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# Novel supermultiplet energy levels for doubly excited He

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The authors propose a novel "supermultiplet" classification of doubly excited states for two electrons in the same shell, constructed from more limited $O(4)$ multiplets of earlier classification schemes. The supermultiplets are found to give a much more efficient classification, and bring to light new features of the spectrum, including accidental near-degeneracies of certain levels having different values of the angular momentum. When viewed with these supermultiplets, the intrashell spectrum is found to bear a striking similarity to a cutoff rotation-vibration spectrum of a linear triatomic molecule. This structure is interpreted with rotations and bending-mode vibrations for a strongly coupled electron pair; energies for these apparent excitations are found to have approximate separability.

## I. INTRODUCTION

Doubly excited atoms are difficult to treat theoretically because of the problem of electron correlation. In recent years this difficulty has led to several approaches for classifying doubly excited states of the prototypical two-electron atom, including hyperspherical radial coordinates,[1-3] group theory from atomic shell structure,[4-12] and even semiempirical analysis of configuration-interaction studies of the Schrödinger equation.[13] Thus far, however, no one has presented a picture of the doubly excited atom that is conceptually easy to grasp and that also explains energy levels without a great deal of numerical effort. This problem is especially difficult for the case of low-lying "intrashell" states, in which two electrons occupy orbitals in the same shell. There the combination of configuration mixing within the degenerate manifold, plus strong intershell correlation, produces an extremely complex spectrum involving many different symmetry terms.

Our present study of doubly excited two-electron atoms indicates that a satisfactory resolution of this difficult problem may well be close at hand. This work is a direct outgrowth of an earlier study[14] which linked certain representations of the group $O(4)$ to cut-off rotorlike spectra for intrashell levels, which could originate in collective rotations of the atom as a floppy, linear $XYX$ "molecule" with $X$'s electrons and $Y$ the nucleus. We now consider the possibility that other, nonrotational types of energy might be linked to a heretofore unrecognized "supermultiplet" classification of intrashell states originating in the $O(4)$ shell theory of the atom. Basically then we are investigating novel mathematics for two-electron atoms and using it to probe the spectrum for new insight into the underlying electron correlation. From this we hope to construct a simple picture of the atom which one can use to interpret energy levels and to understand transitions between these levels.

Our main concern is with presenting these novel results so that experimentalists and theorists alike can understand them and appreciate their significance for atomic-structure theory. We therefore describe only key concepts and results; most of the mathematical details will be presented subsequently. For now, we note only that our work parallels dynamical symmetry interpretations in other areas of physics, such as collective motion[15] and shell structure[16] of nuclei, and elementary particles.[17]

We illustrate results using the $N=3$ shell of helium, which is sufficiently complicated that one sees the full power of the supermultiplet approach. This will be described using successively higher classification schemes. Section II gives the usual single-configuration approach and explains why this method fails. Section III gives a similar classification using the group $O(4)$, which takes into account configuration-mixing effects. We then present our supermultiplet classification in Sec. IV and show how it reveals new spectral features which were not at all obvious in the earlier classifications. We summarize, interpret, and discuss the significance of these results in Sec. V.

## II. SINGLE-CONFIGURATION CLASSIFICATION

This approach emphasizes a picture of the atom in which each electron occupies an orbital with fixed angular momentum $l$. There is a total of six configurations $(ll')$ for the $N=3$ shell, corresponding to two electrons in $3s$, $3p$, and $3d$ orbitals. Each configuration leads to a multiplet of levels described by the usual atomic term symbol $^{2S+1}L^{\pi}$, in which values of the total orbital angular momentum are determined from the Clebsch-Gordan series $|l-l'| \leq L \leq l+l'$ for the two-electron product group $O(3)_1 \times O(3)_2$. These multiplets are shown in Fig. 1, which includes a total of 19 $S$,

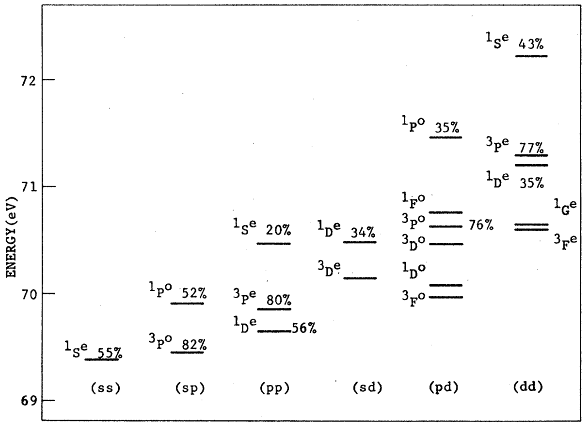

FIG. 1. Configurational classification of helium-atom doubly excited energy levels for two electrons in the same shell $N=3$. Percentages indicate contribution of configuration to the wave function computed in Ref. 7. Energies are in electron volts above the ground state.

