# A NOTE ON ELECTRONIC OSCILLATOR STRENGTHS IN CONJUGATED AND AROMATIC HYDROCARBONS

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The standard Hückel method (without overlap) predicts oscillator strengths which for the $N \rightarrow V_1$ transition are 3—4 times too large. It is shown that an essential improvement can be obtained if varying the resonance integrals with bond lengths as required by the SC LCAO MO method. The results are however still too large, being for intensive bands almost exactly twice as large as found experimentally.

## 1. Introduction

The calculation of positions of absorption bands and of their intensities have been the subject of many papers. A fair success has been already achieved in the interpretation of the position of maxima of the bands, particularly in the case of aromatic and conjugated hydrocarbons. However, the explanation of the observed intensities is usually rather troublesome.

Let $\psi_I$ be the electronic wave function of the ground state, $\psi_{II}$ — of the excited state, and $\vec{r}_i$ let be the radius vector of the electron $i$. Theoretically, the intensity of a band is characterized best by what is called the oscillator strength, $f$. According to Mulliken and Rieke (1941),

$$f = \frac{8\pi^2 mc}{3h} \nu Q^2 = 1.085 \cdot 10^{-5} \nu Q^2, \tag{1}$$

where $\nu$ is the average frequency of the transition (in $cm^{-1}$), and $\vec{Q}$ is the transition dipole moment (in Å),

$$\vec{Q} = \int \psi_I \sum \vec{r}_i \psi_{II} \, dV. \tag{2}$$

On the other hand,

$$f_{\text{exp}} = \frac{mc^2}{\pi e^2 N} \int_{\text{(band)}} \varepsilon_\nu d\nu, \tag{3}$$

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where $e$ is the electronic charge, $m$ — its mass, $c$ is the velocity of light in vacuum, $N$ is Avogadro's number and $\varepsilon_\nu$ is the molecular extinction coefficient for a radiation of frequency $\nu$.

In this paper we compare the oscillator strengths calculated with the Hückel method and also the SC LCAO MO method, with experiment.

## 2. *Details of calculations*

The Hückel method and its application to the calculation of oscillator strengths is described in books on quantum chemistry (*e.g.* Pullman and Pullman 1952; Daudel *et al.* 1959). The SC LCAO MO method is a modification of the Hückel method in which an allowance is made for a variation of resonance integrals $\beta_{rs}$ with the bond lengths $R_{rs}$ (Gołębiewski and Nowakowski 1964),

$$\beta_{rs} = \text{const} \cdot \exp\ (-4\Delta E R_{rs}), \tag{4}$$

where $\Delta R_{rs} = R_{rs} - 1.397\text{Å}$. The method requires a knowledge of bond lengths, $R_{rs}$. They are settled by the requirement that

$$\Delta R_{rs} = 0.180\ (p_{rs} - 2/3), \tag{5}$$

where $p_{rs}$ is the mobile bond order.

The oscillator strengths, calculated with these assumptions for some alternant conjugated and aromatic hydrocarbons, are listed in Table I. Some explanation is necessary. For bond angles in polyene-chains we always took 120°. The bond lengths assumed are those calculated with Eq. (5). The rings in benzenoid hydrocarbons are certainly not regular; let us denote by $a, b, c, d, e, f$ the sides of a ring, and by $x$ the diagonal which is parallel to the sides $a$ and $d$. We have assumed, that approximately $x = \frac{1}{2}(a+d)+\frac{1}{4}(b+c+e+f)$.

## 3. *Comparisons*

It is well-known that Hückel's method predicts oscillator strengths which are much too high (Pullman and Pullman 1952; Daudel *et al.* 1959). One can also see it from Table I. If one takes atomic overlap into account, the agreement with experiment is still worse; the overlap makes the oscillator strengths almost twice as large as without overlap (Coulson 1948). Certainly, a way out is to make extensive and elaborate calculations with the use of a more explicit hamiltonian and with the mixing of configurations. However, there is always some interest in simple theories, in which the physical arguments are much easier to follow, and the calculations are comparably short. Indeed, assuming the validity of Eq. (4) and (5) we could interpret the transitions in alternant hydrocarbons and some $\pi$-complexes in a more compact and clear way than it was possible with the standard Hückel method. Hence we thought it worthwhile to find how much the SC procedure does affect the oscillator strengths.

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We learn from Table I that errors $\Delta f = f_{calc} - f_{exp}$, which follow from the application of the Hückel method, are now reduced by 20—30% for benzenoid hydrocarbons and by 45—55% for butadiene and vinyl compounds. For polyacenes the SC theory is not much

TABLE I

Oscillator strengths of the $N \rightarrow V_1$ transition of some hydrocarbons

| Molecule | $Q$ Hückel | $Q$ SCLCAO | $\nu$ kK* | $f$ Hückel | $f$ SCLCAO | $f$ exp.* | $f$** ASMOCI |
|---|---|---|---|---|---|---|---|
| Diphenyl-butadiene (assumed trans) | 2.86 | 2.23 | 28.4 | 2.53 | 1.54 | 0.77 | — |
| Stilbene (trans) | 2.23 | 1.90 | 32.0 | 1.73 | 1.25 | 0.62 | — |
| Butadiene (trans) | 1.66 | 1.41 | 47.7 | 1.43 | 1.03 | 0.53 | 0.60 |
| Diphenyl (assumed planar) | 1.74 | 1.60 | 41.0 | 1.34 | 1.14 | 0.41 | — |
| Stilbene (cis) | 1.62 | 1.35 | 37.0 | 1.06 | 0.73 | 0.39 | — |
| Perylene | 2.44 | 2.10 | 23.0 | 1.48 | 1.10 | 0.36 | — |
| Etylene | 0.94 | 0.94 | 61.5 | 0.59 | 0.59 | 0.34 | — |
| Naphthalene | 1.17 | 1.08 | 36.4 | 0.54 | 0.46 | 0.18 | 0.26 |
| Anthracene | 1.32 | 1.17 | 26.7 | 0.51 | 0.40 | 0.10 | 0.39 |
| Tetracene | 1.45 | 1.30 | 21.0 | 0.48 | 0.38 | 0.08 | 0.44 |

* Data for ethylene from Platt, Klevens and Price (1949). Remaining data from Pullman and Pullman (1952).

** Butadiene according to Coulson and Jacobs (1951), The other data according to Pariser (1956).

worse than the more elaborate Pariser and Parr method (Pariser 1956); indeed, the predicted strength is worse in the case of naphthalene, but for tetracene the opposite seems to be true.

Anyhow, the oscillator strengths predicted by the SC LCAO MO theory are still too large. It may be of some practical interest to know that for intense bands $f_{exp}$ seems to be equal to $\frac{1}{2} f_{SCLCAO}$. For low intensities this relation still overestimates the oscillator strength by 0—0.15.

In hexatriene and octatetraene we know nothing about the statistical weights of cis and trans forms. It we assume trans forms only, the oscillator strengths $f_{calc}$ should exceed $f_{exp}$ slightly more than usually. We find

| | $f_{Hückel}$ | $f_{SCLCAO}$ | $f_{exp}$ |
|---|---|---|---|
| Hexatriene | 2.76 | 1.80 | 0.7 |
| Octatetraene | 4.70 | 3.05 | 0.9 |

We see, that the SC procedure reduces the error by about 50%. As expected, $\frac{1}{2} f_{SC} > f_{exp}$, particularly in the case of octatetraene.

A further improvement within the assumption of an effective single-electronic hamiltonian does not seem to us possible.

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