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Use of the Fock expansion for ^1S-state wave functions of two-electron atoms and ions

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The exact representation of a two-electron wave function near the origin is the Fock expansion, i.e., a double summation over powers of R and of $\ln R$ [where $R \equiv (r_1^2+r_2^2)^{1/2}$] with coefficients dependent on the five remaining angular variables. Using a representation of hyperspherical harmonics, we present here the first numerical solution of the equations for the Fock coefficients. We present also a general procedure for matching a linear combination of Fock-series solutions onto a basis of adiabatic hyperspherical functions at a matching radius R_0. This matching procedure ensures that the proper asymptotic boundary conditions are satisfied. Exploratory numerical results are presented for ^1S wave functions of He and H^- in which four Fock-series solutions are matched onto the lowest ^1S adiabatic hyperspherical wave function at a matching radius near the first antinode in the adiabatic wave function.

I. INTRODUCTION

Bartlett[1] showed that an acceptable series solution of the Schrödinger equation for a two-electron atom or ion is the following series representation at the nucleus,

$$\sum_{n,j} C_{nj} R^n (\ln R)^j , \tag{1}$$

where R is the hyperspherical radius introduced by Gronwall:[2,3]

$$R \equiv (r_1^2+r_2^2)^{1/2} . \tag{2}$$

In particular, series representations in terms of only the variables r_1, r_2, $r_{12} \equiv |\mathbf{r}_1-\mathbf{r}_2|$, and/or R—i.e., ignoring $\ln R$ terms—were shown *not* to exist.[1,4] Fock[5] independently demonstrated that Eq. (1) provides an acceptable series solution near the origin of the two-electron Schrödinger equation for ^1S states. He also discussed in detail the procedure for calculating the coefficients C_{nj}, which depend on five angular variables and hence obey rather complicated differential equations. Demkov and Ermolaev[6] showed that Fock's expansion applies generally to an N-electron wave function of arbitrary symmetry.

The usefulness of the series representation in Eq. (1) is dependent on its convergence properties as a function of the system energy.[7] Macek[8] proved its convergence in the mean (L^2 of the hypersphere) for values of R less than $(2|k|)^{-1}$, where the energy E (in a.u.) of the two-electron system relative to the double ionization threshold is related to k by

$$E = k^2/2 . \tag{3}$$

More recently, Morgan[9] has proved the convergence of the Fock expansion for S states pointwise (L^∞ of the hypersphere) for all values of R and has indicated that the expansion coefficients C_{nj} are analytic functions of E. Although other studies of the Fock expansion have been carried out,[10,11] the major application of Bartlett's and Fock's work has been to provide a better representation of the two-electron wave function in variational calculations.[12–14] In particular, while the mathematical necessity of the logarithmic terms in Eq. (1) is acknowledged and the faster convergence their presence permits in variational calculations is known,[13] the physical consequences of these logarithmic terms remain unknown.

In this paper we present a numerical solution of Fock's equations[5] for the coefficients in Eq. (1) based on an expansion of the coefficients in hyperspherical harmonics. Although the properties of hyperspherical harmonics and the representation of the Coulomb matrix in terms of them have been studied,[8,15–21] detailed expressions suitable for numerical computation have not been given.

Because boundary conditions must be introduced and because a series representation for the wave function is inefficient far from the nucleus, we present here also a procedure for matching the series representation of the wave function onto the hyperspherical adiabatic channel representation[22] at some fixed radius R_0. The matching procedure minimizes the difference between the inner and outer wave functions on the hypersphere $R=R_0$. We show that the first derivatives (with respect to R) become smooth across $R=R_0$ as the number N_F of Fock series in the inner region and the number N_C of channel functions in the outer region becomes infinite (i.e., complete). Our matching procedure does not require equality of N_F and N_C.

As a first application, we have computed ground-state wave functions and energies for the He atom and the H^- ion as well as s-wave continuum wave functions for the $e^- + H$ system. We have employed four Fock-series solutions in the inner region, $R \leqq R_0$, and one adiabatic channel function in the outer region, $R \geqq R_0$. Our motivations for this pilot study are fourfold. First, it is known that the adiabatic approximation in hyperspherical coordinates gives a reasonably accurate representation of the wave function and energy of two-electron-system ground states.[23,24] Second, Christensen-Dalsgaard[25,26] and Macek[27] have pointed out that the major defect of the adiabatic channel functions is their slow convergence to the usual close-coupling representation as R increases to large

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values. Third, Cavagnero[28] has proposed that the major effects of configuration interaction may be understood in terms of avoided crossing of the adiabatic hyperspherical potential curves in regions of R space corresponding to the outer atomic shells of atoms. In other words, each of these three instances implies that the adiabatic hyperspherical approximation is adequate at small values of R. With our use of the Fock expansion to represent the two-electron wave function near the origin, we are able to test these earlier findings. Last, an alternative series expansion procedure in hyperspherical coordinates has been employed by Haftel and Mandelzweig[29,30] to calculate ground-state energies, among other quantities, for He and H^-. Comparison of our formulation with theirs tests the convergence behavior of the two approaches.

In Sec. II we review the equations satisfied by the Fock coefficients. In Sec. III we introduce the symmetrized hyperspherical harmonics, and in Sec. IV we present the representation of the Coulomb interaction operator in terms of them. Section V gives the representation of the Fock coefficients in terms of symmetrized hyperspherical harmonics.

Our procedure for matching the Fock-series solutions at a radius R_0 onto an adiabatic hyperspherical coordinate representation is given in Sec. VI. Our numerical results for He and H^- are given in Sec. VII and are discussed in Sec. VIII. Appendix A presents the explicit equations from which we have calculated the Fock coefficients as represented in terms of symmetrized hyperspherical harmonics. Finally, Appendix B discusses an approximation which permits an explicit solution of the Fock equations and which we have used to test our computer codes numerically.

II. DIFFERENTIAL EQUATIONS FOR THE FOCK COEFFICIENTS

The hyperspherical coordinate system for two electrons outside of a massive center is defined by introducing the mean-square radius of the two electrons from the nucleus, R [cf. Eq. (2)], and a corresponding angular coordinate α, defined by

$$\tan\alpha = r_2/r_1 \ . \tag{4}$$

The radius R measures the "size" of the two-electron state, while the angle α measures the radial correlation of the two electrons.

In this system of coordinates the nonrelativistic two-electron Schrödinger equation becomes (in atomic units)

$$\left[\frac{d^2}{dR^2}+\frac{5}{R}\frac{d}{dR}-\frac{\Lambda^2}{R^2}+\frac{C}{R}+2E\right]\Psi=0 \ . \tag{5}$$

In Eq. (5) Λ^2 is the hyperspherical angular operator,

$$\Lambda^2 = -(\sin\alpha\cos\alpha)^{-2}\frac{d}{d\alpha}(\sin^2\alpha\cos^2\alpha)\frac{d}{d\alpha} + \frac{L_1^2}{\cos^2\alpha}+\frac{L_2^2}{\sin^2\alpha} \ , \tag{6}$$

where L_1 and L_2 are the orbital angular momentum operators for electrons 1 and 2, and C comprises the Coulomb potential interaction terms,

$$C(\alpha,\theta_{12}) = 2Z(1/\cos\alpha + 1/\sin\alpha) - 2(1-\sin 2\alpha\cos\theta_{12})^{-1/2} \ , \tag{7}$$

where

$$\cos\theta_{12} = \hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2 \ . \tag{8}$$

The differential equation for the Fock coefficients in Macek's representation[8] is obtained as follows. Divide Eq. (5) by $-k^2$, where k and E are related by Eq. (3), and represent R in units of ιk. Equation (5) becomes, then,

$$\left[\frac{d^2}{dR^2}+\frac{5}{R}\frac{d}{dR}-\frac{\Lambda^2}{R^2}+\frac{C/\iota k}{R}-1\right]\Psi=0 \ . \tag{9}$$

Note that for two-electron energies E below the double ionization threshold, i.e., $E \leqq 0$, k is given by

$$k = \iota(2\,|\,E\,|\,)^{1/2} = \iota\kappa \tag{10}$$

so that $C/\iota k$ in Eq. (9) may be replaced by $-C/\kappa$, which is explicitly real.

