Potential Harmonic Calculations of Helium Triplet States

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ABSTRACT

The hyperspherical harmonics (HH) provide a complete basis for the expansion of atomic wave functions, but even for two particles the number of harmonics for a given order is not trivial and, as the number of electrons increases, this degeneracy becomes absolutely prohibitive. We modify the method by selecting a subset of the basis that, we feel, will yield the physically most important part of the wave function, and test the idea on simple systems.

In a previous work (with M. Haftel) of the ground and first excited $^1S_0$ states of the helium atom we found that the error in the binding energy of the $^1S_0$ ground state was of the order of 1 part in $10^4$ and that it decreased for the first excited state.

We now have applied our method to the equivalent triplet $^3S_1$ states. We report on this work, and our results, and hope to draw attention to the interesting accuracy that we obtain with the relatively simple wave functions of our formulation.
Introduction

The bound states of the helium atom have been studied by using several methods. The most accurate results have been achieved by variational calculations where the states are described by wave functions which include more than 200 parameters [1]. Other, more recent, calculations have been performed using expansions in hyperspherical harmonics (HH), where the convergence was speeded up by the introduction of a correlation factor describing the average behaviour of the wave function at short and long ranges [2]. The residual part of the wave function was expanded in HH. This leads to an accuracy of about nine figures in the binding energy, but with a nonuniform convergence as the number of HH is increased.

In our approach to the many body problem, we select the HH occurring in the wave function by following a scheme in which the basis elements are introduced according to the degree of complexity of the correlations that they describe.

In the first approximation, a HH of minimal degree (because of the Pauli principle) defines the state. In the next approximation, terms will appear in our equations consisting of the product of the HH of minimal degree and the potential. The basis elements that can correctly reproduce these terms form our Potential Harmonic basis [3], which we use in this work. A further approximation would be obtained by applying the potential to the wave function, including the correlations already obtained from the previous order and by taking into account the new basis elements generated by this product.

In the analysis of the ground and first excited $^1S_0$ state of the helium atom [4], what was studied was the accuracy obtained by using the PH basis. The resulting expansion of the wave function provides a simple structure where one and two body contributions are exactly separated. It leads to a simple description of the wave function.

We found that the error in our calculation of the binding energy of the $^1S_0$ ground state was of the order of $10^{-4}$ and decreased for the first excited state.

Our purpose, then, in this paper was to study the worth of the method for triplet $^3S_1$ states. Since the potential basis is complete in so far as describing the independent motion of the electrons (i.e. when the interaction between the electrons is neglected), the missing energy must come from the Coulomb interaction between the two electrons. In the $^1S_0$ state this interaction is maximum at short distances and is expected to be larger in the space symmetric $^1S_0$ states than in the space anti-symmetric $^3S_1$ states, where the effect of this interaction damps out at small distances where the wave function goes to zero. We were therefore very hopeful that our method would be even more satisfactory for the triplet than for the singlet.
Formalism

In the HH expansion method the coordinates are expressed in polar form in a $D$-dimensional space where $D = 3N$ is the number of independent space degrees of freedom. $N = 2$ for two electrons with position vectors $\vec{x}_1$ and $\vec{x}_2$, relative to the nucleus with nuclear charge $Z$ and polar coordinates $(r_i, \vec{\omega}_i)$, $i = 1, 2$, where the $\vec{\omega}_i$ denote the two standard angle measures for the $i$th electron, the hyperspherical coordinates $(r, \Omega)$ are chosen to be the hyperradius $r = \sqrt{r_1^2 + r_2^2}$ and the set $\Omega$ of five angular coordinates, $\vec{\omega}_1$, $\vec{\omega}_2$ and $z$, where $r_1 = r \cos \phi$, $r_2 = r \sin \phi$ and we replace $\phi$ by

$$z = \cos 2\phi = \frac{r_1^2 - r_2^2}{r^2} \quad (1)$$

The Schrödinger equation for the helium atom, in atomic units ($\hbar = m = e = 1$),

$$\left\{-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_{12}}\right) - E\right\} \Psi = 0, \quad (2)$$

is then transformed, in hyperspherical coordinates, into

$$\left\{-\frac{1}{2}\left[\frac{\partial^2}{\partial r^2} + \frac{L^2(\Omega)}{r^2}\right] - \frac{\sqrt{2Z}}{r} \left(\frac{1}{\sqrt{1+z}} + \frac{1}{\sqrt{1-z}}\right) + \frac{1}{r} + \frac{1}{r^2}\right\} \Phi(r, \Omega) = 0 \quad (3)$$

