

Classification of Doubly Excited States of Two-Electron Atoms

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(Received 17 June 1983)

Based upon the analysis of electron correlations in hyperspherical coordinates, a classification scheme for all doubly excited states of two-electron atoms is presented. A new set of correlation quantum numbers, K , T , and A , is introduced, where (K, T) describes angular correlations and A describes radial correlations. It is shown that states with different L , S , and π but identical $(K, T)^A$ have isomorphic correlations. Such isomorphism is shown to result in the *general* supermultiplet structure of doubly excited states.

PACS numbers: 31.30.+z, 31.20.Tz

Since the identification of doubly excited states of He in 1963,¹ it has been recognized that understanding these states requires a new *language* for describing the correlation of two excited electrons. The independent-particle model, which forms the basis for almost all areas of microscopic physics, no longer suffices as a first-order description of these states. Because of the lack of understanding of electron correlations, a first-order description of doubly excited states as well as a complete classification scheme for these states have not been available so far.

In the past few years partial understanding of two-electron correlations has emerged gradually. In particular, Lin² has introduced the graphical display of two-electron correlation patterns in hyperspherical coordinates and Herrick and Kellman³ have emphasized the supermultiplet structure of *intrashell* doubly excited states. In this Letter I report a *complete* classification scheme of doubly excited states based upon the analysis of electron correlations in hyperspherical coordinates. It is shown that the supermultiplet structure is quite general for doubly excited states and its origin is attributed to isomorphic correlation patterns.

According to the independent-particle model, the two-electron wave function within the LS coupling scheme is represented by $|n_1 l_1, n_2 l_2, L, S, \pi\rangle$. Since configuration mixing is quite large for doubly excited states, a given state is represented as the admixture of many configurations with different n_1 , n_2 , l_1 , and l_2 such that these individual quantum numbers are no longer adequate to *identify* the state. Mixings of l_1 and l_2 within given n_1 and n_2 were introduced by Herrick and Sinanoglu⁴ in their doubly excited-state basis (DESB) functions. Two new quantum numbers, K and T , were introduced to replace l_1 and l_2 such that each state is now represented by $|nNKTLS\pi\rangle$, where n

and N represent the principal quantum numbers of the outer and the inner electrons, respectively. However, DESB functions in general do not represent radial correlations of doubly excited states adequately,⁵ so that further superpositions of DESB functions are required.

Doubly excited states have also been studied in hyperspherical coordinates.⁶ With use of the assumption of quasiseparability,⁷ the wave function is expressed as $F_\mu^n(R)\Phi_\mu(R; \Omega)$, where $R = (r_1^2 + r_2^2)^{1/2}$, $\Omega \equiv (\alpha, \hat{r}_1, \hat{r}_2)$, and $\alpha = \arctan(r_2/r_1)$. In this first-order approximation, μ is the channel index, $\Phi_\mu(R; \Omega)$ is the channel function, and $F_\mu^n(R)$ is obtained by solving the one-dimensional radial equation with channel potential $U_\mu(R)$. Despite the success of this approach, it has not been possible to relate the channel index μ to some apparent quantum numbers. Through the analysis of electron correlations for different L , S , and π states, I show in this Letter that *each channel is identified by a set of correlation quantum numbers, K , T , and A* . Channels with identical $(K, T)^A$ but different L , S , and π are shown to have isomorphic correlations. This isomorphism is shown to result in the general supermultiplet structure of doubly excited states. The physical meanings, the rules of assigning these quantum numbers, and the spectroscopic consequence are discussed. For example, in Fig. 1 the potential curves for 1^3P^o and 1^3D^e of He below $N=3$ are labeled with these $(K, T)^A$ quantum numbers. It is evident that channels with identical $(K, T)^A$ have very similar potential curves.

