)$$

(The symbol $[L]$ indicates that the set of quantum num-

bers includes projections as well as the grand angular momentum L).

For total angular momentum zero (S states), the PH functions are defined in terms of the kinetic rotation vectors

$$\mathbf{R}(\varphi) = \mathbf{x}_1 \cos\varphi + \mathbf{x}_2 \sin\varphi , \qquad (9)$$

where φ is a parameter. The basis of PH functions

$$P^0_{2k}(\Omega,\varphi) = \pi^{-3/2} C^1_k(2R^2(\varphi)/r^2 - 1) , \qquad (10)$$

where C^1_k is a Gegenbauer polynomial of degree k, is complete for functions of $|R(\varphi)|$. Hence for $\varphi=0$, the $P^0_{2k}(\Omega,0)$ constitute a complete basis for functions of r_1, and for $\varphi=\pi/2$ the $P^0_{2k}(\Omega,\pi/2)$ constitute a complete basis for functions of r_2. The individual PH functions $P^0_{2k}(\Omega,\varphi)$ are expressible as linear combinations of hyperspherical-harmonic functions of grand orbital angular momentum $L=2k$, so they are also eigenfunctions of the grand orbital angular momentum. Finally, since

$$2R^2(0)/r^2 - 1 = \cos(2\phi) \equiv z , \qquad (11a)$$

and

$$2R^2(\pi/2)/r^2 - 1 = -\cos(2\phi) = -z , \qquad (11b)$$

and $C^1_k(-z) = (-1)^k C^1_k(z)$, the PH basis for functions of r_1 and r_2, respectively, differ trivially by only a phase factor. Therefore the function $U(r_1,r)$ [or $F(r_1,r)$] is expandable in terms of the PH functions

$$U(r_1,r) = \sum_k u_k(r) P^0_{2k}(\Omega,0), \qquad (12)$$

with $U(r_2,r)$ having the same expansion except $U_k(r) \to (-1)^k u_k(r)$. Furthermore symmetric (antisymmetric) combinations of $U(r_1,r)$ and $U(r_2,r)$ are likewise expanded with contributions coming only from even (odd) k. Since the product forms like $\phi_1(r_1)\phi_2(r_2)$ are also expandable as products of Gegebauer polynomials, and since products of Gegenbauer polynomials are expressible in terms of single Gegenbauer polynomials, the products in Eq. (2) are fully expandable in PH functions (as are their symmetrized and antisymmetrized forms). Note that the independent electron solution is only a special case of Eq. (3), so that the PH expansion implied by Eq. (3) allows a more general description of the wave function, mainly through the dependence on the collective coordinate r.

In order to solve the Schrödinger equation (1) we expand the Coulomb potential in potential harmonics. According to Ref. [4] the PH expansion of a potential $V(r_i)$ is given by

$$V(r_i) = \sum_k P^0_{2k}(\Omega,\varphi_i) V_k(r) , \qquad (13)$$

where

$$V_k(r) = \int V(r\cos\phi) P^0_{2k}(\Omega,\varphi_i) d\Omega , \qquad (14)$$

and where the integral is taken over the surface of the unit hypersphere with $d\Omega = \frac{1}{4}\sin^2 2\phi \, d\phi \, d\omega_1 d\omega_2$, and $\varphi_i = 0$, $\pi/2$ for $i=1,2$. One finds

$$\frac{1}{r_i} = \frac{16\sqrt{\pi}}{r} \sum_k (-1)^k \left[\frac{(k+1)}{(2k+1)(2k+2)} \right] P^0_{2k}(\Omega,\varphi_i) . \qquad (15)$$

As a consequence of the parity relation $P^0_{2k}(\Omega,\pi/2) = (-1)^k P^0_{2k}(\Omega,0)$, the symmetric combination

