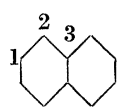


(2) Application to the case of the benzyl radical, with all bond lengths equal to 1.39 Å, yields a delocalization energy of 34.4 kcal; the average bond order calculated differs a little from the value of $\frac{2}{3}$ ($\equiv 1.39$ Å), and after an allowance of 5.7 kcal (calculated by the methods described by Pritchard & Sumner 1955*a*) a resonance energy of 28.7 kcal is obtained, in good agreement with the experimental value of 24.5 kcal (see, for example, Pritchard & Sumner 1955*b*).

Thus, it seems clear that the approximation gives slightly better results on the whole than does the Hückel method for hydrocarbon systems. It is also clear, however, that, since the charge densities are no longer all the same, the effective electro-affinities of all the atomic orbitals are no longer equivalent, and an allowance should be made for this fact; the results for naphthalene are presented in detail in table 1 as an example. In practice, it turns out that the correction is negligible for hydrocarbon systems, but it is most essential when we come to discuss hetero-atom systems later in the paper.

TABLE 1

		first cycle value	self-consistent value
 naphthalene	total π -energy	16.834 χ_C	16.776 χ_C
	resonance energy	0.953 χ_C	0.896 χ_C
	electron densities, q_r		
	1	1.008	1.008
	2	1.011	1.004
	3	0.962	0.976
	bond orders, p_{rs}		
	1-2	0.724	0.731
	2-3	0.558	0.552
	1-1'	0.599	0.590
3-3'	0.513	0.525	

The method of correction is based on the fact that the total electronic energies of a series of ions of the same atomic number lie very closely on a parabola (see, for example, Pritchard & Skinner 1954). In figure 1 are shown the relative energies of the three valence states required to define the p -electro-affinity of a 4-valent carbon atom: we construct through these three points a parabola; the first derivative of the electronic energy with respect to q , the occupation number of the orbital being considered, is $\frac{1}{2}(I + E)$ at the point $q = 1$ —precisely Mulliken's definition of the electro-affinity of this orbital. Accepting that this is the fundamental basis of the electro-affinity scale, it is now an easy matter to write down the electro-affinity for the given orbital for the whole range of occupation numbers $0 \leq q \leq 2$; it is meaningless to consider values of q outside these limits. Table 2 presents the relevant valence state data for the atoms considered in this paper. Thus, having calculated the charge densities assuming all atoms to be equivalent, it is a fairly easy matter to adjust the various Coulomb integrals according to the formulae in table 2, to alter the exchange integrals accordingly and to re-solve the secular determinant. It has to be remembered also that the overlap integrals vary with occupation number (since the effective nuclear charges are affected), but the correction is easily made with the aid of Slater's rules. They also vary with bond order (which alters the distance between the overlapping orbitals), but here again the

correction is easily made via the standard bond order-bond length relationship; a similar alteration to the exchange integrals is also necessary. A number of cycles of the calculation were carried through on the naphthalene molecule to find the effect of these corrections; the approximation does not converge readily but tends to oscillate, probably due to the inaccuracy of the bond order-bond length relationship which is used to determine the overlap and exchange integrals for the succeeding cycle; however, the effect is quite small, as can be seen from the self-consistent values given in the last column of table 1. The total π -electron energy is altered by about 0.4% ($\equiv 8$ kcal/mole), and the bond orders and charge densities are similarly only slightly affected.

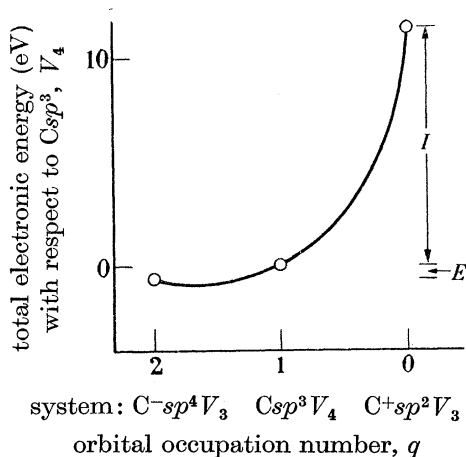


FIGURE 1. Variation of total electronic energy with orbital occupation number for carbon.

TABLE 2. VALENCE STATE EXCITATION ENERGIES (IN eV)
AND ORBITAL ELECTRO-AFFINITIES

process	E	I	χ	type of molecule
$B^2-sp^4V_3 \rightarrow B^{-sp^3}V_4 \rightarrow Bsp^2V_3$	(-5.8)	0.12	3.08-5.92 q	boron trifluoride
$C^{-sp^4}V_3 \rightarrow Csp^3V_4 \rightarrow C^+sp^2V_3$	0.58	11.42	16.84-10.84 q	benzene
$N^{-sp^5}V_2 \rightarrow Nsp^4V_3 \rightarrow N^+sp^3V_2$	1.58	14.49	20.95-12.91 q	pyridine
$Nsp^4V_3 \rightarrow N^+sp^3V_4 \rightarrow N^2+sp^2V_3$	12.26	28.86	37.16-16.60 q	pyrrole
$Fs^2p^5V_1 \rightarrow F^+s^2p^4V_2 \rightarrow F^2+s^2p^3V_1$	18.06	39.63	50.42-21.57 q	boron trifluoride

(a) Application to pyridine

The principal difficulty in applying the method to non-hydrocarbon systems is to find the most convenient route to a self-consistent solution, because in the zero-order approximation, charge densities differing from integral values by as much as 0.3 electron appear which so profoundly affect the S and χ for the next cycle that oscillation occurs. The simplest method was found to be the one which is generally applicable to all π -electron systems: that is, to take for the first cycle the nuclear framework with all the π -electrons removed and to solve the secular determinant containing χ , S , etc., corresponding to $q = 0$ for all the orbitals; this cycle is completely superfluous in the case of homonuclear systems, and at first sight, apparently so in the pyridine case, but here it yields a zero-order solution which does not cause such violent oscillation in the succeeding solutions. The approximate condition of