Channel invariants and SU(3) classification for two-electron atoms

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Previous studies showed the configuration-mixed excitation channel structure of two-electron atoms to be classified by two quantum numbers K and T. Three new aspects of the classification are considered here: (i) K and T are shown to be limiting cases of two exact invariants for channels in the asymptotic regime $r_2 \gg r_1$. The invariants classify channels for the entire isoelectronic series. Sum rules, quantum number correlation diagrams for isoelectronic series, and perturbation formulas for the invariants are described. (ii) The K, T spectrum is shown to be contained in a chain SU(4)⊃SU(3)⊃SU(2) defined mathematically on the two-electron channels. Possible physical connection with O(6) quantum numbers for noninteracting particles in hyperspherical coordinates is discussed. (iii) An empirical link is established between autoionization stability of heliumlike atoms, and unitarity of irreducible representations for a SU(2,1) channel scheme. The noncompact classification also includes channels for double ionization.

I. INTRODUCTION

Recent investigations[1-6] revealed an interesting group theoretical structure for excitation channels in two-electron atoms. Double excitation states are characterized by strong Coulomb configuration mixings which render the usual independent particle angular momentum quantum numbers l_1 and l_2 inadequate for classifying channels. For heliumlike atoms where a long-range Coulomb attraction dominates when $r_2 \gg r_1$, each excitation channel contains a Rydberg series of states. The group theory provides at the outset a configuration-mixed, spatially correlated basis which reproduces in large part mixings in computed wave functions. Two integer quantum numbers K, T were found[2] to label configuration-mixed channels, and excitation and decay characteristics of the series display some striking regularities when viewed in the K, T classification. Radiative excitation of ^1P helium to Rydberg series converging on the $N = 1, 2, \ldots$ ionization thresholds, for instance, shows a strong selectivity for channels having $K = N - 2$, $T = 1$, while excitation to other channels is substantially weaker.[2] Although the channel structure emerges clearly in theoretical calculations of energies and wave functions, there exists at present no detailed explanation for those results directly—in terms of group-theoretical properties of the full three-body Hamiltonian. Rather, the K, T quantum numbers have been deduced from group theoretical analysis of approximate wave functions for the two-electron states.

Sinanoğlu and Herrick[6] and Wulfman[7] showed independently that mixings of degenerate hydrogenic configuration wave functions for $n_1 = n_2$ are well described by group-theoretical diagonalization of the operator $(\vec{b}_1 - \vec{b}_2)^2$, where $\vec{b}$ is the Runge-Lenz vector for SO(4) symmetry of the hydrogen atom. Mixings of degenerate configurations are not well described by $(\vec{b}_1 - \vec{b}_2)^2$ when $n_1 \neq n_2$. Previous attempts to classify degenerate mixings using $(\vec{b}_1 + \vec{b}_2)^2$ had been unsuccessful.[8-13] Wulfman's classification for fixed n_1, n_2 used the traditional P, Q quantum numbers for rotations in four dimensions.[14] In contrast the K, T quantum numbers[2,6] were defined to reflect inherent channel characteristics of the overall two-electron spectrum. Isoelectronic series configuration-interaction (CI) computations with nondegenerate hydrogenic configurations showed, for instance, an approximate block diagonalization of the energy with respect to K and T.[2] In this sense the K, T classification appears more characteristic of the two-electron Hamiltonian itself, rather than of degenerate hydrogenic configurations. The CI channel classification remained strong even in the extreme case of H^-, where a hydrogenic n_1, n_2 classification of states is grossly inaccurate. Some additional insight to the channel structure was subsequently offered in a variable-dimensionality model for two-electron atoms.[3] There, K governed configuration mixings exactly in the one-dimensional limit.

The hydrogenic CI wave functions did not take into account screening for the radially more diffuse electron.[2] A group-theoretical model classifying channels in the asymptotic regime, where $r_2 \gg r_1$, was offered in (I).[1] K, T quantum numbers were derived for that model in the limit of strong electron-electron coupling. In Sec. II of the present paper we again address the problem of classifying the asymptotic channels. K and T are shown to be merely limiting forms of two exact invariants for asymptotic channels, valid for the entire isoelectronic series. We describe several properties of the invariants, including matrix elements, sum rules, and eigenvalue correlation diagrams.

Although the classification in Sec. II offers substantial new insight to the channel structure, it fails to identify K and T group theoretically as quantum numbers for irreducible representations of a continuous group. We therefore explore in Sec. III a possibility first discussed in (I), that there might exist an underlying SU(3) channel classification. Our approach is a phenomenological one, and we simply define representations of SU(3) on the channel spectrum. One consequence of this definition, however, is that the complete numerology of a K, T type spectrum is then contained in $SU(4) \supset SU(3) \supset SU(2)$. Possible connection with Dragt's[15] SU(3) classification of states for three noninteracting particles is discussed.

In Sec. IV the question is raised whether a related noncompact SU(2,1) classification for channels might be more appropriate than SU(3). Earlier suggestions[4] for noncompactness have been disputed.[16] The present analysis establishes an empirical link relating unitarity of irreducible representations to the stability of heliumlike atoms against autoionization.

II. ASYMPTOTIC CHANNELS

Full details for constructing asymptotic channels appear in (I). Briefly, configuration channel states $|Nl_1 l_2 LM\rangle$ represent products of hydrogenic states ($0 \leq l_1 \leq N-1$) for electron 1 and angular momentum states ($l_2 = 0, 1, \ldots$) for electron 2, coupled to yield total angular momentum quantum numbers L, M. Configuration-mixed channels obtain[17,18] from diagonalization of $A = l_2^2 + 2\lambda r_1 \cos\theta_{12}$ in channel subspaces of constant N. λ is a coupling parameter, equal to $1/Z$ for the helium isoelectronic sequence. A is an effective total angular momentum in the coupled radial Schrödinger equations for large r_2. Diagonalization of A decouples the asymptotic radial equations, and eigenvalues of A thus label possible decay channels for ejection of a single electron. The problem of systematically classifying these eigenvalues is therefore of some importance. How do we represent A group theoretically?