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{32\sqrt{\pi}}{r} \sum_{k \text{ even}} \left[\frac{(k+1)}{(2k+1)(2k+3)} \right] P^0_{2k}(\Omega,0) \qquad (16)$$

contains only harmonic for even k. Making use of the relationship [4]

$$P^0_{2k}(\Omega,0)P^0_{2k'}(\Omega,0) = \pi^{-3/2} \sum_{k''} P_{2k''}(\Omega,0) ,$$

$$(k'' = |k-k'|, |k-k'|+2, \ldots, k+k') , \qquad (17)$$

we obtain

$$\langle P^0_{2k}(\Omega,0)|P^0_{2k''}(\Omega,0)|P^0_{2k'}(\Omega,0)\rangle = \pi^{-3/2} ,$$

$$(k+k', k'' \text{ even} , |k-k'| \le k'' \le k+k') , \qquad (18)$$

and we derive the matrix element (for $k+k'$ even)

$$\left\langle P^0_{2k}(\Omega,0) \left| \frac{1}{r_1} + \frac{1}{r_2} \right| P^0_{2k'}(\Omega,0) \right\rangle = \frac{32}{\pi r} S^{k'}_k , \qquad (19)$$

where

$$S^{k'}_k = \sum_{k''} \frac{(k''+1)}{(2k''+1)(2k''+3)}$$

$$(k'' = |k-k'|, |k-k'|+2, \ldots, k+k') . \qquad (20)$$

Substituting the expansion (12) into the reduced Schrödinger equation

$$\left[\frac{\partial^2}{\partial r^2} + \frac{\mathcal{L}^2(\Omega)}{r^2} + 2Z \left[\frac{1}{r_1} + \frac{1}{r_2} \right] + 2E \right] U(r_1,r) = 0 , \qquad (21)$$

and taking the inner product with $P_{2k}(\Omega,0)$, one obtains the coupled equations for $u_k(r)$

$$\left[\frac{d^2}{dr^2} - \frac{(2k+\frac{3}{2})(2k+\frac{5}{2})}{r^2} + 2E \right] u_k(r)$$

$$+ \sum_{k'} U^{k'}_k u_{k'}(r) = 0 , \qquad (22)$$

where

$$U^{k'}_k = \frac{64ZS^{k'}_k}{\pi r} . \qquad (23)$$

For singlet states k and k' are even, and for triplet states they are odd.

Table I contains the value of the energy $|E|$ when Eq. (22) is truncated to $k,k' \le k_{\max}$, for increasing values of $k_{\max}$ up to $k_{\max} = 36$. Of course, $|E|$ must converge to the exact independent-electron value of 4.0 a.u. Table I also contains an extrapolated value of $|E|$ for $k_{\max} \to \infty$.

TABLE I. Potential-harmonic predictions of the ground-state He atom total energy for independent electrons (no e-e repulsion). The units are atomic units (a.u.). The extrapolated value is to $k_{max} \to \infty$, carried out as described in the text.

k_{max}	Total energy (a.u.)
20	3.998 906 42
24	3.999 326 21
28	3.999 556 23
32	3.999 692 55
36	3.999 778 35
Extrapolated	4.000 000 00±0.000 000 05

Since theoretically $\Delta E(k) = E(k) - E(k-4)$ should decrease as k^{-4} [13] for large k, we obtain the extrapolated value by making a least-squares fit of $\Delta E(k)$ to the form $[k^2(A + Bk + Ck^2)]^{-1}$ using the results for k (i.e., k_{max}) of 24, 28, 32, and 36 as input. We see that with the calculations just for $k_{max} \leq 36$ we can extrapolate to the exact result with an error only in the eighth decimal place. The accuracy of this type of extrapolation will be more than enough to assess the quality of our other PH calculations.

We now introduce the e-e repulsion $1/r_{12}$, but retain the structure (3) of the wave function. This procedure is similar in spirit to the Hartree-Fock approach, but somewhat more general in that it allows an r dependence. To compute matrix elements of $1/r_{12}$, we utilize Eq. (17) and the relationships [4]

$$\frac{1}{r_{12}} = \frac{16}{r} \left[\frac{\pi}{2} \right]^{1/2} \sum_k (-1)^k \left[\frac{(k+1)}{(2k+1)(2k+3)} \right]$$

