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Pairing model for doubly excited atoms

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A model is investigated for doubly excited states, in which two electrons move on the surface of a spherical shell with restricted angular momentum to account for a hydrogenlike shell structure. Hybridized two-electron wave functions are constructed for the short-range part of the intrashell interaction potential using a modified version of hybridization theory originally developed by Pauling for molecules. The highest energy level obtained by this approach is identified as being invariant under SO(4) rotations on the restricted-shell basis, and is thus seen to be compatible with the SO(4) structure and rotation-vibration levels in a recent "supermultiplet" theory of doubly excited states. The highest energy level in each shell has ^1S symmetry, and is interpreted as a "perfect pairing" level which maximizes the electron density at values of the interelectronic angle $\theta_{12}=0°$, and hence is an exact eigenstate of a δ-function interaction between the two electrons. Formulas are described for the explicit θ_{12} dependence of related ^1S states for SO(4), and these give rise to approximate decoupling of the radial Schrödinger equation for two electrons in the same shell.

I. INTRODUCTION

Recent work[1-3] identified an interesting "supermultiplet" energy level structure for doubly excited atoms with two electrons in the same shell. The supermultiplets were interpreted using two highly different, yet evidently compatible views of the atom. In the first approach[1,2] supermultiplets are embedded within the framework of the group SO(4), which is the exact symmetry group of the problem in the high-Z limit. In the second approach[1,3,4] the intrashell levels were interpreted as being like cut-off spectra for a model of the atom as a quasirigid linear rotor-vibrator. The linear "geometry" of this structure is associated with a minimum in the electron repulsion operator $1/r_{12}$ when the interelectronic angle has the value $\theta_{12}=180°$. The vibrational part of the energy is then associated with small-angle bending motions of the electrons which decrease the value of θ_{12} from its equilibrium value. The compatibility of these two views of the spectrum was seen in a simple model of the atom with electrons on the surface of a spherical shell, and the electron-electron interaction near $\theta_{12}=180°$ described by dipole coupling of SO(4) Lie algebra generators for the electrons. At certain values of the coupling strength the model energy could be described exactly[2] using Casimir invariants for a subgroup chain $\mathrm{SO}(4)\supset\mathrm{SO}(3)$ for the two-electron group. Wave functions for states in irreducible representations of the coupled SO(4) have a configuration-mixed structure, which accounts for electron correlation and hence a relatively high degree of localization of electrons near the linear geometry. Those states were similar to ones identified earlier[5,6] for configuration mixing in hydrogenic orbital bases, whose properties with regard to θ_{12} have been illuminated in great detail.[7]

Although the SO(4) spherical-shell model could account for qualitative features of the intrashell spectrum, it did not address the question of what role the short-range part of the potential energy near $\theta_{12}=0$ plays in the approximate SO(4) symmetry of the two-electron atom. This region is obviously very important because of the Coulomb singularity. In the present paper we will investigate the spherical-shell model and show that there is an approximate SO(4) symmetry associated with states that are highly localized near $\theta_{12}=0$. Generators for the group turn out to be the same ones described earlier[2] for the SO(4) group which described electron correlation near $\theta_{12}=180°$. We thus offer further evidence for the compatibility of the SO(4) approach and the rotor-vibrator interpretation, as well as new insight to the electron correlation in these states. The approximate SO(4) symmetry we describe for the short-range interaction between two electrons in the same shell accounts for the fact noted in earlier SO(4) studies[1,5,6] with $1/r_{12}$, that generally the totally symmetric representation of the group describes the *highest* energy level in each shell. This is the state whose wave function remains invariant under the SO(4) group rotations, and it lies highest in energy because the short-range part of the potential is highly repulsive. This situation contrasts with the analogous situation in nuclear-shell models, where it is more appropriate to consider pairing of nucleons due to a short-range attraction. The pairing interaction is central to group theoretical seniority classifications of states in shell models, stemming from Racah's description of atomic multiplets.[8] Generalized Racah tensors have been constructed for SO(4) (Ref. 9), but that approach was found to give an inadequate description of the Coulomb repulsion in atoms. In the present paper we describe "pairing" of two electrons from a different point of view, which gives a more physical interpretation of the electron correlation and configuration mixing in terms of orbital "hybridization" for the electron pair.[2,10] In particular, we demonstrate in Sec. II the extension of ideas originally introduced by Pauling[11] to describe orbital hybridization in molecules, to include now similar geometrical effects for the electron-pair correlation. The connection of this approach to SO(4) is established for the spherical-shell model in Sec. III. Correlated SO(4) channels and coupled radial equations are described in Sec. IV, and Sec. V contains a summary of our results.

II. HYBRIDIZED PAIR WAVE FUNCTIONS

We consider the angular correlation of two electrons interacting within the same shell, neglecting radial parts of the wave function entirely. Each shell is labeled by a principal quantum number N, and the orbital-angular-momentum quantum numbers for the electrons are restricted to the hydrogenlike values $0 \leqslant l_1, l_2 \leqslant N-1$. Only spatial wave functions will be described, since spin for two electrons is linked by the Pauli principle to the spatial exchange symmetry $P_{12} = +1$ ($S=0$) or $P_{12} = -1$ ($S=1$). We use the usual labels L and M to describe rotational symmetry of the atom, and thus explicitly consider only the case of an isolated electron pair. In a many-electron (i.e., more than two) system the spherical pair symmetry would be broken by the noncentral field of the other electrons. In the limit of very high N, the two-electron model includes a large number of angular-momentum states for each electron, and hence would begin to approach the classical limit of charged particles on a spherical shell.

In order to treat the problem of electron correlation and configuration mixing in the intrashell model, we now develop a simple hybridization method for configuration mixing which is qualitatively consistent with results from extensive computed double excitation spectra.[1,2] Pauling's original ideas about hybridization were an attempt to explain simple bond angles in molecules,[11] including only angular parts of the wave function. Zimmerman and Rysselberghe have described some aspects of hybridization including radial effects.[12] The key idea in Pauling's approach is maximization of the bond strength; this is achieved by taking suitable linear combinations of atomic orbitals $Y_{lm}(\theta,\phi)$ so as to maximize the value of a normalized wave function along the z axis. The sp^3 hybridization orbital, for example, is described by the linear combination $s+\sqrt{3}\,p_z$ for the $N=2$ shell. The two-electron intrashell states are described by analogous mixing of configurations:

$$\Psi_{NLM} = \sum_{l,l'} a^L_{ll'} \chi_{ll',LM} , \tag{1}$$

in which $a^L_{ll'}$ is a linear mixing coefficient and $\chi_{ll',LM}$ represents the Clebsch-Gordan-coupled configuration

$$\chi_{ll',LM} = \sum_{m,m'} \langle lm, l'm' | LM \rangle \times Y_{lm}(\theta_1, \phi_1) Y_{l'm'}(\theta_2, \phi_2) . \tag{2}$$