An explicit group theoretical construction of the channel invariant A on the configuration channel basis can be accomplished using generators of the hydrogenic SO(4) algebra for 1, and a noncompact, angular O(3,2) Lie algebra for 2. The projection $\vec{r} \to (3/2)N\vec{b}$ was used in (I). SO(4) commutation relations are

$$[l_x, l_y] = il_z, \quad [l_x, b_y] = ib_z, \quad [b_x, b_y] = il_z. \tag{1}$$

Construction of the unit vector $\hat{r}$ with O(3,2) generators for spherical harmonics has been described by Herrick and Sinanoğlu.[19] Thus A is in fact well-defined group theoretically, and in principle one expects to exploit this operator representation for classification of two-electron channels. We establish some general properties of the physical channel states in the following sections.

A. Exact invariants

In terms of SO(4) the first channel invariant becomes

$$A = l_2^2 + \mu\vec{b}_1 \cdot \hat{r}_2, \tag{2}$$

with $\mu = 3N\lambda$. Both the total angular momentum $\vec{L} = \vec{l}_1 + \vec{l}_2$, and parity $\Pi = \Pi_1\Pi_2$, commute with A. The projection of $\vec{L}$ along the vector $\vec{R} = \mu\hat{r}_2 - 2\vec{b}_1$ is defined by

$$W = \vec{L} \cdot \vec{R}, \tag{3}$$

or

$$W = \mu\vec{l}_1 \cdot \hat{r}_2 - 2\vec{b}_1 \cdot \vec{l}_2 \tag{4}$$

when orthogonality of $\vec{l}_2$ and $\vec{r}_2$, and of $\vec{l}_1$ and $\vec{b}_1$ is taken into account. One easily verifies using SO(4) commutation relations that $[W, A] = 0$. W is therefore a new, second-channel invariant for *all* values of μ. There are two distinct ways of labeling the physical channels.

The first way has L^2, L_z, A, and W diagonal. When $W \neq 0$ each eigenvalue of A for $0 < \mu < \infty$ is doubly degenerate, due to invariance of A under either positive or negative rotations about $\vec{R}$. The two eigenvalues of W for these degenerate states have equal magnitude, but different sign. Eigenvalues of A for the case $W = 0$ are nondegenerate. Parity is not conserved in this first classification, since $\Pi W \Pi = -W$.

The second classification has L^2, L_z, A, W^2, and Π diagonal. In this scheme two degenerate eigenvalues of A exist for each nonzero value of W^2: one for an even parity state and the other for an odd parity state. Parity is not a "long-range" quantum number for two-electron atoms, since these even and odd parity channels define identical effective centrifugal potentials for the radial coordinate r_2. The existence of W^2 as a second channel invariant thus explains the parity degeneracies for A found in (I).

Physically, diagonalization of W and A corresponds to a transformation of channel states from space-fixed (external) coordinates to a rotating (internal) frame. R is the figure axis about which angular momentum is conserved. In this way eigenvalues of A are analogous to energy levels of a rigid rotor, with N playing the role here of a generalized angular momentum quantum number. In this connection, transformation from channel states having W diagonal to those states having

W^2 diagonal resembles the Wang[20] transformation for ordinary asymmetric top wave functions. Diagonalization of A also bears a similarity to solution[21,22] of the second-order Dirac equation for hydrogen.

We cannot offer at present a complete diagonalization of the channel invariants valid for all values of μ. However, exact diagonalization for the strong coupling ($\mu=\infty$) limit is described in Sec. II B. There then follows in Sec. II C a partial O(4) diagonalization for the weak coupling ($\mu=0$) limit. Explicit representations of A and W in the strong coupling basis appear in Sec. II D. Additional properties of A, including sum rules, empirical correlation diagrams for quantum numbers, and classification of H^- states are discussed in the remaining sections.

B. Strong coupling

For large μ the channel invariants become $A \sim \mu\vec{b}_1\cdot\hat{r}_2$ and $W\sim\mu\vec{L}\cdot\hat{r}_2$. Diagonalization is achieved in two steps, in a way analogous to that described in (I). First we diagonalize $\vec{L}\cdot\hat{r}_2\equiv -Q$ in the basis

$$|Nl_1QLM\rangle=\sum_{l_2}|Nl_1l_2LM\rangle(2l_2+1)^{1/2}\begin{pmatrix} l_1 & l_2 & L\\ Q & 0 & -Q\end{pmatrix}. \tag{5}$$

The eigenvalues are $Q=0,\pm1,\ldots,\pm\min(L,N-1)$. When $L>N-1$ the restriction on the maximum value of Q results from the limit $0\leq l_1\leq N-1$ for hydrogenic states. The second step diagonalizes $\vec{b}_1\cdot\hat{r}_2\equiv -K$, and corresponds to Stark mixing of degenerate hydrogenic states[23] with respect to the $\hat{r}_2$ axis[1]

$$|NKQLM\rangle=\sum_{l_1}|Nl_1QLM\rangle(-)^Q(2l_1+1)^{1/2}\begin{pmatrix} a & a & l_1\\ \alpha & \beta & -Q\end{pmatrix}. \tag{6}$$

Here $a=\frac{1}{2}(N-1)$, $\alpha=\frac{1}{2}(Q-K)$, and $\beta=\frac{1}{2}(Q+K)$. The coefficients in Eqs. (5) and (6) are $3-j$ symbols. In terms of $T=|Q|$, values for K are $K=N-T-1$, $N-T-3,\ldots,-N+T+1$. Wave functions for $|NKQLM\rangle$ are spatially correlated, having $\cos\theta_{12}=-K/N$ diagonal in subspaces of constant N.

Parity representations are

$$\Pi|NKQLM\rangle=(-)^L|NK,-Q,LM\rangle, \tag{7}$$

$$\Pi_1|NKQLM\rangle=(-)^{N-1}|N,-K,QLM\rangle. \tag{8}$$

When $Q=0$ the parity is $(-)^L$. For $Q\neq0$, parity-diagonal states are

$$|NKTLM\Pi\rangle=(|NKQLM\rangle\pm|NK,-Q,LM\rangle)/\sqrt{2}, \tag{9}$$

where + gives $\Pi=(-)^L$, and − gives $\Pi=(-)^{L+1}$.

