Theoret. chim. Acta (Berl.) 10, 342—351 (1968)

Semi-Empirical LCAO—SCF Molecular Orbital Calculations for Selected Homo-Substituted Benzenes

B. FORD
Department of Mathematics, The University of Nottingham
University Park, Nottingham

Received January 9, 1968

Methods of parameter compilation, for calculating the excited singlet energy levels of substituted benzenes using the Pariser-Parr-Pople method, are compared for selected cases. A process of optimisation is employed to achieve the best fit to the observed spectra of the mono-substituted benzenes. The optimum parameters are then used to calculate the spectra of the di- and tri-homo-substituted cases. Conclusions as to a best set of data are drawn from comparison of the calculated results with the observed spectra of the di- and tri-substituted cases.

Methoden der Parameterwahl im Rahmen des PPP-Verfahrens werden für den Fall einiger substituierter Benzole verglichen. Die Parameter werden bei den monosubstituierten Verbindungen bezüglich der experimentellen Spektren optimalisiert und zur Berechnung der entsprechenden Daten für die di- und trisubstituierten Analoga verwendet. Aus dem Vergleich dieser Ergebnisse mit dem Experiment lassen sich Rückschlüsse auf die verschiedenen Parameter-Verfahren ziehen.

On compare sur des cas choisis les méthodes de détermination des paramètres, pour le calcul des états excités singulets des benzènes substitués, par la méthode de Pariser-Parr-Pople. Un procédé d'optimisation permet d'obtenir le meilleur accord avec les spectres observés des benzènes monosubstitués. Ces paramètres optimum sont alors utilisés pour calculer les spectres des dérivés di et tri homosubstitués. Des conclusions sur un ensemble de données optimum sont tirées de la comparaison des calculs avec les spectres observés des composés di et tri substitués.

Introduction

The Pariser-Parr-Pople [1, 2] method for computing SCF molecular orbitals for closed systems has been successfully applied to a wide variety of aromatic hydrocarbons and compounds with ring hetero-atoms. There have been comparatively few studies for non-ring substituents [3–12]. The aim of this paper is to determine the best procedure for data compilation within the PPP method, with particular reference to non-ring substituent calculations. The basis of the determination is comparison of calculated results with experimental values of the four lowest singlet energy levels from spectral data for selected substituted benzenes.

A process of optimisation is employed to achieve the best fit to the spectra of the mono-substituted benzenes. The optimum parameters are then used to calculate the spectra of the di- and tri-homo-substituted cases. The results, from the various methods of data compilation, are calculated using a programme written by the author.

The PPP method is based on the LCAO approximation of the Hartree-Fock SCF procedure for closed shells. With the assumption of $\sigma-\pi$ separability [13], in the π-electron approximation and adopting the zero differential overlap approximation, the Hartree Fock core Hamiltonian operator F gives

$$F_{\mu\mu} = U_{\mu\mu} + \tfrac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} + \sum_{\lambda \neq \mu} (P_{\lambda\lambda} - Z_\lambda)\gamma_{\mu\lambda}$$

$$\begin{aligned} F_{\mu\nu} &= \beta_{\mu\nu}^{\text{core}} - \tfrac{1}{2} P_{\mu\nu}\gamma_{\mu\nu} \quad (\mu \neq \nu)\ \mu, \nu \text{ nearest neighbours} \\ &= -\tfrac{1}{2} P_{\mu\nu}\gamma_{\mu\nu} \quad (\mu \neq \nu) \text{ otherwise}. \end{aligned}$$

A completely conjugated model is assumed. Every carbon atom contributes one electron to the π-system, every substituent is considered as contributing two (a lone pair). The geometry of the molecular models considered is basically hexagonal, with the substituents added radially with the required bond length. All angles are 120°. The bond lengths are taken as:

Carbon-Carbon	1.39 Å
Carbon-Fluorine	1.30 Å
Carbon-Chlorine	1.69 Å

Parameters

Core Matrix Elements

a) $\beta_{\mu\nu}^{\text{core}}$

Pariser and Parr [1] in their original elucidation describe $\beta_{\mu\nu}^{\text{core}}$ as dependent on the type and length of the bond $\mu\nu$ and the atoms μ and ν, but not sensibly on the neighbouring bonds or atoms. Hence $\beta_{\mu\nu}^{\text{core}}$ may be carried from molecule to molecule, and treated as a basic empirical quantity. A semi-empirical method is suggested for fitting $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ (discussed below) to give the lowest singlet excited state of benzene and ethylene. In other hydro-carbons an exponential form in bond length for $\beta_{\mu\nu}^{\text{core}}$ is suggested. This semi-empirical approach is the standard method for work in hydrocarbons. The value of $\beta_{\text{cc}}^{\text{core}}$ ($r = 1.39$ Å) in benzene is of particular importance since so many hydrocarbons and heteromolecules have a basic benzenoid structure. The value $\beta_{\text{cc}}^{\text{core}}$ ($r = 1.39$ Å$) = -2.371$ is almost invariably employed.

For heteromolecules and substituted benzenes Kon [13] proposed $\beta_{\mu\nu}^{\text{core}}$ inversely proportional to $r_{\mu\nu}^6$. Other workers [10, 11] have treated the value of $\beta_{\mu\nu}^{\text{core}}$ as one of two parameters (the other γ_{ss}) which are varied to achieve a satisfactory spectral fit. Bloor et al. suggested that the value be restricted to the range -2 eV to -3 eV.

Some confusion has been caused in the literature by a footnote in the original Pariser and Parr [1] paper. It reads 'For theoretical purposes $\beta_{\mu\nu}^{\text{core}}$ is better thought of as defined by

$$\beta_{\mu\nu}^{\text{core}} = \beta_{\mu\nu} + \tfrac{1}{2} S_{\mu\nu}(\alpha_\mu^{\text{core}} + \alpha_\nu^{\text{core}})$$

which takes more realistic account of the overlap integral $S'_{\mu\nu}$. This has its foundations in the work of Mulliken [14], and forms part of the earlier orthodox SCF model. Its insistence on the use of the overlap integral puts it outside the semi-empirical SCF model with its assumption of zero differential overlap. But the attraction of a developed theoretical justification has led to its use in the PPP method [5, 12], despite the contortions and contradictions in both model and method that ensue.

It would appear that the value of $\beta_{cs}^{\mathrm{core}}$ is now generally accepted as an adjustable parameter within the range -2 eV to -3 eV, which can be used to achieve a suitable fit to experimental data. The only exception is the value of $\beta_{cc}^{\mathrm{core}}$, for which the value in benzene suggested by Pariser is employed, and for other bond lengths the exponential derivation is available. Coherence of method is maintained by ignoring any derivation employing the overlap integral. SCF calculations are not intensitive to this parameter. This may in part explain its importance in the PPP method whilst having so little sound theoretical justification.

b) $\alpha_\mu^{\mathrm{core}}$

Pariser and Parr describe the coulomb integral $\alpha_\mu^{\mathrm{core}}$ as dependent on the bonding of atom μ, and the neighbours of μ, and hence it cannot be carried from molecule to molecule. Using the Goeppert-Mayer and Sklar approximation

$$\alpha_\mu^{\mathrm{core}} = W_\mu - \sum_{\nu \neq \mu} (\gamma_{\mu\nu} + (\nu : \mu\mu)) - \sum_{\xi} (\xi : \mu\mu)$$

where W_μ is the appropriate atomic valence state ionization potential and $(\nu : \mu\mu)$ and $\langle \xi : \mu\mu \rangle$ are coulomb penetration integrals between ϕ_μ and the neutral atoms ν (of the charged core) and ξ (from the uncharged core).