Normally the configuration-mixing coefficients are found by numerical procedures involving diagonalization of the energy matrix in the configuration basis. Here we consider the possibility of obtaining reasonable estimates of mixings for some of the highest energy levels in each shell, using a hybridization approach that can be solved in closed form. The quantity we consider analogous to Pauling's bond strength in molecules will be called the electron "pair strength;" it is the value of the function Ψ_{NLM} when the two electrons occupy the same position in space, with $\theta_1 = \theta_2 \equiv \theta$ and $\phi_1 = \phi_2 \equiv \phi$. From standard angular-momentum coupling theory we find the pair-strength function is given generally by the formula

$$S_{LM} = \frac{(-1)^L}{\sqrt{4\pi}} Y_{LM}(\theta,\phi) \sum_{l,l'} a^L_{ll'} D^L_{ll'} , \tag{3}$$

with the coefficient defined in terms of a 3-j angular-momentum symbol as

$$D^L_{ll'} = [(2l+1)(2l'+1)]^{1/2} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} . \tag{4}$$

Owing to symmetry properties of the 3-j symbol, the pair-strength function S_{LM} vanishes unless the total parity satisfies $\Pi(-1)^L = +1$ and the exchange is $P_{12} = +1$. In addition to the pair strength, it will be convenient to define also a related pair density function which is independent of direction:

$$\rho_L = \frac{16\pi^2}{(2L+1)} \sum_M |S_{LM}|^2 . \tag{5}$$

This represents the mean-square pair strength over the surface of the spherical shell.

Following Pauling's procedure for maximizing the molecular bond strength,[11] we maximize the pair-strength function subject to constant normalization on the sphere. This leads immediately to the result that $a^L_{ll'} \propto D^L_{ll'}$, and taking into account the normalization of states to unity we find

$$a^L_{ll'} = D^L_{ll'} / \rho_L^{1/2} , \tag{6a}$$

$$\rho_L = \sum_{l,l'} (D^L_{ll'})^2 \,. \tag{6b}$$

Notice the method only provides one set of mixing coefficients for each value of L, and this is presumably related to the state with highest repulsion energy. In addition, although we speak directly to the problem of a hydrogenlike shell with the restriction $0 \leq l \leq N-1$ for each shell, the same hybridization procedure may be used for other restrictions on l and l' in Eq. (1). Comparisons between the coefficients for maximum pair strength and ones from numerical calculations with the repulsion operator $1/r_{12}$ will be given in Sec. III.

Our procedure for estimating configuration-mixing coefficients of high-energy states has thus far emphasized a hybridization picture of the electron correlation in these states. In Pauling's molecular theory, other equivalent orbitals are found by orthogonalization procedures.[11] Similarly, we would like to devise a procedure for extending the classification of two-electron states to include levels not described by the condition of maximum pair strength. This question will be considered in Sec. III in connection with approximate invariance.

We conclude this section by noting an important link between the hybridization approach and the usual pairing concept from atomic- and nuclear-shell theories.[8,13] Specifically, the states we have constructed for maximum pair strength are found to be eigenstates of a short-range interaction potential $V_\delta = 2\delta(1-\cos\theta_{12})$ in the finite configuration basis for each shell N. This leads to a set of equations involving a pairing repulsion energy ϵ_L:

$$D^L_{ll'} \sum_{j,j'} D^L_{jj'}\, a^L_{jj'} = \epsilon_L\, a^L_{ll'} \,. \tag{7}$$

The coefficients we described in Eq. (6) are solutions of Eq. (7) with $\epsilon_L = \rho_L$. All other states, which are orthogonal to the maximum pair-strength ones, have zero repulsion energy. In the two-electron atomic-shell model this degeneracy would be broken by the full Coulomb repulsion operator including all interelectronic angles $0 \leq \theta_{12} \leq 180°$, in addition to the short-range part. Values of the electron pair-strength density ρ_L for several low-lying shells are given in Table I. These values were computed specifically for a hydrogenlike shell, with the angular-momentum restriction $0 \leq l, l' \leq N-1$, and are seen to satisfy the ordering $\rho_0 > \rho_1 > \rho_2 > \cdots > \rho_{2N-2}$. The ${}^1S^e$ density is found generally to be given by the formula $\rho_0 = N^2$, and has the highest repulsion energy. The ${}^1P^o$ level has $\rho_1 = N(N-1)$. We can also derive the following sum rule for pair-strength densities in each shell:

$$\sum_{L=0}^{2N-2} (2L+1)\rho_L = (\rho_0)^2 = N^4 \,. \tag{8}$$

TABLE I. Pair density function [cf. Eq. (6b)] ρ_L for intrashell states with maximum electron pair strength at $\theta_{12} = 0°$.

N	ρ_0	ρ_1	ρ_2	ρ_3	ρ_4	ρ_5	ρ_6
1	1						
2	4	2	$\frac{6}{5}$				
3	9	6	$\frac{162}{35}$	$\frac{90}{35}$	$\frac{50}{35}$		
4	16	12	$\frac{212}{21}$	$\frac{152}{21}$	$\frac{1240}{231}$	$\frac{700}{231}$	$\frac{700}{429}$

We note that these results describe only the states with maximum pair strength. Energy levels for doubly excited intrashell states of helium were illustrated in Fig. 7 of Ref. 2 for each shell $N \leq 5$. It is very clear there that the ordering of states for the highest energy for each L has an overall L dependence much like that of ρ_L described above. The correspondence between values of L for maximum pair strength and the supermultiplet quantum numbers d and T is found to be described by the formula $L = 2d - T$ with the values $T = 0$ and 1 for even and odd L, respectively. The even values of L are found to correspond with the highest energy level in the largest rotorlike series $[2d, 0]^+$ in each d supermultiplet of Ref. 2, while the odd values of L correspond with the second largest rotor series $[2d-1, 1]^+$ in that classification of states. This illustrates the basic difference between the present approach and the rotor-vibrator interpretation of doubly excited states.[1-3] The rotor-vibrator model focuses on low-lying levels related to the long-range part of the electron repulsion near $\theta_{12} = 180°$, while the maximum pair-strength approach focuses on high-lying intrashell levels related to the behavior of the repulsion near $\theta_{12} = 0°$. Our analysis of levels in helium shows that the condition of maximum pair strength at $\theta_{12} = 0°$ does indeed give a reasonable qualitative description of this part of the spectrum. We have investigated the possibility that low-lying states might also have a similar description with a maximum pair-strength function defined at $\theta_{12} = 180°$ instead of 0°. However, this approach is found *not* to give a useful set of configuration mixings for electron correlation.

