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Nonadiabatic hyperspherical approach to two-electron systems

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Energy values for the ground and three lowest excited singlet S states of helium have been calculated using hyperspherical coordinates in a variational basis consisting of Sturmian functions in R, Legendre polynomials in θ_{12}, and problem-optimized functions in α. No adiabatic hypothesis is made. The convergence and energy values are superior to previous calculations using similar methods, but not as good as calculations in which r_{12} is explicitly included. Plots of $(H-E)\Phi(R,\alpha,\theta_{12})$ versus R and α are presented, and they show that the greatest departure from zero is in the $\alpha\approx 0$ region.

I. INTRODUCTION

Hyperspherical coordinates, first introduced into atomic physics by Bartlett,[1] have been extensively applied to two-electron atoms, usually by means of an adiabatic hypothesis.[2-4] These studies have been primarily concerned with the correlation structure of doubly excited states, although other applications have been reported. Feagin *et al.*[5] have investigated the helium ground state as well as S-wave e-H scattering and Christensen-Dalsgaard[6] has also performed a hybrid hyperspherical coordinate and close-coupling calculation for S-wave e-H scattering. The adiabatic hyperspherical approach has provided an economical and quite accurate method for studying low-lying doubly excited states, but has been less successful for the ground state.[5]

In order to obtain further insight into the suitability of hyperspherical coordinates for two-electron systems, we have begun a study of both the ground and low excited states as well as doubly excited states using a hyperspherical basis without the adiabatic hypothesis. In this paper we report very precise energy values for the $(1s^2)$, $(1s2s)$, $(1s3s)$, and $(1s4s)^1S$ states of helium. Results concerning doubly excited states will be forthcoming in a subsequent paper. We use a product basis consisting of Sturmian functions in the hyperspherical radius R, specially constructed functions in the pseudo angle α (to be described in Sec. II) and Legendre polynomials in θ_{12}.

Other, nonadiabatic studies[7,8] have investigated the ground state only and have used hyperspherical harmonics for the α,θ_{12} dependence. We achieve a lower energy with fewer terms than used in these studies due to the basis functions in α. It is our experience that hyperspherical harmonics do not converge well for a description of the ground state, and the situation worsens considerably for singly excited states. That the hyperspherical approach has difficulties when the two electrons are far apart has been recognized and is implicit in the calculational method devised by Christensen-Dalsgaard[6] to describe electron scattering.

An additional advantage of the basis selected here is the ease with which matrix elements can be calculated. The nonlinear parameter ζ in the Sturmian basis can be varied to achieve an optimum energy without recalculating the entire matrix since it appears just as a scale factor.

In Sec. II we present the computational method and in Sec. III the results. In Sec. IV we include some plots of Φ and $(H-E)\Phi$ versus R and α to investigate the limitations of the wave function, and there are concluding remarks in Sec. V.

II. COMPUTATIONAL METHOD

The Schrödinger equation for a two-electron atom with an infinitely heavy nucleus reads

$$\left[-\tfrac{1}{2}(\Delta_1+\Delta_2)-Z\left[\frac{1}{r_1}+\frac{1}{r_2}\right]+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2)=E\Psi(\mathbf{r}_1,\mathbf{r}_2)\ . \qquad (1)$$

The hyperspherical coordinate system is defined in the usual way by

$$R=(r_1^2+r_2^2)^{1/2} \text{ and } \alpha=\tan^{-1}(r_2/r_1)\ . \qquad (2)$$

In order to describe a two-electron state completely, the remaining coordinates can be chosen as

$$\theta_{12}=\cos^{-1}\left[\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1r_2}\right] \qquad (3)$$

and the three Euler angles. The wave function for S states does not depend on the overall orientation of the system and can be written as

$$\Psi(R,\alpha,\theta_{12})=\frac{1}{r_1r_2}\Phi(R,\alpha,\theta_{12}) \ . \tag{4}$$

The Schrödinger equation in hyperspherical coordinates is

$$\left\{-\frac{1}{2}\left[\frac{\partial^2}{\partial R^2}+\frac{1}{R}\frac{\partial}{\partial R}+\frac{1}{R^2}\frac{\partial^2}{\partial\alpha^2}+\frac{1}{R^2}\left[\frac{1}{\sin^2\alpha}+\frac{1}{\cos^2\alpha}\right]\left[\cot\theta_{12}\frac{\partial}{\partial\theta_{12}}+\frac{\partial^2}{\partial\theta_{12}^2}\right]\right]-\frac{Z}{R}\left[\frac{1}{\cos\alpha}+\frac{1}{\sin\alpha}\right]\right.$$
$$\left.+\left[\frac{1}{R\cos\alpha}\sum_{\nu=0}^{\infty}\tan^{\nu}\alpha P_{\nu}(\cos\theta_{12})\right]_{r_1\geq r_2}+\left[\frac{1}{R\sin\alpha}\sum_{\nu=0}^{\infty}\frac{1}{\tan^{\nu}\alpha}P_{\nu}(\cos\theta_{12})\right]_{r_1<r_2}\right\}\Phi=E\Phi \ . \tag{5}$$

