Application of the Fock Expansion to Doubly Excited States of the Helium Atom

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The formal properties of the Fock expansion of helium-atom wave functions provide a frame within which the behavior of doubly excited ^1P states can be simply expressed. The convergence of the expansion is investigated.

I. APPLICATION TO DOUBLY EXCITED STATES OF HELIUM

FOR many applications of wave mechanics to two-electron systems it is important to have a good representation of the wave function in the region of configuration space where both electrons are near the nucleus. This is just the region where most methods represent the wave function in only an average way. An expansion developed by Fock[1] and generalized by Demkov and Ermolaev[2] seeks to represent the wave function exactly when both electrons are near the nucleus. The method has been applied by Ermolaev and Sochilin[3] and by Frankowski and Pekeris[4] to the calculation of ground-state energies of atomic helium in the nonrelativistic approximation with favorable results.

It has become evident in the last few years that $^1P^0$ auto-ionizing states of helium converging to the $n=2$ level of the positive helium ion exhibit remarkable properties which have been qualitatively related to the magnitude of their wave functions in the region of $\mathbf{r}_1,\mathbf{r}_2$ space where both electrons are near the nucleus.[5,6] In the ultraviolet absorption experiments of Madden and Codling, two Rydberg series of such levels were found which exhibited greatly different decay widths and oscillator strengths. Cooper, Fano, and Prats[6] argued that the existence of two ^1P series with greatly different widths and oscillator strengths would imply that the wave functions for these states could not be of the form $2snp$ and $2pns$, but would instead be $\frac{1}{2}\sqrt{2}(2snp+2pns)$ and $\frac{1}{2}\sqrt{2}(2snp-2pns)$. The states whose wave functions were $\frac{1}{2}\sqrt{2}(2snp+2pns)$ were called $2n+$ states and those with wave functions $\frac{1}{2}\sqrt{2}(2snp-2pns)$ were called $2n-$ states. In the region near the nucleus, the plus state is much larger than the corresponding minus state, hence its overlap with the ground state would be much larger. This would then account for the difference in widths and oscillator strengths of the two series. Detailed calculations of the doubly excited ^1P wave functions did indeed bear out this interpretation,[7-9] but also predicted the existence of a third series called $2pnd$, whose states have decay widths smaller by a factor of 10 than the $2n-$. An analysis[10] of the wave functions for these states showed that their magnitude was also very small near the nucleus even though they contained large mixtures of the $2snp$ and $2pns$ configurations. The design of detailed calculations has not been suited to provide any clear indication of the physical mechanism from which these properties arose. On the other hand, the classification scheme of Copper, Fano, and Prats, while certainly relevant, did not provide a framework within which to include three rather than two series. The physical mechanism is still unknown, but we will show in this paper how the Fock expansion may provide a more suitable framework for the description of the empirical evidence. A method of approximate solution of the Schrödinger equation within this framework is being developed.

Previous applications of the Fock expansion have been limited to obtaining good trial functions to use in a variational principle for lower-lying bound-state energy levels. For these purposes, a proof of the convergence of the expansion was not of great importance. Since, in this paper, we are assuming a general validity of the Fock expansion over an extended energy range, the question of its convergence is much more important. It will be shown that for sufficiently small values of the mean-square distance of the two electrons from the nucleus, the Fock expansion converges in the sense that the integral of the square of the wave function over all coordinates, except the mean-square distance of the two electrons from the nucleus, converges.

The basic idea of the Fock expansion is to write the wave equations for two electrons in the field of an atomic nucleus in the coordinates $R=(r_1^2+r_2^2)^{1/2}$ and five angular coordinates,[11] then expand the wave

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function in powers of R and $\ln R$. The five angular coordinates may be chosen in a variety of ways, but for definiteness the set $\hat{r}_1,\hat{r}_2$, and α, where $\tan\alpha=r_2/r_1$, will be used here.