Diagrams of K and T for different values of N appear in (I), where a parity-diagonal basis similar to Eq. (9) was used. The T basis suffers from the disadvantage of inconvenient normalization factors[1] in matrix elements of A for finite μ. A useful result of the present theory is that eigenvalues of A can be computed directly in the Q basis.

C. Weak coupling

When $\mu=0$ the explicit two-electron coupling in A vanishes, and the eigenvalues reduce to the ordinary form $l_2(l_2+1)$ for one electron. However, for each N and L there may occur several channels having the same value of l_2. This "accidental degeneracy" for A is explained in the present theory by the second invariant, W. When $\mu=0$ one can choose either W or l_1^2 diagonal. The more natural choice is to diagonalize $W=-2\vec{b}_1\cdot\vec{l}_2$, so that weak coupling states connect smoothly with channel states for $\mu>0$. W mixes configuration channel states having $\Delta l_1=\pm1$, but it leaves l_2 unchanged. Although the case $\mu=0$ corresponds to an independent particle limit for A, there remains a residual "weak" configuration mixing due to W.

We now derive a partial classification of W for weak coupling channels using an O(4) Lie algebra generated by $\vec{L}=\vec{l}_1+\vec{l}_2$ and $\vec{C}=\vec{b}_1+\vec{l}_2$. Irreducible representations of the rotation group in four dimensions are commonly labeled with pairs of integers (p,q), which specify O(3) subgroup representations as follows: $p\geq l\geq|q|$.[14] Bound state hydrogenic wave functions for fixed N have the representation $(N-1,0)$, while spherical harmonics for fixed l_2 correspond to (l_2,l_2) in O(4). Reduction of the product[14] of these two O(4) representations on the configuration channel basis yields irreducible representations $(N-1+\tau,\tau)$, where τ is an integer having all values

$$\max(l',l'')\leq\tau\leq\min(l_2,L). \tag{10}$$

Here $l'=|a-l_2|-a$, $l''=|a-L|-a$, and $a=(N-1)/2$. Explicit coupled states are

$$|N\tau l_2LM\rangle=\sum_{l_1}(-)^c|Nl_1l_2LM\rangle[(N+\tau)\times(2l_1+1)]^{1/2}\begin{Bmatrix} l_1 & l_2 & L\\ a+\tau & a & a\end{Bmatrix}, \tag{11}$$

with $c=l_1+l_2+L-2a-\tau$. The possible values for l_2 are $\max(0,L-N+1)\leq l_2\leq N-1+L$ for fixed N,L.

Using O(4) Casimir invariants[14] $L^2+C^2=p(p+2)+q^2$ and $L\cdot C=q(p+1)$, we can rewrite W as

$$W=[l_2(l_2+1)+L(L+1)-2\tau(N+\tau)]-l_1^2. \tag{12}$$

The portion in brackets is constant for O(4) states,

but l_1^2 is not diagonal in the $|N\tau l_2 LM\rangle$ basis. Thus the O(4) classification of W is only an approximate one. Nevertheless, τ describes the degeneracy of A, via Eq. (10). When $N \gg L$ and $N \gg l_2$, Eq. (12) becomes $W \sim -2N\tau$. τ is similar to the strong coupling quantum number Q in this limit.

The O(4) channels resemble states defined by Nikitin and Ostrovsky[5] for hydrogenic configurations. When $n_2 \gg n_1$ and $L \gg n_1$, $\vec{b}_1 \cdot \vec{l}_2$ becomes diagonal in their basis in a way similar to Eq. (12) here. They offered no physical justification for diagonalization of $\vec{b}_1 \cdot \vec{l}_2$, however. Diagonalization for this operator is predicted in our channel classification at $\mu = 0$. Moreover, the invariant W applies to the entire isoelectronic sequence.

D. SU(2) construction for A, W

Both A and W mix zero-order strong coupling states having different values of K and Q. The explicit evaluation of matrix elements is omitted here. Instead, we offer a simple model which reproduces those results. The model involves three mutually commuting SU(2) angular momentum "particles" $\vec{j}$, $\vec{k}$, and $\vec{J}$. By imposing suitable constraints on these particles, we generate representations of the channel invariants.

The product basis $|j\alpha, k\beta, J\gamma\rangle$ for $\vec{j}$, $\vec{k}$, and $\vec{J}$ has $(2j+1)(2k+1)\cdot(2J+1)$ substates. α, β, and γ are eigenvalues of diagonal components j_0, k_0, and J_0, respectively. Quantum numbers N, K, Q, and L for the physical channels are embedded in this product space and are specified in part by the restrictions $j = k = a$, $J = L$, and $\alpha = \frac{1}{2}(Q-K)$, $\beta = \frac{1}{2}(Q+K)$. The requirement $j = k$ originates with the SU(2) × SU(2) decomposition of SO(4) for hydrogen. The third particle $\vec{J}$ describes the total orbital angular momentum. The particles are not independent for physical channels. In order to completely specify states requires the additional constraint

$$j_0 + k_0 + J_0 = 0\,, \tag{13}$$

which has the form of a conservation law. Thus $\alpha + \beta + \gamma = 0$, and hence $\gamma = -Q$. This completes the construction of physical channel numbers in the SU(2) states.

Evaluation of matrix elements verifies the following representation of channel invariants

$$A \to (\vec{j} + \vec{k} + \vec{J})^2 + \mu(j_0 - k_0)\,, \tag{14}$$

$$W \to \mu J_0 - 2(\vec{j} - \vec{k}) \cdot \vec{J}\,. \tag{15}$$

In this way $\vec{j} + \vec{k}$, $\vec{j} - \vec{k}$, and $\vec{J}$ represent versions of $\vec{l}_1$, $\vec{b}_1$, and $\vec{L}$, respectively; in a rotating frame consistent with Eq. (6). We leave for future study the question whether these representations—including nonphysical values of $\gamma \neq -Q$—can be exploited in a more useful manner.

