is zero at threshold[25] because of the PW density of states, the α term rises from zero with an initially infinite slope, reaching a maximum only 2 eV above threshold (photon energy 12.5 eV). This behavior, resulting from contributions to α that are proportioned to k rather than to k^5 as in the PW expression for $\beta/2$ in eq 13, produces two maxima in the dependence of $(d\sigma/d\Omega)_\perp$ on photon energy. The high-energy maximum is similar to those in Figure 1, but shifted about 5 eV to higher energy and reduced in height as described above. The question remains as to whether the OPW procedure[26] will confirm the chemical trends found in the PW cross sections.

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(25) By contrast, the exact cross section for the photoionization of the H atom (ref 3) is a maximum at threshold. An improved procedure might be the combination of OPW matrix elements with the density of states appropriate to the H atom continuum.

(26) For an OPW study of anthracene applied to the photoconductivity of the crystal, see R. D. Sharma, *J. Chem. Phys.*, **46**, 2841 (1967).

ω-Type Calculations on π-Electron Systems with Inclusion of Overlap Charges. I. Ionization Potentials of Some Alternant Hydrocarbons

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Abstract: ω-Type calculations have been performed on π-electron systems with inclusion of overlap charges. Ionization potentials of some alternant hydrocarbons have been calculated and the results obtained compared with those obtained from the SCF–MO method and with experimental values.

In recent years much attention has been paid to the Hückel equation.[1] A simple argument shows that the coulomb integral $H_{\mu\mu}$ for a carbon atom μ in a π lattice for which the electron density q_μ is not unity cannot be treated as a parameter. If $q_\mu < 1$, the net positive charge $(1 - q_\mu)$ means that the screening "seen" by any one electron is reduced and the coulombic attraction to the nucleus is increased. $H_{\mu\mu}$ for such a carbon should have a more negative value. Conversely, a carbon with a net negative charge should have a less negative value of $H_{\mu\mu}$. Wheland and Mann[2] proposed that the value of $H_{\mu\mu}$ should be linearly related to the charge. Their proposal may be formulated as

$$H_{\mu\mu} = \alpha_0 + (1 - q_\mu)\omega \tag{1}$$

$$H_{\mu\nu} = \beta_{\mu\nu} \tag{2}$$

in which α_0 and ω are treated as empirical parameters whose value may be chosen so as to give best agreement with experimental results. The resonance integral $\beta_{\mu\nu}$ is supposed to be zero unless μ and ν are directly bonded; for all directly bonded μ,ν, it is given a constant value.

Thus the dependence of the coulomb integral upon the net charge of an atom introduces some electron repulsion within the framework of the simple LCAO method.[3] The use of this method in the literature is still rather limited, but it has been shown to lead to improved calculated dipole moments for hydrocarbons[2,4] and greatly improved energy values for organic cations.[3,5] The ω technique also involves an iterative procedure like the SCF equation. In the first iteration the Hückel charge distributions are used as a first approximation. However, in a semiempirical treatment, the iterative procedure is generally omitted.

Inclusion of Overlap Charges in the ω Technique (IOC ω Technique)

All investigators who have used the ω technique have neglected the overlap charges in their calculations. Therefore, according to Harris,[6] if we include the overlap, take the net charge on atom μ as that resulting when all overlap charges are divided equally among the atoms involved, and use the Wolfsberg–Helmholtz[7] form for $H_{\mu\nu}$, we have

$$H_{\mu\mu} = \alpha_0 + \omega[1 - {}^1/_2\sum_\sigma(p_{\mu\sigma}S_{\mu\sigma} + p_{\sigma\mu}S_{\sigma\mu})] \tag{3}$$

$$H_{\mu\nu} = {}^1/_2KS_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu}) \tag{4}$$

where K is a dimensionless constant and $p_{\mu\sigma}$ is defined as

$$p_{\mu\sigma} = 2\sum_i^{\text{occ}} c_{i\mu}c_{i\sigma} \tag{5}$$

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in which $c_{i\mu}$ and $c_{i\sigma}$ are coefficients of atomic orbitals in the ith molecular orbital.

Now it is apparent that if the overlap integral $S_{\mu\sigma}$ is neglected in eq 3 unless $\mu = \sigma$, the equation will reduce to eq 1. However, in the present calculations $S_{\mu\sigma}$ is given a constant value, say S, for μ,σ bonded and is supposed to be unity for $\mu = \sigma$.