Pople has $\alpha_\mu^{\mathrm{core}} = U_{\mu\mu} - \Sigma Z_\alpha \gamma_{\mu\alpha}$ with the penetration integral terms included in the $U_{\mu\mu}$ [15]. Kon [13] appears to have been the first to ignore the penetration integrals finding they made little, if any, difference. This has become standard practice. Hence $U_{\mu\mu}$ is dependent only on atom μ. Bloor [10] stresses the importance of choosing the appropriate valence state ionization potential, a particular problem in substituent calculations due to the lone pair contribution to the π system. In fact there is no agreement in the literature as to what does constitute an appropriate value. This, in part, is due to disagreement as to the particular states from which calculations should start. For this reason in the calculations below $U_{\mu\mu} = -I_\mu$ is taken as a first approximation, and the value then treated as an empirical parameter, with $\beta_{\mu\nu}^{\mathrm{core}}$, to achieve optimum fit to experimental data. Again the carbon value is excepted, $U_{cc} = -11.14$ eV.

Repulsion Integrals

a) One Centre Integrals

For one centre integrals Pariser and Parr suggested $\gamma_{\mu\mu} = I_p - \mathrm{A}_p$, where I_p is the valence state ionization potential of the neutral atom and A_p its electron affinity. This has been widely used for calculation in both hydrocarbons and heteromolecules. However in many cases it is a difficult task to find good experimental values of I.P. and E.A.

Pariser [16] later evaluated the one centre and nearest neighbour integrals semi-empirically for work in hydrocarbons. To obtain these he constructed an empirical $\gamma_{\mu\nu}/r_{\mu\nu}$ graph from values obtained by equating the theoretical to the experimental excited state energies of benzene.

Paolini [17] deals specifically with the problem of $\gamma_{\mu\mu}$ when the atom μ contributes two electrons to the π system. He circumvents the problems of which are the appropriate I.P. and E.A. by the suggestion that $\gamma_{\mu\mu}$ is proportional to $Z_{\mu\mu}$ (Slater's effective nuclear charge). This hypothesis is tested for first row atoms and it is found that $\gamma_{\mu\mu} = 3.294\, Z_{\mu\mu}$ is a 'fairly good approximation' ($\pm 3\%$) both for atoms once or twice ionized in the molecular core, in a pure p state or hybridised. For second row atoms, for a pure p valence state only, $\gamma_{\mu\mu} = 1.794\, Z_{\mu\mu}$ is proposed.

In the calculations below the Pariser value of $\gamma_{cc} = 10.959$ eV is employed for the benzene core. A thorough comparison of results derived from calculations using the Pariser-Parr (the Standard Tables [18, 19] of the results) or the Paolini formulation (for fluorine and chlorine, a 1st and 2nd row atom) showed that it was impossible to differentiate between the two approaches. Further the results from both formulations are sound.

b) Two Centre Integrals

Pariser and Parr [1] proposed a classical electrostatic method, replacing each $\bar{\phi}_\mu \phi_\mu e$ by a pair of tangent uniformly charged non-conducting spheres of diameter $R_\mu = (4.597/Z_{\mu\mu}) \times 10^{-8}$ cm. $\gamma_{\mu\nu}$ is then computed from

$$\gamma_{\mu\nu}(r) = \frac{7.195}{r}\left\{\left[1+\left(\frac{R_\mu - R_\nu}{2r}\right)^2\right]^{-\frac{1}{2}} + \left[1+\left(\frac{R_\mu + R_\nu}{2r}\right)^2\right]^{-\frac{1}{2}}\right\} \quad \text{for} \quad r \geqq 2.80\,\text{Å}\,.$$

For $r < 2.8$ Å the $\gamma_{\mu\nu}$ are extrapolated from the relationship

$$\gamma_{\mu\nu}(r) = \tfrac{1}{2}(\gamma_{\mu\mu} + \gamma_{\nu\nu}) - ar - br^2$$

where a and b are evaluated from $\gamma_{\mu\nu}(2.8)$ and $\gamma_{\mu\nu}(3.7)$.

Later Pariser [16] employed a multipole expansion, used in conjunction with the empirical method, described above, for one centre and nearest neighbour terms.

Nishimoto and Mataga [20] took $\gamma_{\mu\nu} = \dfrac{e^2}{a_{\mu\nu} + r_{\mu\nu}}$.