$P$, $D$, $F$, and $G$ levels for $N=3$ doubly excited helium. These data were computed in Ref. 7, taking into account both intrashell and intershell configuration-mixing effects; similar levels would be seen using data from Lipsky *et al.*[13] for $S$, $P$, $D$, and $F$ states.

Because of the configuration-mixing problem, it is difficult to assign these levels purely on the basis of a single, dominant orbital configuration in the wave function. We have indicated this in cases where the single-configuration scheme breaks down, by including the percent contribution of the "dominant" configuration to the wave function. This is quite low in some cases, owing to very strong mixing with other configurations of the same symmetry. The configuration interaction also perturbs the energies of the states. This can change the ordering of levels one expects for a single-configuration state and Hund's rules. For example, the usual ordering in a $(pp)$ multiplet is $^3P^e < {}^1D^e < {}^1S^e$, but here we find a different ordering, $^1D^e < {}^3P^e < {}^1S^e$, due largely to the interaction of $^1D^e$ levels in $(pp)$ and $(sd)$. Overall then, Fig. 1 offers little evidence which might suggest a useful picture of the electron correlation.

## III. $O(4)$ CLASSIFICATION

Applications of the $O(4)$ group in atoms originate in the exact degeneracy of hydrogen-atom levels due to commutation of the energy with the $O(4)$ generators $\vec{l} = \vec{r} \times \vec{p}$ for $O(3)$ angular momentum, and the energy-weighted Lenz vector $\vec{b} = N[\vec{p}(\vec{r}\cdot\vec{p}) - \vec{r}(p^2 - 1/r)]$.[18] In classical mechanics the Lenz vector lies along the major semiaxis of an elliptical Kepler orbit, while $\vec{l}$ is perpendicular to the orbit plane. In quantum mechanics $\vec{b}$ mixes degenerate hydrogenic orbitals having different $l$; for example, $b_z|2s\rangle = |2p_z\rangle$. The generators are therefore useful for describing approximately the configuration mixing found in two-electron atoms.

Neglecting spin, the degenerate manifold of hydrogenic orbitals $l=0, 1, \ldots, N-1$ is contained in a single irreducible representation of $O(4)$ labeled $[N-1, 0]$. Similar $O(4)$ representations $[P, T]$ are found in two-electron atoms, and these label multiplets of $O(3)$ terms with angular momemtum $L=T, T+1, \ldots, P$.[19] $P$ and $T$ designate two $O(4)$ quantum numbers, which replace the two quantum numbers $l$ and $l'$ from the single-configuration picture. The number of configurations $(ll')$ resulting from two electrons in the same shell is $\binom{N}{2} = \frac{1}{2}N(N-1)$. Likewise there is a total of $\frac{1}{2}N(N-1)$ multiplets $[P, T]$ in the intrashell $O(4)$ picture. These two-electron representations are seen in the following $O(4)$ Clebsch-Gordan series:

$$[N-1, 0]_1 \times [N-1, 0]_2 = \sum [P, T], \tag{1}$$

which includes the values $T=0, 1, \ldots, N-1$ and $P=T, T+2, \ldots, 2N-2-T$. Earlier two-electron studies[4(b),6] identified the generators $\vec{L} = \vec{l}_1 + \vec{l}_2$ and $\vec{B} = \vec{b}_1 - \vec{b}_2$, and configuration mixings follow from diagonalization of the operator $\vec{B}^2$. A set of diagonal operators for the $O(3)$ terms $T \leq L \leq P$ contained in each $O(4)$ multiplet $[P, T]$ is given by $\vec{L}^2 = L(L+1)$, $L_z = M$, $\vec{B}^2 = P(P+2) + T^2 - L(L+1)$, and $|\vec{L}\cdot\vec{B}| = T(P+1)$. The $O(4)$ states we consider for two-electron atoms are chosen to have definite symmetry for parity $(\Pi)$ and exchange $(P_{12})$ of spatial coordinates of the electrons. By the Pauli principle, levels which correspond to spatial exchange $P_{12}=+1$ and $P_{12}=-1$ have singlet $(S=0)$ and triplet $(S=1)$ electron spin, respectively. The quantum number $T$ is associated with the magnitude of the total orbital angular momentum projected along the internal axis $\vec{B}$. Only the magnitude is important because the operator $\vec{L}\cdot\vec{B}$, which has eigenvalues $\pm T(P+1)$ in a mixed-parity basis, anticommutes with $\Pi$ and $P_{12}$ operations. The inequality $L \geq T$ is consistent with the angular momentum interpretation of $T$. When $T=0$, there is one atomic term $^{2S+1}L^{\pi}$ for each value of $L$, and this term has definite parity and exchange symmetry, owing to the fact that $\vec{L}\cdot\vec{B}=0$. When $T>0$, on the other hand, there are *two* terms for each value of $L$, and these terms have opposite parity and exchange.