The wave equation for the helium atom when written in the coordinates $\hat{r}_1$, $\hat{r}_2$, R, and α, and in atomic units is[12]

$$\left[\frac{d^2}{dR^2}+\frac{5}{R}\frac{d}{dR}-\frac{\Lambda^2}{R^2}+\frac{C(\alpha,\theta_{12})}{R}+k^2\right]\psi=0, \quad (1)$$

where

$$\Lambda^2=-\frac{1}{\sin^2\alpha\cos^2\alpha}\frac{d}{d\alpha}\left(\sin^2\alpha\cos^2\alpha\frac{d}{d\alpha}\right)+\frac{\mathbf{L}_1^2}{\sin^2\alpha}+\frac{\mathbf{L}_2^2}{\cos^2\alpha}, \quad (2)$$

and

$$C(\alpha,\theta_{12})=2z/\sin\alpha+2z/\cos\alpha-2/(1-\sin2\alpha\cos\theta_{12})^{1/2}, \quad (3)$$
$$\cos\theta_{12}=\hat{r}_1\cdot\hat{r}_2.$$

The operators $\mathbf{L}_1^2$ and $\mathbf{L}_2^2$ are the usual orbital angular-momentum operators for the two electrons. The operator Λ^2 is Casimir's operator for the O_6 group.

Dividing (1) by $-k^2$, expressing R in units of ik, expanding ψ as

$$\psi=e^{-R}\sum_{n=0}^{\infty}\sum_{j=0}^{[n/2]}R^{n+\nu}(\ln R)^j U_n^{(j)}(\alpha,\hat{r}_1,\hat{r}_2)/j!,$$

where

$$[n/2]=n/2, \quad n \text{ even}$$
$$=(n-1)/2, \quad n \text{ odd}, \quad (4)$$

substituting into (1), and equating to zero like powers of R and $\ln R$ gives

$$[-\Lambda^2+(n+\nu)(n+\nu+4)]U_n^{(j)}$$
$$=[-C/(ik)+2(n+\nu)+3]U_{n-1}^{(j)}$$
$$+2(n+\nu+2)U_n^{(j+1)}-2U_{n-1}^{(j+1)}+U_n^{(j+2)}, \quad (5)$$

where it is understood that $U_n^{(j)}=0$ if $j>[n/2]$.

This is essentially the Fock expansion, although it differs in form from that employed by Fock in that the series is multiplied by e^{-R} and a factor of $1/j!$ is introduced to simplify the recurrence relation.

The method of solving the set of equations (5) has been discussed by Fock.[1] Here we are primarily interested in the equation for $U_0^{(0)}$, that is

$$\{-\Lambda^2+\nu(\nu+4)\}U_0^{(0)}=0, \quad (6)$$

which will be called the "idicial equation." Once this equation has been solved, all other coefficients are determined uniquely (for a given L,M, parity, and symmetry) with the exception that the coefficients $U_n^{(0)}$, where n is even, may have added to them any eigensolution of the equation

$$\{-\Lambda^2+(n+\nu)(n+\nu+4)\}f=0. \quad (7)$$

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We shall remove this arbitrariness by a standardizing convention, namely, by requiring $U_n^{(0)}$ to be orthogonal to all eigenfunctions of Λ^2 with eigenvalue $(n+\nu)\times(n+\nu+4)$ if n is even. Since each $U_n^{(j)}$ will now be unique, the power series will be unique. These solutions to the Schrödinger equation will be called "standardized solutions."

Different standardized solutions exist whose $U_0^{(0)}$'s are, respectively, equal to all different eigenfunctions of Λ^2. Because Λ^2 has an infinite number of eigenvalues, an infinite number of standardized solutions will exist for each energy. Solutions which satisfy the physical boundary conditions at large R should be regarded as superpositions of standardized solutions.