A. Angular correlations.—The angular-correlation quantum numbers, K and T , are those used by Herrick and Sinanoglu⁴ in their DESB functions. In the present context, however, they are *not* related to DESB functions directly. Instead, they are used to label asymptotic dipole states,⁸ i.e., the Stark states in the asymptotic

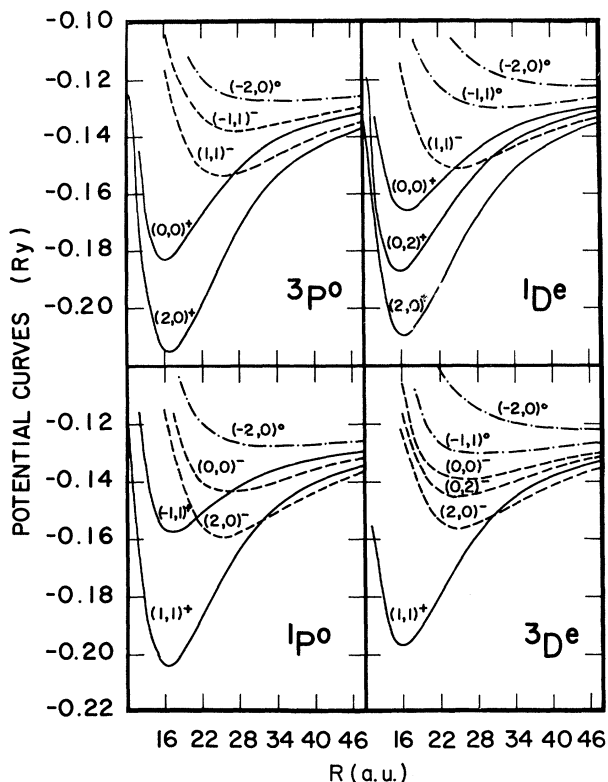


FIG. 1. Potential curves for $1,3P^o$ and $1,3D^e$ of He below $N=3$. The curves are labeled by the quantum numbers $(K, T)^{\pi\alpha}$ as described in the text. Reduced units ($Z=1$) are used.

region ($R \rightarrow \infty$). According to Ref. 4, the ranges of K and T are determined as follows:

$$\begin{aligned} T &= 0, 1, \dots, \min(L, N-1), \\ \pm K &= N-T-1, N-T-3, \dots, 1 \text{ (or 0)}. \end{aligned} \quad (1)$$

For states where $\pi = (-1)^{L+1}$, $T=0$ is not allowed. The quantum number K is proportional to $\langle \cos \theta_{12} \rangle$, with large positive K corresponding to $\theta_{12} \sim \pi$, and T^2 is proportional to the square of the average of $\hat{I}_1 \cdot \hat{r}_2$ (r_2 refers to the outer electron), with $T=0$ corresponding to the situation where the two electrons orbit on the same plane. In this asymptotic region, $\alpha \rightarrow 0$ (or $\pi/2$), and there is no radial correlation. Thus K and T describe angular correlations only.

B. Radial correlations.—Previous work^{2b} has shown that angular correlation within a given channel is independent of R . Thus the asymptotic K and T quantum numbers can be used to describe angular correlations for the whole channel. To distinguish different radial correlations, channel functions which exhibit exact antinodal (e.g., all $1S^e$ channels) or approximate antinodal structure

at $\alpha = 45^\circ$ are assigned^{9,10} to have $A = +1$; channels with exact nodal (e.g., all $3S^e$ channels) or approximate nodal structure at $\alpha = 45^\circ$ are assigned to have $A = -1$. Other states, like the $2pnd$ $1,3P^o$ series, do not have definite parity at $\alpha = 45^\circ$ and are assigned to have $A = 0$. In general, all L, S , and π symmetries have channels with $A = +1, -1$, and 0 (see Fig. 1) except for $L > 2(N-1)$ where all the channels have $A = 0$. According to this prescription, the conventional single excited states $1sns$ $1S^e$, $1sns$ $3S^e$, and $1snL$ $1,3L$ have $(K, T)^A = (0, 0)^+, (0, 0)^-,$ and $(0, 0)^0$, respectively. The three $1P^o$ doubly excited states for $N=2$ have $(K, T)^A = (0, 1)^+, (1, 0)^-,$ and $(-1, 0)^0$. Notice that this choice of $A = \pm 1$ coincides with the work of Cooper, Fano, and Prats.⁹ The $+/-$ designation emphasizes whether the two electrons approaching the nucleus are in phase or out of phase and thus whether the wave function vanishes (for $-$) or not (for $+$) at $r_1 = r_2$. For all $+$ states, symmetry condition imposes that⁴