$$\times P^0_{2k}(\Omega, 3\pi/4) , \qquad (24)$$

$$\langle P^0_{2k}(\Omega, 0) | P_{2k'}(\Omega, 3\pi/4) \rangle$$

$$= \begin{cases} 0 & (k \text{ odd}) \\ (-1)^{k/2} \dfrac{\delta_{kk'}}{(k+1)} & (k \text{ even}) \end{cases} \qquad (25)$$

to obtain

$$\left\langle P^0_{2k}(\Omega, 0) \left| \frac{1}{r_2} \right| P^0_{2k'}(\Omega, 0) \right\rangle = \frac{8\sqrt{2}}{\pi r} \sigma^{k'}_k , \qquad (26)$$

where

$$\sigma^{k'}_k = \sum_{k''} (-1)^{k''/2} / [(2k''+1)(2k''+3)] \qquad (27)$$

with $k'' = |k-k'|, |k-k'|+2, \ldots, k+k'$, and with k, k' both having the same parity. Equation (22) still holds, but with

$$U^{k'}_k = \frac{64}{\pi r} \left[ZS^{k'}_k - \frac{\sqrt{2}}{4} \sigma^{k'}_k \right] \quad (k+k' \text{ even}) . \qquad (28)$$

Table II gives the convergence of the energy with k_{max} as in Table I, but with the e-e repulsion included. We obtain an extrapolated energy of 2.879 028 76 a.u., compared to the Hartree-Fock result of 2.861 7 a.u. [12]. Therefore, with no more computational difficulty than in-

TABLE II. Potential-harmonic predictions of the ground-state He atom total energy using the $P^0_{2k}(\Omega, 0)$ basis only, where e-e repulsion is included. The Hartree-Fock result is from Ref. [12].

k_{max}	Total energy (a.u.)
20	2.877 013 59
24	2.877 774 70
28	2.878 197 22
32	2.878 449 86
36	2.878 609 91
Extrapolated	2.879 028 76±0.000 000 06
Hartree-Fock	2.8617

volved in the Hartree-Fock method, we get a much better variational energy. Indeed, even truncation at low k_{max} (like $k_{max} = 20$, which involves solving only ten coupled equations), the PH method gives a lower energy than that of the Hartree-Fock.

The solution of (22) with the potential matrix (28) does not contain the two-body correlations produced by $1/r_{12}$. In a previous work [14] one of us (M.F.R.) has shown that the $k_{max} \to \infty$ limit of (22) is equivalent to the two-variable partial differential equation

$$\left[\frac{\partial^2}{\partial r^2} - \frac{15}{4r^2} + \frac{4}{r^2 W(z)} \frac{\partial}{\partial z} (1-z^2) W(z) \frac{\partial}{\partial z} \right.$$

$$\left. + \frac{2\sqrt{2}}{r} \left[\frac{Z}{\sqrt{1+z}} + \frac{Z}{\sqrt{1-z}} - \frac{1}{\sqrt{1+|z|}} \right] + 2E \right]$$

$$U(z,r) = 0 , \qquad (29)$$

where $W(z) = (1-z^2)^{1/2}$, and where we express the reduced wave function $U(r_1, r)$ as a function of $z = \cos 2\phi$ (and r) instead of r_1 (and r). The $Z/\sqrt{1+z}$ and the $Z/\sqrt{1-z}$ terms are the e-nucleus Coulomb potentials, while the $1/\sqrt{1+|z|}$ term is the angle average e-e repulsion

$$\frac{1}{2} \int_{-1}^{1} \left[\frac{1}{1 - x\sqrt{1-z^2}} \right]^{1/2} dx = \frac{\sqrt{2}}{\sqrt{1+|z|}} , \qquad (30)$$

where x is the cosine of the angle between the electrons, and the integrand is the repulsive potential $1/r_{12}$. Since Eq. (29) ignores the x dependence of the e-e potential, except to average over it, it ignores the feature of the potential that produces two-electron correlations. So we conclude that Eq. (22) [or (29)] represents the wave function in the absence of two-body correlations. We now proceed to include these correlations.