where $x$ is the cosine of the angle between the two electrons, $(x = \vec{x}_1 \cdot \vec{x}_2 / (r_1 r_2) = \cos \theta)$, $L^2(\Omega)$ is the grand orbital operator, and $\Psi$ and $\Phi$ are related by

$$\Psi = r^{-5/2} \Phi(r, \Omega). \quad (4)$$

We note that if $Y_{L}^{j}(\Omega)$ is a HH, with $r^L Y_{L}^{j}(\Omega)$ the associated harmonic polynomial of degree $L$, then $L^2(\Omega)$ in equation (3) satisfies

$$[L^2(\Omega) + \mathcal{L}(\mathcal{L} + 1)] Y_{L}^{j}(\Omega) = 0 \quad (5)$$

with $\mathcal{L} = L + 3/2$ in the six dimensional space spanned by the coordinates $\vec{x}_1$ and $\vec{x}_2$. Also, the Hamiltonian in (3) is an even function of $z$ and therefore the wave function can have a definite $z$-parity. The $z$-parity is associated, according to (1), with the parity in the exchange of the two electrons, i.e. it is even for the singlet $^1S_0$ states and odd for the triplet $^3S_1$ states.

When the interaction between the electrons is set to zero, equation (3) is separable and the wave function for $S$-states can be written either as a product of individual wave functions

$$\Psi = \phi_{n_1l_1}(r_1) \phi_{n_2l_2}(r_2) \pm \phi_{n_2l_1}(r_1) \phi_{n_1l_2}(r_2) \quad (6)$$

where $+$(-) is for space (anti)symmetric wave functions, or as a function

$$\Psi = \frac{\phi(z, r)}{r^{5/2}} \quad (7)$$

with a $z$-parity even(odd) for space (anti)symmetric wave functions. Both descriptions are equivalent.
Let the HH expansion of the wave function in (3) be

\[ \Phi(r, \Omega) = \sum_{[L]} Y_{L_1}(\Omega) u_{L_1}(r) \]  

where \([L]\) is the set of the five quantum numbers \([L, l_1, l_2, m_1, m_2]\) associated with the five degrees of freedom \((\vec{\omega}_1, \vec{\omega}_2, z)\). The \((l_i, m_i)\) are the orbital quantum numbers and \(L = 2k + l_1 + l_2\) where \(k\) is the quantum number associated with \(z\).

The coupled equations for the partial waves \(u_{L_1}(r)\) are

\[ \left\{ \frac{1}{2} \left[ -\frac{d^2}{dr^2} + \frac{L(L+1)}{r^2} \right] - E \right\} u_{L_1}(r) + \sum_{[L']} \langle Y_{L_1}|V(r, \Omega)|Y_{L_1'} \rangle u_{L_1'}(r) = 0 \]  

where in our problem \(V(r, \Omega)\) is the potential occurring in equation (3).

In equation (8) the sum starts from a minimal degree \(L_m\). In the hypercentral approximation (HCA) only the first term in equation (8) is taken into account and equation (9) is reduced to a hyperradial equation

\[ \left\{ \frac{1}{2} \left[ -\frac{d^2}{dr^2} + \frac{L_m(L_m+1)}{r^2} \right] + U_{L_m}(r) - E \right\} u_{L_m}(r) = 0 \]

where

\[ U_{L_m}(r) = \langle Y_{L_m}|V(r, \Omega)|Y_{L_m} \rangle . \]

For a normalized HH

\[ \int |Y_{L_m}(\Omega)|^2 d\Omega = 1 . \]

Here, the surface element of the unit hypersphere is

\[ d\Omega = d\vec{\omega}_1 d\vec{\omega}_2 (\sin \phi \cos \phi)^2 d\phi = d\vec{\omega}_1 d\vec{\omega}_2 \frac{1}{8} \sqrt{1-z^2} dz . \]

For \(S\)-states

\[ Y_{[2k,0,0,0,0]}(\Omega) = \pi^{-3/2} C_k^1(z) \]

and

\[ d\Omega = \pi^2 \sin \theta d\theta \sqrt{1-z^2} dz . \]

