B.5.4. Visualization of Electron Correlations in Intrashell Triply Excited States of Atoms-- *Toru Morishita and C. D. Lin*

One of our eventual goals in the study of triply excited states of atoms is to be able to find a new classification scheme. This goal cannot be reached until we have a full understanding of how the three electrons are correlated. Information on electron correlations is buried in the channel wavefunction, as given in Eq.(4) of Section B.5.2. The channel function contains eight spatial degrees of freedom, plus spins. By removing the three degrees of freedom for the overall rotation and summing over the spins, we are still left with five degrees of freedom. To simplify the problem further we thus confine ourselves to intrashell states where the radial distance of each electron is set at a radius where the wavefunction is near the maximum. In other words we consider three electrons confined on the surface of a sphere. This leaves us with three degrees of freedom. There still remain two issues: (1) how to choose the three angles, and (2) how to display the correlation. We have succeeded partially in answering these questions in the last grant period.

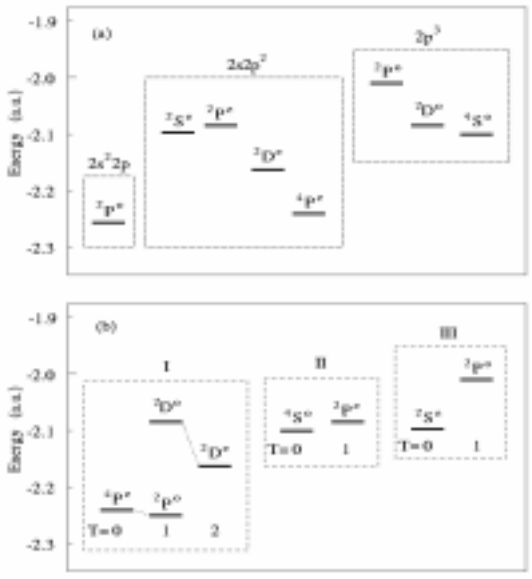

Figure 1. The energy levels of the eight $2\ell 2\ell' 2\ell''$ triply excited states of Li. (a) The states are arranged in terms of the single-particle electronic configurations. (b) The states are arranged according to their internal wavefunctions to show the rotational level structure (from Publication #95).

To make the explanation easier to follow, let us consider the eight intrashell $2\ell 2\ell' 2\ell''$ triply excited states of Li. The energy levels of the eight states are ordered according to the independent electron approximation, shown in Fig. 1(a). We rearranged these eight states as shown in Fig. 1(b). In so doing the states within the same box, distinguished by I, II and III groups, would have the same correlation patterns, as are clearly seen in Fig. 2. Without even

knowing what has been plotted, it is clear that the states within the same group do have nearly identical patterns. While the details are given in Publication #95, we explain the geometric meaning of the distributions of the three electrons in Fig. 2:

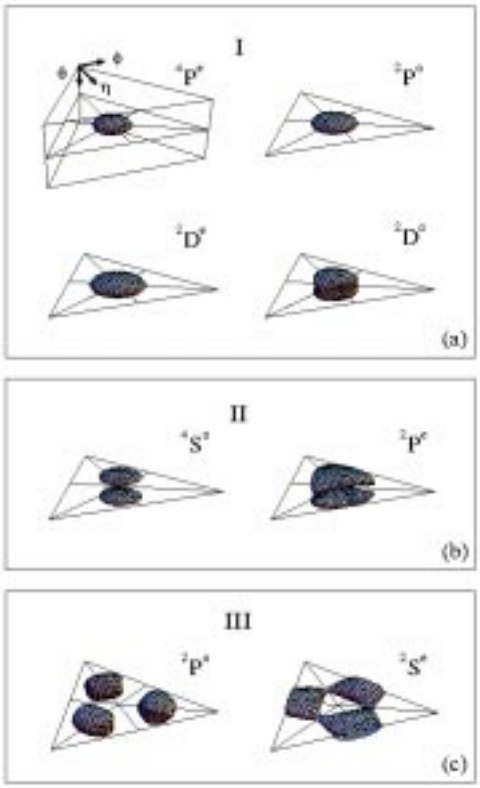

Figure 2. The equi-density surface plots of the three-electron wavefunctions for the eight intrashell states at $r_1=r_2=r_3$. The surface represents 60% of the maximum density that is located at the center of each surface (from Publication #95). Note that the center of the triangle shown in the figure corresponds to an equilateral geometry in physical space.

(1) In group I, the wavefunction peaks at the coplanar equilateral triangle configuration, where the three electrons are at the vertices of the triangle and the nucleus at the center. The states in this group have geometry resembling a planar molecule like BF_3.

(2) In group II, the wavefunction vanishes at the plane of the equator. The three electrons form an equilateral triangle, but cannot be coplanar. The distribution has a nodal plane and thus these states have higher energies. The states in this group have a geometry resembling the NH_3 molecule.

(3) In group III, the wavefunction vanishes at the equilateral triangular geometry, but it can be coplanar. We are not aware of any molecules having this configuration.

The arrangement of energy levels in Fig. 1(b) is analogous to the rotational level ordering of a symmetric top. However, the electrons are not rigid. In the middle frame of Fig. 2 we can see pronounced deviations, indicating that quantum number T, which is the projection of the angular momentum with respect to the axis perpendicular to the plane of the three electrons, is only an approximate quantum number. More complete analysis of the correlation of the three electrons has been reported in Publication #107. The correlation in the radial degrees of freedom and the correlation of doubly excited states have also been analyzed in Publication #107. A report based on the conference-invited talk is published in Publication #106.