A particular state $\Psi_{\nu m_\nu}$ may be expanded as

$$\Psi_{\nu m_\nu} = R^\nu \exp(-R)\sum_{n=0}^{\infty}\sum_{j=0}^{[n/2]} R^n(\ln R)^j U_n^{(j)}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)/j! \ , \tag{11}$$

where ν is the leading power of R and m_ν is a degenerate substate among all those having leading power R^ν, and where

$$[n/2] = \begin{cases} n/2 \ , & \text{for } n \text{ even} \\ (n-1)/2 \ , & \text{for } n \text{ odd} \ . \end{cases} \tag{12}$$

Substituting Eq. (11) in Eq. (9), and equating to zero the coefficients of like powers of R and $\ln R$, gives[31] (for $E \leqq 0$)

$$\begin{aligned}\{-\Lambda^2+(\nu+n)(\nu+n+4)\}U_n^{(j)} &= \{-C/\kappa+2\nu+2n+3\}U_{n-1}^{(j)} \\ &\quad -2(\nu+n+2)U_n^{(j+1)}+2U_{n-1}^{(j+1)}-U_n^{(j+2)} \ .\end{aligned} \tag{13}$$

Equation (13) is solved subject to the condition, implied by Eq. (11), that $U_n^{(j)}=0$ for $j>[n/2]$; there would be too many unknowns otherwise. Note also that there is an implicit dependence of the coefficients $U_n^{(j)}$ on ν and m_ν, which are defined explicitly in Sec. V as hyperspherical harmonic eigenvalues. The hyperspherical harmonics are discussed in Sec. III. A general wave function is represented as a linear combination of Fock-series functions, $\Psi_{\nu m_\nu}$, with expansion coefficients determined by asymptotic boundary conditions.

III. SYMMETRIZED HYPERSPHERICAL HARMONICS

Solution of Eq. (13) for the Fock coefficients is complicated by the noncommutativity of the hyperspherical angular momentum operator Λ^2 and the Coulomb interaction operator C. We have carried out the solution by ex-

panding each Fock coefficient in the eigenstates of Λ^2, the hyperspherical harmonics, which we discuss here. The most time-consuming part of the numerical work consists, then, of calculating the matrix elements of the Coulomb operator C in hyperspherical harmonics, which we discuss in Sec. IV. Our algorithm for obtaining the expansion coefficients for each Fock coefficient is presented in Sec. V.

A. Definition

The eigenstates $u_{l_1 l_2 m_\lambda}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$ of the hyperspherical angular momentum operator satisfy the following equation:

$$\Lambda^2 u_{l_1 l_2 m_\lambda}=\lambda(\lambda+4)u_{l_1 l_2 m_\lambda}\ , \tag{14}$$

where $\lambda\equiv l_1+l_2+2m_\lambda$, and m_λ must be either zero or a positive integer in order that $u_{l_1 l_2 m_\lambda}$ is finite at $\alpha=\pi/2$; l_1 and l_2 are the orbital angular momentum quantum numbers of the two electrons; and L, S, M, and parity are assumed to be good quantum numbers for the two-electron system. Note that the parity of the state, $(-1)^{l_1+l_2}$, is the same as that of the eigenvalues λ, since the allowed eigenvalues increase in steps of $2m_\lambda$, where m_λ is an integer.

The α, $\hat{\mathbf{r}}_1$, and $\hat{\mathbf{r}}_2$ dependences of $u_{l_1 l_2 m_\lambda}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$ may be written in the following symmetrized form *for* $l_1\neq l_2$,

$$u_{l_1 l_2 m_\lambda}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=(2^{1/2}\sin\alpha\cos\alpha)^{-1}\{f_{l_1 l_2 m_\lambda}(\alpha)\mathscr{Y}_{l_1 l_2 LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)+(-1)^{l_1+l_2+L+S+m_\lambda}f_{l_2 l_1 m_\lambda}(\alpha)\mathscr{Y}_{l_2 l_1 LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\}\ , \tag{15a}$$

and in the following way *for* $l_1=l_2=l$,

$$u_{llm_\lambda}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=(\sin\alpha\cos\alpha)^{-1}f_{llm_\lambda}(\alpha)\mathscr{Y}_{llLM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ . \tag{15b}$$

Here

$$\mathscr{Y}_{l_1 l_2 LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\equiv\sum_{m_1 m_2}Y_{l_1 m_1}(\hat{\mathbf{r}}_1)Y_{l_2 m_2}(\hat{\mathbf{r}}_2)(l_1 m_1 l_2 m_2\,|\,LM) \tag{15c}$$

describes the coupling of the spherical harmonics for each individual electron to form a two-electron state of well-defined total angular momentum L and projection M using the Clebsch-Gordan coefficients.

B. Eigenvalue equation in α

Substituting either Eq. (15a) or Eq. (15b) in Eq. (14) gives the following eigenvalue equation in α only:

$$-\frac{d^2}{d\alpha^2}f_{l_1 l_2 m}(\alpha)+\left[\frac{l_1(l_1+1)}{\cos^2\alpha}+\frac{l_2(l_2+1)}{\sin^2\alpha}\right]f_{l_1 l_2 m_\lambda}(\alpha)=(\lambda+2)^2 f_{l_1 l_2 m}(\alpha)\ , \tag{16}$$

where, again, $\lambda\equiv l_1+l_2+2m_\lambda$ and m_λ is either zero or a positive integer. The solution of Eq. (16) that is finite at $\alpha=0$ and $\pi/2$ is[3]

$$f_{l_1 l_2 m_\lambda}(\alpha)=N_{l_1 l_2 m_\lambda}F(-m_\lambda,l_1+l_2+m_\lambda+2\,|\,l_2+\tfrac{3}{2}\,|\,\sin^2\alpha)(\sin\alpha)^{l_2+1}(\cos\alpha)^{l_1+1}\ , \tag{17}$$

where the hypergeometric function in Eq. (17) is a Jacobi polynomial of $m_\lambda+1$ terms:[32]

$$F(-m_\lambda,l_1+l_2+m_\lambda+2\,|\,l_2+\tfrac{3}{2}\,|\,\sin^2\alpha)$$
$$=m_\lambda!\frac{\Gamma(l_2+\frac{3}{2})}{\Gamma(l_2+\frac{3}{2}+m_\lambda)}\sum_{s=0}^{m_\lambda}(-1)^{m_\lambda-s}\begin{bmatrix}m_\lambda+l_2+\frac{1}{2}\\ s\end{bmatrix}\begin{bmatrix}m_\lambda+l_1+\frac{1}{2}\\ m_\lambda-s\end{bmatrix}(\sin\alpha)^{2(m_\lambda-s)}(\cos\alpha)^{2s}\ . \tag{18}$$

The normalization constant $N_{l_1 l_2 m_\lambda}$ in Eq. (17) is defined such that

$$\int_0^\pi d\alpha\, f_{l_1 l_2 m_\lambda}^2(\alpha)=1 \tag{19}$$

and is given by[33]

$$N_{l_1 l_2 m_\lambda}=\frac{1}{\Gamma(l_2+\frac{3}{2})}\left[\frac{2(2m_\lambda+l_1+l_2+2)\Gamma(m_\lambda+l_1+l_2+2)\Gamma(m_\lambda+l_2+\frac{3}{2})}{m_\lambda!\Gamma(m_\lambda+l_1+\frac{3}{2})}\right]^{1/2}\ . \tag{20}$$

C. Exchange symmetry

The exchange symmetry of the two-electron wave functions in Eqs. (15a) and (15b) is determined by interchanging the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. This implies an interchange of $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$ and of α with $\pi/2-\alpha$ or, alternatively, of $\sin\alpha$ with $\cos\alpha$. Under these transformations the coupled spherical harmonics and the α-dependent functions transform as follows:[34]

$$\mathscr{Y}_{l_1 l_2 LM}(\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_1)=(-1)^{l_1+l_2+L}\mathscr{Y}_{l_2 l_1 LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\ , \tag{21}$$

$$f_{l_1 l_2 m_\lambda}(\pi/2-\alpha)=(-1)^{m_\lambda} f_{l_2 l_1 m_\lambda}(\alpha) \ . \tag{22}$$

Employing Eqs. (21) and (22) in Eqs. (15a) and (15b) gives the symmetry of our hyperspherical harmonics under particle interchange *in the case* $l_1 \neq l_2$ as

$$u_{l_1 l_2 m_\lambda}(\pi/2-\alpha,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_1)=(-1)^S u_{l_1 l_2 m_\lambda}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) \tag{23a}$$

and *in the case* $l_1=l_2=l$ as

$$u_{llm_\lambda}(\pi/2-\alpha,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_1)=(-1)^{m_\lambda+L} u_{llm_\lambda}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) \ . \tag{23b}$$

Since the two-electron spin wave function has an exchange symmetry of $(-1)^{1+S}$, we see that for $l_1 \neq l_2$ the overall exchange symmetry is (-1), as required, while for $l_1=l_2$ the exchange symmetry is $(-1)^{m_\lambda+L+1+S}$. Hence for $l_1=l_2$ we must have $m_\lambda+L+S=$even. In particular, for the important case of $L=0$, we must have $m_\lambda=$even for $S=0$ and $m_\lambda=$odd for $S=1$.

