# Visualization of correlations in intrashell triply excited states of atoms

Toru Morishita, Yong Li, and C. D. Lin

*Department of Physics, Cardwell Hall, Kansas State University, Manhattan, Kansas 66506*

(Received 11 February 1998)

The internal wave functions of the eight lowest intrashell triply excited states of Li atoms are analyzed. By visualizing the equidensity surfaces we show that in four of the eight states the most probable shape of the three electrons is a coplanar equilateral triangle with the nucleus at the center. The relative energies of these four states resemble the rotational spectrum of a symmetric top. The remaining four states have nodal surfaces in their internal wave functions and thus have higher excitation energies. [S1050-2947(98)00311-4]

PACS number(s): 31.10.+z, 31.15.Ja, 31.25.Jf

Microscopic few-body systems are often described in terms of the independent-particle model where each particle is moving in the mean field of all the other particles. In atomic structure calculations, electron correlation has often been defined as the deviation from the independent electron approximation. However, this definition fails to address how the electrons are correlated. For an $N$-electron atom, the spatial part of the wave function is described by a $3N$-dimensional function. Visualization of such a function on a two-dimensional space, which would reveal information on how the electrons are correlated, is thus a daunting task.

The need of a new treatment of electron correlation first occurs in the description of doubly excited states of atoms. Great strides have been made on this subject in the past two decades. It has been shown that a subset of doubly excited states perform motion akin to the rotation and vibration of a molecule [1–5]. The correlated motion of the two electrons is understood to be similar to the antisymmetric stretch and the bending vibration of a linear triatomic molecule. A new set of quantum numbers that describe the correlated motion have been proposed and are widely in use now. We can say that the correlations in doubly excited states of atoms are now well understood. The next challenge then is to characterize the correlations in triply excited states of atoms. These states lie way up in the spectrum of a three-electron atom such that they are difficult to observe or to calculate. While there are several previous investigations of this subject, the analysis has often been done only for a few states [6,7] or for model atoms [8,9]. Experimentally triply excited states of Li are being intensively investigated at synchrotron facilities [10,11]. In the meanwhile the energies and decay widths of some of these states have been calculated [12–15]. These studies provide useful information on the triply excited states of Li but none of them addresses the correlation properties directly.

In this paper we will focus on the lowest few intrashell triply excited states of Li. Within the independent electron model there are eight intrashell states that can be formed from the $2s$ and $2p$ orbitals. They are $2s^2 2p\ ^2P^o$, $2s2p^2$ ($^4P^e$, $^2S^e$, $^2P^e$, $^2D^e$) and $2p^3$ ($^4S^o$, $^2D^o$, $^2P^o$). Each state has well-defined total angular momentum $L$, total spin $S$, and parity $\pi$. In Fig. 1(a) we display the energy levels of these eight states, arranged according to their configurations. For each configuration, according to Hund's rule, which is valid within the independent electron approxima-

tion, the state with the highest $S$ has the lowest energy and for a given $S$, the state with higher $L$ has lower energy. For $2s2p^2$ we note that Hund's rule is followed except between $^2S^e$ and $^2P^e$, and for $2p^3$ Hund's rule is followed. The empirical Hund's rule does not explain the observed relative energies. In this paper we set out to explain their ordering in terms of the internal motion of the three electrons. This is achieved by a proper display of the equidensity surfaces of the electron cloud, which allows us to visualize the most probable configurations of the electrons in an atom and to identify the collective modes in these states.