With the Gegenbauer polynomials \(C_k^1 = 1\) and \(C_k^1(z) = 2z\), the hypercentral potential for the \(^1S_0\) and \(^3S_1\) ground states are, for \(k = 0, 1\) respectively,

\[ U_{[0]}(r) = \frac{1}{\pi} \int V(r, \Omega) \sin \theta d\theta \sqrt{1-z^2} dz \]

and

\[ U_{[2]}(r) = \frac{4}{\pi} \int V(r, \Omega) \sin \theta d\theta z^2 \sqrt{1-z^2} dz \]

where the integrals are taken in the domain \(0 \leq \theta \leq \pi\) and \(-1 \leq z \leq 1\).
For a Coulomb potential, the integrals (13) and (14) are simply proportional to $1/r$, and therefore the HCA equation (10) can be solved analytically [3]. In order to go further, another variable must be introduced. An expansion of $r_{12}^{-1}$ in terms of Legendre polynomials is obtained from the generating function

$$\sum_{\ell=0}^{\infty} P_{\ell}(u) z^\ell = (1 - 2zu + z^2)^{-1/2},$$

leading to

$$\frac{1}{r_{12}} = \frac{1}{r \sqrt{1 - \sin 2\phi \cos \theta}} = \frac{1}{r} \sqrt{\frac{2}{1 + |z|}} \sum_{\ell=0}^{\infty} \left( \frac{1 - |z|}{1 + |z|} \right)^{\ell/2} P_{\ell}(x).$$

(16)

We expand the wave function for electrons in $S$-states in terms of normalized Legendre polynomials:

$$\Phi(r,z,x) = \sum_{\ell=0}^{\infty} \mathcal{P}_{\ell}(x) u_{\ell}(z,r),$$

(17)

where $\mathcal{P}(x) = \sqrt{\ell + 1/2} P_{\ell}(x)$. Introducing this form for the wave function into Eq. (3), we obtain an infinite system of coupled second order partial differential equations for the partial waves $u_{\ell}(z,r)$:

$$\left\{ \frac{\partial^2}{\partial r^2} + \frac{L^2(l,z)}{r^2} + 2\sqrt{2} \frac{Z}{r} \left[ \frac{1}{1+z} + \frac{1}{1-z} \right] + 2E \right\} u_{\ell}(z,r)$$

$$= 2 \sum_{\ell'='0}^{\infty} <\mathcal{P}_{\ell'}|\frac{1}{r_{12}}|\mathcal{P}_{\ell'}> u_{\ell'}(z,r)$$

(18)

where

$$L^2(l,z) = -\frac{15}{4} \frac{1}{r^2} + \frac{4}{\sqrt{1-z^2}} \frac{\partial}{\partial z} (1-z^2)^{3/2} \frac{\partial}{\partial z} - \frac{4}{1-z^2} \ell(\ell + 1)$$

(19)

and the matrix element

$$\left< \mathcal{P}_{\ell} | \frac{1}{r_{12}} | \mathcal{P}_{\ell'} \right> = \sqrt{\left( \ell + \frac{1}{2} \right) \left( \ell' + \frac{1}{2} \right)} \int_{-1}^{1} P_{\ell}(x) \frac{1}{r_{12}} P_{\ell'}(x) dx$$

where $r_{12}^{-1}$ is given by (10) in terms of $r$, $z$ and $x = \cos \theta$. Rather than try to solve this system of coupled two-variable second order partial differential equations to atomic accuracy, we expand $\Phi(r,z,x)$ in hyperspherical harmonics. To then solve exactly equations (18) requires the complete Zernike-Brinkman basis [3] $\cal HE$ for two particles in $S$-states, i.e. a basis complete in the variable $z$ for each value of $\ell$ in the expansion (17). This would lead us to a large number of coupled equations (1) to be solved for a given accuracy and we try to reduce the size of the basis and choose the potential basis.
This basis consists of: (i) the basis for \( \ell = 0 \) which is complete for an expansion of any function of \( z \) only (in particular of the potential \( r_1^{-1} + r_2^{-1} \)), and (ii) the basis needed for a complete expansion of \( r_{12}^{-1} \). This implies that equation (3) can then be solved with a harmonic expansion which includes only two orthogonal elements for each grand orbital \( L = 2k \), except when \( L = 0 \).

The PH approximation selects the partial waves in expansion (8) which are coupled to the largest components, \( L = 0 \) (\( L = 2 \)), of the \( ^1S_0 \) \((^3S_1) \) ground states of the wave function respectively. We call this the optimal subset.

