Classification of Doubly Excited States of Two-Electron Atoms

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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 \( \pi \) but identical \( (K, T) \) have isomorphic correlations.
Such isomorphism is shown to result in the general supermultiplet structure of doubly
excited states.

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Since the identification of doubly excited states of He in 1963,\(^1\) it has been recognized that under-
standing 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 micro-
scopic 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, Lin\(^2\) has introduced the graphical display of two-electron correlation patterns in
hyperspherical coordinates and Herrick and Kell-
man\(^3\) have emphasized the supermultiplet struc-
ture 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 co-
dinates. 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 \( LS \) cou-
pling scheme is represented by \( \ell_1\ell_2n_1n_2L,S,\pi \). Since configuration mixing is quite large for doubly
excited states, a given state is represented as the admixture of many configurations with differ-
ent \( n_1, n_2, \ell_1, \) and \( \ell_2 \) such that these individual quantum numbers are no longer adequate to iden-
tify the state. Mixings of \( \ell_1 \) and \( \ell_2 \) within given \( n_1 \) and \( n_2 \) were introduced by Herrick and Sinanoglu\(^4\) in
their doubly excited-state basis (DESB) func-
tions. Two new quantum numbers, \( K \) and \( T \), were
introduced to replace \( \ell_1 \) and \( \ell_2 \) such that each
state is now represented by \( |nKNKLST\rangle \), where \( n \)
and \( N \) represent the principal quantum numbers
of the outer and the inner electrons, respective-
ly. 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 as-
sumption of quasiseparability,\(^7\) the wave function
is expressed as \( F_\mu (R)\Phi_\mu (R;\Omega) \), where \( R = (r_1^2 + r_2^2)^{1/2}, \Omega = (\alpha, \gamma_1, \gamma_2), \) and \( \alpha = \arctan(r_2/r_1) \). In
this first-order approximation, \( \mu \) is the channel
index, \( \Phi_\mu (R;\Omega) \) is the channel function, and
\( F_\mu (R) \) is obtained by solving the one-di-

Despite the success of this approach, it has not
been possible to relate the channel index \( \mu \) to
some apparent quantum numbers. Through the
analysis of electron correlations for different \( L, \)
\( S, \) and \( \pi \) states, I show in this Letter that each
channel is identified by a set of correlation quan-
tum numbers, \( K, T, \) and \( A \). Channels with identi-
\( (K, T) \) but different \( L, S, \) and \( \pi \) are shown to
have isomorphic correlations. This isomor-
phism is shown to result in the general super-
multiplet structure of doubly excited states. The
physical meanings, the rules of assigning these
quantum numbers, and the spectroscopic conse-
quence are discussed. For example, in Fig. 1
the potential curves for \( \lambda^3P^o \) and \( \lambda^3D^o \) of He below \( N = 3 \) are labeled with these \( (K, T) \) quantum
numbers. It is evident that channels with identi-
\( (K, T) \) have very similar potential curves.

A. Angular correlations.—The angular-corre-
lation quantum numbers, \( K \) and \( T, \) are those
used by Herrick and Sinanoglu\(^4\) in their DESB
functions. In the present context, however, they
are not related to DESB functions directly. In-
stead, they are used to label asymptotic dipole
states,\(^8\) i.e., the Stark states in the asymptotic
region ($R \to \infty$). According to Ref. 4, the ranges of $K$ and $T$ are determined as follows:

$$T = 0, 1, \ldots, \min(L, N - 1),$$

$$\pm K = N - T - 1, N - T - 3, \ldots, 1 \text{ (or 0).}$$

(1)

For states where $\pi = (-1)^{L+1}$, $T = 0$ is not allowed. The quantum number $K$ is proportional to $\langle \cos \vartheta_{12} \rangle$, with large positive $K$ corresponding to $\theta_{12} \sim \pi$, and $T^2$ is proportional to the square of the average of $\vec{r}_1 \cdot \vec{r}_2$ ($\vec{r}_2$ 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, $\alpha = 0$ (or $\pi/2$), and there is no radial correlation. Thus $K$ and $T$ describe angular correlations only.

B. Radial correlations.—Previous work$^2$ 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 $1S^0$ channels) or approximate antinodal structure at $\alpha = 45^\circ$ are assigned$^{5,10}$ to have $A = +1$; channels with exact nodal (e.g., all $3S^0$ channels) or approximate nodal structure at $\alpha = 45^\circ$ are assigned to have $A = -1$. Other states, like the $2p_n d_{1,3}^1 P^0$ series, do not have definite parity at $\alpha = 45^\circ$ and are assigned to have $A = 0$. In general, all $L$, $S$, and $\pi$ 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 $lsnL_{1/2}^1 S^0$, $lsnL_{3/2}^3 S^0$, and $lsnL_{1/2}^1 L$ have $(k, T)^A = (0, 0)^+$, $(0, 0)^-$, and $(0, 0)^0$, respectively. The three $1P^0$ 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 $r_2 = r_\infty$. For all $+$ states, symmetry condition imposes that

$$K + S + L + I_\pi = \text{odd},$$

(2)

where $I_\pi$ 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 $\pi$ of interest, and the number of $-$ channels from the possible intrashell states of the other spin symmetry. For example, $3s3d^2$, $3p^2$, and $3d^2$ for $1D^0$ and $3s3d3D^0$ are intrashell states. Thus there are three $+$ channels and one $-$ channel for $1D^0$ and one $+$ channel and three $-$ channels for $3D^0$. 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 $1^p\sigma$, $3^p\sigma$, $3^d\sigma$, and $1^d\sigma$ symmetries of $H^-$ are shown at $R = 20$. Similar plots for the $(2,0)^* 1^p\sigma$ and $(-2,0)^* 1^p\sigma$ 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 $U_\rho(R)$. 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 $1^p\sigma/3^p\sigma$ pair as well as in the $1^d\sigma/3^d\sigma$ pair. In fact, there are similar pairs such as $2^p\sigma/2^d\sigma$, $3^p\sigma/3^d\sigma$, $1^p\sigma/3^p\sigma$, etc., for $N = 3$ and for higher $N$ manifolds so long as each pair has identical $(K, T)^A$.

Another spectral regularity occurs for channels which have identical $(K, T)^A$ but different $L$. Their differences in potential curves occur most likely 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 Kellman 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, $1^S^0/3^p^0/1^d^0/3^d^0$, discussed in Ref. 3, is due to the isomorphism of these states, with $(K, T)^A = (-2,0)^*$. There are similar rotor series, $1^S^0/3^p^0/3^d^0/1^p^0$, $3^p^0/3^d^0$, and $1^p^0/3^d^0$, corresponding to $(K, T)^A = (-2,0)^*$, $(1,1)^*$, and $(1,1)^*$, respectively. These 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 $n, N, (K, T)^A, L, S, \sigma$ 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.

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Fig. 2. The rotation-averaged surface charge densities for the $(1,1)^*$ channel for $1^p\sigma$, $3^p\sigma$, $1^d\sigma$, and $3^d\sigma$ of $H^-$ at $R = 20$. All four graphs have identical orientations as shown in the lower-left corner.

Fig. 3. Similar to Fig. 2 but for the $(2,0)^* 1^p\sigma$ and $(-2,0)^* 1^p\sigma$ channels of He at $R = 24$.  

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8C. D. Lin and J. H. Macek, to be published.
9See the recent review by U. Fano, Rep. Prog. Phys. 46, 97 (1983), and references therein.
10The validity of quasiparallelability has been shown directly by comparing with large-scale configuration-interaction wave functions. See Ref. 2d.