We will analyze the wave functions of these intrashell states obtained using the hyperspherical approach in the
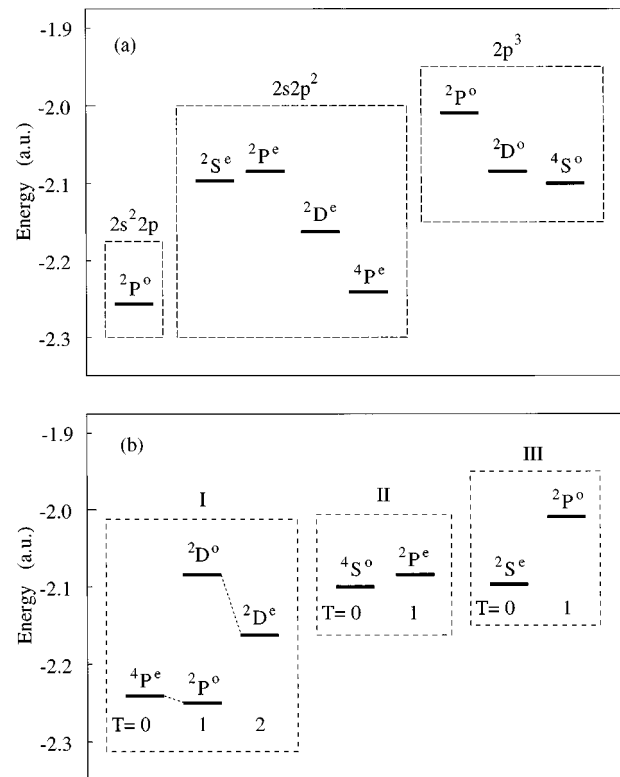


FIG. 1. The energy levels of the eight intrashell triply excited states of Li. (a) The states are arranged in terms of the electronic configurations. (b) The states are rearranged according to their internal wave functions to show the rotor structure. Data from Ref. [12] for $^4S^o$ and from Ref. [13] for other symmetries.
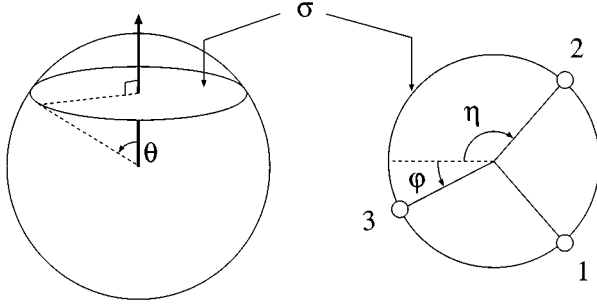
FIG. 2. Definition of the three angles used to describe the three electrons on a sphere. The three electrons form a $\sigma$ plane. On the plane (the right figure) the three electrons are confined to a circle.

adiabatic approximation. In the adiabatic approximation the total wave function for each state is given by [16,17]

$$\psi_{\nu}^{LS\pi}=F_{\nu}^{LS\pi}(R)\left(\sum_{S_{12}}\Phi_{\nu}^{LS\pi,S_{12}}(\Omega;R)\chi_{S_{12}}^{S}\right), \quad (1)$$

where $R=\sqrt{r_1^2+r_2^2+r_3^2}$ is the hyperradius and $\Omega$ collectively denotes the eight hyperangles, namely, ($\alpha_1=\tan^{-1}(r_1/r_2),\alpha_2=\tan^{-1}[\sqrt{(r_1^2+r_2^2)/r_3}],\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2,\hat{\mathbf{r}}_3)$. In the equation above, $F_{\nu}(R)$ is the hyperradial function, $\Phi_{\nu}(\Omega;R)$ is the adiabatic channel function, and $\chi_{S_{12}}^{S}$ is the total spin function. The size of the atom is measured by $F_{\nu}(R)$. The channel function $\Phi_{\nu}(\Omega;R)$, which depends parametrically on $R$, contains all the information about electron correlations for states within the channel $\nu$. To visualize the ''shape'' of the three electrons in an atom, we consider the internal wave function of the atom and display the electron density distributions after integrating over the overall rotation $\Omega_E$ and summing over the parent spin $S_{12}$,

$$\rho_{LS\pi}^{\nu}(\Xi,\alpha_1,\alpha_2;R)=\sum_{S_{12}}\int d\Omega_E|\Phi_{\nu}^{LS\pi,S_{12}}(\Omega;R)|^2, \quad (2)$$