Equation (6) is an eigenvalue equation for ν which has been solved by Morse and Feshbach.[11] The solutions which have total $\mathbf{L}^2$ ($\mathbf{L}=\mathbf{L}_1+\mathbf{L}_2$) and parity as good quantum numbers, and which are symmetric or antisymmetric under exchange of the spatial coordinates of particles 1 and 2, can be taken to be

$$U_0^{(0)}=\tfrac{1}{2}\sqrt{2}[f_{l_1l_2mLM}(\alpha,\hat{r}_1,\hat{r}_2)+(-1)^{S+l_1+l_2-L+M}\times f_{l_2l_1mLM}(\alpha,\hat{r}_1,\hat{r}_2)] \quad (8)$$

with

$$S=\text{spin}, \quad \nu=l_1+l_2+2m, \quad m=0,1,\cdots$$

and

$$f_{l_1l_2mLM}(\alpha,\hat{r}_1,\hat{r}_2)$$
$$=\left[\frac{(l_1+l_2+2m)(m+l_1+l_2+2)!(m+l_1+\frac{3}{2})!}{m!(l_2+\frac{3}{2})!(m+l_1+\frac{3}{2})!}\right]^{1/2}$$
$$\times(\cos\alpha)^{l_1}(\sin\alpha)^{l_2}F(-m,m+l_1+l_2+2|l_2+\tfrac{3}{2}|\sin^2\alpha)$$
$$\times\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2).$$

The function $F(-m,m+l_1+l_2+2|l_2+\frac{3}{2}|\sin^2\alpha)$ is a Jacobi polynomial in $\sin^2\alpha$ and $\mathcal{Y}_{l_1l_2LM}$ is defined in terms of spherical harmonics and Wigner coefficients as

$$\mathcal{Y}_{l_1l_2LM}(\hat{r}_1,\hat{r}_2)=\sum_{\mu}Y_{l_1,\mu}(\hat{r}_1)Y_{l_2M-\mu}(\hat{r}_2)\times(l_1,\mu,l_2M-\mu|l_1l_2LM). \quad (9)$$

The symmetry or antisymmetry of (8) under exchange of the spatial coordinates of particles 1 and 2 follows from the relation[11]

$$F(-m,m+a|c|Z)=\frac{\Gamma(c)\Gamma(1-c+a+m)}{\Gamma(1+a-c)\Gamma(m+c)}\times F(-m,m+a|a-c+1|1-Z) \quad (10)$$

and the fact that $\sin\alpha\rightarrow\cos\alpha$ under interchange of the particles. The parity of $f_{l_1l_2mLM}(\alpha,\hat{r}_1,\hat{r}_2)$ under inversion of the coordinate axes is $(-1)^{l_1+l_2}=(-1)^{\nu}$, where $\nu=l_1+l_2+2m$.

The first coefficient $U_0^{(0)}$ is determined by its quantum numbers, ν, l_1, l_2, L, and M. The higher coefficients are completely determined by recurrence relation (5), the standardizing convention, and the requirement that

the wave function ψ have L, M, and parity as good quantum numbers and that it be either symmetric or antisymmetric under interchange of the spatial coordinate of the two electrons. Because Λ^2 and C do not commute, the different standardized solutions must be added together in such a way that the boundary conditions at large R are satisfied. To do this would require an explicit determination of all the $U_n^{(j)}$'s, which has not yet been done. For small values of R, however, only the first few terms of the power series will be important, and these few terms are determined to within a few constants. The central point of this paper is that even though the helium wave-function problem has not actually been solved, some of the properties of the doubly excited states of helium can be related to the order of magnitude of the first few constants. The wave functions for the doubly excited $^1P^0$ states of helium will be considered from this point of view.

Since ν has the parity of the wave function, its lowest value is 1 for $^1P^0$ states. The next lowest value is 3, but now there are two possibilities, $l_1+l_2=1$, $m=1$ and $l_1+l_2=3$, $m=0$. The fact that the wave functions for the $2n+$ states are large near the nucleus implies that they would have a large component of the power series which starts as R to the first power; conversely, the $2n-$ states would have a small component of the power series which starts as R to the first power and a large component which starts as R to the third power. If the zero-order wave functions of Cooper *et al.* are expanded as power series in R, this is indeed found to be the case. In fact, if instead of the function $2snp-2pns$ one chooses $a(2snp)-b(2pns)$ as a zero-order solution, where $b/a=\frac{2}{3}\sqrt{3}(1-1/n^2)^{1/2}\approx 1.155$, one finds that such a function has a series which starts as R to the third power. Furthermore, the coefficient of R^3 is a constant times $\sin\alpha F(-1, 4|\frac{5}{2}|\sin^2\alpha)Y_{1M}(\hat{r}_1)$, as it must be since the indicial equation also applies to the zero-order helium wave functions. (This eigenfunction corresponds to $\nu=3$, $l_1+l_2=1$, $m=1$.) Near $R=0$, the term $-\Lambda^2/R$ in Eq. (1) is approximately $-\nu(\nu+4)/R^2$, which can be viewed as a generalized angular-momentum barrier. Electrons in the minus states see a higher generalized angular-momentum barrier than electrons in the plus states.