III. THE POTENTIAL-HARMONIC BASIS WITH TWO-BODY CORRELATIONS

To fully include all two-body correlations in the wave function, one must extend the ansatz (3) to include a term $F_c(r_{12}, r)$. This is equivalent to supplementing the $P_{2k}(\Omega, 0)$ harmonics with the harmonics $P_{2k}(\Omega, 3\pi/4)$, which describe functions of r_{12} and r in the wave function, not just in the potential. From a practical

viewpoint, we need only introduce that part of the basis which is orthogonal to the $P^0_{2k}(\Omega,0)$. We will call this orthogonal part $P^\perp_{2k}(\Omega_{12})$, where $\Omega_{12}=(\Omega,3\pi/4)$. Since according to Eq. (25) $P^0_{2k}=(\Omega,0)$ and $P_{2k}(\Omega,3\pi/4)$ are already orthogonal for odd k, we need only orthogonalize for even k. Hence $P^\perp_{2k}(\Omega_{12})=P_{2k}(\Omega,3\pi/4)$ for odd k, and for even k

$$P^\perp_{2k}(\Omega_{12})=C_k[P^0_{2k}(\Omega,3\pi/4)-\langle 0|12\rangle P^0_{2k}(\Omega,0)] , \quad (31)$$

where $\langle 0|12\rangle$ is the overlap integral given by Eq. (25), and C_k is the normalization constant

$$C_k=\frac{k+1}{\sqrt{k(k+2)}} . \quad (32)$$

The PH form of the wave function is now (for singlet states)

$$\psi(\mathbf{x}_1,\mathbf{x}_2)=F(r_1,r)+F(r_2,r)+F_c(r_{12},r) , \quad (33)$$

where the correlation amplitude $F_c(r_{12},r)$ is expanded [14]

$$F_c(r_{12},r)=r^{-5/2}\sum_k P^\perp_{2k}(\Omega_{12})u^\perp_k(r) . \quad (34)$$

The coupled Schrödinger equations now become

$$\left[\frac{d^2}{dr^2}-\frac{(2k+\frac{3}{2})(2k+\frac{5}{2})}{r^2}+2E\right]u_k(r)$$
$$+\sum_{k'}[U^{k'}_k u_{k'}(r)+U^{k'\perp}_k u^\perp_{k'}(r)]=0 , \quad (35a)$$

$$\left[\frac{d^2}{dr^2}-\frac{(2k+\frac{3}{2})(2k+\frac{5}{2})}{r^2}+2E\right]u^\perp_k(r)$$
$$+\sum_{k'}[U^{k'}_{k\perp}u_{k'}(r)+U^{k'\perp}_{k\perp}u^\perp_{k'}(r)]=0 , \quad (35b)$$

where $U^{k'}_k$ is given by (23), and

$$U^{k'\perp}_k=\frac{16\sqrt{2}}{\pi r}\left[\frac{E(k')(k'+1)}{\sqrt{k'(k'+2)}}\left[\frac{(-1)^{k/2}}{(k+1)}S^{k'}_k-\frac{(-1)^{k'/2}}{(k'+1)}\sigma^{k'}_k\right]-O(k')\frac{(-1)^{k/2}}{(k+1)}S^{k'}_k\right] , \quad (36a)$$

$$U^{k'}_{k\perp}=U^{k\perp}_{k'} , \quad (36b)$$

$$U^{k'\perp}_{k\perp}=\frac{64}{\pi r}\left[O(k)O(k')\left[Z\sigma^{k'}_k-\frac{\sqrt{2}}{4}S^{k'}_k\right]\right.$$
$$+\frac{\sqrt{2}}{4}O(k)E(k')\frac{\sqrt{k'(k'+2)}}{(k'+1)}S^{k'}_k+\frac{\sqrt{2}}{4}O(k')E(k)\frac{\sqrt{k(k+2)}}{(k+1)}S^{k'}_k$$
$$+E(k)E(k')\frac{(k+1)(k'+1)}{\sqrt{k(k+2)k'(k'+2)}}\left\{Z\left[\sigma^{k'}_k-(-1)^{(k+k')/2}\frac{S^{k'}_k}{(k+1)(k'+1)}\right]\right.$$
$$-\frac{\sqrt{2}}{4}\left[\left[1-\frac{1}{(k+1)^2}-\frac{1}{(k'+1)^2}\right]\right.$$
$$\left.\left.\left.\times S^{k'}_k+(-1)^{(k+k')/2}\frac{\sigma^{k'}_k}{(k+1)(k'+1)}\right]\right\}\right] , \quad (36c)$$