The $O(4)$ classification of levels for the $N=3$ shell of helium is given in Fig. 2. This represents the same data as Fig. 1, but viewed from a different perspective. Herrick and Sinanoğlu described the configuration mixing in wave functions for these

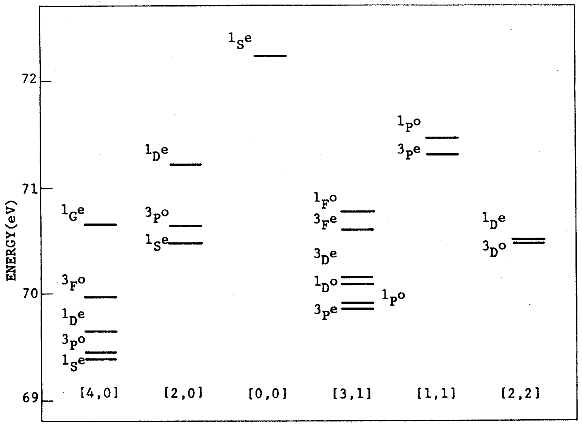

FIG. 2. $O(4)$ classification of helium-atom doubly excited energy levels for two electrons in the same shell $N=3$; levels are the same ones shown in Fig. 1. Each $O(4)$ multiplet $[P,T]$ contains levels with $T\leq L\leq P$.

states, using a slightly different $O(4)$ quantum number $K$ which they defined to take into account the strong intershell correlation as well.[7] Our present construction of $O(4)$ multiplets is related to the earlier work by the identity $P=N-1+K$ for intrashell levels.

Note that there are six $O(4)$ multiplets in Fig. 2, just as there were six configurational multiplets in Fig. 1. The $O(4)$ multiplets lend a more ordered structure to the spectrum of helium, however, and energies increase with $L$ in each multiplet. The parity $\Pi$ of each level satisfies $\Pi(-1)^L=+1$ when $T=0$. There are two levels for each value of $L$ in a multiplet when $T>0$. These are nearly degenerate, and the level with $\Pi(-1)^L=+1$ lies slightly higher in energy than the level with $\Pi(-1)^L=-1$. These trends were seen in the earlier studies[6,7] of helium levels with $K$ and $T$. Here we call the splitting of these conjugate pairs of levels "$T$ doubling" and note further that it tends to increase with $L$ in each $O(4)$ multiplet and decrease with higher $T$ between different multiplets. It is convenient for us to distinguish between the two types of levels with multiplets designated $[P,T]^+$ or $[P,T]^-$, for the two types of parity $\Pi(-1)^L=+1$ or $-1$, respectively. In addition, we note that the exchange symmetry of each level is given by the expression $P_{12}=\Pi(-1)^T$. Taking into account electron spin, we see this gives the intrashell identity $\Pi(-1)^{S+T}=+1$ for all levels, including both singlet ($S=0$) and triplet ($S=1$) total spin. This is a useful result to remember, because it helps explain selection rules for energy matrix elements or transitions. Radiative $E1$ transitions, for example, conserve total spin but change the parity of the atomic state; consequently, these transitions can occur between two intrashell multiplets only when $\Delta T$ is odd.

