

### Comment on "Classification of Doubly Excited States of Two-Electron Atoms"

In a recent Letter<sup>1</sup> Lin has reported a classification of doubly excited states of two-electron atoms based on quantum numbers  $(K, T)^A$ . He argued that the supermultiplet structure discovered by Herrick and Kellman for intrashell levels<sup>2</sup> is of more general applicability. This structure is associated with isomorphic correlations patterns for states of distinct symmetries.

In fact, a conceptually simple picture of correlation in doubly excited states already exists, the *collective rovibrational* or *molecular* interpretation of supermultiplet structure, introduced by Kellman and Herrick.<sup>3</sup> This model developed from  $O(4)$ -based descriptions of doubly excited states.<sup>4,5</sup> Graphical studies of rotationally averaged two-electron densities<sup>6-8</sup> have confirmed its validity, especially with accurate wave functions,<sup>8</sup> for low- $Z$ ,  $N=2$  intrashell states.

There is no difficulty extending either the supermultiplet scheme or the molecular model to *intershell* states. Excitations of one electron from a particular intrashell state to a higher shell are associated with *stretching vibrations* of the electron-nucleus vector, like a local mode in an  $H_2O$  molecule. The lowest  $S$  states of an intershell manifold correspond to symmetric ( $^1S$ ) or asymmetric ( $^3S$ ) superpositions of local-mode excitations. Higher levels in the manifold correspond to bending/rotation excitations of the bond-excited molecule. Electron densities for  $n_1=2$ ,  $n_2=3$   $^1S^e/3P^o$  and  $^3S^e/1P^o$  states confirm this view.<sup>8</sup>

The isomorphic correlation patterns noted by Lin are a natural consequence of *collective* motion in two-electron atoms. Along a rotor series, for example, the wave function approximately factors into an almost-invariant intrinsic part and an external rotational part.

The relation between the  $(K, T)^A$  quantum numbers and the molecular quantum numbers is as follows: For a state connecting asymptotically with a one-electron state with quantum number  $N$ , the number of nodes or near nodes in the bending ( $\theta_{12}$ ) wave function between 0 and  $\pi$  is  $(N-1-K-T)/2$ . The number of bending quanta  $\nu_2=N-1-K$ .  $\nu_2$  increases as  $K$  decreases, so that  $\langle\theta_{12}\rangle$  decreases as  $K$  decreases.  $T$  is the number of quanta of vibrational angular momentum along the molecular axis. For separable stretching vibrations  $A=(+)$  or  $(-)$ , corresponding to symmetric or antisymmetric linear combinations of bond vibrations. In excited states with  $L > 0$ , there is not

necessarily a well-defined node or antinode at  $r_1=r_2$ , and Lin arbitrarily sets  $A=0$  here.

The molecular character of the states considered by Lin is readily apparent. In Fig. 2 of Ref. 1, the  $^3P^e/1P^o$  pair corresponds to  $\nu_2=1$ ,  $T=1$ , and no stretching or rigid-rotor excitation. Adding one quantum of rigid-rotor excitation generates the  $^1D^o/3D^e$  pair. In Fig. 3 of Ref. 1, the  $(2, 0)^- 1P^o$  state is a one-quantum rotor state with  $\nu_2=0$  and antisymmetric bond excitation. The  $(-2, 0)^0 1P^o$  state has four additional quanta in the bending vibration. The apparent lack of angular correlation in the  $(-2, 0)^0 1P^o$  channel wave function, which has relatively small amplitude at  $r_1=r_2$ , reflects a transition to more independent-particle-like angular behavior, as observed in model calculations for particles on concentric spheres.<sup>9</sup>

In conclusion, all features of correlation in doubly excited states of two-electron atoms discussed in Ref. 1 can be understood in terms of a collective molecular model.

Gregory S. Ezra

Department of Chemistry  
Cornell University  
Ithaca, New York 14853

R. Stephen Berry

Department of Chemistry and  
The James Franck Institute  
The University of Chicago  
Chicago, Illinois 60637

Received 16 January 1984

PACS numbers: 31.10.+z, 31.20.Tz

<sup>1</sup>C. D. Lin, Phys. Rev. Lett. **51**, 1348 (1983).

<sup>2</sup>D. R. Herrick and M. E. Kellman, Phys. Rev. A **21**, 418 (1980); D. R. Herrick, M. E. Kellman, and R. D. Poliak, Phys. Rev. A **22**, 1517 (1980).

<sup>3</sup>M. E. Kellman and D. R. Herrick, J. Phys. B **11**, L755 (1978), and Phys. Rev. A **22**, 1536 (1980).

<sup>4</sup>C. E. Wulfman, Chem. Phys. Lett. **23**, 370 (1973), and Phys. Rev. Lett. **51**, 1159 (1983).

<sup>5</sup>O. Sinanoglu and D. R. Herrick, J. Chem. Phys. **62**, 886 (1975).

<sup>6</sup>P. Rehmus, M. E. Kellman, and R. S. Berry, Chem. Phys. **31**, 239 (1978); P. Rehmus and R. S. Berry, Chem. Phys. **38**, 247 (1979).

<sup>7</sup>H.-J. Yuh, G. S. Ezra, P. Rehmus, and R. S. Berry, Phys. Rev. Lett. **47**, 497 (1981).

<sup>8</sup>G. S. Ezra and R. S. Berry, Phys. Rev. A **28**, 1974 (1983).

<sup>9</sup>G. S. Ezra and R. S. Berry, Phys. Rev. A **25**, 1513 (1982), and **28**, 1989 (1983).