

Origin of Two-Electron Atomic Supermultiplets in U(4) Group Embedding

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The origin of the supermultiplet classification of collective rotor-vibrator states of doubly excited atoms is investigated by embedding the O(4) structure of the problem in a larger U(4) group. This results in the supermultiplets for the physical states, suggesting an approximate U(4) symmetry of the two-electron Hamiltonian, acting within the O(4) basis derived from hydrogenic theory.

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Two-electron atoms continue to elicit intense interest as the simplest prototype of electron correlation, a central problem in atoms, molecules, and condensed systems. Starting in 1978, Herrick and Kellman (hereafter referred to as HK) published several papers [1–6] aimed at a coherent picture, in terms of collective modes, of the electron correlation in doubly excited atoms. (These are systems where both electrons are excited from the ground state.) HK devised a “supermultiplet” scheme for classifying and grouping the atomic terms into regular patterns. They interpreted the supermultiplets in terms of a model of the two-electron atom as a quasirigid linear structure with the electrons on opposite sides of the nucleus, similar to a highly nonrigid triatomic molecule. In this model the two-electron excitations are described as moleculelike rotations and bending vibrations. Since the appearance of these papers, both the supermultiplet classification and the collective rotor-vibrator interpretation have received a wide measure of acceptance. The supermultiplets were constructed by collecting together approximate two-electron O(4) multiplets, originating in the exact O(4) symmetry of the nonrelativistic one-electron Coulomb problem, into larger entities—the supermultiplets. However, despite compelling physical motivation and the remarkable spectral patterns that it revealed, one fundamental aspect of this procedure was mysterious from the start and remains so even now. This is the formal grounds, in a group larger than O(4), of the larger classification represented by the supermultiplets. In particular, the supermultiplets did not appear to correspond to irreducible representations of a larger group encompassing the two-electron O(4) as a subgroup.

In this Letter, I address this question by embedding the O(4) group structure in a larger group, U(4). By this means U(4) lends its structure to a larger organization scheme—precisely the supermultiplets—than can be obtained from O(4) alone. An important question regarding the embedding, related to the fact that a U(4) origin for the supermultiplets had not been suspected earlier, concerns the physical significance of the larger U(4) classification, since it contains states not included in the $O(4)_1 \times O(4)_2$ basis obtained from hydrogenic theory. This is considered at the end.

There have been significant developments since the work of HK which give further impetus to a reexamination of the group theoretical basis of the supermultiplets. Hunter and Berry [7] analyzed wave functions of atomic systems in terms of a basis with collective bending vibrations and localized, i.e., single-particle Morse oscillators for the radial motion. Ezra *et al.* [8] developed a semiclassical treatment of the radial motion of a collinear atom and found evidence for radial motions that can be described as an antisymmetric stretch. Rost *et al.* [9,10] gave a unified “molecular orbital” treatment of the radial, bending, and rotational motion. They found an intricate interweaving of bend and stretch excitations, rather more like what might be expected in the highly nonrigid system envisaged by HK than like the naive Born-Oppenheimer separability of a near-rigid triatomic molecule. These investigations support the idea of the atom as being like a highly nonrigid triatomic molecule, but now understood to have a systematic involvement of radial motion in the classification which HK never attempted to describe.

The use here of U(4) in the two-electron problem shares some aspects of the “vibron” model [11] of molecular rotation-vibration motion, which in turn is related to an early treatment of rigid and nonrigid molecular systems in terms of correlation diagrams [12,13]. A basic idea of the vibron model is to treat radial and angular degrees of freedom of each oscillator with as much generality as possible by means of the U(4) group, then to correlate the vibron states to various limiting cases, such as a rigid or nonrigid molecule, by means of Hamiltonians built out of operators from appropriate subgroup chains. The work presented here is based on the observation that the pattern of correlation [13] from nonrigid to rigid states in linear molecules results in groupings analogous to the atomic supermultiplets, except that molecules have independent stretching degrees of freedom, in addition to the rotations and bending vibrations of doubly excited atoms. The basic similarity is that the atomic O(4) shell structure for each N parallels the structure of a U(4) vibron. The essential difference is that each atomic O(4) shell has a more limited basis than the U(4) vibron shell, related to the absence in the atom of independent stretching modes.