In order to extract this subset, we introduce the kinematic rotation vector \( \vec{R}(\varphi) = \vec{r}_1 \cos \varphi + \vec{r}_2 \sin \varphi \), with parameter \( \varphi \), where \( \vec{R}(0) = \vec{r}_1 \), \( \vec{R}(\pi/2) = \vec{r}_2 \), \( \vec{R}(3\pi/4) = (\vec{r}_2 - \vec{r}_1)/\sqrt{2} \), and we define \( z(\varphi) = 2R^2(\varphi)/r^2 - 1 \), with \( z(0) = \cos 2\varphi = z \), leading to

\[
\begin{align*}
1/r_1 & = \frac{\sqrt{2}}{\sqrt{1+z}}, \quad 1/r_2 = \frac{\sqrt{2}}{\sqrt{1-z}}, \quad 1/r_{12} = \frac{1}{r\sqrt{1+z(3\pi/4)}} \quad (20)
\end{align*}
\]

for \( \varphi = 0, \pi/2, \) and \( 3\pi/4 \), respectively.

The Potential Harmonics for the \( S \)-state are given in terms of the kinematic angle \( \varphi \) by

\[
P^{0}_{2k}(\Omega, \varphi) = \pi^{-3/2}C^{1}_{k}(z(\varphi))
\]

where \( C^{1}_{k} \) is a Gegenbauer polynomial of even grand orbital \( L = 2k \). We use the notation \( P^{0}_{2k}(\Omega_i), \quad i = 1, 2, 12, \) for \( P^{0}_{2k}(\Omega, \varphi_i) \), where \( \varphi = 0, \pi/2, 3\pi/4 \) refer to the respective choices of the kinetic angle parameter for each coordinate. The PH expansion of \( r_{i}^{-1} \), for \( i = 1, 2, 12 \), is then given in (3) for \( n = -1 \) by

\[
\frac{1}{r_i} = \frac{16\sqrt{\pi}}{r} \sum_k (-1)^k \frac{k+1}{(2k+1)(2k+3)} P^{0}_{2k}(\Omega_i), \quad i = 1, 2
\]

where \( P^{0}_{2k}(\Omega_2) = (-1)^k P^{0}_{2k}(\Omega_1) \), according to the parity of the Gegenbauer polynomial, and

\[
\frac{1}{r_{12}} = \frac{8\sqrt{2\pi}}{r} \sum_k (-1)^k \frac{k+1}{(2k+1)(2k+3)} P^{0}_{2k}(\Omega_{12}).
\]

In a PH expansion of the wave function for the singlet \( S \)-state, the optimal subset consists of: (i) \( P^{0}_{2k}(\Omega_1) \) for \( k \) even and (ii) that part of \( P^{0}_{2k}(\Omega_{12}) \) orthogonal to \( P^{0}_{2k}(\Omega_1) \). One uses the orthonormalized base \( B_{k}(\Omega) = \mathcal{P}^{0}_{2k}(\Omega_1) \) for \( k \) even, \( B^{\perp}_{k}(\Omega) = \mathcal{P}^{0}_{2k}(\Omega_{12}) \) for \( k \) odd, and \( B^{\perp}_{k}(\Omega) = \frac{1}{\sqrt{k(k+2)}} \left[ \mathcal{P}^{0}_{2k}(\Omega_{12}) - \frac{1}{(k+1)} \mathcal{P}^{0}_{2k}(\Omega_1) \right] \) for \( k \) even, where the matrix elements

\[
< \mathcal{P}^{0}_{2k}(\Omega_2) | \mathcal{P}^{0}_{2k}(\Omega_1) > = (-1)^k
\]

and

\[
< \mathcal{P}^{0}_{2k}(\Omega_i) | \mathcal{P}^{0}_{2k}(\Omega_{12}) >= \begin{cases} 0 & \text{if } k \text{ odd} \\ (-1)^{k/2} & \text{if } k \text{ even} \end{cases}
\]

are used in agreement with equation (25) of reference [3].
For triplet $S$-states the $B_k(\Omega)$ for $k$ odd are suitable for the motion of the two electrons around the nucleus, but $P_{2k}^0(\Omega_{12})$ is not appropriate since it is even in the exchange of the two electrons. In order to find the second set of HH we note that, since the normalized PH are proportional to Gegenbauer polynomials (21), then

$$< P_{2k}^0(\Omega, \varphi) | P_{2k'}^0(\Omega, \varphi) > = \delta_{k,k'} .$$

By taking the derivative with respect to $\varphi$, noting

$$< \frac{\partial P_{2k}^0}{\partial \varphi} | P_{2k'}^0 > = 0 ,$$

one generates the additional basis elements

$$\frac{\partial P_{2k}^0(\Omega, \varphi)}{\partial \varphi} = \frac{2}{\pi^{3/2}} \left[ x \sqrt{1 - z^2} \cos 2\varphi - z \sin 2\varphi \right] C_{k-1}^2 \left( z \cos 2\varphi + x \sqrt{1 - z^2} \sin 2\varphi \right) .$$

