Correlated Electrons in Lithiumlike Hollow Atoms

Lars Bojer Madsen and Klaus Mølmer
Institute of Physics and Astronomy, University of Aarhus, 8000 Aarhus C, Denmark
(Received 26 March 2001; published 11 September 2001)

We present a scheme for the explicit construction of highly correlated triply excited hollow states in Coulombic three-electron systems. Our analytical ansatz for the three-electron state is physically well justified and it produces configuration mixing coefficients in good agreement with data obtained from *ab initio* calculations.

DOI: 10.1103/PhysRevLett.87.133002 PACS numbers: 31.25.Jf, 32.80.Hd

The description and understanding of electron-electron correlations in multiply excited Coulombic systems represent one of the outstanding problems in modern atomic physics. Using synchrotron radiation with photon energies about 60 eV, Madden and Codling in the 1960s observed resonances ascribed to autoionizing doubly excited states in the He atom [1]. These states were described theoretically by Fano [2], who pointed out the important role of the electron repulsion and the effective description of the states as superpositions of coupled angular momentum eigenstates (configuration mixing). Subsequently, alternative approaches were developed for the theoretical description of the doubly excited states. The two-electron (three-body) problem has been addressed in hyperspherical coordinates [3], and a close investigation of the electron correlations displayed in these coordinates [4] confirms the validity of group theoretical classifications [5], and it supports molecular pictures [6,7]. Further progress on the group theoretical description is reported in Ref. [8], and references therein. For states with both electrons in the same principal shell, the group theoretical method was proven to be equivalent to a description where the two electrons occupy Stark states which are subsequently rotated to account for the total angular momentum quantum numbers [9].

Recent progress in advanced light sources delivering photon energies of hundreds of eV has enabled experimental investigations of highly correlated triply excited states embedded in the continua of the singly and doubly ionized atom. In lithium, triply excited states were observed by photoabsorption [10], photoion [11,12], and also in photoelectron [13,14] measurements. Triply excited states of even parity were investigated [15], as well as states with empty $n = 1$ and 2 shells [16,17]; several Rydberg series were identified [18–23], and angle-resolved photoelectron spectrometry was reported [24]. The experimental results were compared with R-matrix [13–16,18–20,24] and Dirac-Fock calculations [12,17] and very accurate calculations using the saddle-point complex rotation method [16,25]. In addition, the hyperspherical coordinate method has been applied to the three-electron problem [26], and it has revealed a propensity for the three excited electrons to arrange themselves in the corners of an equilateral coplanar triangle with the nucleus in the center—a spatial arrangement similar to the three-pointed star displayed on Mercedes Benz vehicles. This arrangement minimizes the electron repulsion, and it was already suggested 25 years ago to play an important role in the three-electron-ejection Wannier problem [27] (see also [28] for a semiclassical treatment of triply excited states based on the same geometry). To date, however, no quantum mechanical description has invoked this physical picture to provide an explicit construction of the quantum mechanical state of the triply excited system well below the Wannier threshold. We suggest and we verify, by a quantitative comparison with *ab initio* calculations, that hollow three-electron atoms which have no electrons in the inner Bohr orbital can be accurately described by a simple analytical product wave function with a spatial arrangement of the three electrons in a coplanar equilateral triangle. As in molecular and nuclear physics, a rotor series of states with appropriate spatial symmetry is identified by a subsequent rotational average of this "intrinsic rotor" state.

In the following, we consider hollow states for the case of three electrons moving in the Coulomb field of a point-like nucleus of charge Z, corresponding to the nonrelativistic lithiumlike Hamiltonian,

$$H = \sum_{j=1}^{3}\left(-\frac{\hbar^2}{2\mu}\nabla_j^2 - \frac{Ze^2}{r_j}\right) + \sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \qquad (1)$$

where μ is the reduced electron mass and e is the electron charge.

In theoretical descriptions, as the configurational interaction or the R-matrix approaches, the electron-electron interaction enforces quantum "entanglement" and the electron correlations are accounted for in terms of linear combinations of angular momentum and spin-multiplet wave functions [12–25], which cannot be factorized into a product of single-particle states. However, in the present approach, the electron-electron interaction will be taken care of by a simple product of three carefully chosen single-particle states. Entanglement is subsequently enforced by spin, exchange, and rotational symmetry.