For our atomic problem, the basic results are the following. First, the $O(4)$ states of the one-electron Coulomb problem are embedded in a $U(4)$ group. Then the states of the two-electron problem are embedded in a coupled $U(4)_1 \times U(4)_2$ group. The two-electron states are classified in terms of the subgroup chain

$$U(4)_1 \times U(4)_2 \supset U(4)_{12} \supset O(4)_{12} \supset O(3)_{12}, \quad (1)$$

and analyzed with a model Hamiltonian closely related to this chain. The outcome is that the supermultiplets are in one-to-one correspondence with the irreducible representations of the $U(4)_{12}$ group in (1).

First, I outline the construction of the supermultiplets. Then I present the embedding of the two-electron problem in $U(4)_1 \times U(4)_2$ and the obtaining of the supermultiplet scheme using the subgroup chain (1).

In the early 1970s, Herrick and Sinanoglu [14] and Wulfman [15] showed that the states of two-electron atoms with both electrons excited from the ground state obeyed an approximate $O(4)_{12}$ symmetry. Within the intrashell basis with both electrons in the same shell of hydrogenic orbitals, the two-electron states are classified by the labels $[P, T]$ of the irreducible representations of $O(4)_{12}$. These ideas were greatly expanded upon by Herrick and Sinanoglu [16] to include intershell states.

HK then explored the grouping of states onto $O(4)_{12}$ multiplets, and later the aggregations of multiplets which they called supermultiplets, as a device for recognizing novel energy-level patterns in the two-electron spectrum. In 1978, they proposed [1] the initial step in a classification in terms of collective molecular-type excitations. They focused on the $O(4)_{12}$ multiplet with $T = 0$ and $P = N - 1$, the highest value of P allowed within the intrashell manifold. They interpreted the excitations in this multiplet as rotational excitations of a quasirigid linear structure for the two-electron atom, similar to a highly nonrigid molecule.

The next step was to collect the entire set of $O(4)_{12}$ multiplets for a shell into supermultiplet schemes [2,3]. I focus here on the d -supermultiplet scheme, which HK recognized as having the more fundamental significance. From among the set of $O(4)_{12}$ multiplets obtained within an intrashell basis, multiplets with a common value of

$$d = P + T/2 \quad (2)$$

are collected into a d supermultiplet. The intrashell manifold (N, N) contains N supermultiplets $\{d\}_{\text{super}}$ with $d = 0, \dots, N - 1$. The different supermultiplets $\{d\}_{\text{super}}$ represent excitations of the bending vibration with $\nu_\rho = d$ quanta in the polar coordinate of the two-dimensional, i.e., doubly degenerate, bending mode, and angular momentum $l = 0$ along the molecule axis [2,4]. The lowest energy state within a supermultiplet is a ${}^1S^e$ intrinsic state. This intrinsic state is the lowest member of an $O(4)_{12}$ multiplet constituting a sequence of rotational excitations. The other $O(4)_{12}$ manifolds within the supermultiplet are rotor series built on $l > 0$ bending excitations of the ${}^1S^e$ intrinsic state. Thus, each supermultiplet $\{d\}_{\text{super}}$

contains rotational progressions built on $|l| \geq 0$ bending excitations, all built on the ${}^1S^e$ intrinsic state with $\nu_\rho = d$ quanta in the polar coordinate of the bending mode. The entire rotor-vibrator supermultiplet scheme can be described as a hierarchy of atomic terms and corresponding molecular rotor-vibrator quantum numbers as follows:

$$(N, N) \longrightarrow \sum_{d=0}^{N-1} \{d\}_{\text{super}}, \quad (3a)$$

with $O(4)_{12}$ decomposition

$$\{d\}_{\text{super}} = \sum [P, T] = [2d, 0], [2d - 1, 1], \dots, [d, d], \quad (3b)$$

and the following relations of atomic and molecular quantum numbers:

$$\begin{aligned} l &= T, \\ \nu_\rho &= N - 1 - d, \\ \nu_b &= 2(N - 1 - d) + l, \\ \nu_3 &= 2(d - l), \\ P &= 2N - 2 - \nu_b. \end{aligned} \quad (3c)$$

Within an $O(4)_{12}$ multiplet, L takes the values $L = T, T + 1, \dots, P$. Here, L and l are the total spatial angular momentum and the projection along the molecule axis; ν_b is the number of bending quanta; ν_ρ is the number of quanta in the polar coordinate of the doubly degenerate bend; and ν_3 is a quantum number not considered by HK, the number of radial, i.e., stretching quanta. This has been associated with motion similar to an antisymmetric stretch [8], hence the standard [17] molecular notation ν_3 . (In terms of the notation of Rost *et al.* [9,10], we use $\nu_\rho = n_\lambda$; $\nu_3 = n_\mu$.) It should be recognized that the collinear states treated in Ref. [8] can perhaps be described just as well in terms of symmetrized "local mode" stretches, in analogy to the local mode model of the stretches in the H_2O molecule [18]. The radial motion of $(2s, 3s)$ states is described in Ref. [7] by wave functions with symmetrized combinations (symmetric and antisymmetric, respectively, in the spatial functions) of localized Morse oscillator stretches.

The supermultiplet classification presented in 1980 was for states derived from intrashell configurations with both electrons in the same shell N . However, as HK recognized at the time, the scheme is readily extended [5] to intershell manifolds (N, n) with $n \geq N$. For the manifold (N, n) one obtains N supermultiplets which here are labeled $\{d, f\}_{\text{super}}$

$$[N, n] \longrightarrow \sum_{d=0}^{N-1} \{d, f\}_{\text{super}}, \quad (4a)$$

where f is a new label given by

$$f = n - N.$$

(In this new labeling, the intrashell supermultiplets denoted above as $\{d\}_{\text{super}}$ are now denoted $\{d, 0\}_{\text{super}}$.) The $O(4)_{12}$ decomposition is [cf. Eq. (3b)]

$$\begin{aligned} \{d, f\}_{\text{super}} &= \sum [P, T] \\ &= [2d + f, 0], [2d + f - 1, 1], \dots, [d + f, d]. \end{aligned} \quad (4b)$$

The supermultiplets $\{d, f\}_{\text{super}}$ for (N, n) are in one-to-one correspondence with those of (N, N) but with $f = n - N$ additional terms in each of the $O(4)_{12}$ rotor series.

With this background, we now consider the embedding of the problem in $U(4)$ and the obtaining of the supermultiplets. The $N + 1$ shell of the hydrogen atom constitutes a representation $[P, T] = [N, 0]$ of $O(4)$. We embed this in the totally symmetric representation $\{N, 0, 0, 0\}$ of $U(4)$. For example, the $N = 3$ hydrogenic shell is embedded in $\{2, 0, 0, 0\}$. This decomposes as $\{2, 0, 0, 0\} = [2, 0] + [0, 0]$. The nine-dimensional $[2, 0]$ is the set of states in the $N = 3$ shell, and the one-dimensional $[0, 0]$ is an extraneous or at least "extra" member of $\{2, 0, 0, 0\}$. The extra members will be retained at this stage; their status will be considered at the stage of the $U(4)_{12} \supset O(4)_{12}$ decomposition of the coupled two-particle representations.