For $\varphi = 0$ one obtains the set of HH where electrons in a $p$-state are coupled to form an $S$-state obviously orthogonal to $B_k(\Omega)$, where both electrons are in an $s$-state. For $\varphi = 3\pi/4$, one obtains the required basis $zC_{k-1}^2(x\sqrt{1 - z^2})$, which however must be normalized and has to be made orthogonal to $B_k(\Omega)$ for $k$ odd. The desired basis elements are

$$B_{k}^\perp(\Omega) = \begin{cases} 
\frac{2\sqrt{3}}{\pi^{3/2} \sqrt{k(k+2)}} z C_{k-1}^2(x\sqrt{1 - z^2}) & k > 0 \text{ even} \\
\frac{2\sqrt{3}}{\pi^{3/2} \sqrt{k(k+2)-3}} \left[ z C_{k-1}^2(x\sqrt{1 - z^2}) - \frac{(-1)^{(k-1)/2}}{2} C_{k}^1(z) \right] & k > 1 \text{ odd}
\end{cases}$$

It is worthwhile to note that, since $z(3\pi/4) = r_{12}^2/r^2 - 1$, the basis element $B_{k}^\perp$ describes the electron pair in an $S$-state. Then, in the expansion

$$\Psi = r^{-5/2} \sum_{k,k_\perp} \left( B_k u_k(r) + B_{k}^\perp u_{k_\perp}(r) \right)$$

the electrons are individually in $s$-states in $B_k$. (Here and in the appendix, we sometimes emphasize that indices take on the values that are associated with the perpendicular set by using the notation $k_\perp$ or $k'_\perp$. Where there is no room for confusion, we drop the $\perp$. This means that in our approximation the space wave function becomes the sum of two functions. In the singlet state

$$\Psi_S = \psi_S(r_2^2 - r_1^2, r) + \psi_S^\perp(r_{12}, r)$$

where $\psi_S$ and $\psi_S^\perp$ are even in an exchange of the two electrons for the singlet state, while in the triplet state

$$\Psi_T = \psi_T(r_2^2 - r_1^2, r) + (r_2^2 - r_1^2) \psi_T^\perp(r_{12}, r)$$

where $\psi_T$ is odd in the exchange of the two electrons.
The partial waves are solutions of the system of coupled second order differential equations

\[
(T_k - E)u_k + \sum_{k',k'_\perp} (U^{k'}_k u_{k'v} + U^{k'\perp}_k u^{\perp}_{k'_\perp}) = 0 \quad (22)
\]

and

\[
(T_{k\perp} - E)u_{k\perp} + \sum_{k',k'_\perp} (U^{k'_\perp}_{k\perp} u^{\perp}_{k'_\perp} + U^{k'}_{k\perp} u_{k'\perp}) = 0 \quad (23)
\]

where

\[
T_k = -\frac{d^2}{dr^2} + \frac{\mathcal{L}_k(\mathcal{L}_k + 1)}{r^2}
\]

and \(\mathcal{L}_k = 2k + 3/2\), (both valid for \(k\) and \(k_\perp\)).

The matrix elements of the potential matrix are given in Appendix A.
Results and Analysis

The $r$ dependence of the coupling matrix is simply $1/r$ (i.e. multiplying a matrix of constant coefficients). To solve the resulting coupled differential equations, we take advantage of a method developed by V. Mandelzweig and M. Haftel [2] - and embodied in one of their numerical programs. It was used by Haftel and us (here, Fabre and Larsen) to obtain results for the singlet [4]. Michael kindly made available to us his program, that we used for the triplet.

Its essence is to calculate the wavefunction and its logarithmic derivative by using expansions - and, then, obtain the matrices of coefficients (of these expansions) by numerical recursions.

We solve the set of equations for a number of values of $k_{\text{max}}$, such as 33, 37, 41 ... and extrapolate the result to infinite order. We can compare our results to a wealth of reliable data [1, 6].

Singlet

As noted above, the results have been published [3]. The result for the ground state is that we obtained an extrapolated value of 2.903471 atomic units, compared to the more accurate variational result of 2.903724. (We truncate all our numbers to 6 decimals.) The error was thus $\sim 0.01\%$.

For the excited state, the extrapolated value was 2.145825 compared with a variational value of 2.145974. The resulting error was thus $\sim 0.007\%$.