III. APPROXIMATE SO(4) SYMMETRY

In this section we will demonstrate an approximate SO(4) symmetry for the short-range part of the intrashell repulsion as described by the condition of maximum pair strength. In view of the equivalence of the pair-strength hybridization approach and a δ-function pairing model, our work is implicitly related to a generalized Racah seniority classification of terms. Although generalized SO(4) seniority-type methods have been considered for mixed atomic configurations in the past[9,14-16] they failed to uncover the approximate SO(4) symmetry which was eventually found[5,6] for two-electron atoms by other means. The main difficulty lies in the assignment of relative phases for coupled two-electron generators, as described in Ref. 2. In the hydrogen atom the SO(4) degeneracy group is generated locally by the angular-momentum operator $\vec{l}=\vec{r}\times\vec{p}$ and the Pauli-Lenz operator $\vec{b}=N[\vec{p}(\vec{r}\cdot\vec{p})-\vec{r}(p^2-1/r)]$ for each shell. When constructing representations of the group for two electrons, one is faced with the choice of two SO(4) groups generated by $\vec{L}=\vec{l}_1+\vec{l}_2$ and $\vec{A}=\vec{b}_1+\vec{b}_2$, or $\vec{L}$ and $\vec{B}=\vec{b}_1-\vec{b}_2$. The assignment of the group with $\vec{B}$ as the "physical" one for electron correlation has in the past been made by investigation of matrix elements of generators and comparisons with actual configuration mixings for the operator $1/r_{12}$. Additional justification for this choice was seen in the earlier angular correlation model[2] based on leading-order contributions to the electron repulsion near $\theta_{12}=180°$. Our present work is important because it identifies a simple criterion for assigning relative phases of generators in a generalized seniority classification based on intrashell δ-function pairing. Specifically, we find that the Lie algebra generators must be antisymmetric under simultaneous application of the operations for particle exchange, time-reversal, and (Hermitian) conjugation.

A. Unitary invariance of the $^1S^e$ state

We begin our analysis of approximate invariance of the states with maximum pair strength by considering the totally symmetric $^1S^e$ state. This state has the strongest pairing of electrons near $\theta_{12}=0$, and therefore has the highest repulsion energy within a shell. Neglecting an overall normalization factor, we see from Eqs. (1) and (6) the wave function

$$\Psi_{00}=\sum_{l,m}Y^*_{lm}(\theta_1,\phi_1)Y_{lm}(\theta_2,\phi_2)\,, \tag{9}$$

in which we have used the standard Condon-Shortley convention for angular wave functions. The two-electron wave function Ψ_{00} is real, and is symmetric with respect to parity inversion and exchange of electrons 1 and 2. Using the notation $\underline{Y}$ for a column matrix which contains the complete intrashell one-electron orbital basis, we note Eq. (9) may be written more compactly as

$$\Psi_{00}=\underline{Y}_1^\dagger\underline{Y}_2=\underline{Y}_2^\dagger\underline{Y}_1\,. \tag{10}$$

This form of the wave function emphasizes the construction of the $^1S^e$ pairing state as a unitary invariant, for if we change each one-electron orbital basis by the unitary transformation $\underline{Y}=\underline{U}\underline{Y}$, then

$$\Psi_{00}=\underline{X}_1^\dagger\underline{U}^\dagger\underline{U}\underline{X}_2=\underline{X}_1^\dagger\underline{X}_2\,, \tag{11}$$

due to the unitary condition $\underline{U}^\dagger\underline{U}=1$. For example, the $N=2$ shell basis may be described with a set of four equivalent sp^3 hybridized orbitals $\chi_1,\chi_2,\chi_3,\chi_4$ for each electron. The angle between these orthogonal orbitals is 109.47°, representing a tetrahedral geometry associated with sp^3 hybridization. From Eq. (11) we see the $^1S^e$ state with maximum pair strength may be written as

$$\Psi_{00}(N=2)=\sum_{k=1}^{4}\chi_k(1)^*\chi_k(2)\,. \tag{12}$$

A similar equation for sp^3 hybridization orbitals in the $N=2$ shell was found in previous work[10] using a different approach. Here we see that (12) describes an invariant for the unitary group in four dimensions. This is generalized to the unitary group in N^2 dimensions for the case of an arbitrary hydrogenlike shell. On the other hand, if we restrict the sum in Eq. (9) to include only a *single* value of l, we have the usual totally symmetric state for Racah-type seniority pairing.[17]

In the paragraph above we demonstrated one type of invariance for the $^1S^e$ state with maximum pair strength. We now describe a second type of invariance that is related to coupling of two electrons. We assume a unitary representation of a group G defined on the one-electron orbital basis. In the case of the hydrogenlike intrashell basis we will want to consider the group SO(4), but for the moment let us keep G arbitrary. We wish to construct a two-electron product representation of the group, denoted G_{12}, which satisfies the invariance condition

$$G_{12}\Psi_{00}=\Psi_{00}\,. \tag{13}$$

That is, we will assume the highest pair-strength state is totally symmetric with respect to all group operations. Obvious elements of G_{12} would, in general, include the total parity Π, two-particle exchange P_{12}, and time-reversal θ. The time-reversal operator is antiunitary,[18] and corresponds in the case of spatial wave functions to complex conjugation. In general, for two-particle states the operator satisfies $\theta\theta=1$, even when particle spin is taken into account.[18] The key point we wish to make is that the simple Kronecker product representation G_1G_2 does not, in general, satisfy the condition in Eq. (13), and is therefore not always the appropriate representation for carrying out a seniority analysis. This is a very subtle point that was evidently missed in the initial attempts to introduce a generalized seniority approach to atomic shells for two electrons.[9] In order to clarify this point, we now note that the correct way of coupling representations is

$$G_{12} = G_1 \theta^{\dagger} G_2 \theta \ , \tag{14}$$

except for an arbitrary overall phase which is unimportant. That G_{12} defined in Eq. (14) indeed satisfies Eq. (13) may be seen directly using the definition of Ψ_{00} in Eq. (10).

It is clear from Eq. (14) that the product representation is also unitary $G_{12}^{\dagger} G_{12} = 1$. In addition, the representation G_{12} may be seen to be symmetric under simultaneous application of the three operations: (i) Hermitian conjugation, (ii) particle exchange, and (iii) time reversal. The product of these three operations is thus related to a type of CPT invariance for two-particle intrashell coupling, in which the "*P*" stands for the exchange operation P_{12} instead of parity. For the special case of a Lie group defined by $G = \exp(ig)$ in which g represents an Hermitian Lie algebra generator, we find the following infinitesimal version of Eq. (14):

$$g_{12} = g_1 - \theta^{\dagger} g_2 \theta \, . \tag{15}$$

This satisfies $g_{12}^{\dagger} = g_{12}$ because g_1 and g_2 are Hermitian for unitary representations. In contrast to the group elements, which were symmetric under the CPT-like operation, the Lie algebra generator is seen to be antisymmetric under the same operation:

$$(\theta P_{12}) g_{12}^{\dagger} (\theta P_{12})^{\dagger} = -g_{12} \, , \tag{16}$$

due to the factor $i = \sqrt{-1}$ in the Lie group exponentiation.