$$K + S + N + I_\pi = \text{odd}, \quad (2)$$

where I_π is an even (odd) integer for even (odd) parity states.

C. Correlation diagram for potential curves.

—Under the requirement that the correlation pattern for a given channel remain invariant with R , the potential curves are shown to follow these correlation rules: (1) In the large- R limit, assign (K, T) quantum numbers from below starting with the largest value of K and then in order of decreasing K . For a given K , larger T values correspond to lower curves. The allowed pairs of (K, T) are calculated from Eq. (1). (2) Find the number of possible $+$ channels by enumerating the possible intrashell states for the given L, S , and π of interest, and the number of $-$ channels from the possible intrashell states of the other spin symmetry. For example, $3s3d$, $3p^2$, and $3d^2$ for $1D^e$ and $3s3d$ $3D^e$ are intrashell states. Thus there are three $+$ channels and one $-$ channel for $1D^e$ and one $+$ channel and three $-$ channels for $3D^e$. The rest of the channels have $A = 0$. (3) Find the K values for the $+$ channels from Eq. (2). All the $+$ curves have deeper potential well and have minima occurring at smaller values of R . Assign $(K, T)^+$ values to all the $+$ curves following rule (1) and join each curve to the asymptotic region that has identical (K, T) . All the $+$ curves are not allowed to cross each other. Then follow the same procedure for $-$ curves. The $-$ curves are not allowed to cross each other but

they may cross + curves any number of times. The rest are the $A=0$ curves which are not allowed to cross each other, nor + or - curves. Notice that these rules are followed by the potential curves in Fig. 1.

D. Isomorphism and supermultiplet structure.

—The correlation quantum numbers contain information about internal correlation patterns of the two electrons. In Fig. 2, the surface charge densities $\rho(R; \alpha, \theta_{12})$ for the $(1, 1)^+$ channel for ${}^1P^\circ$, ${}^3P^e$, ${}^3D^e$, and ${}^1D^\circ$ symmetries of H^- are shown at $R=20$. Similar plots for the $(2, 0)^-$ ${}^1P^\circ$ and $(-2, 0)^0$ ${}^1P^\circ$ channels of He at $R=24$ are shown in Fig. 3. These plots clearly illustrate that the $+/-$ quantum number describes radial correlations and (K, T) describes angular correlations. In evaluating $\rho(R; \alpha, \theta_{12})$ for $L \neq 0$ states, we average over the rotations of the atom.

According to the present classification, channels labeled with identical $(K, T)^A$ have essentially isomorphic correlation patterns. As illustrated in Fig. 2, the major features of correlation patterns shown are identical, despite the fact that these channels have different L and S . Such isomorphism also results in nearly identical potential curves $U_\mu(R)$. For channels which have identical $(K, T)^A$ and L , the potential curves are nearly degenerate throughout the whole range of R and thus the eigenenergies for all the states belonging to these channels are nearly degenerate. Thus we expect near degeneracy in eigenenergies (labeled by n) for all $(1, 1)^+$ states in the ${}^1P^\circ/{}^3P^e$ pair as well as in the ${}^1D^\circ/{}^3D^e$ pair. In fact, there are similar pairs such as ${}^3P^\circ/{}^1P^e$, ${}^3D^\circ/{}^1D^e$, ${}^1F^\circ/{}^3F^e$, etc., for $N=3$ and for higher N manifolds so long as each pair has identical $(K, T)^A$.