Inclusion of overlap charges in the ω technique apparently approximates SCF equations by bringing in an approximate correction for two-center, two-electron repulsion integrals *via* the relationship (3), while the ω technique approximates only one-center, two-electron repulsion integrals. The present communication deals with the application of new matrix elements to π-electron systems. This is the first time that anybody has performed ω-type calculations on π-electron systems with inclusion of overlap charges.

Ionization Potentials of Alternant Hydrocarbons

The energy of each of the occupied orbitals is an approximation to one of the ionization potentials. The first ionization potential, I, of an even alternant hydrocarbon corresponds to the energy of the highest occupied molecular orbital[8] (Koopmans' theorem[9]). Therefore, from the approximate version of simple molecular orbital theory, if ψ_n is the highest occupied molecular orbital, the ionization potential, I, of an even alternant hydrocarbon is given as

$$-I = \sum c_{n\mu} H_{\mu\nu} c_{\mu\nu} \tag{6}$$

$$= \sum_{\mu} c_{n\mu}{}^2 H_{\mu\mu} + 2\sum_{\mu<\nu} c_{n\mu} H_{\mu\nu} c_{n\nu} \tag{7}$$

Here summations are over all μ,ν. For alternant hydrocarbons it can easily be shown that

$$p_{\mu\mu} = 1$$

and

$$p_{\mu\sigma} = p_{\sigma\mu} \tag{8}$$

so that eq 3, 4, and 8, when applied in eq 7, lead to

$$-I = \alpha_0 + mKS\alpha_0 - \omega S \sum_{\mu} \sum_{\sigma\neq\mu} c_{n\mu}{}^2 p_{\mu\sigma} - K\omega S^2 \sum_{\mu<\nu} \sum_{\lambda\neq\mu} \sum_{\sigma\neq\nu} c_{n\mu} c_{n\nu} (p_{\mu\lambda} + p_{\nu\sigma}) \tag{9}$$

where

$$m = 2\sum_{\mu<\nu} c_{n\mu} c_{n\nu} \tag{10}$$

Here summations like $\Sigma_{\sigma\neq\mu}$ are only over directly bonded atoms; the summation $\Sigma_{\mu<\nu}$ is over only μ,ν bonded, as it occurs with S which is defined only for bonded atoms.

Before using eq 9 for evaluation of the ionization potentials, one must first determine the values of α_0 and ω empirically, using the known I values of some compounds. However, $\alpha_0 = -9.40$ and $\omega = -9.44$ eV with $K = 2$ and $S = 0.25$ have been found to give quite satisfactory results. As an approximation, the simple HMO coefficients are used for the present purpose.

Results and Discussion

In Table I, we have listed the ionization potentials of some alternant hydrocarbons calculated by us from eq 9 and those calculated by Dewar, *et al.*,[10] using Pople's approximate SCF–MO theory, along with the observed ones.[11] All the calculated values listed in Table I refer to the vertical ionization potentials, since the geometry of the molecule has not been changed while performing the calculations. As a comparative study is to be made among the calculated and observed values, we have listed only the electron-impact data for the observed ones, as on some bases they have been proved to be the vertical ionization potentials.[10]

Table I. Calculated and Observed Ionization Potentials of Some Alternant Hydrocarbons

			Ionization potential, eV		
No.	Compound	m	IOC ω technique	SCF–MO method	Obsd
1	Ethylene	1.00	10.56	10.14	10.56
2	Benzene	1.00	9.38	9.35	9.38
3	Naphthalene	0.618	8.31	8.45	8.26
4	Anthracene	0.414	7.72	7.83	7.55
5	Phenanthrene	0.605	8.19	8.28	8.03
6	Tetracene	0.295	7.37	7.42	
7	3,4-Benzophenanthrene	0.568	7.98	8.09	7.84
8	Styrene	0.662	8.73	8.71	8.86
9	Biphenyl	0.705	8.31	8.45	8.30
10	Butadiene	0.618	9.15	9.02	9.18

We first point out from the present calculations that the inclusion of the overlap charges in the ω technique separates the ionization potentials of ethylene and benzene, which, within the simple HMO method, the HMO method with nearest neighbor overlaps, and also the simple ω technique, are predicted to have the same ionization potential. Further, from Table I, it is clear that the IOC ω technique gives results better even than does the SCF–MO theory. The average percentage deviation of the present calculations from the observed values is only 0.85, while that of SCF–MO calculations is 2.40. Therefore, it may be concluded that the IOC ω technique is much better for giving results of chemical accuracy and hence may be successfully applied to π-electron systems.

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