One consequence of the representations is that perturbation formulas for A and W can be generated in orderly fashion by taking advantage of SU(2) commutation relations and the simple form of the zero-order eigenvalues $A_0 = -\mu K$ and $W_0 = -\mu Q$. Second-order expansions are

$$A = -\mu K + \tfrac{1}{2}[2L(L+1) + N^2 - 1 - K^2 - 3Q^2] - (K/4\mu)[8L(L+1) + N^2 - 1 - K^2 - 15Q^2] + \cdots\,, \tag{16}$$

$$W = -Q\{\mu + 2K + \mu^{-1}[2L(L+1) + N^2 - 1 - K^2 - 3Q^2] + \cdots\}\,. \tag{17}$$

Note that the second-order term in W is proportional to the first-order term in A, and the expansion suggests $W \propto Q$. Eigenvalues are even functions of μ, since both A and W remain invariant under the simultaneous inversions $\hat{r}_2 \to -\hat{r}_2$ and $\mu \to -\mu$.

Two more symmetrical invariants are

$$B_\pm = \tfrac{1}{2}[A - 2a(a+1) - L(L+1) \pm W]\,. \tag{18}$$

In the present representation

$$B_+ = \vec{k} \cdot (\vec{j} + 2\vec{J} - \mu\vec{\sigma})\,, \tag{19}$$

$$B_- = \vec{j} \cdot (\vec{k} + 2\vec{J} + \mu\vec{\sigma})\,, \tag{20}$$

with $\vec{\sigma} = (1, 0, 0)$ for the vector convention $\vec{k} = (k_0, k_1, k_2)$. Eigenvalues of B_+ for μ are identical to eigenvalues of B_- for $-\mu$, since the condition $j = k$ for physical channels renders $\vec{j}$ and $\vec{k}$ identical particles under exchange.

E. Sum rules for A

Although operators yielding K, T quantum numbers directly have been found only in the strong coupling limit, K and T also label eigenvalues of A in the intermediate coupling range $0 \leq \mu < \infty$. Values of K and T can be found by comparison of eigenvalues with Eq. (16). Henceforth we regard K and T as quantum numbers for exact channel invariants.

For fixed N and L, the sum of eigenvalues of A is a quantity independent of μ. That is, $\mathrm{Tr}(A)$ is constant. $\mathrm{Tr}(A)$ is also constant within fixed-parity subspaces, so that two trace invariants exist for fixed N, L. Theory from previous sections says, however, that eigenvalues of A for states having $T \geq 1$ are identical for both $\Pi = (-)^L$ and $\Pi = (-)^{L+1}$. By difference, we thus establish that *the sum of eigenvalues of A for channels having $T = 0$ is a quantity independent of μ.* The precise value of the sum can be calculated in the strong coupling representation.

First define the general sum

$$\sigma_\mu(NTL) = \sum_K A\,, \tag{21}$$

from which

$$\sigma_\infty(NTL) = (N-T)[L(L+1)+\tfrac{1}{2}(N^2-1-3T^2) - \tfrac{1}{6}(N-T)^2+\tfrac{1}{6}] \tag{22}$$

follows upon substitution of Eq. (16) for A. $\sigma_\mu(NTL)$ is found in some cases to be a slowly varying function of μ. The sum is independent of μ when $T=0$ as noted above. It is also μ independent when $T=1, L=1$ since the only possible values for T are 0 and 1 when $L=1$. Thus

$$\sigma_\mu(N0L) = N[N^2-1+3L(L+1)]/3 \tag{23}$$

and

$$\sigma_\mu(N11) = N(N^2-1)/3\,. \tag{24}$$

Note also that $\sigma_\mu(N11) = \sigma_\mu(N00)$.

F. Correlation diagrams for A

It is useful to construct *correlation diagrams* connecting eigenvalues of A in the strong and weak coupling limits. Without exact eigenfunctions for invariants these diagrams are difficult to construct from first principles. We therefore report some empirical correlation rules for the weak coupling quantum number l_2 in terms of K and T. The rules were formulated from computed eigenvalues of A for $N \leq 3$, and have been verified for $N=4$ channels. For fixed N, T, and L we define a cutoff value of K as follows:

$$K_c = 2L - T - N + 1\,. \tag{25}$$

We find that

$$l_2 = L-K\,, \text{ if } K \leq K_c$$
$$= (N-1-K+T)/2\,, \text{ if } K \geq K_c\,. \tag{26}$$

For $L=0$ this yields $l_2 = \frac{1}{2}(N-1-K)$; and when $L \geq N-1, l_2 = L-K$.

There is a simple graphical construction for l_2 in Eq. (26), illustrated in Fig. 1 for the case

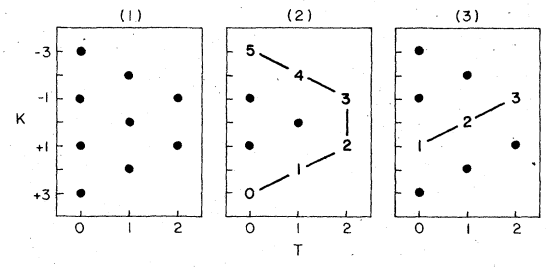

FIG. 1. Graphical construction for l_2 values on the K,T channel spectrum for $N=4$, $L=2$, according to rules (1)–(3) in Sec. II F. The complete diagram appears in Fig. 2.

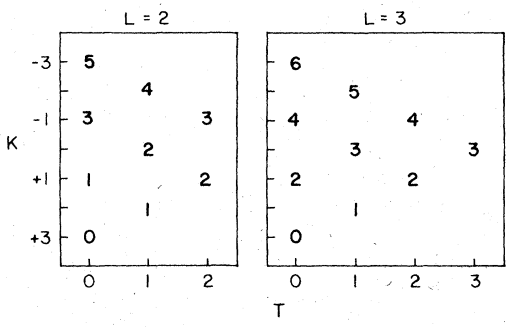

FIG. 2. Correlation diagrams for $N=4$ and $L=2,3$ illustrating values of l_2 for different K,T channels. $A = l_2(l_2+1)$ when $\mu=0$, and $A \sim -\mu K$ when $\mu \to \infty$.