To solve for the energy of this Hamiltonian we employ Sturmian functions in R, Legendre polynomials in θ_{12}, and problem optimized functions in α, $f_m(\alpha)$. The Sturmians are defined by[9]

$$S_n(\zeta R)=\left[\frac{(n-2)!}{2(n+1)!}\right]^{1/2}(\zeta R)^2e^{-\zeta R/2}L_{n-2}^{(3)}(\zeta R) \ , \tag{6}$$

where $L_{n-2}^{(3)}(\zeta R)$ is an associated Laguerre polynomial. The trial function is given in the product form by

$$\Phi(R,\alpha,\theta_{12})=\sum_{n,l,m}c_{nlm}S_n(\zeta R)P_l(\cos\theta_{12})f_m(\alpha) \ . \tag{7}$$

To achieve the required symmetry, $f_m(\alpha)=f_m(\pi/2-\alpha)$ for singlet and $f_m(\alpha)=-f_m(\pi/2-\alpha)$ for triplet states, the following boundary conditions are imposed on $f_m(\alpha)$. These are

$$\left.\frac{df_m}{d\alpha}\right|_{\alpha=\pi/4}=0$$

for singlet states, and (8)

$$f_m(\pi/4)=0$$

for triplet states. Furthermore, the function $f_m(\alpha)$ has to vanish at $\alpha=0$.

The question is how to make an effective choice of the α basis functions $f_m(\alpha)$. We began by using suitably modified sine functions. This seems natural because the boundary conditions are easy to apply, and these functions are closely related to the hyperspherical harmonics. The energy of the ground state, however, converged very slowly and in terms of the size of the basis, the results were inferior to those of Petrov, Jarovay, and Babaev.[7] We found also that excited states are very difficult, if not impossible, to calculate due to the poor convergence of these sine functions. As an example, the energy of the first excited state using ten radial functions, three Legendre polynomials, and ten sine functions is $E_1=-2.0826$ a.u., i.e., 0.07 a.u. too high and the higher excited states are not even bound.

Our approach to accelerate the convergence of the α basis is to determine the coefficients $\tilde{c}_{nlm}$ by using a basis $\tilde{f}_m(\alpha)$ of trial functions (e.g., sine functions). One obtains a first approximation to the α eigenfunctions $\tilde{g}_n^{(l)}(\alpha)$ given by

$$\tilde{g}_n^{(l)}(\alpha)=\sum_m\tilde{c}_{nlm}\tilde{f}_m(\alpha) \ . \tag{9}$$

Then we try to find basis functions $f_m(\alpha)$ which simulate the functions $\tilde{g}_n^{(l)}(\alpha)$. Plots of the functions $g_n^{(l)}(\alpha)$ for $l=0$ using the final basis are shown in Fig. 1 for the ground state and two excited states. Curves for $l\neq0$ look very similar but are smaller in magnitude. There are two apparent features: (a) The amplitude of $g_n^{(l)}(\alpha)$ decreases rapidly for increasing n. Thus, e.g., no more than five Sturmians should be adequate for the ground state. (b) The functions $g_n^{(l)}(\alpha)$ only oscillate in the left region $(0<\alpha<\pi/8)$ and in the right region $(\pi/8<\alpha<\pi/4)$ there is no structure present; here the $g_n^{(l)}(\alpha)$ appear to behave exponentially.