II. CONVERGENCE OF THE FOCK EXPANSION

The Fock expansion will be a solution of the Schrödinger equation in the region over which the series converges. The physical solutions are superpositions of the standardized solutions, and it is possible that a superposition of the standardized solutions will converge even though the standardized solutions diverge. However, the convergence of the standardized solutions would be a sufficient condition for the convergence of the physical solutions.

In this section, it will be shown that the Fock expansion converges in the sense that $\psi(R,\alpha,\hat{r}_1,\hat{r}_2)$ is square integrable over the five angular coordinates for $|R|<\frac{1}{2}$, where R is measured in units of ik.

The analysis of convergence is most conveniently carried out if the recursion relation (5) is expressed in integral form. The modified Green's functions for the operator $\{-\Lambda^2+(n+\nu)(n+\nu+4)\}$ is, in the coordinated representation,

$$G_{n+\nu}=\sum_m{}' \sum_{l_1 l_2} \frac{f_{l_1 l_2 m LM}(\alpha,\hat{r}_1,\hat{r}_2) f_{l_1 l_2 m LM}(\alpha',\hat{r}_1,\hat{r}_2)}{\lambda(\lambda+4)-(n+\nu)(n+\nu+4)}, \quad (11)$$

where $\lambda=l_1+l_2+2m$, and the prime means that the terms for which $\lambda=n+\nu$ are omitted. It is more convenient to sum over the variable λ rather than m, and to this end the basis functions are redefined as $f_{l_1 l_2 m LM}=f_{l_1 l_2 LM}{}^{\lambda}$. In the following discussion the subscripts LM can be dropped since they are not summed over. For conciseness, the integral $\int G_{n+\nu}(\alpha,\hat{r}_1,\hat{r}_2,\alpha',\hat{r}_1,\hat{r}_2')\times\phi(\alpha,\hat{r}_1',\hat{r}_2)d\Omega$ will be written in operator form as $G_{n+\nu}\phi$.

We shall now show that the function

$$\psi(R,\alpha,\hat{r}_1,\hat{r}_2)=\sum_{n=0}^{\infty}\sum_{j=0}^{[n/2]} R^{n+\nu}(\ln R)^j U_n{}^{(j)}(\alpha,\hat{r}_1,\hat{r}_2)/j! \quad (12)$$

is square integrable over α, $\hat{r}_1$, and $\hat{r}_2$ for sufficiently small values of R. This will be shown by using the fact that

$$\|\psi(R,\alpha,r_1,r_2)\|\equiv\left[\int d\Omega\,\psi^*\psi\right]^{1/2}$$

$$\leq\sum_{n=0}^{\infty}\sum_{j=0}^{[n/2]}|R|^{n+\nu}|\ln R|^j\|U_n{}^{(j)}\|/j!, \quad (13)$$

$d\Omega=\sin^2\alpha\cos^2\alpha d\alpha d\hat{r}_1 d\hat{r}_2$, and then showing that the series

$$\sum_{n=0}^{\infty}\sum_{j=0}^{[n/2]} R^{n+\nu}|\ln R|^j\|U_n{}^{(j)}\|/j! \quad (14)$$

converges.