$L=2, N=4$. General rules for fixed N and L are as follows:

(1) Construct the K,T channel diagram so that $K=N-1$ lies at the lower left corner.

(2) Fill in the values $\max(0, L-N+1) \leq l_2 \leq L+N-1$ in increasing order along the boundary defined by the maximum value of T for $K=N-1$, $N-2, \ldots, 1-N$. The lower right vertex of the diagram always has $l_2 = L$.

(3) For each value of l_2 in step (2), fill in values $l_2' = l_2-1, l_2-2, \ldots$ in order along the diagonal having $K+T$ constant. The smallest value of l_2' lies at $T=0$.

Complete correlation diagrams for $N=4$ and $L=2,3$ appear in Fig. 2. Eigenvalues $A = l_2(l_2+1)$ at $\mu=0$ satisfy the sum rule Eq. (23). For large μ, $A \sim -\mu K + L(L+1) + \frac{1}{2}(N^2-1-K^2-3T^2)$.

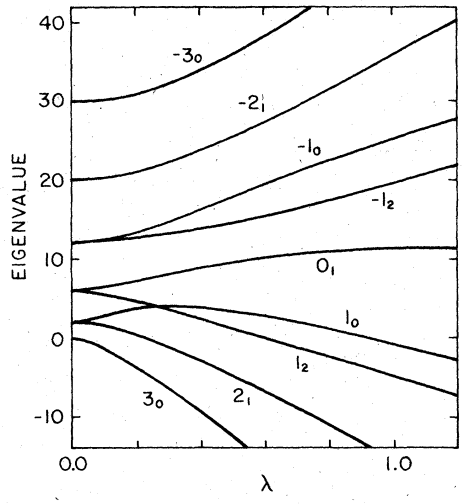

FIG. 3. Eigenvalues of A for the case $N=4$, $L=2$ for different values of the coupling parameter λ. The isoelectronic sequence H^-, He, $Li^+, \ldots$ has $\lambda = 1, \frac{1}{2}, \frac{1}{3}, \ldots$. Curves are labeled with K,T channel quantum numbers as K_T. Note the level crossing of 1_0 and 1_2 at $\lambda \simeq 0.286$.

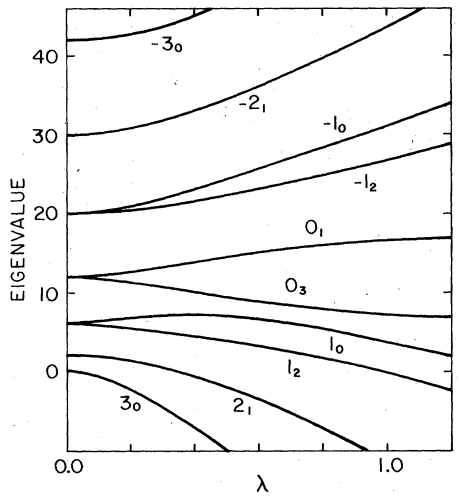

FIG. 4. Eigenvalues of A for the case $N=4$, $L=3$, using notation of Fig. 3. The curves for channels 0_3 and 1_0 appear to suffer a broad avoided crossing in the region $\lambda \simeq 0.7$.

An important feature of the diagram for $N=4$, $L=2$ is the implied crossing of eigenvalues of A between the strong and weak coupling limits for channels having $K=1$. In the large-μ regime the eigenvalue for $T=2$ lies below that for the $T=0$ channel. At $\mu=0$, however, the ordering of the two levels is inverted. Computed eigenvalues for $L=2$ displayed in Fig. 3 as continuous functions of λ in fact show a crossing. In contrast, the correlation diagram for $N=4, L=3$ channels suggests no such crossing. Eigenvalues of A for the $L=3$ channels are displayed in Fig. 4.

Equation (26) leads to similar predictions of crossings for channels when $N>4$. However, the rule has not yet been tested for those channels. Investigation of the higher N channels is left for future work. Exact crossings in the spectrum of A for fixed values of N and L are one consequence of the second channel invariant W^2. Two channels can have the same value of A if they have different values of W^2.

G. H^- channels

Eigenvalues of A for H^- appeared in (I). Neglecting fine structure for thresholds, only channels having $A<-\frac{1}{4}$ can support series of autoionizing states.[18] Of interest here is the maximum value of $L, L_{\max}$, for which $A<-\frac{1}{4}$ in each K, T channel. Second-order perturbation theory for A gave poor estimates of $L_{\max}$ for the larger values of K. We note here that exact values[1] of $L_{\max}$ for $N \leq 4$ seem to follow a regular pattern when viewed in the K, T classification. For instance, $L_{\max} = 2(N-1)$ for the channel $K=N-1, T=0$. Similarly, $L_{\max}=2(N-2)$ for the channel $K=N-2$, $T=1$. The simple form of these results for $N \leq 4$ has at present no obvious explanation. Systematics for $N>4$ will offer additional insight to the classification of H^- channels according to K and T, and would also bear on the problem of electron scattering off high Rydberg states of hydrogen.