The parameter $a_{\mu\nu}$ is determined

a) for homonuclear two centres by $a_{\mu\nu} = \dfrac{e^2}{\gamma_{\mu\mu}}$,

b) for heteronuclear two centres by $a_{\mu\nu} = \dfrac{2e^2}{(\gamma_{\mu\mu} + \gamma_{\nu\nu})}$.

Knowlton and Carper [11] took $\gamma_{\mu\nu} = \dfrac{1}{r_{\mu\nu} + A\exp(-br_{\mu\nu})}$ where $A = \dfrac{1}{\gamma_{\mu\mu}}$ and b is evaluated by fitting the $\gamma_{\mu\nu}$ to the γ_{12}, γ_{13} and γ_{14} values obtained by Pariser for benzene. Comparable results for substituents were then interpolated.

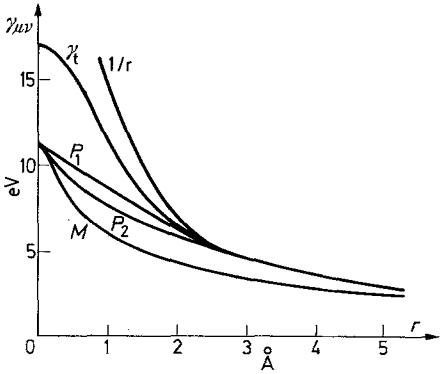

Fig. 1. Graphs of $\gamma_{\mu\nu}$ against r. A comparison of semi-empirical derivations of $\gamma_{\mu\nu}$, the two centre, two electron repulsion integral. γ_t, the theoretical curve. p_1, the Pariser-Parr model. p_2, the Pariser multipole expansion. M, the Nishimoto-Mataga model

In the calculations below the exponential form suggested by Knowlton and Carper is ruled out by its need of $\beta_{\mathrm{cs}}^{\mathrm{core}} < -3$ eV (in fact $\beta_{\mathrm{cf}}^{\mathrm{core}} = -3.80$ eV and $\beta_{\mathrm{c,cl}}^{\mathrm{core}} = -3.62$).

Otherwise the methods mentioned fall into two distinct groups; the Nishimoto-Mataga approach, and the other formulations. This is most clearly shown by the graph. The weakness of the Pariser multipole expansion is the need to evaluate the nearest neighbour term separately [21]. Hence whilst the values suggested by Pariser ($\gamma_{12} = 6.895$, $\gamma_{13} = 5.682$, $\gamma_{14} = 4.978$) were used for the benzene core, it was decided to compare results obtained using the uniformly charged sphere approximation of Pariser and Parr with a total Nishimoto-Mataga formulation ($\gamma_{11} = 10.959$, $\gamma_{12} = 5.325$, $\gamma_{13} = 3.869$, $\gamma_{14} = 3.517$). Within the bounds mentioned, the Nishimoto-Mataga approach gives an optimal fit to the monobenzenes of $\pm 1.07\%$ to the experimental values. The Pariser-Parr model allows a fit of only $\pm 3.83\%$ due to the ^1B system. Hence for di- and tri-substituted benzenes the results for the former must be regarded as more significant than those of the latter.

For the Nishimoto-Mataga calculations of the di- and tri-substituted cases, apart from a discrepancy of 11% for ^1L_a transition of 1–3 Dichlorobenzene, agreement with experimental results is within $\pm 4.61\%$. A disturbing feature throughout is the separation of the levels of the ^1B transitions in the calculations, particularly for the chlorobenzenes.

The Pariser-Parr model gives agreement within $\pm 4.92\%$ of experimental results. (2.75% apart from the ^1L_a transition of 1–4 Dichlorobenzene). The form of the ^1B transitions is predicted correctly.

However the Nishimoto-Mataga approach predicts Ionization Potentials values considerably closer to the experimental results. Hence due to this, and the difficulties regarding the initial optimal fit, it is concluded that the Nishimoto-Mataga formulation generally affords a better fit to the experimental data.