B. Application to intrashell SO(4)

As we noted above in Sec. III A, the invariance criterion in Eq. (14) or the equivalent form in Eq. (16) have not been explicitly taken into consideration in previous work for intrashell two-electron atomic coupling. We therefore now consider their import for an SO(4) group defined on the one-electron intrashell angular basis. Without going into details of matrix elements of generators, we note that it is sufficient to consider a representation identical to the one generated by the angular momentum $\vec{l}$ and the Pauli-Lenz operator $\vec{b}$ for the hydrogen atom as described above in the introduction to this section. These SO(4) Lie algebra generators are seen to satisfy the properties $\vec{l}^{\dagger} = \vec{l}$, $\theta^{\dagger} \vec{l} \theta = -\vec{l}$, and $\vec{b}^{\dagger} = \vec{b}$, $\theta^{\dagger} \vec{b} \theta = \vec{b}$. Application of the invariance condition in Eq. (15) to the case $g = \vec{l}$ leads to the usual operator $\vec{L} = \vec{l}_1 + \vec{l}_2$ for the total angular momentum of two particles. In the case of $g = \vec{b}$, however, we note this procedure leads to the coupled two-particle SO(4) generator $\vec{B} = \vec{b}_1 - \vec{b}_2$, due to the fact that $\vec{b}$ is symmetric with respect to time reversal. We thus see that our assumption of invariance for the $^1S^e$ state with maximum pair strength is entirely consistent with previous work which identified $\vec{B}$ as the physical SO(4) generator for two-electron correlation. This is a very pleasing result, as it thereby establishes a link between SO(4) groups for long-range ($\theta_{12} = 180°$) and short-range ($\theta_{12} = 0°$) angular correlation effects.[1,2]

C. Configuration mixings

In Sec. III A we described conditions on group generators such that the $^1S^e$ state is left invariant under operations of the group for two electrons; in Sec. III B we investigated these using an SO(4) classification of hydrogenlike shells. We now show that the SO(4) group describes configuration-mixing wave functions which are very similar to the ones in Sec. II that were obtained from the condition of maximum pair strength. In this way we demonstrate that the SO(4) group generated by $\vec{L}$ and $\vec{B}$ describes an approximate symmetry for the short-range part of the intrashell interaction.

Tables II and III contain configuration-mixing coefficients for the highest intrashell state for each value of L in the shells $N = 3$ and 4, respectively. There are three sets of coefficients for each state, including ones from Eq. (6) for the method of maximum pair strength (MPS), SO(4) mixings, and ones computed from diagonalization of $1/r_{12}$ in a basis of coupled hydrogenic wave functions. The coefficients shown here include renormalization to ac-

TABLE II. Comparison of intrashell configuration mixings determined by the method of maximum pair strength (MPS), SO(4) theory, and numerical diagonalization of $1/r_{12}$ in a hydrogenic basis (HYD) for level $N = 3$. States for $L = 3$ and 4 are described with single configurations $(3p3d)\,^1F^0$ and $(3d3d)\,^1G^e$.

$^1S^e$	$3s3s$	$3p3p$	$3d3d$
MPS	0.333	−0.577	0.745
HYD	0.331	−0.586	0.739
SO(4)	0.333	−0.577	0.745
$^1P^0$	$3s3p$	$3p3d$	
MPS	0.577	−0.817	
HYD	0.634	−0.774	
SO(4)	0.667	−0.745	
$^1D^e$	$3s3d$	$3p3p$	$3d3d$
MPS	0.657	0.509	−0.556
HYD	0.571	0.563	−0.597
SO(4)	0.408	0.500	−0.763

TABLE III. Configuration mixings for intrashell states in the level $N=4$ (cf. Table II for $N=3$). Single-configuration states are $(4d4f)^1H^0$ and $(4f4f)^1I^e$.

$^1S^e$	$4s4s$	$4p4p$	$4d4d$	$4f4f$	
MPS	0.250	−0.433	0.559	−0.661	
HYD	0.265	−0.462	0.582	−0.615	
SO(4)	0.250	−0.433	0.559	−0.661	
$^1P^0$	$4s4p$	$4p4d$	$4d4f$		
MPS	0.408	−0.577	0.707		
HYD	0.480	−0.636	0.605		
SO(4)	0.500	−0.632	0.592		
$^1D^e$	$4s4d$	$4p4p$	$4d4d$	$4p4f$	$4f4f$
MPS	0.445	0.345	−0.376	−0.597	0.430
HYD	0.493	0.420	−0.433	−0.491	0.390
SO(4)	0.346	0.340	−0.458	−0.317	0.673
$^1F^0$	$4s4f$	$4p4d$	$4d4f$		
MPS	0.526	0.596	−0.607		
HYD	0.454	0.700	−0.551		
SO(4)	0.387	0.700	−0.600		
$^1G^e$	$4p4f$	$4d4d$	$4f4f$		
MPS	0.705	0.516	−0.487		
HYD	0.642	0.617	−0.456		
SO(4)	0.447	0.500	−0.742		

count for the exchange symmetry of each configuration. Hydrogenic SO(4) mixings including radial functions were described in earlier work as an approximate basis for diagonalizing $1/r_{12}$ (Refs. 5 and 6). This agreement is evident in the tables. We also see there a very close agreement with the MPS coefficients; the different methods give the same relative signs but slightly different magnitudes for coefficients. Both the SO(4) method and the MPS method give the same mixing coefficients for the $^1S^e$ state. It is interesting to note that in some cases the MPS mixings give a better description of $1/r_{12}$ mixings than do the SO(4) mixings. One advantage of the MPS approach is that it provides a nice interpretation of the electron correlation underlying these mixings, in terms of a strongly coupled pair that is associated with the short-range δ-function potential.

IV. θ_{12} DEPENDENCE OF SO(4) WAVE FUNCTIONS

In Sec. III we analyzed intrashell states with maximum pair strength and found they were described approximately by the group SO(4) defined on the intrashell angular basis. The SO(4) method is a very useful one because it also provides estimates of configuration mixings for other (i.e., non-MPS) states as well. These other levels are the ones that are degenerate with zero repulsion energy in the δ-function model. Earlier work has established that SO(4) mixings give a good description of electron correlation due to $1/r_{12}$ in low-lying intrashell levels. Our concern in the present section is with the explicit θ_{12} dependence of the SO(4) states approximated by the intrashell angular model. Kellman and Herrick[3] described a rotor-vibrator model of intrashell doubly excited states which gives a simple qualitative interpretation of the correlation. That model showed that the number of nodes in the θ_{12} part of the wave function was a constant $N-d-1$ within each d supermultiplet of levels; the full range of supermultiplets is described by the sequence $d=0,1,\ldots,N-1$ for each shell. One can therefore assess the overall θ_{12} correlation qualitatively, by considering only the lowest level in each supermultiplet. These so-called "intrinsic states" for intrashell supermultiplets were identified[3] as the set of $^1S^e$ levels for each shell. Levels with $L>0$ involve rotational excitations of the electrons; these distort the intrinsic distribution of θ_{12} but do not introduce new nodes to the wave function. In the present work we will describe the θ_{12} dependence of the set of intrinsic $^1S^e$ states for the angular intrashell SO(4) model. These results provide a very useful qualitative description of the types of angular correlation that will be important at very high N near the double detachment limit for doubly excited states.

