Bond Integrals and Spectra

With an Analysis of Kynch and Penney's Paper on the Heat of Sublimation of Carbon*

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THE use of the molecular orbital method in making connections between spectra, dissociation energies, and resonance energies is described. These quantities are all expressed in terms of the "bond integral" β, whose nature is discussed, and whose values for various bonds in carbon and hydrogen compounds are determined empirically from available data. The values of $-\beta$ are all about 3 to 4 ev. They are rather well correlated with the true bond strengths. By "true bond strength" is here meant energy of dissociation into atoms with each carbon atom in the tetrahedral valence state.

Computed overlap integrals S are obtained for various carbon-carbon bonds. These should form a measure of bond strength according to the "criterion of maximum overlapping," but actually they prove in general not to be proportional to the true bond strengths. Pauling's definition of the "strength of a bond orbital" is found, in general, not to be well correlated either with the S values or with the true bond strengths.

The value of β as a function of internuclear

distance has been evaluated from the resonance energy of benzene together with infra-red and Raman data.

The use of molecular orbitals constructed from atomic orbitals with adjusted values of the effective nuclear charge Z is discussed. Good results are noted for computed intensities of electronic transitions in the hydrogen molecule when suitable different Z values are used for normal and excited states. The extension to other molecules may account for the considerable factor by which existing computed intensities exceed observed intensities. The theoretical computation of singlet-triplet separations in molecules is briefly discussed.

The nature of the bond integral α of the atomic orbital approximation is examined, and values of both α and β obtained by various methods are tabulated and critically discussed. Kynch and Penney's theoretical treatment of certain spectra of butadiene, hexatriene, and benzene is critically analyzed, and it is shown that it gives no basis for decision as to the true value of the heat of sublimation L of carbon. The value $L=124$ kcal./mole remains the most probable. Kynch and Penney's identification of their computed excited states with the observed first excited states of butadiene and hexatriene is invalid.

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* The complete paper was not ready in time for inclusion here, but will probably be ready fairly soon for publication elsewhere.

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