where $d\Omega_E$ denotes the volume element of the rotation angles, and $\Xi$ represents three independent relative angles yet to be specified. This density is a function of six variables. Under the adiabatic approximation this function is expected to change smoothly with $R$. Therefore we will focus on Eq. (2) for $R\simeq3$ a.u. where the hyperradial function $F_{\nu}(R)$ for the intrashell states is near the maximum. For intrashell states the three electrons are at about the same distance from the nucleus and the maximum of the density peaks at $(\alpha_1,\alpha_2)=(\pi/4,\tan^{-1}\sqrt{2})$, i.e., at $r_1=r_2=r_3$ for all the eight states. The differences in the wave functions among the eight intrashell states are not in the $R$, $\alpha_1$, and $\alpha_2$ coordinates, but rather in the three relative angles $\Xi$.

There are many different ways to choose the three relative angles among the three electrons. One can choose the angles between each pair of electrons with respect to the nucleus [7]. However, to illustrate the correlation among the three electrons, other choices of angles are preferred [8,9]. For the configuration $r_1=r_2=r_3$, the three electrons lie on the surface of a sphere. We define a $\sigma$ plane formed by the three electrons. This plane makes an angle $\theta$ with respect to the
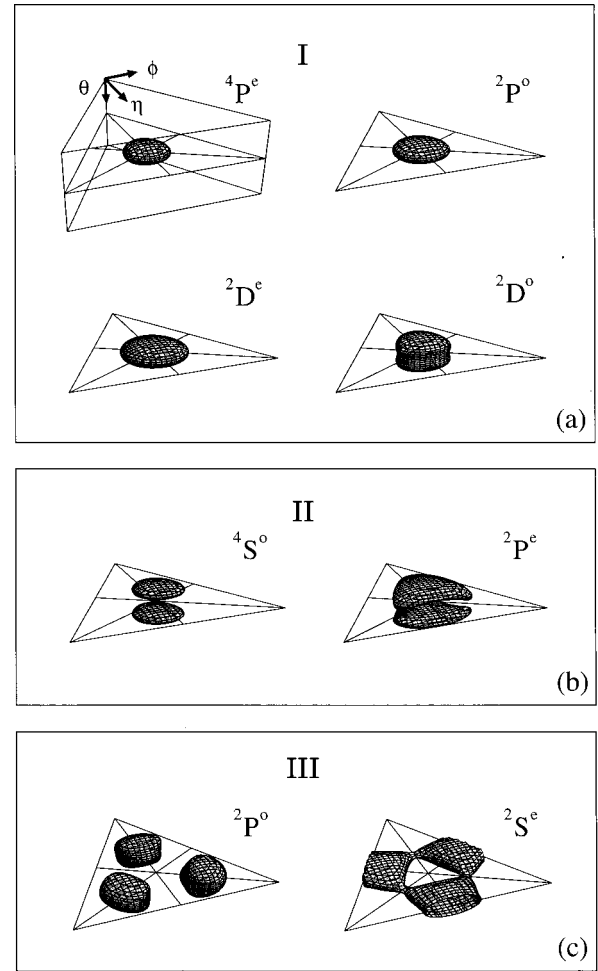


FIG. 3. The equidensity surface plots of the three-electron wave functions for the eight intrashell states at $r_1=r_2=r_3$. The surface represents 60% of the maximum density. Each ''slice'' represents the whole range of the three angles ($0\le\theta\le\pi$, $0\le\eta\le\pi$, $-\eta\le\phi\le\eta$). See text for detailed discussion of these plots.