A. Wave functions

The set of $^1S^e$ wave functions for each shell are described by functions ψ_{Nd} which depend on θ_{12} through the coordinate $x\equiv\cos\theta_{12}$. The quantum number $d=0,1,\ldots,N-1$ labels the sequence of d supermultiplets for the shell; the functions are real and satisfy the intrashell orthonormality

$$\int_{-1}^{+1}\psi_{Nd}\psi_{Nd'}\,dx=\delta_{dd'}\,. \tag{17}$$

Two functions in different shells are not orthogonal, because the intershell orthogonality would be contained in the radial part of the total wave function. Here we are considering only the set of angular SO(4) states for $L=0$. In describing our results it will be convenient to use a function H_{Nd} that is related to ψ_{Nd} by the formula

$$\psi_{Nd}=(d+\tfrac{1}{2})^{1/2}H_{Nd}\,. \tag{18}$$

From earlier descriptions (cf. Ref. 2) of angular SO(4) configuration mixings we find the $^1S^e$ spatial wave functions have the form

$$H_{Nd}=(-1)^{N-d-1}\sum_{l}(2l+1)W(aaaa;dl)P_l(x)(-1)^l\,, \tag{19}$$

where $P_l(x)$ is a Legendre function and $W(aaaa;dl)$ is a Racah coefficient with $a\equiv\frac{1}{2}(N-1)$. Equation (19) does not describe a particularly convenient form of the function H_{Nd} for interpreting the correlation near $x=-1$ for $\theta_{12}=180°$. Our investigation of this function shows it may be reexpressed in terms of a number of different orthogonal polynomials whose well-known properties may be exploited. We find these alternate forms by expanding the right-hand side (RHS) of (19) in a power series

$$H_{Nd}=\sum_k h_{dk}\left(\frac{x-1}{2}\right)^k, \tag{20}$$

in which the coefficient h_{dk} is found to be

$$h_{dk}=(-1)^{N-1-d}\sum_l(-1)^l(2l+1)W(aaaa;dl)\,\frac{(l+k)!}{(l-k)!} \tag{21a}$$

$$=(-1)^d\binom{N+k}{2k+1}\binom{2k+1}{k-d}. \tag{21b}$$

where $\binom{n}{m}=n!/m!(n-m)!$ is the binomial coefficient. The form of the coefficient h_{dk} permits us to recognize the S states for the angular SO(4) as being related to a Jacobi polynomial:

$$H_{Nd}=\left(\frac{1-x}{2}\right)^d P^{(2d+1,0)}_{N-d-1}(x), \tag{22}$$

which has several alternate representations involving

$$H_{Nd}=(-1)^d\sum_k\binom{N+d}{k}\binom{N-1-d}{k}\times\left(\frac{x+1}{2}\right)^k\left(\frac{x-1}{2}\right)^{N-1-k}, \tag{23}$$

a Gauss hypergeometric function,

$$H_{Nd}=\binom{N+d}{2d+1}\left(\frac{1-x}{2}\right)^d\times F(d+1-N,d+1+N;2d+2;\tfrac{1}{2}(1-x)), \tag{24}$$

and a Wigner d function,

$$H_{Nd}=\left(\frac{1-x}{2}\right)^{-1/2} d^{N-1/2}_{-d-1/2,d+1/2}(\theta_{12}), \tag{25}$$

among other forms.[19]

One sees from these formulas that wave functions with $d>0$ vanish when $\theta_{12}=0°$; each function has $N-1-d$ nodes in the range $0°<\theta_{12}<180°$. The state with maximum pair strength is the one with $d=0$, and from Eq. (19) this may be written in the form

$$H_{N0}=N^{-1}\sum_{l=0}^{N-1}(2l+1)P_l(\cos\theta_{12}), \tag{26}$$

which we identify as the same formula which describes a rotation of one of Pauling's equivalent atomic orbitals through an angle θ_{12} (Ref. 11). The ideal molecular bond angles in Pauling's hybridization theory are determined from nodes of the function, this giving the orthogonality of equivalent orbitals. It is very interesting that the same ideal bond angles for molecules arise here as the angles for nodes in the state of highest pair strength. Table IV gives the location of these nodes for several lower shells. At high N we may estimate these using an asymptotic expansion of the Jacobi function[19] representation of states in Eq. (22) when $N\gg d$:

$$H_{Nd}=\frac{\cos[N\theta_{12}-(d+\frac{3}{4})\pi]}{(\sin\frac{1}{2}\theta_{12})^{3/2}(\cos\frac{1}{2}\theta_{12})^{1/2}[\pi(N-d-1)]^{1/2}}+O(N^{-3/2}). \tag{27}$$

This formula predicts nodes at $\theta_{12}=\pi(j+d+\frac{1}{4})/N$, with $j=1,2,\ldots,N-d-1$. At the other extreme, states with high values of d in each shell have a relatively high degree of localization near $\theta_{12}=180°$. Equation (24) is very useful for describing states in this region, since it is a function of the variable $\frac{1}{2}(1-x)=(\cos\beta)^2$ with $\beta=\frac{1}{2}(\pi-\theta_{12})$. The highest degree of localization is seen when $d=N-1$:

$$H_{N\,N-1}=(\cos\beta)^{2N-2}. \tag{28}$$

The angular distributions of the SO(4) states are qualitatively similar to those for rotor-vibrator states described in Ref. 3. Here we note that the vibrational part of those functions may be expressed in terms of a confluent hypergeometric function as

$$\psi_{\text{vib}}=\beta^T\exp(-\tfrac{1}{2}k\beta^2)F(d+1-N,T+1,k\beta^2), \tag{29}$$

with $k\equiv r^{1/2}$, where r is a characteristic shell radius, and the quantum number $T=0,1,\ldots,d$ labels rotations about an internal axis. The intrinsic ${}^1S^e$ states have $T=0$. The angular distribution described by Eq. (29) when $d=N-1$ is similar to the SO(4) distribution in Eq. (28) if we choose $r\propto N^2$; in this case both functions are localized at $\theta_{12}=180°$ with a characteristic width that scales as $N^{-1/2}$. Very little is known currently about angular distributions and threshold behavior for the ejection of two electrons from atoms, either experimentally or theoretically. The approximate rela-

TABLE IV. Angles of nodes in the ${}^1S^e$ intrashell wave function for the state with maximum pair strength $d=0$.