Overall, the $O(4)$ multiplets in Fig. 2 suggest a clearer picture of the intrashell electron correlation than did the configurational multiplets. We note that each $O(4)$ multiplet places a heavy emphasis on collective rotational aspects of the energy. This is illustrated most clearly by the sequence of energy levels in the largest multiplet $[4,0]$, whose spacings were noted earlier[14] to be similar to those of an $XYX$ rigid rotor molecule. This illustrates the value of the approximate symmetry group. It organizes the data into a form which allows us to draw conclusions about the underlying atomic structure. This is similar to uses[16] of approximate symmetry groups in nuclear spectra. However, it is important to note that the mathematical structure of $O(4)$ does not in itself dictate the $XYX$ model. Instead, $O(4)$ originates with the independent-particle picture of the atom, at high $Z$ in the isoelectronic series. It is entirely possible that nonrotor series would be found at high $Z$, where the electron correlation is much weaker than it is in low-$Z$ atoms such as helium. It has already been pointed out, for example, that the $[4,0]$ multiplet spectrum becomes less like that of a rigid rotor if one looks at the data for high values of $Z$.[14] Here we find another interesting result, that $T$ doubling *decreases* with lower values of $Z$, suggesting a similarity of the $T$-doubled levels to the degeneracy one expects for rigid rotations of the $XYX$ linear molecule as a symmetric top. The structure of each $O(4)$ multiplet is too small, however, to allow us to pursue this line of thought any further and include the possibility of other, nonrotational parts of the correlation energy. The $O(4)$ multiplets were very useful for illuminating the rotor characteristics of the spectrum. This is one of the reasons why we consider the possibility that an even larger "supermultiplet" classification scheme would be just as useful for illuminating other parts of the spectrum.

We have found some evidence hidden in the $N=3$ intrashell spectrum which suggests to us that a supermultiplet classification is not entirely a speculative proposition. This bit of evidence may be seen in the unresolved spectrum of Fig. 1 or Fig. 2. Overall, this displays what may be called level clustering, rather than a uniform distribution of energies. Some of this clustering may be accidental, owing to the large number of levels with different symmetries. Some of it may even result from the relatively limited accuracy of current estimates of energies, in comparison to exact solutions of the Schrödinger equation. We are very much struck, however, by the closeness of three levels near 70.5 eV. Two of the levels are identified as the $T$-doubled pair $^1D^e$ and $^3D^0$, belonging to the $O(4)$ multiplet $[2,2]$. The third level is identified as the $^1S^e$ state from the multiplet $[2,0]$. Thus the nearly degenerate cluster involves levels from different $O(4)$ multiplets, as well as different angular momentum symmetry. We have searched the more extensive configuration-interaction data of Lipsky *et al.*[13] and found a similar near-degeneracy of these levels occurring at only slightly lower energy. We have also looked at the available data for $S$, $P$, and $D$ levels in the $N=4$ shell and found other examples of $S$-$D$ degeneracies. These results lead us to take more seriously the possibility that near-degeneracy of levels with different values of $L$ might be a fundamental part of the doubly excited intrashell spectrum. This near-degeneracy is not explained by the $O(4)$ multiplets, nor has it even been recognized in any earlier work, although other examples of apparent accidental degeneracies have been cited for the intershell part of the spectrum.[7] We therefore look in Sec. IV for supermultiplets which could account for this puzzling feature of the spectrum.

## IV. SUPERMULTIPLET CLASSIFICATION

In Sec. III we indicated that supermultiplets would allow one to take a broader view of the intrashell spectrum and hence gain some insight into nonrotational aspects of the correlation energy. We now construct two related types of supermultiplets which achieve this goal. We construct these from the earlier framework of $O(4)$ multiplets and quantum numbers, using a novel invariant for the two-electron atom.

### A. *d* supermultiplets

We identify the first type of intrashell supermultiplet, using the combinations of $O(4)$ generators $\vec{j}=\frac{1}{2}(\vec{L}+\vec{B})$ and $\vec{k}=\frac{1}{2}(\vec{L}-\vec{B})$. It is well known mathematically[18,19] that they generate two commuting SU(2) groups and, in the case of the hydrogen atom, are related to the separability of the energy in parabolic coordinates. However, neither $\vec{j}$ nor $\vec{k}$ is particularly useful by itself for the two-electron atoms, because the operators and the SU(2) invariants are not symmetric under the permutation-inversion symmetry operations. Our investigation shows, however, that an approximate invariance may be associated with a related SU(2) group which takes this into account. We define the SU(2) group using a generator $\vec{J}_>$, which is taken to be the *larger* magnitude vector of $\vec{j}$ and $\vec{k}$. Although this appears to be a somewhat unusual way of defining a generator, it is the preferred way for two-electron atoms. Classically the vectors are related to the relative precession of two degenerate Kepler orbits.