nucleus, see Fig. 2. The distribution of $\rho_{LS\pi}^{\nu}$ with respect to $\theta$ depicts the motion of the plane with respect to the nucleus. On the $\sigma$ plane, the three electrons lie on a circle. The angle between electrons 1 and 2 is defined to be $2\eta$, choosing the arc including electron 3. The angle between electron 3 and the line bisecting electrons 1 and 2 is defined to be $\phi$, see Fig. 2. The range of the angles are ($0\le\theta\le\pi$, $0\le\eta\le\pi$, $-\eta\le\phi\le\eta$). These three angles specify a definite shape of the triangle and the position of the triangle with respect to the nucleus. For $\phi=0$, the three electrons form an isosceles triangle. If $\eta=2\pi/3$ also, then they form an equilateral triangle. If at the same time $\theta=\pi/2$ also, then they form a coplanar equilateral triangle with the nucleus at the center. Obviously the latter has the lowest Coulomb repulsion among the three electrons and is expected to be the most favorable geometry. However, as shown in model studies by Watanabe and Lin [8] and by Bao, Yang, and Lin [9], this geometry is not available to some states. Since each state has good quantum numbers $L$, $S$, and $\pi$, these symmetries would impose nodal surfaces in the multi-dimensional wave functions. The existence of such nodal surfaces tends to increase the excitation energy of the state.

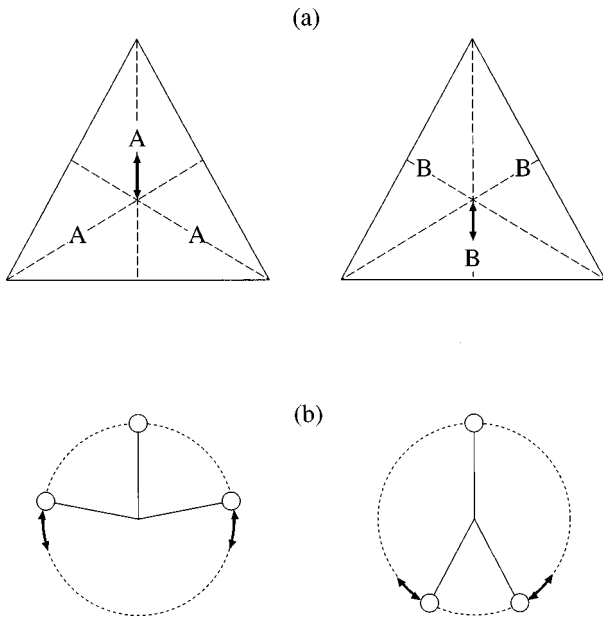For the fixed values of $R$, $\alpha_1$, and $\alpha_2$ given above, the

FIG. 4. Mechanical analog of the motion of the three electrons for group III states. (a) Top figures with $A$ indicating the peak density on the $(\phi, \eta)$ plane for $\theta = \pi/2$ for the $^2S^e$ state and $B$ the same for the $^2P^o$ state. When the three electrons move along the direction of the arrows in (a), the corresponding motion of the two electrons are shown in (b) where the third electron is fixed.

electronic density $\rho_{LS\pi}$ is still a function of three angles $\theta$, $\eta$, and $\phi$, which is not easily visualized. To display the global feature of a function in three dimensions we use the ''equidensity surfaces,'' which is a surface of constant electronic density. We have obtained such surfaces for all the eight intrashell states and the surfaces can be separated clearly into three groups, see Fig. 3.

In the first group, we found that there are four states which have similar equidensity surfaces. They are the $^2P^o$, $^4P^e$, $^2D^e$, and $^2D^o$ states. Each surface is a contour where the density is 60% of the maximum. A contour surface of higher density would fit inside the surface shown in each case. The similarity of the contour surfaces for these four states shows that they have nearly identical internal shape. In fact, the maximum of the density for each figure occurs at $\theta = \pi/2$, $\eta = 2\pi/3$, and $\phi = 0$; that is, the most favorable geometry is a coplanar equilateral triangle. This geometry is similar to that of a BF$_3$ molecule. Since they basically have the same shape, their relative energies are then similar to the rotational excitation of an oblate symmetric top [8,9]. For an oblate symmetric top, the rotation energy is

$$E(L,T) = \frac{1}{2I}[2L(L+1) - T^2], \quad (3)$$

where $I$ is the moment of inertia and $T$ is the projection of $L$ along the direction perpendicular to the plane. The energies of these four states shown in group I of Fig. 1(b) indeed resemble those of a symmetric top.