IV. COULOMB MATRIX ELEMENTS

General expressions for the matrix elements of the Coulomb potential operator C, defined in Eq. (7), between hyperspherical harmonic functions of the form in Eq. (15a) have been derived by Lin[35] in terms of certain integrals over the coordinate α. We have verified Lin's results and derived analytic expressions for the α integrals that are better suited for numerical computation. Although our computer code calculates the Coulomb matrix for arbitrary L and S, we present here the results only for the special case of interest in our applications, the case $L=0$, in which the electrons have equal orbital angular momentum, $l_1=l_2=l$. For simplicity of notation, we write m_λ as m in this section.

The matrix element of the operator C defined in Eq. (7) between two hyperspherical harmonics of the form in Eq. (15b) may be expressed, upon carrying out the integrations over $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$, as

$$\begin{aligned}\langle l'l'm' \mid C \mid llm \rangle &= 2Z\delta_{ll'}\int_0^{\pi/2} d\alpha(\cos^{-1}\alpha+\sin^{-1}\alpha) f_{l'l'm'}(\alpha) f_{llm}(\alpha) \\ &\quad -2\sum_k (l'l' \mid P_k \mid ll)_{LM}\left[\int_0^{\pi/4} d\alpha\, f_{l'l'm'}(\alpha)\frac{\sin^k\alpha}{\cos^{k+1}\alpha} f_{llm}(\alpha)+\int_{\pi/4}^{\pi/2} d\alpha\, f_{l'l'm'}(\alpha)\frac{\cos^k\alpha}{\sin^{k+1}\alpha} f_{llm}(\alpha)\right] .\end{aligned} \tag{24}$$

The $\delta_{ll'}$ and the factor $(l'l' \mid P_k \mid ll)_{LM}$ arise from the integrations over $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$. The summation over k in the second set of terms arises from the following expansion of the interelectron interaction,

$$2[1-\sin(2\alpha)\cos\theta_{12}]^{1/2}=\begin{cases} 2\displaystyle\sum_{k=0}^{\infty}\frac{\sin^k\alpha}{\cos^{k+1}\alpha}P_k(\cos\theta_{12}) & \text{for } \alpha\le\pi/4 \\ 2\displaystyle\sum_{k=0}^{\infty}\frac{\cos^k\alpha}{\sin^{k+1}\alpha}P_k(\cos\theta_{12}) & \text{for } \alpha\ge\pi/4 \ , \end{cases} \tag{25}$$

where $P_k(\cos\theta_{12})$ is a Legendre polynomial. The matrix elements of this polynomial between the coupled spherical harmonics defined in Eq. (15c) may be expressed analytically as

$$(l_1'l_2' \mid P_k \mid l_1 l_2)_{LM}=(-1)^{k+L}[(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2}\begin{pmatrix} l_2' & k & l_2 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & k & l_1' \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} L & l_2 & l_1 \\ k & l_1' & l_2'\end{Bmatrix} , \tag{26}$$

where the large parentheses are $3j$ symbols, and the curly brackets are a $6j$ symbol.

Substituting Eq. (17) in Eq. (24) the α integrations may be performed. The result for the first set of terms in Eq. (24) is[35]

$$\begin{aligned}&\langle l'l'm' \mid 2Z(1/\cos\alpha+1/\sin\alpha) \mid llm \rangle \\ &\quad = Z\bar{N}_{llm'}\bar{N}_{llm}\delta_{ll'}\sum_{s'=0}^{m'}(-1)^{m'-s'}\sum_{s=0}^{m}(-1)^{m-s}A_{s'}(l,l,m')A_s(l,l,m)\{B(l+m'-s'+m-s+\tfrac{3}{2},l+1+s'+s) \\ &\qquad +B(l+1+m'-s'+m-s,l+s'+s+\tfrac{3}{2})\} \ ,\end{aligned} \tag{27}$$

where the new symbols are defined as follows:

$$\bar{N}_{l_1 l_2 m}\equiv N_{l_1 l_2 m}(m!)\Gamma(l_2+\tfrac{3}{2})/\Gamma(l_2+\tfrac{3}{2}+m) \ , \tag{28a}$$

$$A_s(l_1,l_2,m)\equiv\frac{\Gamma(m+l_1+\frac{3}{2})\Gamma(m+l_2+\frac{3}{2})}{\Gamma(l_1+\frac{3}{2}+s)\Gamma(m-s+1)\Gamma(m+l_2+\frac{3}{2}-s)\Gamma(s+1)} \ , \tag{28b}$$

$$B(\mu/2,\nu/2)\equiv 2\int_0^{\pi/2} d\alpha(\sin\alpha)^{\mu-1}(\cos\alpha)^{\nu-1}=\Gamma(\mu/2)\Gamma(\nu/2)/\Gamma(\mu/2+\nu/2)\ . \tag{28c}$$

The result for the second set of terms in Eq. (24) is[35]

$$\begin{aligned}\langle l'l'm' \mid 2[1-\sin(2\alpha)\cos\theta_{12}]^{-1/2} \mid llm\rangle &= 2\sum_k (l'l' \mid P_k \mid ll)_{LM}\bar{N}_{l'l'm'}\bar{N}_{llm}\sum_{s'=0}^{m'}(-1)^{m'-s'}A_{s'}(l',l',m') \\ &\quad\times\sum_{s=0}^{m}(-1)^{m-s}A_s(l,l,m) \\ &\quad\times\{P(l+l'+2s+2s'-k+1,l+l'+2m'+2m-2s'-2s+k+2) \\ &\quad +P(l+l'+2m+2m'-2s-2s'-k+1,l+l'+2s+2s'+2+k)\}\ ,\end{aligned} \tag{29}$$

where $\bar{N}$ and A_s are defined in Eq. (28) and where

$$P(\mu,\nu)\equiv\int_0^{\pi/4}(\cos\alpha)^{\mu}(\sin\alpha)^{\nu}d\alpha\ . \tag{30a}$$

The integral in Eq. (30a) may be expressed analytically in several ways in terms of a sum involving γ functions, but the numerical evaluation of the resulting expression is difficult because of extensive cancellation between the various terms, particularly for large-m values. We have employed the following analytic expression, which is subject to less roundoff error than other expressions:

$$P(\mu,\nu)=(\tfrac{1}{2})^{(\nu+3)/2}\Gamma(\tfrac{1}{2}(\mu+1))\sum_{n=1}^{(\mu+1)/2}(-\tfrac{1}{2})^{n-1}[\Gamma(\tfrac{1}{2}(\mu+3)-n)\Gamma(n)\Gamma(\tfrac{1}{2}(\nu-1)+n)]^{-1}\ . \tag{30b}$$

V. FOCK COEFFICIENT REPRESENTATION IN HYPERSPHERICAL HARMONICS FOR $^1S^e$ STATES

A. First Fock coefficient ($n=j=0$)

The first Fock coefficient, $U_0^{(0)}$, satisfies the hyperspherical harmonic eigenvalue equation [cf. Eq. (13)]

$$\{-\Lambda^2+\nu(\nu+4)\}U_0^{(0)}=0\ , \tag{31}$$

where the eigenvalue is $\nu\equiv l_1+l_2+2m_\nu$. For $^1S^e$ states $l_1=l_2=l$ and $\nu\equiv 2(l+m_\nu)$, where m_ν is an *even* integer. Hence $U_0^{(0)}$ is given by the corresponding hyperspherical harmonic:

$$U_0^{(0)}=u_{llm_\nu}(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\equiv u_{\nu m_\nu}\ . \tag{32}$$

[On the right-hand side of Eq. (32) we have replaced the subscripts llm_ν by νm_ν since $l\equiv\nu/2-m_\nu$.] This equality of the first Fock coefficient with the hyperspherical harmonic having quantum numbers νm_ν identifies the possible degenerate states m_ν for a fixed, *even* value of ν as

$$m_\nu=0,2,\ldots,\nu/2\ . \tag{33}$$

In what follows we make explicit the dependence of the Fock coefficients on the quantum numbers νm_ν of a particular solution by replacing $U_n^{(j)}$ by $U_{nj}^{\nu m_\nu}$. Furthermore, we denote hyperspherical harmonics u_{llm} by $u_{\lambda m_\lambda}$, where $\lambda=2(l+m_\lambda)$, $l=\lambda/2-m_\lambda$, and where m_λ is an even integer (for $^1S^e$ states) less than or equal to $\lambda/2$.