We define a $d$ supermultiplet to be the collection of $O(4)$ intrashell states over which the operator $\vec{J}_>^2$ is invariant. The number $d$ used here is contained in the SU(2) invariant for the supermultiplet,

$$\vec{J}_>^2 = d(d+1)\,, \tag{2}$$

and is given by $d=\frac{1}{2}(P+T)$. Thus each $d$ supermultiplet, which we label as $\{d\}$, is built up from intrashell $O(4)$ multiplets having the same value of $P+T$. We can therefore rewrite the $O(4)$ Kronecker product in Eq. (1) with $d$ supermultiplets as follows:

$$[N-1,0]_1 \times [N-1,0]_2 = \{0\} + \{1\} + \cdots + \{N-1\}\,. \tag{3}$$

Each $d$ supermultiplet in turn has the following $O(4)$ multiplet reduction:

$$\{d\} = [2d,0] + [2d-1,1] + \cdots + [d,d]\,. \tag{4}$$

Neglecting spin, the number of states in each $d$ supermultiplet is $(2d+1)[2d(d+1)+1]$ and generates the sequence of multiplicities 1, 15, 65, 175, 369,.... Neglecting both spin and spatial rotation degeneracies, the number of energy levels contained in each $d$ supermultiplet is $2d(d+1)+1$ and generates the sequence 1, 5, 13, 25, 41,.... It is interesting to note the way a single factor, $2d+1$, accounts for the entire spatial degeneracy of a $d$ supermultiplet in these formulas. The total number of intrashell states is $N^4$, while the total number of energy levels is $\frac{1}{3}N(2N^2+1)$, as illustrated by the 19 levels for $N=3$ in Fig. 1 or 2. The spectrum clearly becomes rapidly more complex with higher values of $N$. Each $d$ supermultiplet also reduces according to the two parity classes, designated $\{d\}^+$ and $\{d\}^-$ for $\Pi(-1)^L=+1$ and $-1$, respectively. The number of states contained in these supermultiplets is $(2d+1)(d+1)^2$ for $\{d\}^+$, and $(2d+1)d^2$ for $\{d\}^-$.

From the preceding mathematical structure of two-electron supermultiplets, we have constructed in Fig. 3 the $d$-supermultiplet classification of term symbols for the $N=3$ shell. We have arbitrarily chosen to place the states in $\{d\}^-$ on the left-hand side of each supermultiplet. The lines between term symbols are a convenience which helps one see the connection between states with the same value of $L$ in the spectrum. The corresponding $d$-supermultiplet representation of the helium spectrum for $N=3$ is shown in Fig. 4. The power of the $d$ supermultiplets for organizing the data is very evident there. There is even some regularity in the level orderings in going from $d=1$ to $d=2$. In the absence of $T$ doubling, each of the $d$ supermultiplets would have a perfect

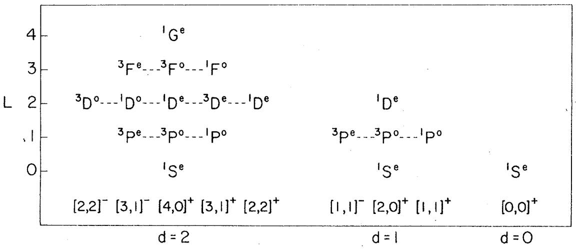

FIG. 3. *d* supermultiplets of intrashell atomic term symbols for doubly excited states in the shell $N=3$. $O(4)$ multiplets are seen vertically above each multiplet symbol $[P,T]^{\eta}$, with $\eta=\Pi(-1)^L$.

left-right mirror symmetry. *T* doubling breaks this symmetry in the case of helium and thus shifts the left side of a supermultiplet slightly lower than the right side. We have also constructed supermultiplets for the $N=2$ shell and find that they have shapes very similar to $d=1$ and $d=0$ in Fig. 4.

### B. *I* supermultiplets

The second type of supermultiplet we consider complements the *d*-supermultiplet picture. The *d*-supermultiplet levels are described by quantum numbers *T* and *L* for two types of rotational excitation in the $O(4)$ states: (i) rotation about an internal axis for the system $(T \geqslant 0)$ and (ii) overall rotation of the system $(L \geqslant T)$. The relative degree of excitation for these two types of rotation may be described with the number

$$I=L-T. \tag{5}$$

We therefore use *I* to investigate intrashell correlation energies associated with other degrees of freedom, between states which have the same degree of rotational excitation. In other words, we say that levels with the same value of *I* belong to the same "*I* supermultiplet." The sequence of supermultiplets for each shell is given by the values $I=0,\ 1,\dots,\ 2N-2$.