The recurrence relation (5) when written in operator form is, for $\nu=0$,

$$U_n{}^{(j)}=G_n[C/(ik)+2(n+\nu)+3]U_{n-1}{}^{(j)}$$
$$+2(n+\nu+2)G_n U_n{}^{(j+1)}$$
$$-2G_n U_{n-1}{}^{(j+1)}+G_n U_n{}^{(j+2)}. \quad (15)$$

Taking the norm of both sides, one has

$$\|U_n{}^{(j)}\|\leq\{\|G_n C\|/|k|+(2(n+\nu)+3)\|G_n\|\}\|U_{n-1}{}^{(j)}\|$$
$$+2(n+\nu+2)\|G_n\|\times\|U_n{}^{(j+1)}\|$$
$$+2\|G_n\|\times\|U_{n-1}{}^{(j+1)}\|+\|G_n\|\times\|U_n{}^{(j+2)}\|\}. \quad (16)$$

It is shown in the Appendix that the norm of G_n is $1/[2(n+\nu)+3]$, so that

$$\|U_n{}^{(j)}\|\leq[K/(n+\nu+1)^{1/2}]\|U_{n-1}{}^{(j)}\|+\|U_n{}^{(j+1)}\|$$
$$+(\|U_n{}^{(j+1)}\|+2\|U_{n-1}{}^{(j+1)}\|+\|U_n{}^{(j+2)}\|)$$
$$\times[2(n+\nu)+3], \quad (17)$$

where $K=(2z+2)/|k|$. This inequality is valid when

$j<[n/2]$, but is not valid when $j=[n/2]$; consequently, (17) does not enable one to relate the norm of $U_n^{(j)}$ to the norm of $U_0^{(0)}$. To obtain an inequality which will enable us to relate $\|U_n^{(j)}\|$ to $\|U_0^{(0)}\|$, we must consider the conditions[1] which determine $U_n^{[n/2]}$. These conditions are that $U_n^{[n/2]}$ is a solution of

$$\{-\Lambda^2+(n+\nu)(n+\nu+4)\}U_n^{[n/2]}=0, \quad (18)$$

and that

$$[-C/ik+2(n+\nu)+3]U_{n-1}^{([n/2]-1)}+2(n+\nu+2)U_n^{[n/2]}$$

be orthogonal to all eigenfunctions of Λ^2 with eigenvalue $(n+\nu)(n+\nu+4)$. If g is a function identical to $U_n^{[n/2]}$, except that it is normalized to 1, the second condition becomes

$$\langle g|[-C/ik+2(n+\nu)+3]|U_{n-1}^{([n/2]-1)}\rangle +2(n+\nu+2)\langle g|U_n^{[n/2]}\rangle=0, \quad (19)$$

which implies

$$\langle g|U_n^{[n/2]}\rangle\leq|\langle g|C|U_{n-1}^{([n/2]-1)}\rangle|/[2(n+\nu+2)|k|]+|\langle g|U_{n-1}^{([n/2]-1)}\rangle|. \quad (20)$$

Now,

$$|\langle g|C|U_{n-1}^{([n/2]-1)}\rangle| \leq\{\langle g|C^2|g\rangle\}^{1/2}\{\langle U_{n-1}^{([n/2]-1)}|U_{n-1}^{([n/2]-1)}\rangle\}^{1/2} \leq[(2z+2)(n+\nu+2)^{1/2}]\|U_{n-1}^{([n/2]-1)}\|, \quad (21)$$

where the last step follows from Eq. (A10). Since $\|U_n^{[n/2]}\|=\langle g|U_n^{[n/2]}\rangle$, we have

$$\|U_n^{[n/2]}\|<[K/(n+\nu)^{1/2}+1]\|U_{n-1}^{[n/2]}\|, \quad K=(2z+2)/|k|. \quad (22)$$

Furthermore, (19) implies that (17) may be modified for $\|U_{n-1}^{[n/2]-1}\|$, so that

$$\|U_{n-1}^{([n/2]-1)}\| <[K/(n+\nu-1)^{1/2}+1]\|U_{n-2}^{([n/2]-1)}\|. \quad (23)$$