The next step is the embedding of the two-electron problem in $U(4)_1 \times U(4)_2$, which is straightforward except for one crucial point. It is essential that the electrons be embedded in *conjugate* representations [19] in order, eventually, to obtain the supermultiplet classification in the chain (1). Thus, the two-electron manifold $(N_1 + 1, N_2 + 1)$ is embedded in the representation $\{N_1, 0, 0, 0\} \times \{\overline{N_2}, 0, 0, 0\}$. An analogy can be made to the $U(3)$ quark model [20]: To obtain the octet, the $q\bar{q}$ must be represented as the conjugate product $3 \times \bar{3} \rightarrow 1 + 8$ rather than as $3 \times 3 \rightarrow 3 + 6$. Embedding the electrons in nonconjugate representations leads to a two-electron classification in which states of constant l are grouped together, rather than states of constant $\nu_\rho = (N - 1 - d)$, as with the supermultiplets [cf. Eq. (3c)]. While physically useful, this alternate classification scheme will not be pursued further here. An underlying physical connection between the type of representations coupled and the resulting two-electron classification is not known at this time.

Now the representation $\{N_1, 0, 0, 0\} \times \{\overline{N_2}, 0, 0, 0\}$ is decomposed under the chain $U(4)_1 \times U(4)_2 \supset U(4)_{12}$ from (1). This is given by

$$\begin{aligned} \{N_1, 0, 0, 0\} \times \{\overline{N_2}, 0, 0, 0\} &= \sum_{d=0}^{N-1} \{2d + n - N, d, d, 0\} \\ &= \sum_{d=0}^{N-1} \{2d + f, d, d, 0\}, \end{aligned} \quad (5)$$

where the labeling $\{2d + f, d, d, 0\}$ of the $U(4)_{12}$ irreducible representations (irreps) is indicative of their eventual relation to the $\{d, f\}$ supermultiplets. For example, $N, n = 3, 3$ gives

$$\{0, 0, 0, 0\} + \{2, 1, 1, 0\} + \{4, 2, 2, 0\} = 1 + 15 + 84.$$

Each $U(4)_{12}$ irrep is next decomposed into a sum of $O(4)_{12}$ irreps. As discussed above, there are extra $O(4)_{12}$ multiplets in this sum because some of the one-electron $U(4)$ members do not correspond to the one-electron hydrogenlike $O(4)$ basis. The result is [21]

$$\begin{aligned} \{2d + f, d, d, 0\} &= [2d + f, 0] + [2d + f - 1, 1] + \dots \\ &\quad + [d + f, d] + (\text{extra terms}). \end{aligned} \quad (6)$$

After exclusion of the extra terms, the remaining states from $\{2d + f, d, d, 0\}$ have precisely the $O(4)_{12}$ labels $[P, T]$ needed to constitute the $\{d, f\}$ supermultiplet [cf. Eq. (4b)]. However, this is still not quite enough to enable the desired identification with the supermultiplets. Suppose, consistent with previous work, that the supermultiplet states with $O(4)_{12}$ labels $[P, T]$ are thought of as originating from an $O(4)_1 \times O(4)_2$ hydrogenlike basis. The supermultiplet states are not automatically identical to the $O(4)_{12}$ states contained in the right hand side of (6). The latter can sometimes be combinations of the two-electron states from hydrogenic theory with the two-electron states formed from the "extra" single-electron levels in the embedding of the shell N in $U(4)$. It is necessary to make sure that we end up with supermultiplet states that come from the hydrogenic theory, and that the "extra" states consist purely of nonhydrogenic states. This can be done by an argument which essentially says that the two-electron interaction has an effective $U(4)_{12}$ symmetry, but that this interaction operates only within the subspace of hydrogenic $O(4)_{12}$ reps, while the nonhydrogenic subspace is separated out and perhaps eliminated altogether. The argument goes as follows.