B. General equation ($n>0$)

In general, we expand the Fock coefficients for $n>0$ in hyperspherical harmonics as follows:

$$U_{nj}^{\nu m_\nu}(\Omega)=\sum_{\lambda'=0}^{\infty}{}'\sum_{m_{\lambda'}=0}^{\lambda'/2}{}' b_{\lambda' m_{\lambda'}}^{\nu m_\nu nj}u_{\lambda' m_{\lambda'}}(\Omega)\ , \tag{34}$$

where the primes on the summations indicate that λ and m_λ have only even values. Substituting Eq. (34) in Eq. (13), multiplying from the left by the hyperspherical harmonic $u_{\lambda m_\lambda}(\Omega)$, where $\Omega\equiv(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$, and integrating over all angles gives the following set of *algebraic* equations for the expansion coefficients $b_{\lambda m_\lambda}^{\nu m_\nu nj}$:

$$\begin{aligned}\{-\lambda(\lambda+4)+(n+\nu)(n+\nu+4)\}b_{\lambda m_\lambda}^{\nu m_\nu nj} &= \sum_{\lambda'=0}^{\infty}{}'\sum_{m_{\lambda'}=0}^{\lambda'/2}{}'\frac{\langle\lambda m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa}b_{\lambda' m_{\lambda'}}^{\nu m_\nu (n-1)j} \\ &\quad +[2(n+\nu)+3]b_{\lambda m_\lambda}^{\nu m_\nu (n-1)j}-2(n+\nu+2)b_{\lambda m_\lambda}^{\nu m_\nu n(j+1)} \\ &\quad +2b_{\lambda m_\lambda}^{\nu m_\nu (n-1)(j+1)}-b_{\lambda m_\lambda}^{\nu m_\nu n(j+2)}\ .\end{aligned} \tag{35}$$

In this equation we have assumed $E<0$ so that we could replace $+C/(ik)$ by $-C/\kappa$, as discussed below Eq. (10). In what follows we discuss the general solution of Eq. (35)

for the expansion coefficients $b_{\lambda m_\lambda}^{\nu m_\nu nj}$ in the way our computer algorithm is written. We start with $n=1$ and proceed to higher values. In Appendix A we give explicit examples for $1 \leqq n \leqq 4$.

C. Solution of Eq. (35) for n odd

For n odd one never has equality of λ with $n+\nu$ since both λ and ν are even integers. Hence Eq. (34) gives the expression of the Fock coefficients and Eq. (35) is used to solve for the corresponding expansion coefficients. Since $U_{nj}^{\nu m_\nu}=0$ for $j>[n/2]$ [cf. Eq. (12)], we have that $b_{\lambda m_\lambda}^{\nu m_\nu nj}=0$ for $j>[n/2]$. We start with the highest allowed value of j and proceed to lower values.

D. Solution of Eq. (35) for n even

When n is even, there is the possibility that $\lambda=n+\nu$ and this case must be treated separately from the case $\lambda \neq n+\nu$. *Consider first the case of* $\lambda \neq n+\nu$. For the highest allowed value of j, which is $n/2$, Eq. (35) becomes

$$\{-\lambda(\lambda+4)+(n+\nu)(n+\nu+4)\} b_{\lambda m_\lambda}^{\nu m_\nu n(j=n/2)}=0 \ . \tag{36a}$$

Since $\lambda \neq (n+\nu)$, the only solution is

$$b_{\lambda m_\lambda}^{\nu m_\nu n(j=n/2)}=0 \ . \tag{36b}$$

For values of $j<n/2$, nonzero coefficients for $n'=n-1$ assure that Eq. (35) is inhomogeneous so that nonzero coefficients for $n'=n$ exist.

For the case $\lambda=n+\nu$, the left-hand side of Eq. (35) is zero so that the coefficients are obtained by setting the right-hand side equal to zero:

$$\begin{aligned} 2(n+\nu+2) b_{\lambda m_\lambda}^{\nu m_\nu nj} &= \sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle \lambda m_\lambda \mid C \mid \lambda' m_{\lambda'} \rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu (n-1)(j-1)} \\ &\quad + \{2(n+\nu)+3\} b_{\lambda m_\lambda}^{\nu m_\nu (n-1)(j-1)} \\ &\quad + 2 b_{\lambda m_\lambda}^{\nu m_\nu (n-1)j} - b_{\lambda m_\lambda}^{\nu m_\nu n(j+1)} \quad \text{for } j \geqq 1 \ . \end{aligned} \tag{37a}$$

This equation determines the expansion coefficients uniquely in the case $\lambda=n+\nu$ for all j values greater than zero. In the case $\lambda=n+\nu$ and $j=0$, however, the coefficients $b_{\lambda m_\lambda}^{\nu m_\nu n0}$ are not uniquely determined since their coefficient vanishes on the left-hand side of Eq. (35). Equation (37a) would determine the $j=0$ coefficients uniquely only if there were coefficients with $j<0$. Since these are not allowed, we adopt the standardization[8]

$$b_{\lambda m_\lambda}^{\nu m_\nu n0}=0 \quad \text{for } j=0 \ . \tag{37b}$$

Any arbitrariness introduced by this requirement is removed when the boundary conditions are applied.

VI. MATCHING OF THE FOCK REPRESENTATION OF THE WAVE FUNCTION TO AN ADIABATIC HYPERSPHERICAL CHANNEL REPRESENTATION

A two-electron wave function may be represented as a linear combination of Fock wave functions of the form given in Eq. (11), as follows:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{\nu,m_\nu} a_{\nu m_\nu} \Psi_{\nu m_\nu}(R,\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) \ . \tag{38}$$

The expansion coefficients $a_{\nu m_\nu}$ are determined by matching the Fock-series representations $\Psi_{\nu m_\nu}$ to two-electron wave functions having the proper asymptotic behavior. In this section we present a variational procedure for matching a wave function of the form in Eq. (38) to a linear combination of adiabatic hyperspherical channel functions at a matching radius, $R=R_0$.

A. Wave-function matching

We consider that the wave function in the inner region is given by a superposition of Fock solutions ψ_Λ, $\Lambda=1,2,\ldots,N_F$, where Λ labels a pair of quantum numbers λm_λ, and that the wave function in the outer region is represented by a superposition of adiabatic[22] channel functions ϕ_μ, $\mu=1,2,\ldots,N_C$, defined by

$$\{-\Lambda^2+RC(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)\}\phi_\mu(R;\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) = \varepsilon_\mu(R)\phi_\mu(R;\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) \ ,$$

with coefficients $F_\mu(R)$ which are functions of the hyperradius R. At the matching radius R_0, these functions are denoted by the constants A_μ. Thus we have

$$\Psi_{\text{inner}} \approx \sum_{\Lambda=1}^{N_F} a_\Lambda \Psi_\Lambda \ , \tag{38'}$$

$$\Psi_{\text{outer}} \approx \sum_{\mu=1}^{N_C} A_\mu \phi_\mu \quad \text{at } R=R_0 \ , \tag{39}$$

and $N_C \leqq N_F$. To simplify the notation we use the convention that repeated Greek indices are summed over. The constants a_Λ and A_μ are to be chosen so that both the function and its derivative match at R_0. Because N_C and N_F are finite and do not include a complete set, this matching can only be done approximately. We match the solutions so that the average deviation of the functions integrated over the hypersphere vanishes. Later we show that this condition suffices to match the derivative also. Denoting the five angular coordinates $\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2$ collectively by Ω, we have

$$\delta \frac{\int \left| \sum_\Lambda a_\Lambda \Psi_\Lambda - \sum_\mu A_\mu \phi_\mu \right|^2 d\Omega}{\int \left| \sum_\Lambda a_\Lambda \Psi_\Lambda \right|^2 d\Omega} = 0 \equiv \delta \frac{N}{D} \tag{40}$$

as the condition that determines the variational parameters a_Λ and A_μ.