III. SU(3) CLASSIFICATION OF CHANNELS

The asymptotic channel invariants provide one explanation for the quantum numbers K and T, but some important questions remain unanswered. How, for instance, can A and W be diagonalized so that K and T label states for all values of μ? The form of the operator $W=\vec{L}\cdot\vec{R}$ suggests possible diagonalization effected by Euler angles for transformations in some generalized coordinate system. Also, what is the group theoretical origin for K and T? Although they relate indirectly to SO(4) as strong coupling limits of A and $|W|$, they do not actually label irreducible representations of SO(4) in subspaces of constant L. A more general question is whether the asymptotic channel invariants are limiting forms of more general operators for a noninvariance group classification of three particles interacting via Coulomb forces. Note, for instance, that exchange symmetry for two electrons is neglected in the asymptotic classification. However, exchange played an important role in the classification of low-lying energy levels within each K, T channel, reflecting correlation effects in the region $r_1 \simeq r_2$.[2]

Putting aside the difficult question of a precise physical origin for the channels, let us take a purely phenomenological approach. Namely, is there a noninvariance group which at least reproduces the numerology of the K, T channel classification? We answer this question in part by constructing mathematically a representation of SU(3) on the channel quantum numbers. This is not to say $SU(3)_1 \times SU(3)_2$ is used here for constructing configuration-mixed channels. Rather, we define an SU(3) algebra directly on the two-electron channels. For convenience, the hierarchy of quantum numbers for parity-diagonal channels is summarized below.

$$
\begin{aligned}
&N=1,2,3,\ldots,\\
&T=0,1,\ldots,N-1 \quad \text{if } \Pi=(-)^L\\
&\quad =1,2,\ldots,N-1 \quad \text{if } \Pi=(-)^{L+1},\\
&K=N-T-1, N-T-3,\ldots,1+T-N,\\
&L=T,T+1,\ldots,\\
&M=L,L-1,\ldots,-L.
\end{aligned}
\tag{27}
$$

The two parity classes will be designated hence-

forth by an index q, equal to 0 or 1, with

$$\Pi = (-)^{L+q}. \tag{28}$$

Furthermore, we shall restrict attention to internal—or energy—channel quantum numbers, and thus M is henceforth set equal to zero. For fixed N and q, $\Psi(KTL)$, or simply Ψ, denotes channels.

A. Definition of representations

Eight operators I_0, I_1, I_2, F, C_1, C_2, D_1, and D_2 which connect different K, T, L channels are defined as follows:

$$\begin{aligned}
&I_0\Psi = \tfrac{1}{2}K\Psi,\\
&I_\pm\Psi = \tfrac{1}{2}[(N - T \mp K - 1)(N - T \pm K + 1)]^{1/2}\Psi(K \pm 2),\\
&F\Psi = (12)^{-1/2}[N - 1 - 3T + 2q]\Psi,\\
&C_\pm\Psi = \tfrac{1}{2}[(N - T + K \pm 1)(2T - 2q + 1 \mp 1)]^{1/2}\\
&\qquad \times \Psi(K \pm 1, T \mp 1, L \mp 1),\\
&D_\pm\Psi = \tfrac{1}{2}[(N - T - K \pm 1)(2T - 2q + 1 \mp 1)]^{1/2}\\
&\qquad \times \Psi(K \mp 1, T \mp 1, L \mp 1),
\end{aligned} \tag{29}$$

where only shifted quantum numbers are indicated, and $I_\pm = I_1 \pm iI_2$, $C_\pm = C_1 \pm iC_2$, $D_\pm = D_1 \pm iD_2$. Commutation relations (Appendix) for the eight operators generate an SU(3) algebra on the two-electron channels. I_0, I_1, and I_2 generate an SU(2) subalgebra having $I^2 = I_0^2 + I_1^2 + I_2^2 = I(I+1)$, with $I = \frac{1}{2}(N - 1 - T)$. Within each SU(3) multiplet

$$\begin{aligned}
&I = 0, \tfrac{1}{2}, 1, \ldots, \tfrac{1}{2}(N - 1 - q),\\
&I_0 = I, I - 1, \ldots, -I.
\end{aligned} \tag{30}$$

Properties of SU(3) defined in this way are summarized by de Swart[24] and Carruthers.[25] The first Casimir invariant, $I^2 + C_1^2 + C_2^2 + D_1^2 + D_2^2 + F^2$, has eigenvalues $[(N - q)(N - q + 1) - 2]/3$. The related irreducible representations are all of the type $D(N - 1 - q, 0)$, with each "triangle" multiplet containing $\frac{1}{2}(N - q)(N - q + 1)$ distinct channels. For $\Pi = (-)^L$ the multiplicities are $1, 3, 6, 10, \ldots$ for $N = 1, 2, 3, 4, \ldots$, respectively. When $\Pi = (-)^{L+1}$ the channel multiplicities are $1, 3, 6, \ldots$ for $N = 2, 3, 4, \ldots$. The connection between these multiplicities and the K, T classification was cited in (I).[26]

For fixed N and q the full spectrum of channel quantum numbers K, T, and L contains an infinite number of identical SU(3) multiplets, since L increases without bound. To distinguish between them we therefore define an additional label d, which is the maximum value of L appearing in a multiplet. Comparison with Eq. (27) shows that $d = N - 1, N, N + 1, \ldots$. Since the generators $C_\pm$ and $D_\pm$ define T and L to change in the same sense, the value of L within a multiplet is $L = d - N + 1 + T$. The smallest value of L in a multiplet is $L_{\min} = d - (N - 1 - q)$.

Consider, for example, the simplest nontrivial case $N = 2, q = 0$. In helium the channels contain configuration-mixed Rydberg series $2snL$, $2pn(L-1)$, and $2pn(L+1)$. In the present classification values of L for each SU(3) triplet of channels are: 0, 1 for $d = 1$; 1, 2 for $d = 2$; 2, 3 for $d = 3$, and so forth.

B. SU(4) ⊃ SU(3)

The SU(3) model requires two quantum numbers N and d in order to determine K, T, L, and Π for each channel. The relationship between N and d is rewritten as follows:

$$d + 1 = 1, 2, \ldots; \quad N - 1 = 0, 1, \ldots, d. \tag{31}$$

The other quantum numbers are accessible via the diagonal operators I_0, F, and I^2, and thus

$$\begin{aligned}
&K = 2I_0, \quad T = N - 1 - 2I, \quad L = d - 2I,\\
&q = \sqrt{3}F - 3I + (N - 1), \quad \Pi = (-)^{L+q}.
\end{aligned} \tag{32}$$

Note that $d + 1$ plays the role of a generalized principal quantum number in Eq. (31). For fixed d and q, $N - 1$ is then an associated generalized angular momentum quantum number [cf. Sec. II-A] labeling different SU(3) multiplets. Together these SU(3) multiplets make up a single irreducible representation of SU(4). SU(4) irreducible representations have been described by Amati *et al.*[27] Here the total number of channels contained in each SU(4) "supermultiplet" is $(d - q + 1)(d - q + 2)(d - q + 3)/6$. For instance, the SU(3) multiplicities contained in either of the representations $d = 3$, $q = 0$ or $d = 4, q = 1$ are $1 + 3 + 6 + 10 = 20$. The entire spectrum of internal channels N, K, T, L is in turn contained in infinite sequences of SU(4) representations: $d = 0, 1, 2, \ldots$ for $q = 0$; and $d = 1, 2, 3 \ldots$ for $q = 1$.