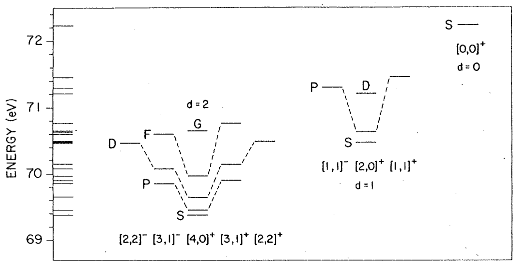

FIG. 4. *d* supermultiplet classification of helium-atom doubly excited energy levels for two electrons in the same shell $N=3$. These are the same levels shown in Figs. 1 and 2. Note unresolved spectrum at left, including level clustering. Notation and term symbols were shown in Fig. 3.

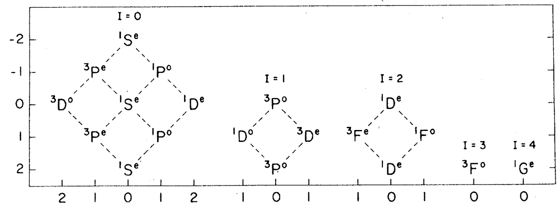

FIG. 5. *I* supermultiplets of intrashell atomic term symbols for doubly excited states in the shell $N=3$. Each *I* supermultiplet contains states from different $O(4)$ multiplets (cf. Fig. 3). For example, the sequence $^1S^e$, $^3P^o,\dots,$ $^1G^e$ seen here as the lowest states in *I* supermultiplets is contained in the single $O(4)$ representation $[4,0]^+$ in Fig. 3.

The *I*-supermultiplet classification of term symbols for $N=3$ is given in Fig. 5. We again place the states with $\Pi(-1)^L=-1$ on the left-hand side of each supermultiplet. Note that each *I* supermultiplet contains terms which in Fig. 4 appeared in different *d* supermultiplets. Thus we are taking yet another view of the spectrum. The corresponding *I*-supermultiplet classification of helium levels in the $N=3$ shell is shown in Fig. 6. The largest of these diamond-shaped supermultiplet spectra has $I=0$. Owing to a similarity between the quantum numbers for these states and earlier ones defined for intershell channels,[7-9] we have chosen to label the terms in *I* supermultiplets using *K* and *T* rather than *P* and *T*. Recall the identity $K=P-N+1$ for intrashell states. The diamondlike shape of each *I* supermultiplet reflects what may be described as approximately equal spacing of levels with decreasing *K* within a supermultiplet. Lower values of *K* give higher energies. *T* doubling is seen for levels with the same values of *K* and *T* within each "diamond." Their splitting increases with higher values of *I*, and hence the

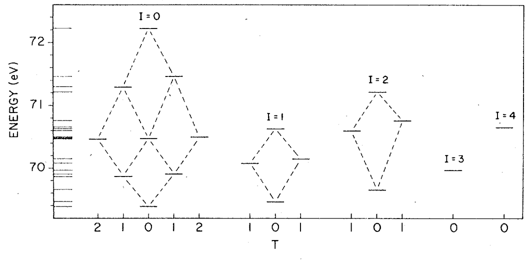

FIG. 6. *I* supermultiplet classification of helium-atom doubly excited energy levels for two electrons in the same shell $N=3$. These are the same levels shown earlier in Figs. 1, 2, and 4. Notation and term symbols were shown in Fig. 5. Note the nearly equal level spacing in the largest of these "diamond" supermultiplets, including near-degeneracy of three levels at 70.5 eV above the ground state.

magnitude of $T$ doubling is evidently linked to the degree of rotational excitation. The degree of rotational excitation is also seen in Fig. 6 as higher energies for the smaller diamonds.

The most striking, and pleasing, feature of the $I$-supermultiplet classification is that it accounts for the near-degeneracy of $S$ and $D$ terms near 70.5 eV. These levels are contained in a single row ($K=0$) in the largest diamond supermultiplet (i.e., $I=0$). This is a very interesting result because the case $I=0$ corresponds to $L=T$; this means that the energy in the system involves internal degrees of freedom, as opposed to overall rotations of the system. It is possible then that the near-degeneracy we have found originates in an approximate separability in some internal coordinate system for the two-electron atom. Our investigation of $S$-$D$ degeneracies in the $N=4$ shell shows they are also in the largest $I$ supermultiplet.