Defining the matrix elements $M_{\Lambda\Lambda'}$ and $X_{\Lambda\mu}$,

$$M_{\Lambda\Lambda'}=\int \Psi_\Lambda \Psi_{\Lambda'} d\Omega \equiv \langle \Psi_\Lambda \mid \Psi_{\Lambda'} \rangle \ , \tag{41a}$$

$$X_{\Lambda\mu}=\langle \Psi_\Lambda \mid \phi_\mu \rangle \ , \tag{41b}$$

and assuming that the adiabatic functions ϕ_μ are normalized to unity, i.e., $\int \phi_{\mu'}\phi_\mu d\Omega=\delta_{\mu'\mu}$, we have for the numerator N and the denominator D in Eq. (40)

$$N=a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'}-2a_\Lambda X_{\Lambda\mu}A_\mu+A_\mu A_\mu \ , \tag{42a}$$

$$D=a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'} \ , \tag{42b}$$

where the summation convention is used. Variation of Eq. (40) gives the relation

$$D\,\delta N-N\,\delta D=0 \ . \tag{43}$$

Variation with respect to $a_{\Lambda''}$ gives

$$a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'}(2a_{\overline{\Lambda}}M_{\overline{\Lambda}\Lambda''}-2X_{\Lambda''\mu}A_\mu)$$
$$-(a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'}-2a_\Lambda X_{\Lambda\mu}A_\mu+A_\mu A_\mu)(2a_{\overline{\Lambda}}M_{\overline{\Lambda}\Lambda''})=0 \tag{44}$$

while variation with respect to A_μ gives

$$-2a_\Lambda X_{\Lambda\mu'}+2A_{\mu'}=0 \ . \tag{45}$$

Equations (44) and (45) are the basic equations of our approach. To solve these equations we substitute Eq. (45) into Eq. (44) to obtain

$$-(a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'})X_{\Lambda''\mu}A_\mu+A_\mu A_\mu a_{\overline{\Lambda}}M_{\overline{\Lambda}\Lambda''}=0 \ . \tag{46}$$

Now define the column array $y_{\Lambda''}$,

$$y_{\Lambda''}=(a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'}/A_\mu A_\mu)X_{\Lambda''\mu}A_\mu \ , \tag{47}$$

so that Eq. (46) becomes

$$a_{\overline{\Lambda}}M_{\overline{\Lambda}\Lambda''}=y_{\Lambda''} \tag{48}$$

with the solution

$$a_\Lambda=y_{\Lambda''}[\underline{M}^{-1}]_{\Lambda''\Lambda} \ . \tag{49}$$

Equation (49) gives us an expression for the coefficients a_Λ relevant to the inner region. These coefficients are given self-consistently through Eq. (46) in terms of the a_Λ's and the A_μ's themselves. Substituting the expression for a_Λ back into the expression [Eq. (45)] for A_μ gives the matrix eigenvalue equation

$$\begin{aligned}A_{\mu'}&=y_{\Lambda''}[\underline{M}^{-1}]_{\Lambda''\Lambda}X_{\Lambda\mu'}\\&=\beta A_\mu[\underline{X}^\tau]_{\mu\Lambda''}[\underline{M}^{-1}]_{\Lambda''\Lambda}X_{\Lambda\mu'}\\&=\beta A_\mu Q_{\mu\mu''} \ ,\end{aligned} \tag{50}$$

where the quantity β is given by

$$\beta=a_\Lambda M_{\Lambda\Lambda'}a_{\Lambda'}/A_\mu A_\mu \tag{51}$$

and is an eigenvalue to be determined from Eq. (50). Equivalently, we have

$$\mathbf{A}\cdot(\beta^{-1}\underline{I}-\underline{Q})=0 \tag{52}$$

and $\mathbf{A}$ is the corresponding eigenvector. Since the dimension of the matrix $\mathbf{X}_\mu^\tau\cdot\underline{M}^{-1}\cdot\mathbf{X}_\mu$ is N_C we obtain N_C eigenvalues and corresponding eigenvectors $\mathbf{A}_j$. The Λth element of the column array $\mathbf{y}_j$ corresponding to a given eigenvalue β_j is

$$y_{\Lambda j}=\beta_j X_{\Lambda\mu}A_{\mu j} \tag{53}$$

which is now completely determined up to a multiplicative constant. This in turn determines the coefficients a_Λ through Eq. (49).

Since the coefficients a_Λ are now fully determined it is a simple matter to obtain the values of $F_\mu(R)$ and the derivative $F'_\mu(R)$ at R_0. We have

$$F_{\mu j}(R)=\langle\Psi_j\,|\,\phi_\mu\rangle=a_{\Lambda j}\langle\Psi_\Lambda\,|\,\phi_\mu\rangle=a_{\Lambda j}X_{\Lambda\mu} \ , \tag{54}$$

where j denotes a particular total wave function. Note that these $F_{\mu j}$'s correspond to solutions in the inner region.

But our construction also interprets the constants $A_{\mu j}$ as values of $F_{\mu j}(R)$ extracted from the outer region evaluated at R_0. To show that these two functions match we substitute for $a_{\Lambda j}$ from Eq. (49) and use the eigenvalue Eq. (52) to obtain

$$\begin{aligned}F_{\mu j}(R_0)&=\beta_j A_{\mu' j}X_{\mu'\Lambda}[\underline{M}^{-1}]_{\Lambda\Lambda'}X_{\Lambda'\mu}\\&=\beta_j A_{\mu' j}\alpha_{\mu'\mu}=\beta_j\beta_j^{-1}A_{\mu j}=A_{\mu j}\end{aligned} \tag{55}$$

(no summation over j is implied) which shows that $F_{\mu j}(R_0)$ equals $A_{\mu j}$. This equality ensures the consistency of the matching of the inner and outer functions.

B. Derivative matching

We also require the derivatives of $F_{\mu j}(R)$ evaluated at R_0. Since we have the Fock solutions Ψ_j for each eigenvalue β_j we can easily form

$$\frac{\partial F_{\mu j}(R)}{\partial R}=\frac{\partial}{\partial R}\langle\phi_\mu\,|\,\Psi_j\rangle \tag{56}$$

at R_0. We then use these values of $F_{\mu j}(R)$ and $F'_{\mu j}(R)$ to start the outward integration of the coupled adiabatic equations from R_0.

It is of some interest to calculate $F'_{\mu j}(R)$ in the outer region by an alternative formula which illustrates the nature of the approximations involved in truncating the basis set in the ϕ_μ's. In the outer region we have

$$\frac{\partial\Psi_j}{\partial R}=\frac{\partial F_{\mu j}}{\partial R}\phi_\mu+F_{\mu j}\frac{\partial\phi_\mu}{\partial R} \ . \tag{57}$$

Forming the inner product with $\phi_{\mu'}$ gives

$$\frac{\partial F_{\mu' j}}{\partial R}=\left\langle\phi_{\mu'}\left|\frac{\partial\Psi_j}{\partial R}\right.\right\rangle-\left\langle\phi_{\mu'}\left|\frac{\partial\phi_\mu}{\partial R}\right.\right\rangle A_{\mu j} \ . \tag{58}$$

Substituting Ψ_j from the inner solution into Eq. (58) and using

$$\left\langle\frac{\partial\phi_{\mu'}}{\partial R}\left|\phi_\mu\right.\right\rangle=-\left\langle\phi_{\mu'}\left|\frac{\partial\phi_\mu}{\partial R}\right.\right\rangle \tag{59}$$

and Eq. (45) for A_μ we find

$$\frac{\partial F_{\mu' j}}{\partial R}=\left\langle\phi_{\mu'}\left|\frac{\partial\Psi_j}{\partial R}\right.\right\rangle+\sum_\mu\left\langle\frac{\partial\phi_{\mu'}}{\partial R}\left|\phi_\mu\right.\right\rangle\langle\phi_\mu\,|\,\Psi_j\rangle \ . \tag{60}$$

If the sum over μ goes over a complete set or if the coupling represented by $\langle(\partial\phi_{\mu'}/\partial R)\,|\,\phi_\mu\rangle$ is weak, then Eq. (60) is equivalent to Eq. (56). In general, we do not use a complete set so that Eq. (60) differs from Eq. (56). This difference reflects the implicit coupling to other adiabatic

channels not included explicitly in the outer region but included implicitly in the inner region.