Inequalities (17), (22), and (23) enable us to relate $\|U_n^{(j)}\|$ to $\|U_n^{(0)}\|$, since, given a value for $\|U_0^{(0)}\|$, we could obtain an upper bound on $\|U_n^{(j)}\|$ by iterating (22) and (17). We may also find a set of numbers $A_n^{(j)}$ which will bound the number $\|U_n^{(j)}\|$ from above if we can find a set of $A_n^{(j)}$'s which satisfy (17), (22), and (23) with the inequality signs reversed and $A_0^{(0)}\geq\|U_0^0\|$. A set of coefficients $A_n^{(j)}$ chosen as follows satisfy these conditions

$$A_n^{(j)}=\{[K/(n+\nu+1)^{1/2}][K/(n+\nu-1)^{1/2}+1]\cdots (K/\nu^{1/2}+1)[K/(n+\nu)^{1/2}+2+2/(n+\nu+\tfrac{3}{2})] \times[K/(n+\nu)^{1/2}+2+2/(n+\nu+\tfrac{1}{2})]\cdots [K/(2j)^{1/2}+2+2/(2j+\nu+\tfrac{3}{2})]\}\|U_0^{(0)}\|, \quad j\neq[n/2],[n/2]-1, \quad (24)$$

$$A_n^{(j)}=[K/(n+\nu)^{1/2}+1][K/(n+\nu-1)^{1/2}+1]\cdots (K/\nu^{1/2}+1)\|U_0^{(0)}\|, \quad j=[n/2],$$

$$A_{n-1}^{(j)}=[K/(n+\nu-1)^{1/2}+1][K/(n+\nu-2)^{1/2}+1]\cdots (K/\nu^{1/2}+1)\|U_0^{(0)}\|, \quad j=[n/2]-1,$$

$$A_n^{(j)}=0, \quad j\geq[n/2].$$

We note that $A_n^{(0)}\geq A_n^{(j)}$, so that

$$\psi\leq R^\nu\|U_0\|+\sum_{n=1}^{\infty}|R|^{n+\nu}A_n^{(0)}\sum_{j=0}^{[n/2]}|\ln R|^j/j! \leq R^\nu\|U_0\|+Re^{|\ln R|}\sum_{n=0}^{\infty}A_{n+1}^{(0)}R^{n+\nu}. \quad (25)$$

By the ratio test, the series (24) converges for $|R|<\frac{1}{2}$; thus the Fock expansion converges in the sense that $\psi(R,\alpha_1,\hat{r}_1,\hat{r}_2)$ is square integrable over the angular coordinates.

This proof of convergence suffers from two limitations, namely, (1) the series has been shown to converge only for $R<\frac{1}{2}$, and (2) the series converges only in the sense that ψ is square integrable over the five angular coordinates. The first limitation is of no consequence for our purposes, since we are interested in the region where R is small; however, because we have bounded $\|G_{n+\nu}U\|$ by $\|G_{n+\nu}\|\,\|U\|$ we can expect that a better bound which takes into account the cancellation of contributions from different parts of the integration region would enable a larger radius of convergence to be shown.

The second limitation is not as serious as it appears. Although the proof given here could mean that the standardized solution ψ could have any finite number of points of discontinuity as a function of the five angular coordinates, the series quite likely has, at most, only one point of discontinuity which is at $\mathbf{r}_1=\mathbf{r}_2$. That this is the case can be seen by studying the Fock expansion for a wave function which is the solution of a Schrödinger equation with $1/r_{12}$ replaced by a finite multipole expansion. In this approximation, the Fock expansion can be shown to converge absolutely; hence the standardized solutions will be continuous functions of all five angular coordinates. The proof fails for the infinite multipole expansions, strongly indicating that the Fock expansion has at most one discontinuity and that this discontinuity would occur only at $\mathbf{r}_1=\mathbf{r}_2$. This possibility is reasonable since the potential is infinite at that point. One would have to include the requirement that the wave functions be continuous at $\mathbf{r}_1=\mathbf{r}_2$ in the boundary conditions on the physical solutions. This requirement in no way changes the discussion presented in Sec. I.