## V. DISCUSSION

We now summarize and discuss our results. We started in Sec. II by illustrating the inadequacy of the single configuration ($ll'$) scheme for classifying levels of helium in the $N=3$ shell. The central-field picture is not a good one for doubly excited states of two-electron atoms, owing to the electron correlation which manifests itself in the wave function as a strong configuration mixing. In Sec. III we exploited previous $O(4)$ theory for configuration mixings, in order to illustrate the same set of $N=3$ levels using multiplets $[P, T]$. These are the irreducible representations of the group for two electrons in the same shell. The $O(4)$ multiplets gave a much clearer picture of the intrashell spectrum and allowed us to make new observations about trends for $T$-doubling energy-level splitting and other electron correlation energy due to rotational excitations. We found evidence, in previously unrecognized near-degeneracies of $S$ and $D$ terms, that $O(4)$ multiplets provide too limited a view of the spectrum for us to interpret nonrotational aspects of the electron correlation. This led us to define and exploit the novel $d$ and $I$ supermultiplets in Sec. IV.

The results we find when we look at the spectrum through the supermultiplets are very startling. They indicate a much higher degree of regularity in the spectrum than could otherwise have been foreseen. This is very surprising to us because of the approximate nature of the group theory involved. There seems to be compelling evidence in the levels of the largest $I$ supermultiplet, however, for a new type of approximate separability in two-electron atoms. The diamond pattern for $I=0$ suggests a type of "linear Stark effect" in an internal coordinate frame. If this Stark analogy were exact, then modified parabolic coordinates involving terms like $1+\cos\theta_{12}$ and $1-\cos\theta_{12}$ might be useful. A more precise set of coordinates leading to the approximate separability has not been identified. We emphasize that our discovery of supermultiplets is an outgrowth of a semiempirical group-theoretical approach. This approach was necessary because of the great difficulty of solving the Schrödinger equation exactly. We think it highly unlikely that the spectral features we describe with supermultiplets could have been found otherwise. Experimental data[20] for doubly excited shells $N \geqslant 3$ are far too limited at present to account for all of the values of $L$ included in the supermultiplets.

There is an alternative and potentially valuable interpretation of the supermultiplets which does not rely on group theory. Instead, it gives a very simple picture of the atom which is much easier to grasp, at least for the present. This view originates in our earlier description of low-$Z$ intrashell rotational collective excitations, which was linked to the $XYX$ rotor model.[14] We now recognize that the entire intrashell spectrum for each $N$ might, in a first approximation, be explained with both rotations and bending vibrations of a linear symmetric $XYX$ structure. These bendings, such as occur in the linear molecule $CO_2$, would account partly for correlated motion of the electrons in atoms involving the interelectronic angle $\theta_{12}$. Although it seems natural to consider bendings in light of Ref. 14, one finds it is not a trivial task to sort out and assign this type of energy level in the complex intrashell spectrum. The supermultiplets solve this problem very nicely. When viewing the $d$ supermultiplets in Fig. 4, molecular spectroscopists will immediately recognize ro-vibrational progressions, similar to those of a highly floppy linear molecule. Shell structure would account for the cutoffs in the ro-vibrational spectrum for the doubly excited atom. Level spacings seen in Figs. 4 and 6 indicate approximate separability for the rotationlike and vibrationlike excitations. There is also separability between these intrashell excitation energies and the energies for transitions to other shells $N=2$ and $N=4$.

In the past, ro-vibrational spectra have not been considered part of the usual atomic spectroscopy. It is probably true to say that rotationlike and vibrationlike progressions of energy levels could originate in a variety of ways. We tentatively assume, however, that the levels we find in the double-excitation supermultiplets originate in combinations of highly nonrigid rotations and very floppy bending vibrations of electrons about an average configuration $\theta_{12}=180°$. The approximate separability of energies would then involve three types of motion: (i) fast radial electronic motion giving the atomic shell structure, (ii) relatively slow collective bending motions of two electrons within a shell, and (iii) even slower collective rotations of two electrons within a shell.