From these graphs it is clear why a sine-function expansion or hyperspherical harmonic expansion is inappropriate for $\alpha>\pi/8$. It is very difficult to find simple functions in α which resemble the features of the α eigenfunctions. The main problem is that each basis function has to satisfy the boundary conditions (8). We constructed two sets of nonorthogonal functions, where each set can represent the eigenfunctions $g_n(\alpha)$ in different regions, i.e., for $0<\alpha<\pi/8$ and $\pi/8<\alpha<\pi/4$. Our basis has the form

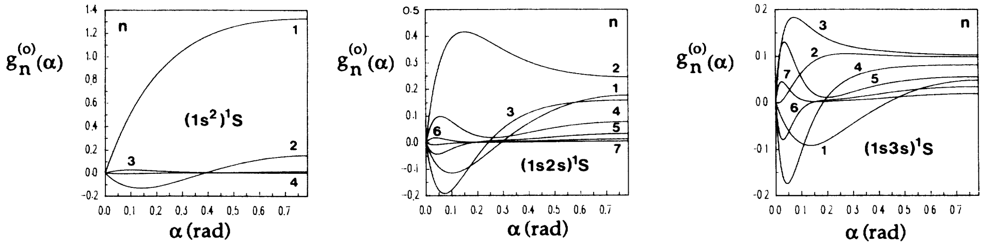

FIG. 1. Eigenfunctions $g_n^{(0)}(\alpha)=\sum_m c_{n0m}f_m(\alpha)$ for ground state, first excited state $(1s2s)^1S$, and second excited state $(1s3s)^1S$ of He.

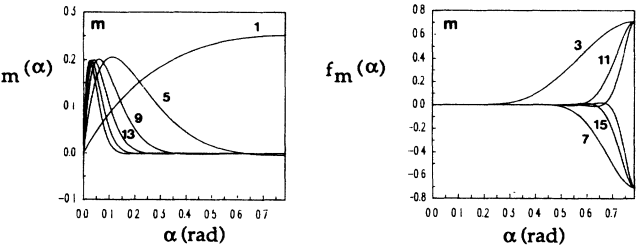

FIG. 2. The $f_m(\alpha)$ basis for $c=1$.

$$f_m(\alpha)=\begin{cases}\dfrac{\sin(m\alpha)}{(1+c\alpha)^{(m/c)(1+c\pi/4)}}, & m=1,5,9,\ldots\\ e^{m\pi/4}e^{-(\pi/4)^2(m/\alpha)}\sin(m\alpha), & m=3,7,11,\ldots\end{cases} \tag{10}$$

where c is a nonlinear parameter to be optimized for each state. Both sets satisfy the boundary conditions and have complementary features which result in an approximate orthogonality to each other.

Figure 2 displays the behavior of $f_m(\alpha)$ for $c=1$. The function set $\{f_m(\alpha)\}$ for $m=1,5,9,\ldots$ is able to describe the oscillating pattern of $g_n(\alpha)$, whereas the set for $m=3,7,11,\ldots$ can represent the constant amplitude near $\alpha=\pi/4$. The principal consideration in the selection of these functional forms was the ability of each member to contribute to the overall function, $g_n(\alpha)$, in only a limited range of α, a behavior which is clear in Fig. 2. There are obviously other possible forms, but these proved easy to use and showed good convergence properties. All matrix elements involving the α basis functions were computed numerically.

III. RESULTS

We foresee the principal application of this basis to be the properties of doubly excited states of two-electron atoms. Nevertheless as a preliminary test of interest in itself we have computed the energies of the ground and low excited states of helium. We anticipate that the basis will become more and more unsuitable as the discrepancy in principal quantum number of the two electrons increases, yet precise energies are found up to the 1s-4s state. We optimize the nonlinear parameters c and ζ for each state. Table I contains the present results.

Two types of calculations are chosen for comparison: approaches using Hylleras coordinates, including r_{12} explicitly,[10–12] and one using hyperspherical coordinates with hyperspherical harmonics.[7] Of course other methods of computing the He ground state exist, some quite accurate and efficient,[13] but these are not directly relevant here. Petrov *et al.*[7] used exponentials and Laguerre polynomials for radial functions and included up to 840 terms in all coordinates.

The comparison, in Table II, shows that the hyperspherical approach, at least with the present formulation, can give very good energies if pushed hard enough, but that the Hylleras coordinates remain the most efficient basis. Our α basis has provided convergence for the excited states as well. Using hyperspherical harmonics, as in Ref. 7, such convergence will be extremely difficult if not impossible. The excited state energies could possibly be lowered further by adding additional radial functions. The amplitudes of the higher indexed Sturmians were quite large in the diagonalizations.

The parameter c has the interesting property of increasing by about unity as each higher excited state is considered. For the ground state we obtained $c\approx 0$, showing that the α basis develops exponential behavior since

$$\lim_{c\to 0}\frac{\sin(m\alpha)}{(1+c\alpha)^{(m/c)(1+c\pi/4)}}=\sin(m\alpha)e^{-m\alpha}\,. \tag{11}$$

Preliminary calculations for ^3S, ^1P, and ^3P excited states were also carried out with the same pattern of results.