In Fig. 3(b) we show the equidensity surfaces for the $^4S^o$ and $^2P^e$ states. They have distinctly different shape from those in Fig. 3(a). The $\theta = \pi/2$ plane is clearly forbidden to the three electrons, indicating that coplanar geometry is not allowed for these two states. Above or below this plane, the
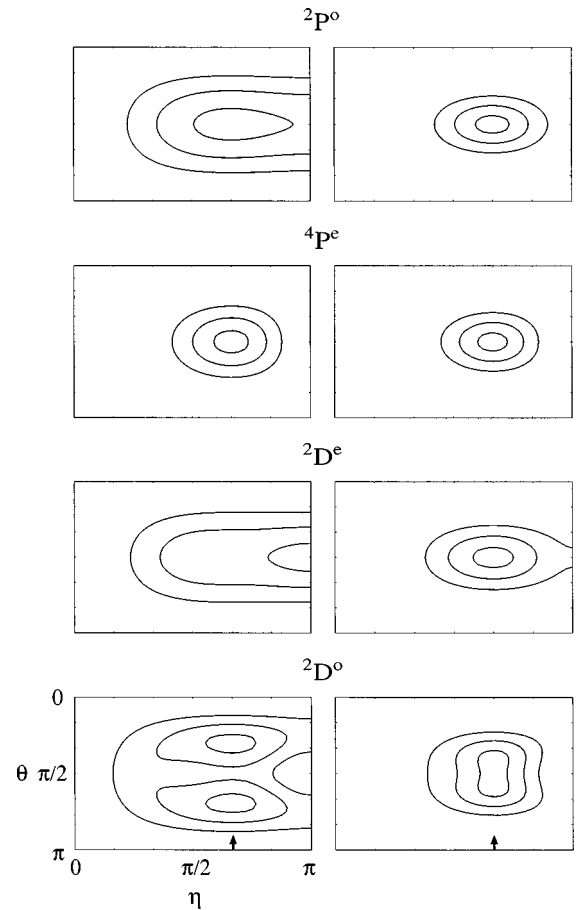


FIG. 5. The effect of angular configuration mixing and the internal shape of the triply excited states. With full angular mixing the three electrons in these four states form an equilateral triangle, as shown in (b). When the wave functions were calculated with only a single angular configuration, the resulting electronic distribution does not resemble an equilateral triangle. The plots are for $\phi = 0$.

three electrons still prefer to form an equilateral triangle. This geometry is similar to the antisymmetric state of the pyramidal NH$_3$ molecule where the wave function vanishes when the plane of the three hydrogen atoms coincides with the nitrogen atom. The existence of a nodal surface when the $\sigma$ plane intersects the nucleus implies higher excitation energy since minimum electrostatic repulsion occurs when the three electrons and the nucleus are coplanar. Note that in Fig. 1(b) the energy levels of group II are higher than the levels in group I except for the highest $^2D^o$ state, which has higher rotational energy.

The remaining two states are shown in Fig. 3(c). Both states have the maximum density at the $\theta = \pi/2$ plane, i.e., the three electrons are coplanar. However, the density vanishes in the middle, indicating that the three electrons cannot form an equilateral triangle. In Fig. 4 we illustrate the motion implied by the distributions shown in Fig. 3(c). In Fig. 4(a) we used $A$ and $B$ to indicate the maxima of the density plots on the $(\eta, \phi)$ plane at $\theta = \pi/2$. Recall each point in the triangle of Fig. 4(a) represents a given geometry. Tracing a point along the diagonal of the triangle represents a hinge mode where the third electron is fixed and the two other electrons are moving toward or away from each other in phase. Such motion is depicted in Fig. 4(b) to show the

analogous mechanical motion of the two modes.