If the qualitative ro-vibrational interpretation is at all realistic, then gross features of the intrashell multiplets should be described by standard molecular-energy formulas for rigid rotations and harmonic-bending vibrations of a linear *XYX* molecule.[21] In terms of the atomic quantum numbers *L* and *T*, this would be

$$E=\omega_2(v+1)+B_e[L(L+1)-T^2], \tag{6}$$

which includes a bending constant $\omega_2$, a rotational constant $B_e$, and a quantum number $v=0, 1, \ldots$ for a two-dimensional oscillator. We will not consider such higher-order effects as anharmonicity and nonrigidity in this paper. We find that the overall level structure predicted by Eq. (6) is similar to that of the atomic supermultiplets if we include cutoffs in the spectrum and if we make the correspondence $v \longleftrightarrow N-1-K$ between the two types of quantum numbers. The approximate separability seen in low-lying levels in Fig. 4 can be described by Eq. (6) when the parameters satisfy $\omega_2/B_e \simeq 12$. This is much smaller than the separability typical of molecular spectra.[21]

Implicit in the simple ro-vibrational energy formula in Eq. (6) are two physical pictures of the *XYX* molecule which could account for similar features in the atomic intrashell spectra. First the near-degeneracy clustering of *S* and *D* terms in the largest diamond supermultiplet would be explained by the degeneracy of a two-dimensional harmonic oscillator, resulting from the two bending degrees of freedom for the *XYX* structure. In a two-dimensional oscillator our quantum number *T* would correspond to a quantum number for what molecular spectroscopists call "vibrational angular momentum," which describes the degenerate states. In the row $K=0$ in the $I=0$ supermultiplet in Figs. 5 and 6, for example, the term $^1S^e$ has no angular momentum, while the two *D* terms each carry two quanta ($T=2$) of angular momentum about the internal axis. In the molecular approach this axis is the one for the *XYX* structure; in the $O(4)$ approach the axis is $\vec{B}$. The second physical picture implicit in Eq. (6) is the one of the *XYX* molecule as a rigid symmetric top. Thus the formula predicts exact degeneracy for each *T*-doubled pair of states, even when the vibrational degeneracy is broken. These features are seen to be consistent with what we find in supermultiplets. It is clear, however, that higher-order effects would have to be considered in a molecular approach to the atom.

From the preceding interpretations we conclude that it is very reasonable to consider that correlation in doubly excited two-electron atoms may be viewed in two approximate ways: (i) with supermultiplets originating in the hydrogenic shell structure at high *Z* or (ii) with a molecular ro-vibrational viewpoint originating in the strong electron correlation at low *Z*. Available data suggest that *T* doubling decreases as one goes to lower *Z* in the isoelectronic series, and thus the *T* doubling becomes more like the degeneracy expected for a symmetric top. We note that the two approaches involve at the outset two very different pictures. In the group-theoretic approach, for example, the totally symmetric representation $[0,0]$ is generally the *highest* $^1S^e$ level in the intrashell spectrum. This has suggested to one of us[22] that the $O(4)$ group theory may be linked to the behavior of the Coulomb-repulsion operator $1/r_{12}$ in the region $\theta_{12}=0°$. In contrast to this, the ground state of the rotor-vibrator corresponds to the *lowest* $^1S^e$ level in each shell and is related to the behavior of $1/r_{12}$ near $\theta_{12}=180°$. Apparently the group-theoretic approach and the collective ro-vibrational approach are reasonably compatible in doubly excited states we have studied thus far. This compatibility is very interesting because of similar connections between group theory and collective motion in nuclei.[15,16] We shall investigate the supermultiplet and ro-vibrational approaches, including higher shells, in considerably more detail in future work.

The full extent of applicability of the ro-vibrational picture and supermultiplets to other systems is not known. However, we note that the configuration-mixing effects in wave functions for intrashell doubly excited states are essentially the same ones important in the valence shells of chemically reactive atoms. In many-electron atoms the present isolated pair correlation picture would be perturbed by antisymmetry and coupling with other electrons. Herrick and Kellman[23] have used pairwise-coupled $O(4)$ invariants for configuration mixings in first-row atoms. Our supermultiplets offer a potentially useful way of classifying pair correlation energies in the many-electron systems. The ro-vibrational picture may also prove useful for sorting out important contributions to the correlation energy in very highly excited levels leading to the threshold for double-ionization processes. Virtual double excitations involving one or more charge centers could also be described with rotations and vibrations in a first approximation; these would affect the contributions of the terms to chemical bonding in both gas and condensed phases. The simplest example of this is the molecule $H_2$, which has Born-Oppenheimer electronic states which correlate with doubly excited states of helium in the united-atom limit. Supermultiplets may therefore have uses in a variety of systems in which pair correlations are important.

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