Programme

The programme was written in Algol and Usercode, a mnemonic form of the basic K.D.F. 9 machine language, for use on the University of Nottingham K.D.F. 9 computer. Operation on the Bond Order matrix was chosen as the means of achieving self consistency.

After three linear iterations to allow movement towards its converged form, an acceleration technique due to Hartree [22] is employed. Matrix consistency (defined by an element maximum difference of less than 10^{-7}) is rapidly achieved. A full first order configuration interaction calculation follows. A complete calculation for chlorobenzene takes 1 minute 10 seconds.

Results

Experimental results for the electronic transitions of homo and hetero-substituted benzenes have been collected by Petruska [23]. These are sufficiently detailed to make comparison of experimental results and semi-empirical calculations for substituted benzenes possible. The cases of mono-, di- and tri-substituted benzenes, with fluorine and chlorine, are considered here. A process of parameter optimisation is employed in each case to achieve the best fit to the spectra of the mono-substituted benzenes. The only limit on such attempts is that the relative charge density of the substituent does not drop below -0.1. Chemical considerations make this limit necessary. Finally adopting the hypothesis of the mutual independence of the substituents, these optimum parameters are used to calculate the spectra of the di- and tri-homosubstituted cases.

Table 1. *Fluorobenzene*

	Nishimoto-Mataga		Pariser-Parr	
	Paolini	Standard Tables [18, 19] (Pariser-Parr)	Paolini	Standard Tables (Pariser-Parr)
β_{cf}^{core}	− 2.667	− 2.667	− 2.667	− 2.667
U_{ff}	−30.61	−34.46	−38.61	−42.61
$\gamma_{ff}[7:7]$	17.129	21.39	17.129	21.39
$\gamma_{cf}[7:1]$	4.225	4.332	5.8	5.934
$\gamma_{cf}[7:2]$	3.083	3.139	3.906	3.906
$\gamma_{cf}[7:3]$	2.792	2.838	3.458	3.458
$\gamma_{cf}[7:6]$	6.057	6.278	8.694	9.433

Table 2

	Nishimoto-Mataga		Pariser-Parr		Experimental Results
	Paolini	Standard Tables (Pariser-Parr)	Paolini	Standard Tables (Pariser-Parr)	
Fluorobenzene	4.71	4.70	4.67	4.67	4.69
	5.86	5.86	5.91	5.91	5.88
	6.77	6.78	6.52	6.52	6.78
	6.79	6.78	6.53	6.53	6.78
Relative charge density	−0.09	−0.09	−0.03	−0.03	—
1-2 Difluorobenzene	4.60	4.57	4.64	4.63	—
	5.63	5.61	5.85	5.85	—
	6.56	6.55	6.48	6.47	—
	6.60	6.58	6.50	6.51	—
Relative charge density	−0.08	−0.08	−0.03	−0.03	—
1-3 Difluorobenzene	4.64	4.61	4.65	4.64	4.70
	5.75	5.74	5.86	5.86	—
	6.54	6.54	6.48	6.48	—
	6.59	6.56	6.51	6.51	
Relative charge density	−0.09	−0.09	−0.03	−0.03	—
1-4 Difluorobenzene	4.52	4.49	4.62	4.61	4.57
	5.67	5.66	5.86	5.86	—
	6.72	6.72	6.51	6.52	—
	6.79	6.78	6.52	6.52	—
Relative charge density	−0.08	−0.09	−0.03	−0.03	—

Table 3. *Chlorobenzene*

	Nishimoto-Mataga		Pariser-Parr	
	Paolini	Standard Tables [18, 19] (Pariser-Parr)	Paolini	Standard Tables (Pariser-Parr)
$\beta^{\text{core}}_{c,cl}$	− 2.134	− 2.134	− 2.134	− 2.134
$U_{cl,cl}$	−21.208	−23.48	−23.908	−26.18
$\gamma_{cl,cl}[7:7]$	10.764	13.03	10.764	13.03
$\gamma_{c,cl}[7:1]$	3.612	3.721	5.16	5.176
$\gamma_{c,cl}[7:2]$	2.724	2.785	3.563	3.563
$\gamma_{c,cl}[7:3]$	2.484	2.535	3.17	3.17
$\gamma_{c,cl}[7:6]$	4.774	4.966	6.862	7.111