N	θ_{12} (deg)			
2	109.47			
3	73.15	133.62		
4	54.88	100.43	145.37	
5	43.91	80.38	116.51	152.35

tionship of the principal quantum number N to binding energies in doubly excited atoms has been described by Read,[20] Wang and Berry,[21] and Herrick *et al.*[2] It will be very interesting to see whether suitable analytic continuation of either the SO(4) angular wave function or the vibrator wave function to energies above threshold provide a realistic model of the electron correlation in that regime.

B. Radial equations for SO(4) channels

Close-coupling equations involving a single radial coordinate are a familiar part of the theoretical treatment of single-ionization processes. In the present section we consider an analogous set of coupled radial equations for two electrons in the intrashell SO(4) angular basis. The potential advantage of this approach lies in the fact that the SO(4) angular channels describe a high degree of angular correlation for the electrons, and may therefore lead to a more compact wave function and approximate decoupling of the radial equations when $r_1 \simeq r_2$ for intrashell states. We investigate this possibility for channels with $L=0$ only.

We construct an intrashell wave function Ψ_N for each level N in terms of the coordinates r_1, r_2, and θ_{12} for S states as follows:

$$\Psi_N = \sum_{d=0}^{N-1} G_{Nd}(r_1, r_2)\psi_{Nd}\,, \tag{30}$$

in which $G_{Nd}(r_1, r_2)$ is a two-electron radial function for the SO(4) angular channel ψ_{Nd}. The radial function is symmetric or antisymmetric under exchange of r_1 and r_2 for singlet or triplet states, respectively. Substitution of Ψ_N into the Schrödinger equation leads to a set of coupled two-electron radial equations,

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + 2E - V_{dd}\right) G_{Nd} = \sum_{d'}{}' \, V_{dd'} G_{Nd'}\,, \tag{31}$$

in which the term $V_{dd'}$ is a radial coupling matrix element between SO(4) channels defined by

$$V_{dd'} = -2Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\delta_{dd'} + \int_{-1}^{+1} \psi_{Nd}\left(\frac{\vec{1}_1^{\,2}}{r_1^2} + \frac{\vec{1}_2^{\,2}}{r_2^2} + \frac{2}{r_{12}}\right)\psi_{Nd'}\,dx\,. \tag{32}$$

An equivalent representation of the intrashell function Ψ_N with a conventional Legendre expansion is

$$\Psi_N = \sum_{l=0}^{N-1} F_{Nl}(r_1, r_2) P_l(x)\,. \tag{33}$$

Using Eqs. (18) and (19) we see that the two sets of radial functions are related by

$$F_{Nl}(r_1, r_2) = (-1)^{N-l-1}(2l+1) \times \sum_{d=0}^{N-1} (-1)^d (d + \tfrac{1}{2})^{1/2} W(aaaa, dl) G_{Nd}(r_1, r_1)\,, \tag{34a}$$

and the inverse transformation

$$G_{Nd}(r_1, r_2) = (-1)^{N-1-d}(d + \tfrac{1}{2})^{1/2} \times \sum_{l=0}^{N-1} (-1)^l W(aaaa; dl) F_{Nd}(r_1, r_2)\,. \tag{34b}$$

If the angular SO(4) we consider described an exact symmetry of two-electron atoms, then the off-diagonal matrix elements $V_{dd'}$ would vanish identically. Clearly this is not possible at all values of the radial coordinates r_1 and r_2. Herrick *et al.*[2] identified an exact symmetry at $r_1 = r_2 = 8N^2$ a.u. for matrix elements of dipole-coupled SO(4) generators. Our present work attempts to identify the regions of approximate SO(4) decoupling of the intrashell radial equations more precisely.

We first consider contributions to $V_{dd'}$ from the electron repulsion term. In general, the interparticle potential $V(r_1, r_2, \cos\theta_{12})$ has a Legendre expansion

$$V(r_1, r_2, \theta_{12}) = \sum_{k=0}^{\bar{N}-1} f_k P_k(x)\,, \tag{35}$$

in the intrashell basis; the cutoff $k \leqslant \bar{N} - 1$ with $\bar{N} \equiv 2N - 1$ originates in the hydrogenlike restriction $0 \leqslant l \leqslant N-1$ for the intrashell orbitals. The function f_k is given by the usual formula $f_k = r_<^k / r_>^{k+1}$ for the Coulomb potential. The angular δ-function interaction we associated with states of maximum pair strength in Sec. II is characterized by the formula $f_k = 2k + 1$. The SO(4) angular expansion analogous to Eq. (35) is defined here by

$$V(r_1, r_2, \theta_{12}) = \sum_{k=0}^{\bar{N}-1} v_k H_{\bar{N}k}\,, \tag{36a}$$

with the radial part related to f_k by the formula

$$v_k = (-1)^k (2k+1) \sum_j (-1)^j W(\overline{aaaa}; kj) f_j\,, \tag{36b}$$

in which $\bar{a} = \frac{1}{2}(\bar{N} - 1)$. In the case of the δ-function interaction noted above, (36b) gives $v_k = \bar{N}\delta_{k0}$ and hence the intrashell part of the potential is described by the single SO(4) function $H_{\bar{N}0}$; this may be seen in Eq. (26) by replacing N with $\bar{N}$. The intrashell Coulomb interaction includes long-range terms with $k > 0$ in addition to a short-range part, and no single term dominates the expansion (36). For example, when $r_1 = r_2 = r$ we find all the SO(4) terms contribute with the same weight $v_k = 1/r$.

Matrix elements of $1/r_{12}$ between SO(4) channels can be evaluated using an approach similar to the usual tensor analysis of the Legendre expansion. We start with a formula for expanding the product of two SO(4) functions:

$$H_{Ni}H_{Nj}=\sum_k C^k_{ij}H_{\bar{N}k}\,. \tag{37}$$

Owing to the orthogonality of functions on the RHS of (38), we can express the coefficient C^k_{ij} as an integral over three SO(4) polynomials:

$$C^k_{ij}=(k+\tfrac{1}{2})\int_{-1}^{+1}H_{\bar{N}k}H_{Ni}H_{Nj}\,dx\,. \tag{38}$$

Corresponding matrix elements of the intrashell Coulomb expansion (36) are then

$$(\psi_{Ni}|1/r_{12}|\psi_{Nj})=[(2i+1)(2j+1)]^{1/2}\times\sum_k C^k_{ij}v_k/(2k+1)\,. \tag{39}$$

In general C^k_{ij} vanishes unless $i+j\leqslant k\leqslant\bar{N}-1$, due to the fact that each function H_{Nd} in (24) contains only terms $(1-x)^s$ with $d\leqslant s\leqslant N-1$. Equations (19)–(25) and (38) lead to several different expressions for the coefficient C^k_{ij}. From the standpoint of computational efficiency we find the most convenient of these expressions, whose explict derivation we omit, is the formula

$$C^k_{ij}=(-1)^{i+j}\left(\frac{2k+1)}{\bar{N}+k}\right)\sum_{p,q}(-1)^{p+q}\binom{N+i}{p}\binom{N-1-i}{p}\times\binom{N+j}{q}\binom{N-1-j}{q}\times\binom{p+q}{\bar{N}-k-1}\binom{\bar{N}+k-1}{p+q}^{-1}. \tag{40}$$