The SU(4) interchannel transitions which change N include possible *decay transitions* from $N_i = d + 1$ to final, lower channels $N_f = 1, 2, \ldots, N_i - 1$. K and T have been used in previous work for devising approximate propensity rules for both excitation and decay processes.[1,2] It is possible that a more comprehensive description of those processes might be formulated with SU(4).

C. Correlation diagrams: SU(3) ⊃ SU(2)

The correlation diagrams of Sec. II-F have a more symmetrical form when viewed in the SU(3) multiplet scheme. We illustrate the case $N = 4, d = 3$ in Fig. 5. Note in particular the constancy of I_2 along diagonals of the multiplet for which $K - T$ is fixed. This behavior is characteristic of Eq.

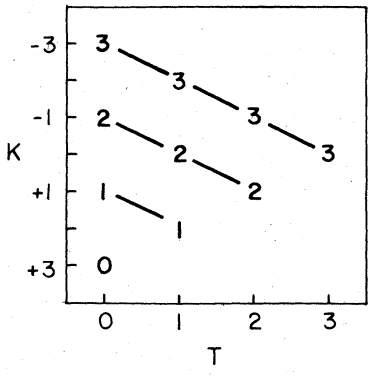

FIG. 5. Correlation diagram illustrating values of l_2 for the SU(3) multiplet $N=4$, $d=3$, $q=0$. The total angular momentum quantum number is $L=T$ for channels in this multiplet. Contrasting diagrams for constant L channels appeared in Fig. 2.

(26). SU(3) generators connecting states along these diagonals are D_1, D_2, and $D_0 \equiv \frac{1}{2}(\sqrt{3}F - I_0)$, which generate an SU(2) subalgebra. The SU(2) states are labeled by the diagonal component $D_0 = \frac{1}{2}(N-1-K-3T+2q)$. It would be premature to conclude that SU(3) $\supset$ SU(2) explains the correlation diagrams for all channels, since applicability of Eq. (26) has not been demonstrated for $N>4$. We have found for $N \leq 4$, however, that $\vec{D}$ commutes with the channel invariant A in the weak coupling limit. The relationship between SU(2) and W^2 is not fully understood. W^2 mixes configuration channel states having $\Delta l_1 = 0, \pm 2$.

D. Hyperspherical coordinates

In 1965 Dragt[15] deduced an SU(3) classification of states for three noninteracting particles, related to O(6) invariance for the kinetic energy in hyperspherical coordinates.[28] Those SU(3) states do not account for Coulomb interactions, however, and are therefore different from the SU(3) model proposed herein. It is thus of considerable interest that computations of atomic energies using hyperspherical coordinates have revealed an "approximate separability" for the two-electron wave functions.[29-31] Channels are labeled using potential energy curves along the hyperspherical radial coordinate $r=(r_1^2+r_2^2)^{1/2}$. In the limit $r \to 0$, O(6) quantum numbers apply. For larger values of r, where the Coulomb interaction mixes states, a K, T classification seems more appropriate.[2]

The connection between the different channel quantum numbers for large r and small r is a problem which is similar to the correlation of the asymptotic invariant A between the strong and weak coupling limits. No single classification of the hyperspherical potential energy curves valid for all values of r has yet been offered. An explanation for the SU(3) characteristics of the channels may possibly be found in a theoretical description of Coulomb interactions within the hyperspherical framework. We note, for instance, the connection between the O(6) and SU(4) Lie algebras.[15] It seems plausible that a single noninvariance group describes the two-electron channels, but in different ways depending on the value of r. At small values of r the channels show characteristics of O(6), while at large values of r the channels exhibit characteristics of SU(4) $\supset$ SU(3). Detailed analysis of hyperspherical symmetry breaking via Coulomb interactions will shed more light on this possibility.

IV. NONCOMPACTNESS

The question has been raised whether[4] or not[16] noncompact versions of two-electron classifications might have physical relevance. At the Lie algebra level the distinction between the compact versus noncompact algebras is trivial, involving only factors of i in generators. At the group level the distinction is nontrivial. Spatial rotations about the z axis, for instance, are described by $\exp(i\alpha L_z)$, which is a periodic function of the angle α. When $\alpha \to i\alpha$, however, the same operator is either exponentially increasing or decreasing depending on the sign of α. We demonstrate below in two different ways importance for noncompactness to the two-electron interaction.

A. Hydrogenic states

Consider the Hamiltonian

$$E=(\tfrac{1}{2})P^2+\lambda/R\,, \tag{33}$$

where $\vec{R}=\vec{r}_1-\vec{r}_2$ and $\vec{P}=-i\partial/\partial\vec{R}$. λ is a coupling parameter, with $\lambda>0$ for a repulsive interaction. Both the relative angular momentum $\vec{\mathfrak{L}}=\vec{R}\times\vec{P}$ and the Runge-Lenz vector

$$\vec{\mathfrak{A}}=\vec{P}(\vec{R}\cdot\vec{P})-\vec{R}(P^2+\lambda/R) \tag{34}$$

commute with E, and

$$\mathfrak{A}^2-\lambda^2=2E(\mathfrak{L}^2+1)\,. \tag{35}$$

$\vec{\mathfrak{L}}$ and the energy-normalized $\vec{\mathfrak{A}}(2E)^{-1/2}$ generate an SO(3,1) algebra, which in the present case is fundamental to the Coulomb repulsion of two particles. Solving Eq. (35) for E yields a group theoretical representation of matrix elements of $1/r_{12}$, since the kinetic energy portion of E can easily be evaluated. For two-electron product wave functions consisting of bound state hydrogenic orbitals for 1 and 2 having principal quantum numbers N and n, respectively, diagonal matrix elements for the Coulomb repulsion thus become

$$(Nn\left|1/r_{12}\right|Nn) = -(N^{-2}+n^{-2})(8\lambda)^{-1} + \left(Nn\left|\frac{\mathfrak{C}^2-\lambda^2}{\mathfrak{L}^2+1}\right|Nn\right)(2\lambda)^{-1}. \quad (36)$$