These were based on calculations for $k_{\text{max}} = 24, 28, 32, 36$ and noting [7] that, asymptotically, the differences between the energies for successively larger values of $k_{\text{max}}$ decrease at least as fast as $k_{\text{max}}^{-4}$. The differences were then fitted to an inverse polynomial:

$$\Delta E(k) = E(k) - E(k - 4) = \frac{1}{k^2(A + B k + C k^2)}$$

and the extrapolated values were obtained by adding the remaining contributions that would result from summing to infinity.

Another point has, in retrospect, proved important. For the ground state, the value for $k_{\text{max}} = 36$ is 2.903067, i.e. this ‘raw’ results is already correct to 4 digits. The extrapolated ‘tail’ only adds a modest amount. For the excited state, the situation is quite different. The ‘raw’ value is 2.129457 and we see that therefore the difference between the resulting energy and the correct value is, roughly, 1%. The contribution of the extrapolated ‘tail’ is very important yielding several more digits in agreement.

Triplet

In Table 1, we present the numerical results (in a.u.) obtained by solving the coupled equations. These need, again, to be extrapolated, so as to take into account the contribution of the higher order potential harmonics, and then compared with good variational estimates: 2.1752495 for the lowest state, 2.068685 for the excited state. Without the $r_{12}$ interaction, the exact result is 2.5 a.u.
Table 1: energies from solving the equations up to $k_{\text{max}}$

| $k_{\text{max}}$ | ground state | excited state | no $r_{12}$ interaction |
|-------------|-------------|--------------|-------------------------|
| 21          | 2.1401236235411021 | 1.92018012535861021 |                          |
| 23          | 2.145902327465288 | 1.9377802892305477  |                          |
| 25          | 2.150482412407837 | 1.952554834156408  |                          |
| 27          | 2.1541746943943439 | 1.9650792663836013 |                          |
| 29          | 2.157174781909449 | 1.975787236977571  |                          |
| 31          | 2.1596321992027180 | 1.9850138971543965 |                          |
| 33          | 2.1616708453178672 | 1.9930169776811079 |                          |
| 35          | 2.163375780590255  | 2.000001772075086  |                          |
| 37          | 2.1648062043495217 | 2.0061315935556941 |                          |
| 39          | 2.1660197311520152 | 2.0115381473492293 |                          |
| 41          | 2.167054234821436  | 2.016328638520296  |                          |
| 43          | 2.1679406196279248 | 2.0205910881663552 |                          |
| 45          | 2.1687046390433931 | 2.0243983641445255 |                          |
| 47          | 2.1693662957017716 | 2.0278112036995569 | 2.4978184400838062      |
| 49          | 2.1699419469276808 | 2.0308805802207102 | 2.4980527934858051      |
| 51          | 2.1704449472143039 | 2.0336495409553854 | 2.4982549671085871      |
| 53          | 2.170862505879244 | 2.036154618675421 | 2.4984302656593832      |
| 55          | 2.1712749122742111 | 2.0384270954208123 | 2.4985829842420010      |
| 57          | 2.1716184476775823 | 2.040983798376949 | 2.4987166244132616      |
| 59          | 2.1719231375119347 | 2.0423774774219713 | 2.4988340592267531      |
| 61          | 2.1721942486212956 | 2.0440984689458583 | 2.4989376603658377      |
| 63          | 2.1745674017990737 | 2.04574017990737  | 2.4990293684706760      |
| 65          | 2.0471192766548691 | 2.4991109122818091 |                          |
| 67          | 2.0484475085284343 | 2.4991835853845747 |                          |
| 69          | 2.4992485787876214 |                          |                          |

The first thing that we notice, then, is that, even for the much higher values of $k_{\text{max}}$ that we have used for the triplet, the difference between our results and the variational ones is still more than 1 part in a thousand for the ground state and 1% for the higher state. If we had limited ourselves to the orders used in the singlet, our errors would have been 1/2% and 3%, respectively!

We were thus driven to higher values of $k_{\text{max}}$ and thus to a greater number of states in the calculations. For example, a $k_{\text{max}}$ of 61 corresponds to a total number of states of 91. Even then, we also had to work harder at the extrapolation than we did for the singlet. The differences were fitted to an inverse polynomial with more coefficients:

$$\Delta E(k) = \frac{1}{A k^4 + B k^3 + C k^2 + D k + E}$$

with the $\Delta$s variously defined as $\Delta E(k) = E(k) - E(k-4)$ and $\Delta E(k) = E(k) - E(k-2)$ and the extrapolated values obtained by using this fit, for the differences, to obtain the higher order contributions.
Examination of the results of the extrapolations then shows that the best strategy consists in fitting the coefficients with the minimum of data points, taken at the highest values of $k_{\text{max}}$. For the ground state, the use of $\Delta(k) = 4$ yields the best result. For the excited state, $\Delta(k) = 2$, is superior.