IV. LIMITATIONS OF THE α BASIS

The ability of our trial functions to give accurate energies for ground and excited states is a confirmation of the applicability of hyperspherical coordinates. However, getting good energy values does not necessarily imply that the trial functions really represent the true wave function over the whole (R,α,θ_{12}) space. Therefore, we have examined the goodness of our approximation to the wave function by plotting the deviation $(H-E)\Phi$ for the ground, first, and second excited states, which is a much more vivid indication of the limitations of the basis set than the expectation value $\langle\Psi|H-E|\Psi\rangle$ or other possible expectation values.

TABLE I. Energies for the lowest four ^1S states of He in the hyperspherical basis, where N_s and N_L denote the number of Sturmians and Legendre polynomials, respectively. The optimized parameters are indicated by ζ_{opt} and c_{opt}.

State (^1S)	Energy (a.u.)	N_S	Included m in α functions $f_m(\alpha)$	N_L	ζ_{opt}	c_{opt}	Matrix size
	−2.902 750	5	1,5,9,13;3	3	4.208	−0.0629	75
	−2.903 300	5	1,5,9,13;3	4	4.208	−0.0629	100
($1s^2$)	−2.903 493	5	1,5,9,13;3	5	4.208	−0.0629	125
	−2.903 576	5	1,5,9,13;3	6	4.208	−0.0629	150
	−2.9037 106	7	1,5,9,13,17;3,7	13	4.208	0.015 08	637
($1s2s$)	−2.145 906	10	1,5,9,13,17;3,7,11,15	3	2.206	0.813 31	270
($1s3s$)	−2.061 101	10	1,5,9,13,17;3,7,11,15	3	1.552	1.769 10	270
($1s4s$)	−2.032 296	10	1,5,9,13,17;3,7,11,15	3	1.134	2.910 31	270

TABLE II. Comparison of previous calculations (Refs. 7, 10, 11, and 12) with the present results.

State (^1S)	This work Energy (a.u.)	Terms in wave function	Other works Energy (a.u.)	Terms in Wave function	Author
			$-2.903\,724\,377$	246	Frankowski *et al.*[a]
($1s^2$)	$-2.903\,711$	637	$-2.903\,724\,377$	230	Freund *et al.*[b]
			$-2.903\,704\,7$	840	Petrov *et al.*[c]
($1s2s$)	$-2.145\,906$	270	$-2.145\,974\,045$	174	Freund *et al.*[b]
($1s3s$)	$-2.061\,101$	270	$-2.061\,271\,989$	174	Frankowski[d]
($1s4s$)	$-2.032\,296$	270	$-2.033\,586\,728$	174	Frankowski[d]

[a] Reference 11.
[b] Reference 12.
[c] Reference 7.
[d] Reference 10.

Figure 3 shows surface plots of Φ and $(H-E)\Phi$ versus R and α for the case $\theta_{12}=\pi$. From these plots it is clear that our α basis does not represent the true wave function for α close to zero. This is the case where one electron is near the nucleus and the other away. The spikes within the graphs arise from the fact that the term in the Hamiltonian, which become singular for $\alpha=0$, are not entirely canceled in $(H-E)\Phi$.

Up to now, we have not correlated the α functions with the Legendre polynomials, and so these singular terms, which come from the single-particle angular momentum operators, cause the spikes. If we take a configuration-interaction approach to the wave function, then the angular momentum operators are handled at the origin by terms in the wave function of the form $r_1^{l+1}r_2^{l+1}$ so for $\alpha\to 0$, we should have α^{l+1} as the lowest power in the coefficient of $P_l(\cos\theta_{12})$. This can be achieved by modifying our α basis to

$$f_m^{(l)}(\alpha)=\begin{cases}\dfrac{[\sin(m\alpha)]^{l+1}}{(1+c\alpha)^{(m/c)(l+1)(1+c\pi/4)}} & \text{for } m=1,5,9\\ e^{m\pi/4}e^{-(\pi/4)^2(m/\alpha)}\sin(m\alpha) & \text{for } m=3,7,11\ .\end{cases} \tag{12}$$

Figure 4 shows the application of the correlated $f_m^{(l)}(\alpha)$ basis for ground, first, and second excited states. The spike in the case of the ground state is almost gone and for the first excited state reduced in size, but for the higher single excited states little improvement has been achieved. Also the corresponding energy is a little bit higher compared to the uncorrelated α basis because the