where k and k' are even, and $k_\perp$ and $k'_\perp$ may be even or odd. In Eq. (36), $O(k)$ is 1 for odd k, zero for even, and $E(k)$ is 1 for even k, zero for odd. The $u_k(r)$ states range over even k only (for S states), while the $u^\perp_k(r)$ states range over all k except $k=0$, which has only one harmonic [i.e., $P^\perp_0(\Omega_{12})$ does not exist].

Table III contains the energies of the He ground state, the excited $2\,^1S$ state, and the H$^-$ ground state, as predicted by the PH expansion, as functions of k_{max}—the maximum k,k' retained in Eq. (35). This table also shows the full set (FS) results [11] for each k_{max}, i.e., the energy when all harmonics for $k\leq k_{max}$ are retained, and also the best correlation-function hyperspherical-harmonic (CFHH) [3] and variational energies [10]. The extrapolation to $k_{max}\to\infty$ proceeds as previously described in Sec. II.

The accuracy of the principal assumption of the PH

method—the ansatz of Eq. (33)—is tested by comparing the PH result with the FS result at given values of k_{max}, or by comparing the extrapolated result with the best available energies calculated by other methods—namely, variational calculations. The error introduced by the PH approximation, so judged, is approximately 0.01% and 0.05% for the ground-state He and H$^-$ systems, respectively. For excited He , the error is about 0.017% for $k_{max}=14$ (the highest k_{max} for which we performed FS calculations), but is only 0.007% when comparing the extrapolated energy with the "exact" (variational) result. So for He*, the discrepancy between the PH and FS results actually decreases with k_{max}. The success of the PH expansion in reproducing FS results for the He* bodes well for the prospects of this method for excited states.

Another important result of Table III is that the PH reduction of the full basis very accurately approximates

TABLE III. Potential-harmonic (PH) and full-set (FS) predictions of the total energy of the ground-state He atom (He), excited $2\,^1S$ He atom (He*), and ground state H$^-$ ion (H$^-$). The PH results are with the full PH basis. Results from the correlation-function hyperspherical-harmonic method (CFHHM) (Ref. [3]) and from the best variational calculations (Ref. [10]) are also included.

k_{max}	He(PH)	He(FS)	He*(PH)	He*(FS)	H$^-$(PH)	H$^-$(FS)
8	2.887 296 35	2.887 543 91	1.947 278 48	1.947 697 49	0.517 474 31	0.517 796 76
10	2.893 334 46	2.893 584 42	1.994 118 84	1.994 575 30	0.520 529 59	0.520 856 00
14	2.898 757 86	2.899 009 20	2.051 112 76	2.051 451 11	0.523 701 27	0.524 030 00
16	2.900 056 43		2.068 961 37		0.524 571 06	
20	2.901 523 00		2.093 134 78		0.525 671 06	
24	2.902 259 77		2.108 152 49		0.526 244 90	
28	2.902 668 47		2.117 993 35		0.526 604 44	
32	2.902 912 72		2.124 713 73		0.526 832 71	
36	2.903 067 40		2.129 457 19		0.526 984 24	
Extrapolated	2.903 471 79$\pm$0.000 000 01		2.145 825$\pm$0.000 007		0.527 427 5$\pm$0.000 000 6	
CFHHM	2.903 724 37		2.145 974			
Variational	2.903 724 38		2.145 974		0.527 751 10	

the influence of all the harmonics coming from large k. The fact that the PH approximation accounts for about 99.9% of the FS differences in energy between successive values of k_{max} in all three systems (for $k_{max} > 8$) evidences this. This property suggests the following systematic improvement of the PH method: Include the full basis up to a certain maximum value of k, and use the PH basis for all k's greater than this. One could then get a very accurate value of the energy in this way while avoiding most of the problems caused by the huge degeneracy in the many-body problem, which is especially acute for large values of k. We concede that while the type of accuracy that the PH approach gives in the two-electron atom problem (four–six significant figures) is not competitive with most modern variational methods, this type of accuracy is desirable for a many-electron system. The accuracy of the PH approach should not seriously degrade with more electrons, nor do the computations grow prohibitively with the number of particles [8,9].