C. Summary

We have established a procedure for determining that superposition of Fock solutions which minimizes the mismatch between these solutions and the adiabatic solutions at some radius R_0. Once this superposition is determined we then form the projection of the Fock solutions on the adiabatic channel functions to determine the radial functions and their derivatives at R_0. The values for these functions then constitute the starting values for outward integration of the coupled adiabatic equations.

VII. RESULTS

A. Numerical details

For ^1S states of H^- and He, we have computed the first four Fock wave functions $\Psi_{\nu m_\nu}$, where $(\nu,m_\nu)=(0,0)$, (2,0), (4,2) and (4,0), by representing the Fock coefficients as an expansion in 32 hyperspherical harmonics $u_{\lambda m_\lambda}$. Aside from the restrictions of symmetry and parity, which require λ and m_λ to be even, we further restricted the electron orbital angular momentum l to the values 0, 1, 2, and 3. [Recall that λ, m_λ and l are related by $\lambda=2(l+m_\lambda)$.] Thus, our 32 hyperspherical harmonics were chosen to be $(\lambda,m_\lambda)=(0,0)$, (2,0), (4,0), (4,2), . . . , (30,12), (30,14), (32,14), and (32,16). Using this basis we solved the equations in Sec. V for the expansion coefficients $b_{\lambda m_\lambda}^{\nu m_\nu nj}$ for each of the following Fock coefficients: $(n,j)=(1,0)$, (2,1), (2,0), (3,1), (3,0), . . . , (6,3), (6,2), (6,1), and (6,0). An analytic test of our calculational procedure is described in Appendix B.

With the first four Fock wave functions $\Psi_{\nu m_\nu}$, we carried out calculations designed to test the adequacy of the adiabatic hyperspherical approximation in a number of simple cases. Specifically, we matched a linear combination of our Fock functions to a *single* adiabatic hyperspherical channel function, $F_\mu(R)\phi_\mu(R;\alpha,\hat{r}_1,\hat{r}_2)$, using Eqs. (47) and (49) of Sec. VI. We then compared the phase shifts, energies, and wave functions given in our Fock representation with those given in the single-channel adiabatic hyperspherical representation.

In the single adiabatic channel case, our program works as follows. First, we designate a wave number $\kappa=(2|E|)^{1/2}$, or $\kappa=(2|E|)^{1/2}=(1-k^2)^{1/2}$ for scattering states, where $\frac{1}{2}k^2$ is now the incident electron's kinetic energy. This κ scales all functions of R such that $R\to\kappa R$. The program then sets up a mesh in R with $R_{\min}$, $R_{\max}$, and ΔR as input and generates the adiabatic channel functions $\phi(R;\Omega)$ by diagonalizing for each R the following equation:

$$\sum_{\Lambda'}\{-\lambda(\lambda+4)+RC_{\Lambda\Lambda'}\}\langle u_{\Lambda'}|\phi\rangle=\varepsilon(R)\langle u_\Lambda|\phi\rangle ,$$

where $\Lambda\equiv(\lambda,m_\lambda)$. Our calculation of the matrix elements $C_{\Lambda\Lambda'}$ reduces all our subsequent calculations to matrix operations. In particular, further integration over hyperangles is unnecessary and the overlap matrix elements needed are computed simply as a vector dot product. With $\lambda_{\max}=32$ we generate $\varepsilon(R)$ over our entire range of R_0 to within 0.1% of the best values obtained by direct integration.

Next, the matching radius R is designated and the expansion coefficients $a_\Lambda(R_0)$ are determined by inverting

$$a_{\bar{\Lambda}}M_{\bar{\Lambda}\Lambda}=X_{\Lambda\mu} .$$

This follows from Eq. (46) and the fact that when there is only a single adiabatic hyperspherical channel μ, Eqs. (45) and (46) imply that $A_\mu=a_{\bar{\Lambda}}M_{\bar{\Lambda}\Lambda}a_\Lambda$. The rectangular arrays $a_\Lambda(R_0)$ and $X_{\Lambda\mu}(R)$ have the same dimensions in Λ and also in the mesh R. The square array $A(R_0,R)$ for $R_{\min}\leqq R_0$, $R\leqq R_{\max}$ is then computed as [cf. Eq. (45)]

$$A(R_0,R)=\sum_\Lambda a_\Lambda(R_0)X_{\Lambda\mu}(R) .$$

The adiabatic channel functions are independent of E and are computed first, once and for all. The overlaps $X_{\Lambda\mu}(R)$ depend on E and must be recalculated as the Fock coefficients change with E. In turn, the coefficients $a_\Lambda(R_0)$ are energy dependent, as are the functions $A(R_0,R)$.

The values of $n_{\max}$ and $\lambda_{\max}$ are read as input data. With $\lambda_{\max}=32$ [as required to obtain accurate values of $\varepsilon(R)$] a value of $n_{\max}>\lambda_{\max}$ is needed for numerical convergence of the Fock expansion. Typically, we have used $n_{\max}=40$ and have generated $n_{\max}j_{\max}=40\times20=800$ terms in the Fock series. For larger values of $n_{\max}$, up to $n_{\max}=60$, we observe only a weak dependence of our results on $n_{\max}$ and presume that the Fock expansion has converged for $R\leqq R_{\max}$, at least for the states we have investigated. The convergence of the Fock coefficients $U_n^{(j)}$ as an expansion in hyperharmonics is slower for larger n but, in general, we achieve an apparent 1% numerical convergence.

B. $e^-+H\ ^1S$ phase shift

We have computed the elastic e^--H ^1S scattering phase shift by matching a linear combination of our four Fock functions $\Psi_{\nu m_\nu}$ onto a single adiabatic hyperspherical channel wave function at a matching radius, $R_0=1.4$ a.u. The phase shift is determined from the asymptotic behavior of the radial adiabatic hyperspherical channel function,

$$F_\mu(R)\to(2/\pi k)^{1/2}\sin(kR+\delta)\ \text{ as } R\to\infty , \qquad (61)$$

where $k^2/2$ is the electron kinetic energy in a.u. Table I compares our Fock results with Lin's[36] single-channel adiabatic hyperspherical results and with Schwartz's[37] variational results, which are the best available. We do not regard the differences between our Fock results and the single-channel hyperspherical results of Lin[36] as significant. They are comparable to the accuracies of each calculation. We conclude that, within the accuracy of our calculation, the Fock representation of the inner-region wave function does not improve upon the elastic scattering phase shift calculated with the single-channel adiabatic hyperspherical wave function.

TABLE I. Elastic e^--H ^1S scattering phase shift (rad).

k (a.u.)	Fock, 1-channel hyperspherical[a]	1-channel hyperspherical[b]	Variational[c]
0.1	2.508	2.513	2.553
0.2	1.968	1.983	2.067
0.3	1.553	1.568	1.696
0.4	1.229	1.242	1.415
0.5	0.973	0.989	1.202
0.6	0.769	0.784	1.041
0.7	0.603	0.618	0.930

[a]Present results: matching of the first four Fock wave functions to the single-channel hyperspherical wave function at a matching radius of 1.4 a.u.
[b]Lin, Ref. 36.
[c]Schwartz, Ref. 37.

C. He and H^- ^1S ground states

We have calculated both the He and H^- ^1S ground-state wave functions and energies by matching our linear combination of four Fock functions $\Psi_{\nu m_\nu}$ to the single adiabatic hyperspherical ground-state channel wave function. In all cases both the wave functions and the energies are very close to those of the single-channel adiabatic hyperspherical approximation.

To determine the energies, we iterated our equations until both the wave function and its radial derivative were smooth at the matching radius. Various matching radii were tried, but consistent results were obtained up to the radius of the first antinode of the radial wave function. In each case our results converged on the single-channel adiabatic hyperspherical ground-state energies:[38] $-0.525\,92$ a.u. for H^- and $-2.895\,17$ a.u. for He. These results are superior to those obtained by Haftel and Mandelzweig:[39] $-0.517\,64$ a.u. for H^- and $-2.893\,58$ a.u. for He.