The $U(4)$ symmetry and effective interaction suggested by (6) can be modeled by an approximate effective Hamiltonian constructed as a sum of commuting Casimir operators of $U(4)_{12}$ and its subgroups in (1), as in the vibron model [11]

$$H = F + AC(U(4)_{12}) + BC(O(4)_{12}) + CC(O(3)_{12}). \quad (7)$$

This effective Hamiltonian is obviously a drastic simplification of the true two-electron Hamiltonian. It is nonetheless a plausible model because it will be seen below to lead to a rotor-vibrator Hamiltonian. The usefulness of such a Hamiltonian in organizing the spectrum comprises much of the original rationale for the supermultiplet classification.

The energy levels of the Hamiltonian (7), for states in the irrep $\{2d + f, d, d, 0\}$ obtained from the manifold $(N, n) = (N_1 - 1, N_2 - 1)$, are given by [11]

$$\begin{aligned} E &= F' + A[-N_1 N_2 + (N_1 - d)(N_1 + N_2) \\ &\quad - (N_1 - d)(N_1 - d - 3)] \\ &\quad + B[P(P + 2) + T^2] + CL(L + 1). \end{aligned} \quad (8)$$

Consider an "extra" $O(4)_{12}$ multiplet $[P, T]$ from the $U(4)_{12}$ irrep $\{2d + f, d, d, 0\}$. There may be several $U(4)_{12}$ irreps each with an extra multiplet with the same $[P, T]$. It turns out that if there is a "nonextra" multiplet with the same $[P, T]$, it is from a different $U(4)_{12}$ irrep than all the extra multiplets. From (8), the states of these multiplets are degenerate term by term if the constant A for the $U(4)_{12}$ Casimir operator $C(U(4)_{12})$ is zero. Assume for now that this is the case. The two-electron states of a degenerate set are combinations of the nonhydrogenic two-electron states with the two-electron states from hydrogenic theory. Therefore, we take linear combinations to get $O(4)_{12}$ states which are, respectively, pure hydrogenic and nonhydrogenic states. If the nonhydrogenic states are assumed to be nonphysical, let the nonhydrogenic one-electron basis state energies go to infinity. This removes the nonphysical two-electron states. For the remaining states, we retain the $U(4)_{12}$ label d : Although it loses its group theoretical significance for the altered states, it retains its physical significance through the energy-level formula (8) and as an index of parentage for the supermultiplets. The important point is that the energy-level formula (8) still holds. We make the identification of Eq. (3c) between P, T, d and molecular quantum numbers, except that $\nu_b = N + n - 2 - P$ for the $\{d, f\}$ supermultiplets. (This quantum number correspondence differs from Eq. 3.47 of Ref. [11]; it follows from a correlation diagram analysis like that of Ref. [13] and the absence of independent stretching modes in the atom.) We have now arrived at the key result: Each rotor-vibrator supermultiplet $\{d, f\}$ of the (N, n) manifold, along with some extra states, has been obtained in correspondence to the irrep $\{2d + f, d, d, 0\}$ of $U(4)_{12}$:

$$(N, n) \longrightarrow \sum_{d=0}^{N-1} \{2d + f = 2d + (n - N), d, d, 0\} \\ \longleftrightarrow \sum_d \{d, f\}_{\text{super}} + (\text{extra terms}). \quad (9)$$

Making use of the quantum number identification (3c), Eq. (8) gives an energy-level formula for a rotor-vibrator spectrum in terms of molecular quantum numbers

$$E = F' + A[-N_1 N_2 + \nu_\rho(N_1 + N_2) - \nu_\rho(\nu_\rho - 3)] \\ - 2B(N_1 + N_2 + 2)(\nu_b + 1) + B(\nu_b + 1)^2 \\ + CL(L + 1) + Bl^2 \\ + 4B(N_1 + N_2) + B(N_1 + N_2)^2 + 3B. \quad (10)$$