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APPENDIX

We must evaluate the norm of the operators

$$G_{n+\nu}C^{(i)}, \quad i=1,3$$

where the $C^{(i)}$'s are the three terms of C in Eq. (3).[13]

The norm of an operator A is defined as

$$\|A\|=\max_{\chi}\|A\chi\|, \tag{A1}$$

where $\|\chi\|=1$. Since $\|y\|=\langle y|y\rangle^{1/2}$, we have, for $A\chi=y$,

$$\langle y|y\rangle^{1/2}=\|A\chi\|=\langle A\chi|A\chi\rangle^{1/2}=\langle\chi|A^{\dagger}A\chi\rangle^{1/2}. \tag{A2}$$

We note that (A2) implies that the eigenvalues of $A^{\dagger}A$ are positive. Using the definition (A1), we see that the norm of $A^{\dagger}A$ is equal to the square root of the largest eigenvalue of $A^{\dagger}A$. If A is partially reduced, that is, diagonal in some of its quantum numbers, one has $\|A\|=\max_i\|A_i\|$, where $\|A_i\|$ is the ith nondiagonal submatrix of the block diagonal matrix A. (In our case, $G_{n+\nu}C^{(1)}$ and $G_{n+\nu}C^{(2)}$ are diagonal in l_1 and l_2; hence $i=[l_1l_2]$.)

Since the largest eigenvalue of $A_i^{\dagger}A_i$ is less than the trace of $A_i^{\dagger}A_i$, an upper limit to $\|A\|$ can be obtained by evaluating $\max_i[\text{trace } A_i^{\dagger}A_i]$. Furthermore, we note that trace $A_i^{\dagger}A_i=$ trace $A_iA_i^{\dagger}$.

Consider $G_{n+\nu}C^{(1)}$. In this case, $A_i=G_{n+\nu,l_1l_2}C^{(1)}$ and $A_i^{\dagger}=C^{(1)}G_{n+\nu,l_1l_2}$, where $G_{n+\nu,l_1l_2}$ is $PG_{n+\nu}P$ and P projects onto the space spanned by the functions $f_{l_1l_2}^{\lambda}$. Thus we have $A_iA_i^{\dagger}=G_{n+\nu,l_1l_2}C^{(1)2}G_{n+\nu,l_1l_2}$. In the $\alpha_1,\hat{r}_1,\hat{r}_2$ coordinate representation, $C^{(1)2}$ is $(2z)^2/\sin^2\alpha$, and a general diagonal element of $G_{n+\nu,l_1l_2}C^{(1)2}G_{n+\nu,l_1l_2}$ is

$$\frac{\langle f_{l_1l_2}^{\lambda}|\,(2Z)^2/\sin^2\alpha\,|f_{l_1l_2}^{\lambda}\rangle}{[\lambda(\lambda+4)-(n+\nu)(n+\nu+4)]^2}. \tag{A3}$$

The matrix element $\langle f_{l_1l_2}^{\lambda}|\,1/\sin^2\alpha\,|f_{l_1l_2}^{\lambda}\rangle$ can be evaluated by using the two forms of the Jacobi polynomials,

$$F(-n,n+a|c|Z)=\sum_{s=0}^{n}(-1)^s \times\frac{n!\Gamma(c)\Gamma(a+n+s)}{(n-s)!s!\Gamma(a+n)\Gamma(c+s)}Z^s \tag{A4}$$

and

$$F(-n,n+a|c|Z)=\frac{Z^{1-c}(1-Z)^{c-a}}{C(C+1)\cdots(c+n-1)}\frac{d^n}{dZ^n} \times[Z^{c+n-1}(1-Z)^{a+n+c}], \tag{A5}$$

and integrating by parts n times. The only term of (A4) which contributes is the term with $s=0$. After the differentiations are carried out, the integral which is left is a β function, and when that is expressed as a ratio of γ functions one obtains the result

$$\langle f_{l_1l_2}^{\lambda}|\,1/\sin^2\alpha\,|f_{l_1l_2}^{\lambda}\rangle=(\lambda+2)/[\Gamma^2(l_2+\tfrac{3}{2})(l_2+\tfrac{1}{2})]. \tag{A6}$$