Similar results were obtained when we compared the radial wave functions directly. Consider Eq. (54), which may be written

$$F_\mu(R)-\sum_\Lambda a_\Lambda(R_0)X_{\Lambda\mu}(R)=0\ . \tag{54'}$$

In this equation we have dropped the subscript j, since we know that we are interested in the ground state, and we have indicated explicitly that the coefficients $a_\Lambda(R_0)$ are constants which are determined at the matching radius R_0. The matrix elements $X_{\Lambda\mu}(R)$, however, are functions of R. When $F_\mu(R)$ is taken to be the adiabatic hyperspherical radial wave function for the ground state, we found that the difference in Eq. (54′) varied smoothly from $+0.43\%$ at $R=0.7$ a.u. to -1.03% at $R=1.4$ a.u. when expressed as a percentage of the value of $F_\mu(R)$ at these radii. Graphical comparison of the two wave functions is shown in Fig. 1. Such wave-function amplitude differences apparently do not affect the ground-state energies (or, in the case of continuum wave functions, the phase shifts) to an extent that is significantly greater than our numerical accuracy.

D. Need for additional adiabatic channels

The expansion of the Fock coefficients in hyperspherical harmonics [cf. Eq. (34)] has coefficients which are energy dependent. We have found that, near $R=0$, the $\mu_{\lambda m_\lambda}$ component having $(\lambda,m_\lambda)=(\nu,m_\nu)$ is always the largest component of the Fock solution $\psi_{\nu m_\nu}$, although as R increases, the other components with $(\lambda,m_\lambda)\neq(\nu,m_\nu)$ become more significant. In our calculations a linear combination of the four lowest Fock solutions $\psi_{\nu m_\nu}$ was matched at R_0 onto the lowest ^1S adiabatic hyperspherical solution, whose angular part behaves near $R=0$ as u_{00}. Therefore, the Fock solution ψ_{00} is dominant near $R=0$ and the others become significant only for larger R values.

That this procedure underweights the Fock solutions $\psi_{\nu m_\nu}$ with $(\nu,m_\nu)\neq(0,0)$ is indicated in our calculations of the e^-+H phase shift. Here, as the energy E of the system approaches that of the $n=2$, ^1S resonant state of H^-

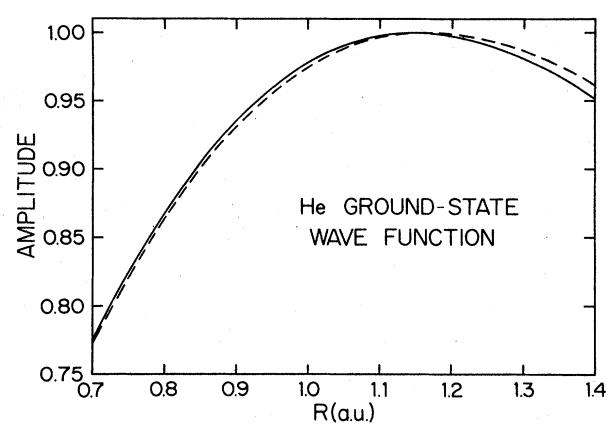

FIG. 1. Comparison of the single-channel adiabatic hyperspherical radial wave function $F_\mu(R)$ (solid line) with the Fock wave function $\sum_{\Lambda=1}^4 a_\Lambda(R_0)X_{\Lambda\mu}(R)$ (dashed line). Each wave function is normalized to unity at its antinode at $R=1.15$ a.u. The matching radius R_0 is 1.4 a.u.

at 9.57 eV we notice a large increase in the u_{20} component of the Fock solutions $\psi_{\nu m_\nu}$. This behavior indicates that our Fock expansion would match well onto the first excited ^1S adiabatic hyperspherical wave function, which is characterized by u_{20} as R approaches zero. Because we have restricted our consideration in these first calculations to only a single adiabatic hyperspherical wave function in the region $R > R_0$, this u_{20} component of our Fock solutions $\psi_{\nu m_\nu}$ is underweighted and hence we see no resonance in our calculated phase shifts. This result indicates that when particular hyperspherical harmonic components $u_{\lambda m_\lambda}$ of the Fock solutions $\psi_{\nu m_\nu}$ become important, the adiabatic basis onto which these solutions are matched must be increased to describe properly the system's wave function.

VIII. DISCUSSION

In this paper we have presented a numerical procedure for obtaining the coefficients of the exact Fock-series representation near the origin for a two-electron wave function. We have also described a general procedure for matching the Fock-series representation onto the adiabatic hyperspherical representation at some finite radius R_0. As discussed in the Introduction, our first numerical applications, presented here, have been motivated by the findings of others[23–28] that the adiabatic hyperspherical coordinate representation is excellent near the nucleus for the ground and low-energy excited states considered here. If this is indeed true, it follows that when the two-electron wave function is represented in terms of a Fock expansion, the wave functions, energies, and phase shifts should be little changed from those of the adiabatic hyperspherical approximation results. Our calculations, presented here, support this conclusion. Future studies of processes for which the adiabatic hyperspherical representation is inadequate—such as excitation processes—are therefore required to identify the physical role played by the logarithmic terms in Eq. (1).

The Fock-series representation apparently is superior to the alternative-series representation of Haftel and Mandelzweig.[30] In their calculations for the ground-state properties of He and H^- they employed up to 25 hyperspherical harmonics. The superiority of our calculated ground-state energies implies that truncation of the number of Fock coefficients is more appropriate than truncation of the number of hyperspherical harmonics.

Finally, some insight into the convergence properties of the wave functions discussed in this paper may be obtained from studies of the variational method. As was discussed long ago by Schwartz[40] and more recently by Klahn and Morgan[41] and by Hill,[42] rates of convergence are controlled by how rapidly basis functions duplicate cusps in the exact wave function one is trying to approximate. It is most important to duplicate first the electron-nucleus cusps, second the electron-electron cusps, and then the three-particle logarithmic cusps. The adiabatic hyperspherical wave functions duplicate the electron-nucleus cusp exactly. They duplicate the electron-electron cusp exactly also except for the truncation of the basis set of (l_1,l_2) pairs used to compute the eigenvalues $\varepsilon(R)$ (cf. Sec. VI A) of the (Λ^2+RC) operator.[22] Thus, for hyperspherical radii $R > R_0$, where there are no logarithmic singularities, our wave function treats all singularities in principle exactly. For $R < R_0$, the truncated Fock-series expansion represents all three cusps approximately. The fact that our combined Fock-hyperspherical adiabatic wave function gives energies and phase shifts that are identical (within our numerical accuracy) to those of a single-channel hyperspherical adiabatic calculation seems to imply that precise treatment of the electron-nucleus and electron-electron cusps in the region $R < R_0$ is not important at our level of accuracy of 10^{-2}–10^{-3} a.u. in energy. However, it would become important in striving for an absolute accuracy of 10^{-4} a.u. or better.[13]

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APPENDIX A: EXPLICIT SOLUTIONS OF EQ. (35)

In this appendix we provide solutions of Eq. (35) for $1 \leqq n \leqq 4$ in order to illustrate the general algorithm for its solution presented in Sec. V.