The eight figures above clearly illustrate the different internal shapes among the intrashell triply excited states. The major distinction being that in group I, the three electrons can form a coplanar equilateral triangle; in group II they can form an equilateral triangle but not coplanar, and in group III they can be coplanar but not an equilateral triangle. The ''forbidden region'' for the latter two groups originates from the quantum symmetry in that a state with well-defined quantum numbers $L$, $S$, and $\pi$ would incur nodal surfaces in a multidimensional wave function. These ''forbidden regions'' are well predicted even within the independent electron model as long as the quantum symmetry is satisfied by the approximate wave functions. However, the precise shape or the internal structure of an atomic state may depend sensitively on the approximations used to describe the wave functions. To illustrate this point, we show in Fig. 5 the density plots for the four states in group I at $\phi=0$. On the left the densities are calculated assuming that each individual electron has a well-defined orbital angular momentum quantum number. We abbreviate such calculations as single angular configuration calculations. On the right the densities are calculated including all the important orbital angular momentum states of the three electrons. They are the multiple angular configuration calculations. Clearly the densities from the two calculations differ significantly except for the $^4P^e$

state. The single angular configuration calculation in general does not predict the coplanar equilateral triangles and the density distribution tends to be more diffuse. Thus it takes the multiple angular configuration calculations to predict the correct coplanar equilateral triangle shape for the three electrons and their collective motion. In Fig. 5 we use an arrow to indicate the location of $\eta=2\pi/3$. Together with $\theta=\pi/2$, they give the coordinates representing an equilateral triangle.

In summary, we have analyzed the internal structure of the wave functions of the eight lowest intrashell triply excited states of Li. We have shown that in four of the states the three electrons exhibit most preferable shape of a coplanar equilateral triangle. Their relative energies can be interpreted as due to the rotational excitation of a symmetric top. We have also shown that the other four states have nodal surfaces in their wave functions, which result in higher excitation energies. The present analysis offers a new direction for understanding the internal modes of triply excited states. While the present analysis was carried out for Li, the result is valid also for He$^-$ and three-electron positive ions, as well as three-valence-electron atoms such as boron and aluminum.

[1] C. D. Lin, Phys. Rev. A **29**, 1019 (1984).

[2] S. Watanabe and C. D. Lin, Phys. Rev. A **34**, 823 (1986).

[3] J. M. Rost and J. S. Briggs, J. Phys. B **24**, 4293 (1991).

[4] R. S. Berry and J. L. Krause, Adv. Chem. Phys. **70**, 35 (1988).

[5] D. R. Herrick and O. Sinanoğlu, Phys. Rev. A **11**, 97 (1975).

[6] S. Watanabe, M. Le Dourneuf, and L. Pelamourgues, J. Phys. (Paris), Colloq. **43**, C2-223 (1982).

[7] Y. Komninos, M. Chrysos, and C. A. Nicolaides, Phys. Rev. A **38**, 3182 (1988).

[8] S. Watanabe and C. D. Lin, Phys. Rev. A **36**, 511 (1987).

[9] C. G. Bao, X. Z. Yang, and C. D. Lin, Phys. Rev. A **55**, 4168 (1997).

[10] D. Cubaynes *et al.*, Phys. Rev. Lett. **77**, 2194 (1996) and references therein.

[11] Y. Azuma *et al.*, Phys. Rev. Lett. **79**, 2419 (1997) and references therein.

[12] B. Davis and K. T. Chung, Phys. Rev. A **42**, 5121 (1990).

[13] K. T. Chung and B. Gou, Phys. Rev. A **52**, 3669 (1995).

[14] K. T. Chung and B.-C. Gou, Phys. Rev. A **53**, 2189 (1996).

[15] K. Berrington and S. Nakazaki, J. Phys. B **31**, 1 (1998).

[16] T. Morishita, C. D. Lin, and C. G. Bao, Phys. Rev. Lett. **80**, 464 (1998).

[17] T. Morishita and C. D. Lin, Phys. Rev. A **57**, 4268 (1998).