The trace of $G_{n+\nu,l_1l_2}C^{(1)2}G_{n+\nu,l_1l_2}$ is

$$\frac{(2Z)^2}{\Gamma^2(l_2+\frac{3}{2})(l_2+\frac{1}{2})}\sum_{\lambda=0}^{\infty}{}'\frac{(\lambda+2)}{[(\lambda+2)^2-(n+\nu+2)^2]}, \tag{A7}$$

where λ goes over even or odd integers as l_1+l_2 is even or odd. An upper limit to the sum (A7) is

$$\int_{3/2}^{n+\nu+3/2}\frac{\mu d\mu}{[\mu^2-(n+\nu+2)^2]^2}+\int_{n+\nu+5/2}^{\infty}\frac{\mu d\mu}{(\mu^2-(\mu+\nu+2)^2)^2},$$

which is of the order $1/(n+\nu)$. Hence the norm of $G_{n+\nu}C^{(1)}$ is less than $2Z/(n+\nu)^{1/2}$. In a like manner, one sees that the norm of $G_nC^{(2)}$ is less than $2Z/(n+\nu)^{1/2}$.

A similar limit on the norm of $G_{n+\nu}C^{(3)}$ is obtained by expressing $G_{n+\nu}$ in the coordinate representation $\beta,\hat{\rho}_1,\hat{\rho}_2$, where $\boldsymbol{\rho}_1=(\mathbf{r}_1-\mathbf{r}_2)/\sqrt{2}$, $\boldsymbol{\rho}_2=(\mathbf{r}_1+\mathbf{r}_2)/\sqrt{2}$, and $\tan\rho=\rho_1/\rho_2$. In this representation, $G_{n+\nu}C^{(3)}$ is block diagonal and $C^{(3)2}$ is just $1/\sin^2\beta$, so we immediately obtain the limit $\|G_nC^{(3)}\|\leq 2/(n+\nu)^{1/2}$. The transformations from the representation $\alpha,\hat{r}_1,\hat{r}_2$ to the representation $\beta,\hat{\rho}_1,\hat{\rho}_2$ is just the "kinematical rotation" discussed by Smith.[12]

The inequality

$$\langle f_{l_1l_2}^{\lambda}|\,1/\sin^2\alpha\,|f_{l_1l_2}^{\lambda}\rangle\leq\lambda+2 \tag{A8}$$

actually holds for a more general function

$$f^{\lambda}=\sum_{l_1l_2}a_{l_1l_2}^{\lambda}f_{l_1l_2}^{\lambda}, \tag{A9}$$

provided that $\|f^{\lambda}\|=1$, since

$$\langle f^{\lambda}|\,1/\sin^2\alpha\,|f^{\lambda}\rangle=\sum_{l_1l_2}(a_{l_1l_2}^{\lambda})\langle f_{l_1l_2}^{\lambda}|\,1/\sin^2\alpha\,|f_{l_1l_2}^{\lambda}\rangle \leq(\lambda+2)\sum_{l_1l_2}(a_{l_1l_2}^{\lambda})^2=\lambda+2. \tag{A10}$$

This inequality and the corresponding one for $C^{(2)}$ and $C^{(3)}$ were used in deriving Eq. (24) of Sec. II.

The norm of $G_{n+\nu}$ itself is the eigenvalue of $G_{n+\nu}$ which is largest in absolute magnitude. A general eigenvalue of $G_{n+\nu}$ is

$$1/[\lambda(\lambda+4)-(n+\nu)(n+\nu+4)], \quad \lambda\neq n+\nu, \tag{A11}$$

which is largest in absolute value when $\lambda=n+\nu-1$ and is $-1/[2(n+\nu)+3]$. Thus the norm of $G_{n+\nu}$ is $1/(2(n+\nu)+3)$.

[13] Much of the discussion given in the Appendix is an application of the general methods of functional analysis which are expounded in A. E. Taylor, *Introduction to Functional Analysis* (John Wiley & Sons, Inc., New York, 1961), pp. 321–364.