Thus far we have considered only the contribution of the electron repulsion term to the coupling matrix $V_{dd'}$. The centrifugal contributions may be evaluated in an entirely straightforward fashion using the Legendre expansion (19), together with the identity

$$l(l+1)=2a(a+1)+(-1)^{N-1-l}2a(a+1)(2a+1)W(aaaa;1l)\,. \tag{41}$$

This leads to the following matrix element for each electron $i=1,2$:

$$(\psi_{Nd}|\vec{l}_i^{\,2}|\psi_{Nd'})=2a(a+1)\delta_{dd'}-2a(a+1)(2a+1)[(2d+1)(2d'+1)]^{1/2}\times[W(dd'aa;1a)]^2\,, \tag{42}$$

which may be seen to vanish unless $\Delta d=0,\ \pm1$.

The nonzero matrix elements may be evaluated from the following simplified expressions:

$$(\psi_{Nd}|\vec{l}_i^{\,2}|\psi_{Nd})=\tfrac{1}{2}[N^2-1-d(d+1)]\,, \tag{43a}$$

$$(\psi_{Nd}|\vec{l}_i^{\,2}|\psi_{Nd+1})=-\frac{(d+1)[N^2-(d+1)^2]}{[4(2d+1)(2d+3)]^{1/2}}\,. \tag{43b}$$

Note that the diagonal term (43a) indicates smaller centrifugal repulsion, and hence lower energies, for SO(4) channels with larger values of d. These are the same channels which have the most favorable two-electron angular correlation.

C. Radial decoupling

We indicated in Sec. III C that a zeroth basis of correlated angular SO(4) channels could lead to approximate radial decoupling in the regime $r_1\simeq r_2$. We now investigate the extent of decoupling by considering the form of the matrix elements $V_{dd'}$ in greater detail. From Eq. (32) we find each matrix element for level N has a finite expansion

$$V_{dd'}=-2Z\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\delta_{dd'}+A\left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)+\sum_{k=0}^{2N-2}B_kt^k/r_>\,, \tag{44}$$

in which $t=r_</r_>$. The coefficients A and B_k are different for each matrix element; A represents the centrifugal term in (43) and B_k is given by the formula

$$B_k=(-1)^{d+d'}2[(2d+1)(2d'+1)]^{1/2}\times\sum_{l,l'}(-1)^{l+l'}(2l+1)(2l'+1)\times W(aaaa;dl)W(aaaa;d'l')\begin{pmatrix}l & l' & k\\ 0 & 0 & 0\end{pmatrix}^2. \tag{45}$$

Tables V–VII contain numerical values of coefficients for levels $N=2$–4. Also shown there are values of a coefficient σ defined by

$$\sigma=\tfrac{1}{4}\sum_k B_k\,, \tag{46}$$

which is related to the matrix of the repulsion

TABLE V. Coefficients for intrashell-potential-coupling matrix elements $V_{dd'}$ in SO(4) angular channels [cf. Eq. (44)] for the shell $N=2$.

	V_{00}	V_{11}	V_{01}
A	1.5	0.5	−0.866
B_0	2	2	0
B_1	1	−1	0.577
B_2	0.6	0.2	−0.346
σ	0.9	0.3	0.058

TABLE VI. Coefficients for intrashell-potential-coupling matrix elements $V_{dd'}$ in SO(4) angular channels [cf. Eq. (44)] for the shell $N=3$.

	V_{00}	V_{11}	V_{22}	V_{01}	V_{12}	V_{02}
A	4	3	1	−2.309	−1.291	0
B_0	2	2	2	0	0	0
B_1	1.333	0	−1.333	0.577	0.516	−0.149
B_2	1.029	−0.229	0.571	0.148	−0.664	0.319
B_3	0.571	−0.429	−0.143	0	0.332	−0.256
B_4	0.317	0.238	0.016	−0.275	−0.061	0.071
σ	1.313	0.395	0.278	0.113	0.031	−0.004

operator $1/r_{12}$ in the SO(4) basis when $r_1=r_2$. We interpret the diagonal and off-diagonal matrix elements separately here below:

1. Diagonal terms

The shapes of these curves are qualitatively similar to potential energy surfaces for a molecular-type reaction $X+YX\rightarrow XY+X$, except that here we have electrons (X) and a nucleus (Y). When $r_1=r_2\equiv r$ the potential for each channel is simply

$$V_{dd}=2A/r^2-4(Z-\sigma)/r\,, \qquad (47)$$

which contains a short-range centrifugal term plus a long-range Coulomb term. Note that σ appears here as a screening constant. The smallest values of σ are seen in Tables V–VII for the channel $d=N-1$ which has the most favorable angular correlation, and these are close to the classical screening constant $\sigma=0.25$ for electrons on a spherical shell when $\theta_{12}=180°$ (Ref. 20). The screening constant increases for channels with decreasing d, and reaches its highest value in the channel $d=0$ which has maximum pair strength and hence the most unfavorable electron correlation. At high Z the potentials described in Eq. (47) have a long-range attraction, indicating states below the threshold for double ejection of electrons at zero energy. At low Z, however, some of the channels with large screening constants satisfy $\sigma>Z$, and hence would have a purely repulsive potential when $r_1=r_2$. The location of the minimum in the attractive channels is found from (47) and (43) to be described by

$$\begin{aligned} r_0&=[N^2-1-d(d+1)]/2(Z-\sigma)\,,\\ V_{dd}^0&=-4(Z-\sigma)^2/[N^2-1-d(d+1)]\ . \end{aligned} \qquad (48)$$

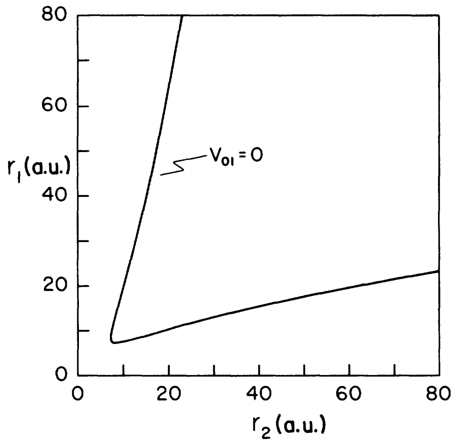

FIG. 1. Line of nodes in the radial coupling matrix element V_{01} between SO(4) channels in the shell $N=2$. Radial coordinates r_1 and r_2 are given in atomic units (1 a.u. = 0.529 Å).