Thus we find that for the ground state, the use of the set of values of $k_{\text{max}}$: $(51,53,55,57,59,61)$ yields $2.175042$, while $(41,45,49,53,57,61)$ gives us our best result $2.175144$ (both results, here, rounded to 6 decimal places). We recall that this must be compared with $2.1752495$.

For the excited case, $(55,57,59,61,63,67)$ gives $2.068704$, while $(47,51,55,59,63,67)$ gives $2.068757$, also rounded at the same place. We compare this with $2.068685$.

Since in our method we only approximate by truncating the basis, both the elements which appear in it and the highest order that we take into account in our calculations, our results must obey the variational principle and must yield upper bounds in the (negative) energies of the states. We can verify that this is indeed the case for our "raw" results, displayed in Table 1. For the extrapolated results, this is only evident for the ground state. Our results for the excited state are slightly deeper than the correct energy.

This is an artifact of the extrapolation. Clearly, our inverse polynomial only imperfectly represents the correct asymptotic behaviour of the differences. In fact taking different sets of points, from which to extrapolate, and trying to 'see' trend lines, we think that we see oscillations and certainly instability and serious limitations in our ability to extrapolate.

Nevertheless, we obtain energies to within 1 or 2 parts in 20,000 for the lowest state and 1 to a few parts in 100,000 for the excited state.

Finally, we note an extrapolation with $\Delta(k)$ of 2, for the case where the electrons are uncoupled. Our result is then $2.499999995$, rounded to nine decimal places, compared to the exact value of $2.5$. In this case our basis is complete, aside from truncation in the order, and we take this result as a confirmation of the soundness of our numerical approach and procedures.
Conclusion

We believe that we have demonstrated that the use of Potential Harmonics is a sound way of obtaining reliable results, at least for 2-electron atoms, to an accuracy of 1 part in $10^4$ or $10^5$. Our aim was to confirm this, with our first two calculations, and then to proceed with higher excited states for these 2-electron atoms and, perhaps more excitingly, with 3-electron atoms!

While this is probably feasible, and in fact the potential harmonics seem to yield better accuracy for the excited states as 3-body and higher correlations become less important, our experience leads us to the following caveat.

We have found many aspects of our effort, such as the calculation of our matrix elements, the necessary extrapolations, to be quite delicate! We would prefer other methods which, using integral equations, would not require them.

Our final and best thought, then, is to draw attention to the simplicity of the form of the wave functions that we have used, and to the fact that, in them, the pairs are, each, in an $s$-state.

Acknowledgment

Sigurd Larsen gratefully acknowledges a sabbatical from Temple University for the year 96-97 and the hospitality of the Physics department of the University of Pretoria, S.A. as well as of the School of Computing and Mathematics of Deakin University, Geelong, Victoria, Australia.
Appendix A

The matrix elements in equations (22) and (23), after making the potential harmonics basis substitution, take the form of integrals of products of three Gegenbauer polynomials. Let us introduce a number of expressions for sums that occur from particular combinations of HHs and PHs:

\[ S_{k}^{k'} = \sum_{m=|k-k'|}^{k+k'} \frac{(m+1)}{(2m+1)(2m+3)}, \]

where \( S_{k}^{k'} = S_{k'}^{k} \),

\[ \sigma_{k}^{k'} = \sum_{m=|k-k'|}^{k+k'} \frac{(-1)^{m/2}}{(2m+1)(2m+3)}, \]

and \( \sigma_{k}^{k'} = \sigma_{k'}^{k} \).

\[ \sum_{k}^{k'} = \sum_{m=|k-k'|+1}^{k+k'+1} \frac{(m+1)(k+k'-m+1)(k-k'+m+1)}{(2m+5)(2m+3)} \times \frac{(k'-k+m+1)(k+k'+m+3)}{(2m+1)(2m-1)}, \]

with \( \Sigma_{k}^{k} = \Sigma_{k'}^{k'} \).

\[ \left( \sum_{k}^{k'} \right)^{\perp} = \frac{1}{16} \sum_{n=|k-k'|}^{k+k'} (-1)^{n/2} \frac{(n+1)}{(2n+1)(2n+3)} \sum_{m=|k-k'|+1}^{k+k'+1} (\delta_{m,n+1} - \delta_{m,n-1}) \times \frac{(m-k+k'+1)(m+k-k'+1)(k+k'+1-m)(k+k'+3+m)}{m(m+2)}, \]

where, by symmetry, \( \left( \sum_{k}^{k'} \right)^{\perp} = \left( \sum_{k'}^{k} \right)^{k'} \).