Table 4

	Nishimoto-Mataga		Pariser-Parr		Experimental Results [23]
	Paolini	Standard Tables (Pariser-Parr)	Paolini	Standard Tables (Pariser-Parr)	
Chlorobenzene	4.60	4.60	4.59	4.59	4.59
	5.53	5.55	5.71	5.72	5.59
	6.52	6.53	6.43	6.43	6.53
	6.59	6.60	6.45	6.45	6.53
Relative charge density	−0.1	−0.1	−0.07	−0.07	—
1-2 Dichlorobenzene	4.43	4.43	4.49	4.49	4.49
	5.19	5.22	5.51	5.52	5.44
	6.08	6.11	6.29	6.30	6.35
	6.29	6.29	6.30	6.31	6.35
Relative charge density	−0.09	−0.09	−0.06	−0.06	—
1-3 Dichlorobenzene	4.48	4.48	4.51	4.52	4.49
	5.42	5.44	5.58	5.60	5.45
	5.92	5.97	6.27	6.29	6.32
	6.16	6.17	6.29	6.29	6.32
Relative charge density	−0.1	−0.1	−0.07	−0.07	—
1-4 Dichlorobenzene	4.34	4.34	4.44	4.44	4.43
	5.22	5.25	5.52	5.54	5.28
	6.57	6.57	6.42	6.42	6.42
	6.58	6.59	6.42	6.43	6.42
Relative charge density	−0.09	−0.09	−0.06	−0.06	—

Table 5. *Chlorine tri-substituted benzene excitation energies*

	Nishimoto-Mataga-Paolini	Nishimoto-Mataga-Standard Tables [18, 19]	Experimental Results [23]
1-2-3 Trichlorobenzene	4.35	4.35	4.37
	5.08	5.10	—
	5.70	5.73	
	5.87	5.89	—
Relative charge density	−0.08	−0.08	—
1-2-4 Trichlorobenzene	4.26	4.26	4.35
	5.10	5.12	—
	5.92	5.96	—
	6.14	6.14	—
Relative charge density	−0.08	−0.08	—
1-3-5 Trichlorobenzene	4.41	4.41	4.40
	5.37	5.39	5.35
	5.88	5.92	6.12
	5.88	5.92	6.12
Relative charge density	−0.09	−0.10	—

Table 6. *Fluorine tri-substituted benzenes excitation energies*

	Nishimoto-Mataga-Paolini	Nishimoto-Mataga-Standard Tables [18, 19]	Experimental Results [23]
1-2-3 Trifluorobenzene	4.53	4.50	—
	5.50	5.48	—
	6.30	6.28	—
	6.36	6.34	—
Relative charge density	−0.08	−0.08	—
1-2-4 Trifluorobenzene	4.46	4.42	4.60
	5.53	5.52	—
	6.47	6.46	—
	6.54	6.51	—
Relative charge density	−0.07	−0.08	—
1-3-5 Trifluorobenzene	4.58	4.59	4.77
	5.68	5.67	—
	6.42	6.41	—
	6.42	6.41	—
Relative charge density	−0.08	−0.09	—