In the coplanar three-pointed star, the interaction between any one electron and the two others is approximately represented by a repulsive field along the direction ζ (with respect to the nucleus) of the electron under concern. For the pure Coulomb potential, the spherical and the polarized Stark bases both span the degenerate n^2-dimensional eigenspace for a given principal shell, n. The Stark states are eigenstates of the hydrogenic Hamiltonian perturbed by a weak external electric field causing only intrashell transitions [29]. Hence, the interelectronic interaction tends to stabilize the electrons in individual Stark states and the appropriate one-electron states are maximally polarized along ζ, $|n, k = n - 1, m = 0\rangle_\zeta$, with k the parabolic and m the magnetic quantum number. Choosing for convenience the xy plane for the directions of orientation of the three electrons, our ansatz for the spatial wave function is simply a product of three Stark states

$$|\Upsilon_R\rangle = |n, n-1, 0\rangle_0 |n, n-1, 0\rangle_{2\pi/3} |n, n-1, 0\rangle_{-2\pi/3}\,, \tag{2}$$

where the subscripts $\{0, \pm 2\pi/3\}$ denote one electron maximally polarized along the x axis and the two others in equivalent states rotated $\pm 2\pi/3$ in the xy plane. It is a remarkable feature that polarized single-electron states are exact solutions of the spherically symmetric Coulomb problem, and that the state of Eq. (2) therefore diagonalizes exactly the single-particle parts of the Hamiltonian of Eq. (1), and according to the above arguments it also diagonalizes approximately the interaction terms. Figure 1 shows the column probability density in the state of Eq. (2), i.e., the electron density integrated over the z coordinate for different values of x and y. One observes a three-pointed distribution, minimizing the Coulomb repulsion between the electrons. The central peak around the atomic nucleus at $(x, y) = (0, 0)$ is a consequence of the attraction between the nucleus and the electron, and the three-pointed star shape which reflects the repulsion between the electrons is therefore present both in the outer region and in the (less populated) inner region near the nucleus.

Note that a product state is the *simplest possible* way to represent a many-particle wave function. We have to supplement, however, our simple ansatz of Eq. (2) with an account of the electronic spin degrees of freedom, and we have to ensure that the states proposed are antisymmetric under exchange of any two electrons (Pauli principle) and that they are eigenstates of total angular momentum, reflecting the rotational symmetry of the problem.

As we consider the spin-independent Hamiltonian of Eq. (1), the spin is accounted for by multiplying the spatial wave function of Eq. (2) by a spin function, $|\chi^S_{M_S}\rangle$, which specifies the conserved total spin of the three electrons S and its projection M_S,

$$|\Psi^{SM_S}_R\rangle = |\Upsilon_R\rangle\, |\chi^S_{M_S}\rangle\,. \tag{3}$$

For three intrashell electrons no physical grounds serve to single out particular values of an intermediate spin of any two of the electrons. Accordingly, we do not follow the usual sequential coupling scheme for spin variables, but instead we propose a new coupling scheme and construct spin functions such as, for example, the spin-doublet eigenstate,

$$|\chi^{S=1/2}_{M_S=1/2}\rangle = \frac{1}{\sqrt{3}}\left(|\downarrow\uparrow\uparrow\rangle + e^{2\pi i/3}|\uparrow\downarrow\uparrow\rangle + e^{-2\pi i/3}|\uparrow\uparrow\downarrow\rangle\right), \tag{4}$$

inspired by the theory of spin waves in solids [30]. This spin state is composed of $i/\sqrt{2}$ intermediate spin-singlet and $1/\sqrt{2}$ intermediate spin-triplet states.

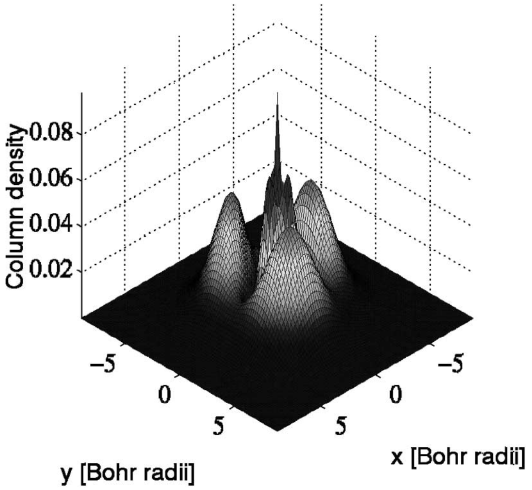

FIG. 1. Column probability density in the xy plane of the state of Eq. (2). The probability densities of the three electrons are added and integrated along the z axis, and one observes a three-pointed distribution, minimizing the Coulomb repulsion energy. The central peak around the atomic nucleus at $(x, y) = (0, 0)$ reflects that the Stark states solve the Coulomb problem. The Bohr radius is $\sim 5.29 \times 10^{-11}$ m.