In previous work [7] one of us (M.F.) has shown that an ansatz like Eq. (33) leads to a transformation of the Schrödinger equation into a integro-differential equation (IDE) for the one- and two-body amplitudes [i.e., the F's of Eq. (33)]. For two-electron atoms, the basic equation that leads to the IDE is

$$(T-E)F(r_i,r)=\frac{Z}{r_i}\psi \quad (i=1,2) , \tag{37a}$$

$$(T-E)F_c(r_{12},r)=-\frac{1}{r_{12}}\psi . \tag{37b}$$

This is the Faddeev decomposition of the Schrödinger equation. The amplitudes $F(r_1,r)$, $F(r_2,r)$, and $F_c(r_{12},r)$ play the roles of $\psi^{(1)}$, $\psi^{(2)}$, and $\psi^{(3)}$ in the usual Faddeev notation, with the additional assumption that the Faddeev amplitude labeled by a certain pair only depends on the relative distance of the pair and on the hyperradius r. If this assumption were exact, the Faddeev equations (37) would be equivalent to the Schrödinger equation, as summing (37) over labels would verify. The correlation amplitude F_c is generated from the one-body amplitudes (F) through the e-e interaction. While the

wave function generated by the solution of Eqs. (37) satisfies the form (33), it is not equivalent to our previous substitution of (33) directly into the Schrödinger equation [leading to Eq. (35)]. In Eqs. (37) we are explicitly demanding that each Faddeev component have a particular form involving its pair label, a restriction not implicit in the form (33). The substitution of (12), (33), and (34) into the Schrödinger equation amounts to an expansion of the wave function in orthogonal basis functions, which guarantees that the energy E is variational. This means that the error in the energy estimate will be of second order in the error in the wave function, and, for the ground state, will be an upper bound to the true energy. This variational property fails to hold for the Faddeev equations (37). The advantage of (37) is that it leads to an integrodifferential equation that sums the PH over all k.

The IDE's are derived by projecting Eqs. (37a) and (37b) onto the r_i and r_{12} spaces, respectively, i.e., onto the $P^0_{2k}(\Omega,0)$ and $P^0_{2k}(\Omega,3\pi/4)$ basis. [Henceforth we will denote $P^0_{2k}(\Omega,3\pi/4)$ as $P^0_{2k}(\Omega_{12})$]. With the definitions

$$F(r_1,r)=\frac{U(z,r)}{r^{5/2}} \quad (z=2r_1^2/r^2-1) , \tag{38a}$$

$$F_c(r_{12},r)=\frac{U_c(r)}{r^{5/2}} \quad (z=r_{12}^2/r^2-1) , \tag{38b}$$

where $U(z,r)$ has a definite z parity, we obtain [8] the projection of $U_c(z,r)$ on the r_1 space given by the integral

$$\langle r_1|F_c(r_{12},r)\rangle=\frac{1}{2r^{5/2}\sqrt{(1-z^2)}}\int_{-z_0}^{z_0}dz'U_c(z',r) , \tag{39}$$

where $z_0=\sqrt{1-z^2}$, while the projection of $U(z,r)$ on the r_{12} space yields

$$\langle r_{12}|F(r_1,r)\rangle=\frac{1}{2r^{5/2}\sqrt{1-z^2}}\int_{-z_0}^{z}dz'U(z',r) . \tag{40}$$

The coupled IDE's for U and U_c then follow

$$(T_z - E)U(z,r) = \frac{\sqrt{2}Z}{r\sqrt{1+z}}\left[U(z,r) + \frac{1}{2\sqrt{1-z^2}}\int_{-z_0}^{z_0} dz' U_c(z',r)\right] ,$$

$$(T_z - E)U_c(z,r) = \frac{-1}{r\sqrt{1+z}}\left[U_c(z,r) + \frac{1}{2\sqrt{1-z^2}}\int_{-z_0}^{z_0} dz' U(z',r)\right] ,$$