The constants on (48) actually describe the location of a saddle point in the full potential-energy curve when values $r_1\neq r_2$ are taken into account; the instability associated with the maximum in the potential at this point is linked to the process of autoionization in doubly excited atoms, as illustrated by $\mathrm{He}^{**}\rightarrow\mathrm{He}^{+}+e^{-}$ in the limit $r_1\rightarrow\infty$ or $r_2\rightarrow\infty$. By analogy with molecular potential-energy surfaces, we note the saddle point in the attractive SO(4) channels describes a type of activated complex for the process $e_1^{-}+\mathrm{He}^{+}\rightarrow\mathrm{He}^{+}+e_2^{-}$.

2. Off-diagonal terms

Owing to the selection rule $\Delta d=0,\pm1$ for centrigugal matrix elements in (42), off-diagonal coupling

TABLE VII. Coefficients for intrashell-potential-coupling matrix elements $V_{dd'}$ in SO(4) angular channels [cf. Eq. (44)] for the shell $N=4$.

	V_{00}	V_{11}	V_{22}	V_{33}	V_{01}	V_{12}	V_{23}	V_{02}	V_{13}	V_{03}
A	7.5	6.5	4.5	1.5	−4.330	−3.098	−1.775	0	0	0
B_0	2	2	2	2	0	0	0	0	0	0
B_1	1.5	0.5	−0.5	−1.5	0.520	0.645	0.423	−0.224	−0.109	0.038
B_2	1.262	0.071	−0.262	0.833	0.322	−0.277	−0.704	0.245	0.327	−0.139
B_3	0.905	−0.429	−0.143	−0.333	0.231	−0.184	0.563	0.043	−0.436	0.227
B_4	0.671	−0.247	0.420	0.091	−0.065	−0.140	−0.256	−0.019	0.304	−0.195
B_5	0.379	−0.136	−0.227	−0.015	−0.131	0.293	0.064	−0.169	−0.109	0.086
B_6	0.204	0.220	0.041	0.001	−0.212	−0.095	−0.007	0.091	0.016	−0.015
σ	1.730	0.495	0.332	0.269	0.166	0.061	0.021	−0.008	−0.002	0.0004

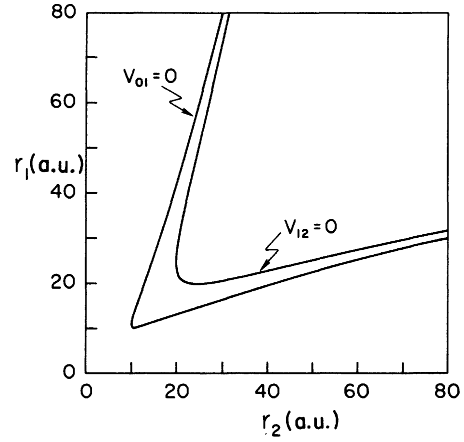

FIG. 2. Lines of nodes for off-diagonal radial coupling matrix elements $V_{dd'}$ between SO(4) channels in the shell $N=3$ (cf. Fig. 1).

terms $V_{dd'}$ which have $|d-d'|>1$ originate entirely in the Coulomb repulsion $1/r_{12}$. The largest of these couplings are found when $r_1=r_2$ at which point they have the value $4\sigma/r_>$. It is evident from values of σ in Tables V–VII that the SO(4) channels approximately diagonalize the Coulomb repulsion when $r_1=r_2$. Radial coupling matrix elements $V_{dd'}$ with $|d-d'|=1$ involve contributions from a positive Coulomb repulsion term and a negative [cf. Eq. (43b)] centrifugal term. Due to a cancellation of these terms, it is possible for the matrix elements to vanish at certain values of r_1 and r_2. Figures 1–3 show the location of the lines of nodes $V_{dd'}=0$ for levels $N=2$–4. These curves are found from (44) to be described by the equation

$$r_> = -A(1+1/t^2)\Big/\sum_k B_k t^k\,, \tag{49}$$

which in the limit of very large $r_>$ gives $r_< = (-A/B_1)^{1/3}(r_>)^{2/3}$. Although there is no single point in the figures where all of the coupling terms vanish, there evidently occurs a relatively high degree of approximate decoupling in a very broad region described by $r_1 \simeq r_2 \simeq 2N^2$ for these levels. It is important to note that the off-diagonal terms $V_{dd'}$, and hence the region of approximate decoupling, are independent of the nuclear charge Z of the atom. Since the characteristic shell radius of atoms scales as $r \propto N^2/Z$ at high Z, we conclude that the approximate decoupling of angular SO(4) channels is strongest in low-Z systems such as H^-. This interpretation is consistent with the Z dependence of supermultiplets[2] and the vibrator model of strongly correlated states at low Z (Ref. 3).

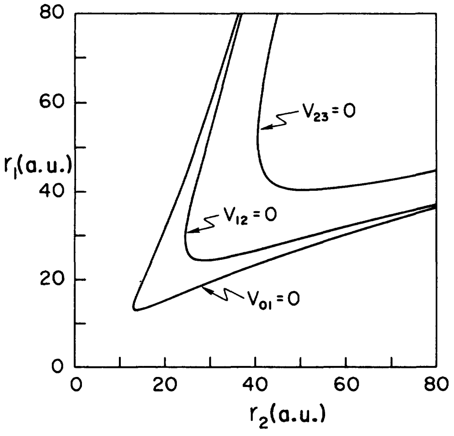

FIG. 3. Lines of nodes for off-diagonal radial coupling matrix elements $V_{dd'}$ between SO(4) channels in the shell $N=4$ (cf. Fig. 1).

V. SUMMARY OF RESULTS

In this work we have described several new results related to the angular correlation of two electrons in doubly excited atoms. In Sec. II we showed how a simple hybridization method for electron-pair surface harmonics accounts for configuration mixing and energy-level orderings of the highest intrashell states in each level N. We interpreted these as pairing states originating in the short-range part of the repulsion within each shell. In Sec. III we investigated an approximate SO(4) symmetry for the angular pairing states in a hydrogenlike shell; the method seems to account for the curious result found in earlier studies that the totally symmetric SO(4) representation for each shell is the *highest* energy level. A key result of our investigation of the short-range correlation was the identification of a CPT-like invariance of intrashell group generators of the approximate symmetry. With this we established a link between the angular SO(4) group for the present short-range correlation model, and a similar group identified in Ref. 2 for long-range correlation effects. We then describe properties of the SO(4) angular channels and the dependence of the states on the interelectronic angle θ_{12}. Although the angular SO(4) channels are not exact eigenfunctions of the Schrödinger equation for doubly excited states, they were found to give an approximate diagonalization of the Coulomb repulsion when $r_1 \simeq r_2$ for levels $N=2$–4. The angular SO(4) states may therefore prove to be a useful model for correlation in highly excited states and threshold behavior for ejection of two electrons. Analytic continuation of the SO(4) states to real wave functions could be obtained using Eq. (24) with $N \rightarrow iN$ and appropriate renormalization. Similar results could be found using SO(4) states for $L>0$ as well.

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