In addition to the spin, the total angular momentum L and projection M are good quantum numbers. To obtain an eigenstate for these conserved quantities we perform the rotational average

$$|\Psi^{LM,SM_S}_{R,M_I}\rangle = N \int d\omega\, \mathcal{D}^L_{MM_I}(\omega)^\star |\Psi^{SM_S}_R\rangle_\omega\,, \tag{5}$$

with $\mathcal{D}^L_{MM_I}(\omega)$ the Wigner function representing finite rotations by Euler angles $\omega = (\alpha, \beta, \gamma)$ [31]. The subscript ω refers the state $|\Psi^{SM_S}_R\rangle_\omega$ to a rotated coordinate frame. N is a normalization constant. The prescription of Eq. (5) is also used in molecular [32] and nuclear physics [33] to ensure the proper external symmetries of states for which the internal correlations are accounted for in a symmetry-broken frame. As in molecular and nuclear physics we then get the explicit picture of an intrinsic rotor (2), which is attributed to angular momentum by the rotational average in Eq. (5). The quantum number M_I in Eq. (5) fixes, by a projection, the magnetic quantum number of the intrinsic rotor with respect to the internal rotor axis. In molecules, this is an important quantum number contributing a term $\sim M_I^2$ to the rotational spectrum. The degeneracy of states with $\pm|M_I|$ is lifted by the Coriolis interaction of rotation and vibrations [32].

Finally a complete antisymmetrization of the state is accomplished by the operator $\mathcal{A} = (1 + C + C^2 - P_{12} - P_{13} - P_{23})$,

$$|\Psi^{LM,SM_S}_{R,M_l,\mathcal{A}}\rangle = N_{\mathcal{A}}\mathcal{A}|\Psi^{LM,SM_S}_{R,M_l}\rangle, \tag{6}$$

where C is a cyclic permutation, and P_{ij} interchanges particle i and j. $N_{\mathcal{A}}$ is a normalization constant.

Equation (6) is our final analytical ansatz for the three-electron hollow states. The Stark states in Eq. (2) have known analytical expressions, and the operations involved in Eqs. (3)–(6) can also be handled analytically. It is thus straightforward to compare our ansatz with the results of elaborate numerical diagonalizations of the three-electron Hamiltonian, i.e., to expand the state of Eq. (6) on the usual multiplet terms, and compare the mixing fractions with the ones obtained numerically. Table I shows a comparison between symmetric rotor and configurational mixing fractions for the lowest lying triply excited ^2P state in the third principal shell. Based on the dominant configuration the state is referred to as the $3s3s3p\,^2P$ atomic resonance. As seen from Table I, the symmetric rotor not only predicts the general trend in the mixing fractions, but actually compares very well with the *ab initio* calculations. Note that, although the mixing fractions in Table I differ slightly, the symmetric rotor and the numerical wave function may have an overlap as large as 0.98 (assuming equal phases of the amplitudes). Also the comparison with the configuration interaction (CI) results for lithiumlike N^{4+} allows us to stress the Z independence of the configuration mixing fractions in our model.

To conclude, we have constructed symmetric rotor states based on the physical assumption that the three electrons in a triply excited intrashell hollow state orient themselves in a three-pointed star. The Stark states are eigenstates of the pure Coulomb problem which are polarized, and our quantum state ansatz for the rotor is simply a product of three Stark states, polarized at 120° with respect to each other. The subsequently antisymmetrized and rotated product states account very accurately for the electron-electron correlations within the system. In parallel to the studies in hollow lithium, work is in progress on triply excited states in He^- (see Ref. [35], and references therein), and our analytical wave function should also represent this system very well. Predictions based on the symmetric rotor will present analytical reference data for future experiments and calculations. Of particular interest will be radiative matrix elements from the ground state and among hollow states [36]. We do not expect the precision of our ansatz to compete with the precision of current elaborate numerical methods. But, we expect it to be sufficient to account for and expose the underlying physics of systematic features [37].

TABLE I. Symmetric rotor mixing fractions for the lowest $n = 3$ triply excited state $^2P(3s3s3p)$ of atomic lithium. The first column gives the antisymmetrized angular momentum and spin-multiplet wave functions. Our numbers in the second column are compared with CI configuration mixing coefficients [17,34], as presented in the last two columns.

LS state	$\lvert\Psi^{L=1,S=1/2}_{R,\mathcal{A}}\rangle$	Ref. 17 (Li)	Ref. 34 (N^{4+})
$\lvert 3s3s3p\,^2P\rangle$	67.44	61.8	64.0
$\lvert 3p3p3p\,^2P\rangle$	18.97	20.0	19.5
$\lvert 3s3p3d\,^2P\rangle$	11.80	13.5	13.2
$\lvert 3p3d3d\,^2P\rangle$	1.79	3.3	

We note that we have provided an explicit construction of the maximally correlated triply excited state, and that the ideas of this Letter have a natural extension to multiply excited states in systems with 4, 6, 8, 12, and 20 electrons, corresponding to the five regular convex polyhedra of $\mathfrak{R}^3$. In view of advances in accelerator-based bright coherent light sources, quadruply excited states may soon be realized in experiment. Based on the experience from doubly excited states [9], we expect that products of less polarized Stark states may form the basis for less correlated rotors and thus account for the other states in the multiply excited manifold. As mentioned, the Stark state construction is fully equivalent to the group theoretical classification of doubly excited states, and we hope that our work will stimulate the search for a firm group theoretical classification of multiply excited states.

L. B. M. is supported by a Steno-talent stipendium (Grant No. 51-00-0569) from the Danish Natural Science Research Council.

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