(41)

$$T_z = -\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} - \frac{15}{r^2} + \frac{4}{r^2 W(z)}\frac{\partial}{\partial z}(1-z^2)W(z)\frac{\partial}{\partial z}\right] .$$

The coupled equations (37), when expanded in PH,

$$F(r_1, r) = \sum_k P^0_{2k}(\Omega, 0)u_k(r)/r^{5/2} , \quad (42a)$$

$$F_c(r_{12}, r) = \sum_k P^0_{2k}(\Omega_{12})u^c_k(r)/r^{5/2} , \quad (42b)$$

converge to solutions identical to the IDE (41) by projecting (37a) onto the $P^0_{2k}(\Omega, 0)$ basis, and (37b) onto the $P^0_{2k}(\Omega_{12})$ basis. As a consequence, coupled equations like (35) result, except the symbol c replaces $\perp$ with the potential matrix

$$U^{k'}_k = \frac{64}{\pi r}ZS^{k'}_k \quad [(-1)^k = (-1)^{k'}] , \quad (43a)$$

$$U^{k'c}_k = \frac{32}{\pi r}Z(-1)^{k'/2}\frac{S^{k'}_k}{k'+1} \quad (k, k' \text{ even}) , \quad (43b)$$

$$U^{k'}_{kc} = -\frac{32\sqrt{2}}{\pi r}(-1)^{k+k'/2}\frac{S^{k'}_k}{k'+1} \quad (k' \text{ even}) , \quad (43c)$$

$$U^{k'c}_{kc} = \frac{16\sqrt{2}}{\pi r}(-1)^{k+k'}S^{k'}_k . \quad (43d)$$

Table IV gives the energy, as a function of k_{max}, for the Faddeev potential harmonics [i.e., Eqs. (37) with the expansions (42), or, equivalently, Eq. (35) with the matrix elements (43)], and the corresponding full-set result. The column labeled distorted Faddeev PH indicates the energy when a set of Faddeev equations, alternative to (37) [9].

$$[T - E + V_0(r)]F(r_i, r) = \left[\frac{Z}{r_i} + \frac{V_0(r)}{3}\right]\psi , \quad (44a)$$

$$[T - E + V_0(r)]F_c(r_{12}, r) = \left[-\frac{1}{r_{12}} + \frac{V_0(r)}{3}\right]\psi , \quad (44b)$$

where $V_0(r)$ is the total potential averaged over the hyperangles $\{\Omega\}$

$$V_0(r) = -\frac{32}{3\pi r}Z + \frac{8\sqrt{2}}{3\pi r} \quad (45)$$

is applied. One can still use Eq. (35) (with $\perp$ replaced by c) by using the matrix elements

$$U^{k'}_k = \frac{64}{\pi r}ZS^{k'}_k - \frac{16\sqrt{2}}{3\pi r}\delta_{kk'} , \quad (46a)$$

$$U^{k'c}_k = \frac{64}{\pi r}(-1)^{k'/2}\frac{(S^{k'}_k - \delta_{kk'}/3)}{k'+1} \quad (k, k' \text{ even}) , \quad (46b)$$

$$U^{k'}_{kc} = \frac{-16\sqrt{2}}{\pi r}(-1)^{k+k'/2}\frac{(S^{k'}_k - \delta_{kk'}/3)}{k'+1} \quad (k' \text{ even}) \quad (46c)$$

$$U^{k'c}_{kc} = \frac{64}{3\pi r}ZS_{kk'} - \frac{16\sqrt{2}}{\pi r}(-1)^{k+k'}S^{k'}_k . \quad (46d)$$

The Faddeev PH gives poor agreement with the full-set results. For $k_{max} = 14$ the Faddeev PH overshoots the FS energy by 1%. Furthermore, the Faddeev PH overshoots the FS differences in energy between successive values of k_{max} by about 20%. The distorted Faddeev PH do much better, giving about 0.1% less binding than the FS result, accounting for about 97% of the FS energy differences between successive values of k_{max}. These trends follow those obtained in nuclear-binding calculations [15], where inclusion of $V_0(r)$ in Eq. (44), when solved as an integrodifferential equation, leads to much more accurate binding energies. However, when the PH ansatz (33) is applied to the wave function itself (Table III), rather than to the Faddeev components, the error in the energy is reduced by yet another factor of 10, no doubt due to the variational nature of the energy in this case.