Equation (30) contains two distinct group theoretical parts. On the one hand are $\mathfrak{L}^2$ and $\mathfrak{C}^2$, which describe exact symmetry properties of E. On the other hand, there is inherent SO(4) symmetry for the bound hydrogenic wave functions. Hence the classification of $1/r_{12}$ in this basis naturally involves SO(4). Note, however, that such a classification fails to recognize the underlying symmetry of the electron-electron repulsion.

This simple model is not intended to suggest SO(3,1) classification for two-electron states. Rather, it illustrates by example that invariance properties of hydrogenic orbitals can be misleading with regard to properties of the Coulomb repulsion.

B. SU(2,1) channels?

The SU(3) model proposed in Sec. III contains the correct numerology for classifying internal quantum numbers for single-ionization channels of two-electron atoms. We offer evidence that a related SU(2,1) classification of channels might be more appropriate. The SU(3) representations[25] are finite dimensional and unitary. In SU(2,1), however, the corresponding finite irreducible representations fall into two classes: (i) one dimensional, unitary, and (ii) multidimensional, nonunitary. For helium the one-dimensional channel representations occur only for $N=1, K=T=q=0$, which contains the $(1snL)L$ singly excited states; and for $N=2, K=0, T=q=1$, which contains $(2pnL)L$ doubly excited states. The important physical connection to note is that none of the states in these unitary SU(2,1) channels decays via Coulomb autoionization. In marked contrast, all other channels for finite N belong to nonunitary representations in an SU(2,1) scheme. These are the configuration-mixed double excitation channels, which contain autoionizing states for helium.[2,4]

Thus a noncompact classification appears to provide a natural distinction between stationary (bound) states and autoionizing (decaying) states, via the respective unitarity or nonunitarity of the channel representation. This connection seems to be more than coincidental, in view of well-known properties[32] of the time evolution operator for bound and decaying states. The question whether autoionization stability of energy levels in helium is in fact governed by the Lie algebra of a noncompact group may also have importance to problems[33] of classical nonergodicity.

There is an additional feature of noncompact channel classification which seems to make it more appropriate for the physical states. Namely, that there also exist infinite-dimensional, unitary representations for a noncompact group. The infinite-dimensional representations of SU(2,1) thus offer one possibility for classification of channels for two-electron escape. The threshold for this double ionization commences in the limit $N\to\infty$.

Finally, it is perhaps noteworthy that the asymptotic channel invariants have a more symmetrical form when constructed with the following vector operators:

$$\vec{h}_0 = 2\vec{L}+\vec{l}_1\,,\quad \vec{h}_1=\vec{l}_2\,,$$
$$\vec{h}_2 = (2^{-5/4})(\sqrt{2}\,\vec{b}_1+\mu\hat{r}_2)\,,\quad \vec{h}_3=(2^{-5/4})(\sqrt{2}\,\vec{b}_1-\mu\hat{r}_2)\,. \quad (37)$$

The first channel invariant thus becomes

$$A = h_1^2+h_2^2-h_3^2\,, \quad (38)$$

a form which admits SU(2,1) invariance under linear combinations of the $\vec{h}_i$. W, however, is not left invariant under these SU(2,1) transformations, since

$$W=\sum_{j,k} W_{jk}(\vec{h}_j\cdot\vec{h}_k)\,, \quad (39)$$

with $W_{jk}=W_{kj}$ and

$$W_{jj}=W_{10}=W_{23}=0\,,$$
$$W_{12}=W_{02}=(1-\sqrt{2})2^{1/4}/6\,, \quad (40)$$
$$W_{13}=W_{03}=-(1+\sqrt{2})2^{1/4}/6\,.$$

V. CONCLUSION

Three primary conclusions have been reached.

(1) In the asymptotic regime the K, T classification for excitation channels is a direct consequence of the invariants A and W^2.

(2) Numerology of internal K, T, L type quantum numbers for single-ionization thresholds is contained in SU(4) ⊃ SU(3) ⊃ SU(2).

(3) In view of (a) stability characteristics of heliumlike systems against Coulomb autoionization, and (b) double-ionization channels, it seems more appropriate to classify channels with SU(2,1) instead of SU(3).

It remains for future work to recast these conclusions together with answers to questions raised herein, in the form of a general theory for two-electron spectra including radiative and autoionization transitions.

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APPENDIX: CHANNEL SU(3)

Nonvanishing commutation relations for the operators defined in Eq. (29) are

$$[I_0, I_\pm] = \pm I_\pm, \quad [F, C_\pm] = \pm \tfrac{1}{2}\sqrt{3}\, C_\pm,$$
$$[I_0, C_\pm] = \pm \tfrac{1}{2} C_\pm, \quad [F, D_\pm] = \pm \tfrac{1}{2}\sqrt{3}\, D_\pm,$$
$$[I_0, D_\pm] = \mp \tfrac{1}{2} D_\pm, \quad [I_+, I_-] = 2I_0,$$
$$[C_+, C_-] = \sqrt{3}\, F + I_0, \quad [D_+, D_-] = \sqrt{3}\, F - I_0,$$
$$[I_-, C_+] = D_+, \quad [C_-, I_+] = D_-,$$
$$[I_+, D_+] = C_+, \quad [D_-, I_-] = C_-,$$
$$[C_+, D_-] = I_+, \quad [D_+, C_-] = I_-,$$

which generate an SU(3) algebra. In de Swart's notation for SU(3) generators,[23] $C_\pm = K_\pm$, $D_\pm = L_\pm$, and $F = M$.

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