

preciable, and that not only  $\delta\Delta$ , but  $\delta\pi$ , varies monotonically throughout this region of the spectrochemical series, which is not unreasonable.

When  $\delta\Delta > 0$ , as with  $\text{NO}_2^-$  and  $\text{CN}^-$ , the effect of the  $\delta\pi$  contribution ought to increase the separation between the states in question. The value for  $\text{NO}_2^-$  remains linear with  $\delta\Delta$ , indicating that the  $\delta\pi$  contribution must be small. However, with  $\text{CN}^-$  the linear relation is no longer observed. In fact, the observed band maximum at  $30,600\text{ cm.}^{-1}$  is at just the predicted wave number for the  ${}^1\text{E}^b$  state when  $\delta\pi = 0$ . The transition  ${}^1\text{A}_1 \rightarrow {}^1\text{B}_2$  is then expected at about  $34,000\text{ cm.}^{-1}$ . From the solution spectra, the separation of the maximum of band II from the onset of transfer is about  $10,000\text{ cm.}^{-1}$  with no indication of another band within this interval. We conclude that (1) the split component  ${}^1\text{B}_2$  must be of very low intensity and be

buried in the high energy tail of the observed band and (2)  $\delta\pi$  must be very close to zero. In support of this argument, a recent e.s.r. study<sup>5</sup> of  $\text{Cr}(\text{CN})_6^{3-}$  indicated that the  $t_{2g}$  set is only slightly antibonding.

The energies and splittings which we have presented also apply to the split components of the  ${}^4\text{T}_1$  and  ${}^4\text{T}_2$  states for  $\text{Cr}(\text{III})$  and those of the  ${}^3\text{T}_2$  and low energy  ${}^3\text{T}_1$  for  $\text{Ni}(\text{II})$ .

(5) H. A. Kuska and M. T. Rogers, *J. Chem. Phys.*, **41**, 3802 (1964).

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## Book Review

**Molecular Orbital Theory.** By C. J. BALLHAUSEN and HARRY B. GRAY. W. A. Benjamin, Inc., New York, N. Y. 1964. ix + 273 pp.  $16 \times 23.5\text{ cm.}$  \$9.00 (clothbound); \$4.95 (paperback).

This is another Benjamin quasi-book, with some 135 pages of text and a skimpy reprint collection of 130 pages (R. G. Parr's "Quantum Theory of Molecular Electronic Structure" by the same publisher contains 340 pages of reprint + 160 of text). Of the twelve reprints, three are by the authors, and four, one each by Mulliken and co-workers and Van Vleck and two by Walsh, are extremely important. The text itself is a rather good introduction to qualitative molecular orbital theory, stressing the importance of symmetry and overlap considerations and eventually directed toward inorganic applications. The spirit of the book is commendable; to quote the final paragraph: "Thus, although we feel it is useful to do simple MO calculations to *help* in interpreting and classifying electronic spectra, it is certainly clear that the calculated MO's must be consistent with a goodly amount of experimental information before they can be taken seriously." The treatment clearly will not appeal to nihilistic purists but it is the only reasonable approach to molecules of some complexity.

The best part of the volume is the discussion of the shapes and spectra of diatomics, triatomics, and some small molecules. Less satisfactory is the last chapter, the most detailed, which describes the kind of Wolfsberg-Helmholz calculations the authors do. There are some bad points in earlier chapters. For instance, a figure, (4-3), claims to show an energy diagram for  $\text{Li}_2$  and two Li atoms with and without hybridization. This is clear nonsense; there exist the real energy levels of two Li atoms and those of a  $\text{Li}_2$  molecule. If one wants to look for hybrids *after* one obtains the correct  $\text{Li}_2$  wave function one may do so; but there is nothing real about hybrids interacting. (Perhaps the point should not be stressed; the authors make excellent

and consistent use of MO arguments, and the hybridization chapter is mercifully short.) Throughout the book there are representations of p and d orbitals which purport to be "boundary surfaces" but which are the end products of artistic license applied to polar diagrams. I wish to recommend in this respect a beautiful extended article in a source probably not familiar to inorganic chemists: C. A. Coulson and E. T. Stewart in "The Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964. Or perhaps Benjamin might harness a computer to produce a useful non-book containing contour diagrams of atomic and molecular orbitals in various stages of approximation.

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### BOOKS RECEIVED

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- RONALD RICH. "Periodic Correlations." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. v + 159 pp. \$8.00.
- WILLIAM L. JOLLY, Editor. "Preparative Inorganic Reactions." Volume 2. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1965. vii + 378 pp. \$14.50.
- GEORGE G. LIBOWITZ. "Solid-State Chemistry of Binary Metal Hydrides." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. v + 139 pp. \$7.25.
- TIBOR S. LASZIO. "Image Furnace Techniques." Technique of Inorganic Chemistry, Volume V. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1965. v + 195 pp. \$12.00.