IV. SUMMARY AND CONCLUSIONS

We have found that the potential-harmonic approximation is an efficient method of calculating the effects of one- and two-body correlations in three-body atomic systems. When only one-body correlations are included [i.e., when only the $P^0_{2k}(\Omega, 0)$ states are included in the basis set], a better total energy (2.8790 a.u.) is obtained for the He ground state than in the Hartree-Fock method (2.8617 a.u.). The PH expansion achieves this with ap-

TABLE IV. Total-energy predictions for the ground-state He atom as calculated with the potential-harmonic expansion of the Faddeev equations (37), the PH expansion of the distorted Faddeev equations (44), and with the full set.

k_{max}	Faddeev PH	Distorted Faddeev PH	Full set
2	2.797 863 83	2.783 921 09	2.784 370 36
4	2.872 812 91	2.847 97	2.850 215 63
6	2.903 072 28	2.873 050 15	2.876 008 22
8	2.916 906 14	2.884 249 37	2.887 543 94
10	2.924 266 02	2.890 103 21	2.893 584 42
12	2.928 427 18	2.893 366	2.896 955 73
14	2.930 984 40	2.895 351	2.899 009 21

proximately the same amount of computation as the Hartree-Fock method. By solving only 18 coupled equations ($k_{max} = 36$) the PH expansion, as applied in the usual hyperspherical-harmonic method, one accounts for about 99.99% of the binding (2.8686 a.u.). One can obtain the full $k_{max} \to \infty$ limit by either solving a two-dimensional partial differential equation or by extrapolating the $k_{max} \leq 36$ energies to infinity. This latter procedure is rather accurate, yielding a final energy accurate to seven to eight significant figures. The desirability of the PH method over the Hartree-Fock method probably stems from allowing the wave function to have variations with a collective coordinate r—the hyperradius—in addition to the usual electron-nucleus correlations. Moreover, the PH expansion might be a better starting point for many-electron atom calculations than the Hartree-Fock method.

When the full PH basis is employed, including the full effect of e-e correlations through the $P_{2k}^{1}(\Omega_{12})$ functions, the error in the total energy is about 0.01% compared with the best full-set calculations. We have confirmed this type of accuracy for a tightly bound ground-state system (the He ground state), a loosely bound ground-state system (H^-), and for a loosely bound excited system (He* $2\,^1S$). Extrapolations to $k_{max} \to \infty$ agree with the best variational calculations [10] (themselves precise up to 12 significant figures) to within 0.01%, with the extrapolations themselves accurate to six–seven significant figures. In addition, the PH basis accounts for about 99.9% of the increase in energy coming from higher hyperspherical harmonics ($k > 8$). This property suggests that the PH method can be improved by including the full set up to a certain k and using the PH basis for larger k.

The version of the PH basis proposed in this paper, based on the PH expansion of the wave function itself rather than the Faddeev components, and using an orthonormal basis, is at least one order of magnitude more accurate than previous versions. Furthermore, it appears possible to extrapolate to $k \to \infty$ to high accuracy by solving relatively small systems of ordinary differential equations as in the hyperspherical-harmonic method.

The main utility of the PH method is not in the three-body problem, where many extremely accurate methods exist, especially in atomic physics. The results of the present paper indicate that the PH expansion is an effective way to drastically reduce the degeneracy of the hyperspherical-harmonic basis with only a small loss in accuracy. The reduction in the number of harmonics becomes an extremely important feature in many-body systems with $N > 3$, where full-set calculations are prohibitive. At the same time, the standards of precision are not as stringent in these many-body calculations, so the type of accuracy obtained in the PH method, which we expect will not seriously degrade in going to many-body calculations, should be quite satisfactory. Finally, a marriage of the PH method with the correlation-function hyperspherical-harmonic method [3], which itself yields up to significant ten-digit precision for the He atom, could lead to still more accuracy for many-body systems.

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