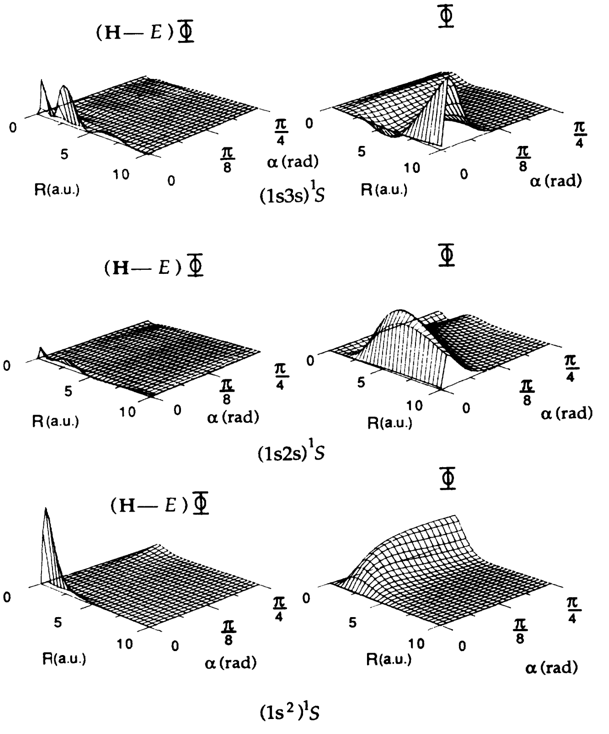

FIG. 3. Surface plots of $(H-E)\Phi$ and Φ as a function of R and α for fixed angle $\theta_{12}=\pi$ using the uncorrelated basis $f_m(\alpha)$.

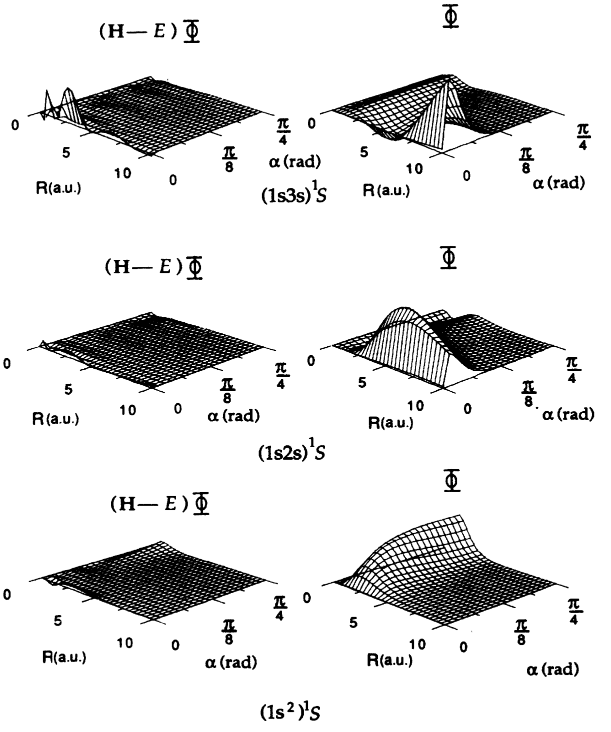

FIG. 4. Surface plots of $(H-E)\Phi$ and Φ as a function of R and α for fixed angle $\theta_{12}=\pi$ using the correlated basis $f_m^{(l)}(\alpha)$.

functions $f_m^{(l)}(\alpha)$ decrease too fast as l increases. The difference in energy is about 1×10^{-5} a.u. The α basis is flexible enough to handle both the singularities in the angular momentum operators and the potential, but the $r_2^2r_1^2$ factor in the differential volume element reduces to a negligible level the contribution of the $\alpha\approx0$ region in the integral. Thus the variational principle does not lead to the optimum determination of coefficients for this range of α.

V. CONCLUSION

We have found a simple variational basis capable of producing very accurate energy values for both ground and excited states of the He atom. We have paid particular attention to the α dependence and were led to use a basis that has properties quite different from the hyperspherical harmonics. We have also investigated the degree to which the wave function is an actual solution to the Schrödinger equation in terms of surface plots of equation $(H-E)\Phi$ versus R and α for $\theta_{12}=\pi$.

The graphical analysis showed that the region around $\alpha=0$ contained the primary departure of $(H-E)\Phi$ from 0. Correlating powers of α with Legendre polynomials improved the situation, but did not entirely remove the problem which has, however, an extremely small effect on the energy. We intend to apply this basis next to study the structure and properties of doubly excited states.

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