If the constant A in Eqs. (8) and (9) is nonzero, the degeneracy invoked in the above argument is removed. To get pure hydrogenic and nonhydrogenic states, a part must then be added to the Hamiltonian which does not have $U(4)_{12}$ symmetry. This shifts the physical levels from the $U(4)_{12}$ formula, Eqs. (8) and (10). From inspection of the calculated supermultiplet levels [3], the constant A in the model (8) is in fact small, and our overall

conclusion remains. It is important to emphasize that if Eqs. (8) and (10) were used to fit molecular spectra, a small value of A would be quite typical. The role of the $U(4)_{12}$ structure in a molecule is therefore in determining the grouping into sets with common ν_ρ . In atoms, we have seen that this is complicated somewhat, though not in the end really compromised, by the limitations imposed by the atomic shell structure.

It is conceivable that the extra states really are physical states not encompassed by the supermultiplets. One possibility might be the "frozen planet" states found semiclassically by Richter *et al.* [22], but I do not believe that the extra $U(4)$ states are the way to set these. The extra states might correspond to some other, as yet unknown collective states in the atom. But the $U(4)$ symmetry might simply function in a novel way as an organizing device for the $O(4)$ states.

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- [1] M.E. Kellman and D.R. Herrick, *J. Phys. B* **24**, L755 (1978).
 - [2] D.R. Herrick and M.E. Kellman, *Phys. Rev. A* **21**, 418 (1980).
 - [3] D.R. Herrick, M.E. Kellman, and R.D. Poliak, *Phys. Rev. A* **22**, 1517 (1980).
 - [4] M.E. Kellman and D.R. Herrick, *Phys. Rev. A* **22**, 1536 (1980).
 - [5] D.R. Herrick, *Adv. Chem. Phys.* **52**, 1 (1983).
 - [6] M.E. Kellman, *Phys. Rev. Lett.* **55**, 1738 (1985).
 - [7] J.E. Hunter III and R.S. Berry, *Phys. Rev. A* **36**, 3042 (1987).
 - [8] G.S. Ezra, K. Richter, G. Tanner, and D. Wintgen, *J. Phys. B* **24**, L413 (1991).
 - [9] J.M. Rost, R. Gersbacher, K. Richter, J.S. Briggs, and D. Wintgen, *J. Phys. B* **24**, 2455 (1991).
 - [10] J.M. Rost and J.S. Briggs, *J. Phys. B* **24**, 4293 (1991).
 - [11] O.S. van Roosmalen, F. Iachello, R.D. Levine, and A.E.L. Dieperink, *J. Chem. Phys.* **79**, 2515 (1983).
 - [12] M.E. Kellman, F. Amar, and R.S. Berry, *J. Chem. Phys.* **73**, 2387 (1980); M.E. Kellman and R.S. Berry, *Chem. Phys. Lett.* **42**, 327 (1976).
 - [13] M.E. Kellman, *Chem. Phys.* **48**, 89 (1980).
 - [14] D.R. Herrick and O. Sinanoglu, *J. Chem. Phys.* **62**, 886 (1975).
 - [15] C.E. Wulfman, *Chem. Phys. Lett.* **23**, 370 (1973).
 - [16] D.R. Herrick and O. Sinanoglu, *Phys. Rev. A* **11**, 97 (1975).
 - [17] G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, New York, 1950).
 - [18] R.T. Lawton and M.S. Child, *Mol. Phys.* **40**, 773 (1980).
 - [19] J.P. Elliott and P.G. Dawber, *Symmetry in Physics* (MacMillan, London, 1979).
 - [20] M. Gell-Mann, *Phys. Lett.* **8**, 214 (1964).
 - [21] B.G. Wybourne and P.H. Butler, *Symmetry Principles and Atomic Spectroscopy* (Wiley, New York, 1970).
 - [22] K. Richter, J.S. Briggs, D. Wintgen, and E.A. Solov'ev, *J. Phys. B* **25**, 3929 (1992).