Table 7. *Ionization potentials for the substituted benzenes*

	Nishimoto-Mataga		Pariser-Parr		Experimental Results
	Paolini	Standard Tables	Paolini	Standard Tables	
Fluorobenzene	9.69	9.66	10.89	10.87	9.20 [24], 9.67 [25]
1-2 Difluorobenzene	9.26	9.22	10.69	10.68	9.31 [24]
1-3 Difluorobenzene	9.38	9.35	10.71	10.70	9.37 [24], 9.3 [24]
1-4 Difluorobenzene	9.11	9.06	10.59	10.57	9.15 [24]
1-2-3 Trifluorobenzene	9.11	9.06			
1-2-4 Trifluorobenzene	8.83	8.78			
1-3-5 Trifluorobenzene	9.27	9.24			
Chlorobenzene	9.23	9.26	10.42	10.43	9.07 [24], 9.42 [25]
1-2 Dichlorobenzene	8.67	8.72	10.01	10.01	9.06 [24]
1-3 Dichlorobenzene	8.88	8.92	10.10	10.10	
1-4 Dichlorobenzene	8.53	8.57	9.85	9.86	8.95 [24]
1-2-3 Trichlorobenzene	8.46	8.51			
1-2-4 Trichlorobenzene	8.22	8.27			
1-3-5 Trichlorobenzene	8.74	8.78			

Conclusions

Employing the empirical method described above satisfactory results were generally achieved.

Calculations with the Nishimoto-Mataga formulation afforded a better fit to experimental results than the Pariser-Parr approach, most notably when the ionization potentials were taken into account. With the Nishimoto-Mataga formulation it was impossible to differentiate between results obtained using Paolini derivation of the one centre substituent integral and those employing a value of the integral taken from the standard tables.

Acknowledgements. The author gratefully acknowledges the teaching, patience and encouragement of Professor G. G. Hall and Dr. A. T. Amos, and the efficient computing facilities given by Dr. E. Foxley and his staff in the University of Nottingham Cripps Computing Centre.

References

1. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
2. Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
3. Peacock, T. E.: Molecular Physics **3**, 453 (1960).
4. Nishimoto, K., and R. Fujishiro: Bull. chem. Soc. Japan **31**, 1036 (1958).
5. Fischer-Hjalmars, I.: Ark. Fysik **21**, 122 (1962).
6. Bloor, J. E., and F. Peradejordi: Theoret. chim. Acta (Berl.) **1**, 83 (1962).
7. Mataga, N.: Bull. chem. Soc. Japan **36**, 1607 (1963).
8. Kwiatkowski, S., and W. Woznicki: Tetrahedron letters **1964**, 2933.
9. Forster, L. S., and N. Nishimoto: J. Amer. chem. Soc. **87**, 1459 (1964).
10. Bloor, J. E., P. N. Daykin, and P. Boltwood: Canad. J. Chem. **42**, 121 (1964).
11. Knowlton, P., and W. R. Carper: Molecular Physics **11**, 213 (1966).
    Russell, B. R., R. M. Hedges, and W. R. Carper: Molecular Physics **12**, 283 (1967).
12. Clark, D. T., and J. M. Emsley: Molecular Physics **12**, 365 (1967).
13. Kon, H.: Bull. chem. Soc. Japan **28**, 275 (1955).
14. Mulliken, R. S.: J. Chim. physique **46**, 479 (1949).

15. Brickstock, A., and J. A. Pople: Trans. Faraday Soc. **50**, 901 (1954).
16. Pariser, R.: J. chem. Physics **24**, 250 (1956).
17. Paolini, L.: Il Nuovo Cimento **4**, 410 (1956).
18. Pritchard, H. O., and H. A. Skinner: Trans. Faraday Soc. **49**, 1254 (1953).
19. Jaffe, H. H., and J. Hinze: J. Amer. chem Soc. **84**, 540 (1962).
20. Nishimoto, K., and N. Mataga: Z. physik. Chem. **12**, 335 (1957).
21. Parr, R. G.: J. chem. Physics **33**, 1184 (1960).
22. Hartree, D. R.: Proc. phys. Soc. (London) A **154**, 588 (1936).
23. Petruska, J.: J. chem. Physics **34**, 1120 (1961).
24. Bralsfond, R., P. V. Harris, and W. C. Price: Proc. Roy. Soc. (London) A **258**, 459 (1960).
25. Morrison, J. D., and A. J. Nicholson: J. chem. Physics **20**, 1021 (1952).

Dr. B. Ford
Mathematics Department
Loughborough University of Technology
Loughborough, Leics./England