For $(n=1, j=0)$, Eq. (35) gives

$$\{-\lambda(\lambda+4)+(\nu+1)(\nu+5)\}b_{\lambda m_\lambda}^{\nu m_\nu 10} = \frac{\langle \lambda m_\lambda \mid C \mid \nu m_\nu \rangle}{\kappa} + (2\nu+5)\delta_{\lambda\nu}\delta_{m_\lambda m_\nu} . \quad \text{(A1)}$$

For $(n=2, j=1)$, Eq. (36b) gives the value zero for all coefficients for which $\lambda \neq \nu+2$. For $\lambda=\nu+2$, Eq. (37a) gives

$$(2\nu+8)b_{\nu+2\, m_\lambda}^{\nu m_\nu 21} = \sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle (\nu+2)m_\lambda \mid C \mid \lambda' m_{\lambda'} \rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 10} + (2\nu+7)b_{\nu+2\, m_\lambda}^{\nu m_\nu 10} . \quad \text{(A2)}$$

For $(n=2, j=0)$, when $\lambda \neq \nu+2$, Eq. (35) gives

$$\{-\lambda(\lambda+4)+(\nu+2)(\nu+6)\}b_{\lambda m_\lambda}^{\nu m_\nu 20} = \sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle \lambda m_\lambda \mid C \mid \lambda' m_{\lambda'} \rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 10} + (2\nu+7)b_{\lambda m_\lambda}^{\nu m_\nu 10} . \quad \text{(A3)}$$

For the case $\lambda=\nu+2$ the coefficients are zero. *For* $(n=3, j=1)$, Eq. (35) gives

$$\{-\lambda(\lambda+4)+(\nu+3)(\nu+7)\}b_{\lambda m_\lambda}^{\nu m_\nu 31}$$
$$=\sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle \lambda m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 21}$$
$$+(2\nu+9)b_{\lambda m_\lambda}^{\nu m_\nu 21} . \tag{A4}$$

For $(n=3, j=0)$, Eq. (35) gives

$$\{-\lambda(\lambda+4)+(\nu+3)(\nu+7)\}b_{\lambda m_\lambda}^{\nu m_\nu 30}$$
$$=\sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle \lambda m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 20}$$
$$+(1-\delta_{\lambda,\nu+2})(2\nu+9)b_{\lambda m_\lambda}^{\nu m_\nu 20}$$
$$-(2\nu+10)b_{\lambda m_\lambda}^{\nu m_\nu 31}+2\delta_{\lambda,\nu+2}b_{\nu+2,m_\lambda}^{\nu m_\nu 21} . \tag{A5}$$

For $(n=4, j=2)$ Eq. (36b) gives zero for all coefficients with $\lambda\neq\nu+4$. When $\lambda=\nu+4$, Eq. (37a) gives

$$(2\nu+12)b_{(\nu+4)m_\lambda}^{\nu m_\nu 42}$$
$$=\sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle (\nu+4)m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 31}$$
$$+(2\nu+11)b_{(\nu+4)m_\lambda}^{\nu m_\nu 31} . \tag{A6}$$

For $(n=4, j=1)$, Eq. (35) gives for the case $\lambda\neq\nu+4$

$$\{-\lambda(\lambda+4)+(\nu+4)(\nu+8)\}b_{\lambda m_\lambda}^{\nu m_\nu 41}$$
$$=\sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle \lambda m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 31}$$
$$+(2\nu+11)b_{\lambda m_\lambda}^{\nu m_\nu 31} , \tag{A7}$$

while for the case $\lambda=\nu+4$, Eq. (37a) gives

$$(2\nu+12)b_{(\nu+4)m_\lambda}^{\nu m_\nu 41}$$
$$=\sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle (\nu+4)m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 30}$$
$$+(2\nu+11)b_{(\nu+4)m_\lambda}^{\nu m_\nu 30}+2b_{(\nu+4)m_\lambda}^{\nu m_\nu 31}-b_{(\nu+4)m_\lambda}^{\nu m_\nu 42}=0 . \tag{A8}$$

For $(n=4, j=0)$, Eq. (35) gives for the case $\lambda\neq\nu+4$

$$\{-\lambda(\lambda+4)+(\nu+4)(\nu+8)\}b_{\lambda m_\lambda}^{\nu m_\nu 40}$$
$$=\sum_{\lambda'=0}^{\infty}{}' \sum_{m_{\lambda'}=0}^{\lambda'/2}{}' \frac{\langle \lambda m_\lambda \mid C \mid \lambda' m_{\lambda'}\rangle}{\kappa} b_{\lambda' m_{\lambda'}}^{\nu m_\nu 30}$$
$$+(2\nu+11)b_{\lambda m_\lambda}^{\nu m_\nu 30}-(2\nu+12)b_{\lambda m_\lambda}^{\nu m_\nu 41}+2b_{\lambda m_\lambda}^{\nu m_\nu 31} , \tag{A9}$$

while for the case $\lambda=\nu+4$, the standardization convention in Eq. (37b) gives zero for the coefficients.

APPENDIX B: SOLUTION OF THE FOCK EQUATIONS IN THE APPROXIMATION THAT THE MATRICES Λ^2 AND C HAVE A SINGLE DIAGONAL ELEMENT

When the system wave function is approximated by a single hyperspherical harmonic,

$$\Psi_\nu(R;\Omega)=F_\nu(R)u_{\nu m_\nu}(\Omega) , \tag{B1}$$

the resulting Fock expansion can be summed analytically since Λ^2 can be replaced by $\nu(\nu+4)$ and the Coulomb matrix by the number $\langle \nu m_\nu \mid C \mid \nu m_\nu\rangle \equiv C_\nu$.

The first coefficient, $U_0^{(0)}$, is equal to $u_{\nu m_\nu}(\Omega)$ and is proportional to all other $U_n^{(j)}$. It is then straightforward to infer that $U_n^{(j>0)}=0$ for all n and that for $n\geq 1$

$$U_n^{(j=0)}=\frac{-C_\nu/\kappa+2(\nu+n)+3}{-\nu(\nu+4)+(n+\nu)(n+\nu+4)}U_{n-1}^{(j=0)} . \tag{B2}$$

By iteration one finds

$$U_n^{(0)}=\prod_{m=1}^{n}\left[\frac{2(m+\nu+\frac{3}{2}-C_\nu/2\kappa)}{m(m+2\nu+4)}\right]u_{\nu m_\nu}(\Omega)$$
$$=\frac{2^n}{n!}\frac{\Gamma(n+\nu+\frac{5}{2}-C_\nu/2\kappa)\Gamma(2\nu+5)}{\Gamma(\nu+\frac{5}{2}-C_\nu/2\kappa)\Gamma(n+2\nu+5)}u_{\nu m_\nu}(\Omega) . \tag{B3}$$

Upon substitution into the Fock expansion in Eq. (11) we recognize that

$$\psi_{\nu m_\nu}(R)=(\kappa R)^\nu e^{-\kappa R}\sum_{n=0}^{\infty}\frac{\Gamma(n+\nu+\frac{5}{2}-C_\nu/2\kappa)}{\Gamma(\nu+\frac{5}{2}-C_\nu/2\kappa)}$$
$$\times\frac{\Gamma(2\nu+5)}{\Gamma(n+2\nu+5)}\frac{(2\kappa R)^n}{n!}$$
$$=(\kappa R)^\nu e^{-\kappa R}\,{}_1F_1(\nu+\tfrac{5}{2}-C_\nu/2\kappa \mid 2\nu+5 \mid 2\kappa R) . \tag{B4}$$

That the hyperspherical wave equation has solutions of the form (B4) for Coulomb potentials C_ν/R has been demonstrated by Peterkop.[43]

One generates in the usual way a Rydberg series of bound states by discarding irregular solutions, which increase with small R as $1/R^{\nu+1}$, by setting

$$\Gamma(\nu+\tfrac{5}{2}-C_\nu/2\kappa)=0 . \tag{B5}$$

Then

$$E_{n'}^{\nu}=\frac{(C_\nu/2)^2}{2(n'+\frac{5}{2}+\nu)^2} , \tag{B6}$$

where $n'=0,1,2,\ldots$ is the radial quantum number. When $a=-n'$, the function ${}_1F_1(a \mid b \mid 2\kappa R)$ in (B4) is a polynomial of degree n'.

The energy E_0^0 from Eq. (B6) represents an upper bound on the true ground-state energy of two-electron systems. That the single hyperspherical harmonic approximation to ground-state wave functions is a poor one is already known from the success of the adiabatic approximation in describing low-lying states of two-electron atoms. For example, for helium we find that $C_{\nu=0}=11.180\,38$, and from Eq. (B6) we have

$$E_0^0(\mathrm{He})=-2.5000 \text{ a.u.} ,$$

which is a poor approximation to the Pekeris[44] value of $E_{gs}(\mathrm{He})=-2.9037$ a.u.

Nevertheless, (B3), (B4), and (B6) provide useful checks on our Fock code. We find that, with the restriction to a single hyperharmonic, our code calculates Fock coefficients in agreement with (B3). Moreover, when the energies are specified according to (B6), our Fock coefficients for $n>n'$ return the value zero, so that our Fock expansion numerically truncates, as required, to a polynomial of order n' and therefore to a regular solution which is finite at $R=0$.

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