The matrix elements

First, consider the contribution from the two electrons separately around the nucleus, where \( k \) and \( k' \) are both odd because of the anti-symmetric requirement of the triplet
wave function.

\[
U_{k}^{k'} = \frac{2}{r} \left\langle B_{k} \middle| \frac{1}{r_{12}} \middle| B_{k'} \right\rangle - \frac{2}{r} \left\langle B_{k} \middle| \frac{Z}{r_{1}} + \frac{Z}{r_{2}} \middle| B_{k'} \right\rangle
\]
\[
= \frac{64}{\pi r} \left[ \frac{\sqrt{2}}{4} \sigma_{k}^{k'} - Z S_{k}^{k'} \right],
\]
(24)

Then, consider the interactions between the electron-electron wave function and the electron-nucleus wavefunctions. Here, we can have \( k \) odd and \( k' \neq 0 \) even,

\[
U_{k}^{k'}_{\perp} = \frac{2}{r} \left\langle B_{k} \middle| \frac{1}{r_{12}} \middle| B_{k'}^{\perp} \right\rangle - \frac{2}{r} \left\langle B_{k} \middle| \frac{Z}{r_{1}} + \frac{Z}{r_{2}} \middle| B_{k'}^{\perp} \right\rangle
\]
\[
= \frac{(-1)^{(k-1)/2}}{\pi r^{\sqrt{k'(k'+2)}} k(k+2)} \sum_{k'}^{k'} \left[ \frac{-1}{2} \frac{k}{k(k+2)} \sum_{k}^{k'} - \frac{-1}{2} \frac{k'}{k'(k'+2)} \right],
\]
(25)

and for the case \( k' \) odd and \( k \neq 0 \) even, we use \( U_{k}^{k'}_{\perp} = U_{k}^{k'} \).

For the case where \( k \) and \( k' \) are both odd,

\[
U_{k}^{k'}_{\perp} = \frac{16 \sqrt{6}}{\pi r^{\sqrt{k'(k'+2)}} - 3} \left[ \frac{(-1)^{(k-1)/2}}{k(k+2)} \sum_{k}^{k'} - \frac{-1}{2} \frac{k}{k(k+2)} \sum_{k}^{k'} - \frac{-1}{2} \frac{k'}{k'(k'+2)} \right],
\]
(26)

Finally, we need to consider the perp-perp matrix elements. Thus, we have for \( k \) and \( k' \) both even:

\[
U_{k}^{k'}_{\perp} = \frac{2}{r} \left\langle B_{k}^{\perp} \middle| \frac{1}{r_{12}} \middle| B_{k'}^{\perp} \right\rangle - \frac{2}{r} \left\langle B_{k}^{\perp} \middle| \frac{Z}{r_{1}} + \frac{Z}{r_{2}} \middle| B_{k'}^{\perp} \right\rangle
\]
\[
= \frac{16}{\pi r^{\sqrt{k(k+2)}} \sqrt{k'(k'+2)}} \left[ \sqrt{2} \sum_{k}^{k'} - 12 Z (\sum_{k}^{k'}) \right],
\]
(27)

\( k \) and \( k' \) both odd,

\[
U_{k}^{k'}_{\perp} = \frac{16}{\pi r^{\sqrt{k(k+2)}} \sqrt{k'(k'+2)}} \times
\]
\[
\left\{ \sqrt{2} \left[ \left( 1 - \frac{3}{k} \frac{k}{k(k+2)} \frac{3}{k'(k'+2)} \right) \sum_{k}^{k'} - 3(-1)^{k-k'/2} \sigma_{k}^{k'} \right] \right. \right.
\]
\[
= 12 Z \left[ (\sum_{k}^{k'}) \frac{k'}{k(k'+2)} \right],
\]
(28)

\( k \) odd and \( k' \) even,

\[
U_{k}^{k'}_{\perp} = \frac{16 \sqrt{2}}{\pi r^{\sqrt{k(k+2)}} \sqrt{k'(k'+2)}} \left( 1 - \frac{3}{k'} \frac{3}{k(k'+2)} \right) \sum_{k}^{k'},
\]
(29)

and finally, with \( k \) even and \( k' \) odd,

\[
U_{k}^{k'}_{\perp} = \frac{16 \sqrt{2}}{\pi r^{\sqrt{k(k+2)}} \sqrt{k'(k'+2)}} \left( 1 - \frac{3}{k'} \frac{3}{k(k'+2)} \right) \sum_{k}^{k'},
\]
(30)
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