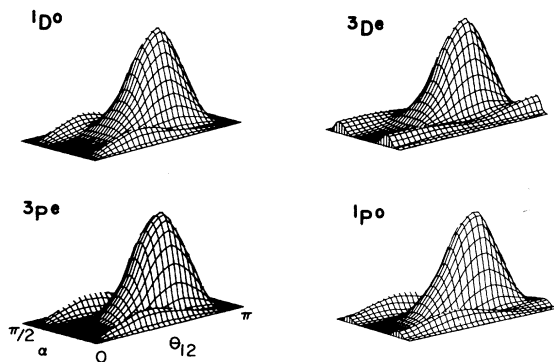


FIG. 2. The rotation-averaged surface charge densities for the $(1, 1)^+$ channel for ${}^3P^e$, ${}^1D^\circ$, ${}^1P^\circ$, and ${}^3D^e$ of H^- at $R=20$. All four graphs have identical orientations as shown in the lower-left corner.

Another spectral regularity occurs for channels which have identical $(K, T)^A$ but different L . Their differences in potential curves occur *mostly* in the large- R region. For low-lying states (small n) the eigenenergies form an approximate rotor series, i.e., they resemble the rotational spectra of a molecule, as pointed out by Herrick and Kellman³ in their study of intrashell states. *In fact, such regularity is quite general for both + and - states and applies to states where $n \neq N$.* For $N=3$, the intrashell rotor series, ${}^1S^e/{}^3P^\circ/{}^1D^e/{}^3F^\circ$, discussed in Ref. 3, is due to the isomorphism of these states, with $(K, T)^A = (-2, 0)^+$. There are similar rotor series, ${}^3S^e/{}^1P^\circ/{}^3D^e/{}^1F^\circ$, ${}^1P^\circ/{}^3D^e$, and ${}^3P^\circ/{}^1D^e$, corresponding to $(K, T)^A = (-2, 0)^-$, $(1, 1)^+$, and $(1, 1)^-$, respectively. The last two combinations have only two members because of the cutoff in angular momentum. For higher N , the "string" for each series is longer. Notice, however, that *no* such rotor-series feature exists for $A=0$ states. In fact, the eigenenergies for these channels are similar to those found in singly excited states; i.e., states with identical $(K, T)^0$ and L are nearly degenerate, with the triplet state slightly lower in energy than the singlet state.

In summary, a complete classification scheme for doubly excited states based upon the analysis of electron correlations in hyperspherical coordinates is presented. It is shown that each state is designated by $|n, N, (K, T)^A, L, S, \pi\rangle$ where $(K, T)^A$ provides important information about radial and angular correlations. Channels with identical $(K, T)^A$ are shown to have isomorphic correlations. Such isomorphism is the underlying reason for the general supermultiplet structure of doubly excited states in two-electron atoms. Similar structure is expected to occur for other doubly excited states in many-electron systems.

I gratefully acknowledge a useful discussion with Birte Christensen-Dalsgaard. This work is supported by the U. S. Department of Energy, Division of Chemical Sciences, and by the Alfred

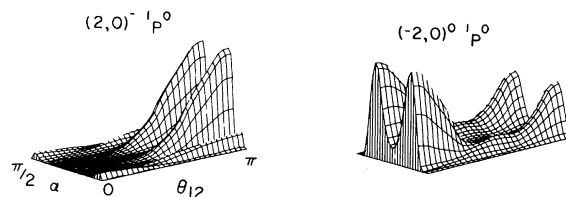


FIG. 3. Similar to Fig. 2 but for the $(2, 0)^-$ ${}^1P^\circ$ and $(-2, 0)^0$ ${}^1P^\circ$ channels of He at $R=24$.

P. Sloan Foundation.

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