

STUDIES

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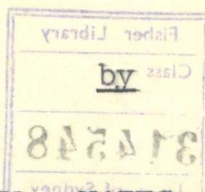
THEORETICAL CHEMISTRY.

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JOHN YATES, B.Sc.

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C O N T E N T S.

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REFINED ANTISYMMETRIC MOLECULAR ORBITAL CALCULATIONS OF THE ENERGY LEVELS OF BENZENE AND HEXAMETHYLBENZENE

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REFINED ANTISYMMETRIC MOLECULAR

ORBITAL CALCULATIONS

OF THE

ENERGY LEVELS OF BENZENE AND

HEXAMETHYLBENZENE.

INTRODUCTION.

The calculation of the energy levels of benzene using the method of Parr, Craig and Ross (1950) was repeated at a higher degree of refinement; the method was also extended to hexamethylbenzene.

The extra detail comprises the inclusion of terms involving

- (i) the exchange interaction between π -electrons and core,
- (ii) the contribution of the hydrogen atoms to the core potential,
- (iii) the carbon-hydrogen or carbon-methyl ionic terms.

A description is therefore given of the antisymmetric molecular orbital method as applied to benzene (including configuration interaction), together with the additional refinements made in our calculations. An attempt is then made to interpret the results obtained in the light of

- (i) experimental data,
- (ii) previous theoretical work, notably the calculation of Parr, Craig and Ross (1950).

A. Antisymmetric Molecular Orbital Treatment of Benzene and Hexamethylbenzene.

Number the nuclei I, II, VI clockwise around the benzene ring. The usual notation is used, where the benzene 2p orbitals perpendicular to the ring are taken as π orbitals, while the σ orbitals are sp^2 hybrids in the plane of the ring. Thus the carbon-carbon bonds in the ring itself are σ -bonds and the C-H or C-CH₃ bonds are also of the σ -type.

Assuming that we can represent a molecular orbital as a linear combination of atomic orbitals, we get for the π -molecular orbital

$$\phi = k_1 I_\pi + k_2 II_\pi + \dots \dots \dots \quad \text{A.1}$$

Here $k_1, k_2, \dots, k_6$ are coefficients yet to be determined, while I VI are the π atomic orbitals on their respective atoms. We have thus taken the π orbitals as being delocalised. Huckel (1931, 1933) showed that the six possible (delocalised) molecular orbitals (one for each π electron) can be written as

$$\phi_l = \frac{1}{\sqrt{6\sigma_l}} [\omega^l I_\pi + \omega^{2l} II_\pi + \dots \dots VI_\pi] \quad \text{A.2}$$

$$\omega = e^{\pi i/3}$$

σ_l = normalising coefficient

$$l \equiv 0, \pm 1, \pm 2, \pm 3$$

It is easy to form a simple product wave-function from some of the equation A.2 orbitals.

$$\psi = \phi_a(l) \bar{\phi}_b(l) \cdots \bar{\phi}_f(l) \quad \text{A.3}$$

Here no bar denotes α spin and a bar means β spin.

Now, for the Pauli principle to be satisfied, it is necessary to antisymmetrise this wave-function (giving a Slater determinant).

$$\begin{aligned} \Psi &= (6!)^{-1} \sum_P \pm P(\phi_a(l) \cdots \bar{\phi}_f(l)) \\ &= (6!)^{-1} |a b c d e f| \end{aligned} \quad \text{A.4}$$

P is the permutation operator. It means that a summation is taken of all the possible permutations of the simple product, odd permutations having a negative sign.

$a, b, c, \dots, f$ can have values of $0, \pm 1, \pm 2$ depending on the determinant required. Any configuration can, in principle, be represented by a sum of determinants like that of equation A.4.

To be a valid configuration for benzene, however, the sum must have the same symmetry properties as benzene has (i.e. it must transform like an irreducible representation of point group D_{6h}).

Up to this point it would appear that the correct result for any particular case should be obtained merely by choosing one configuration only. However, it should be noted that, in practice, we start by calculating a "core potential", and we put the six π electrons one by one into delocalised molecular orbitals. This means that certain π electron interaction terms are omitted due to one of the basic assumptions of the method.

We must allow to interact all the configurations in the symmetry class to which the chosen configuration belongs, and the best combination of antisymmetrised molecular orbital states can be obtained by using the variation method. This just means solving a set of secular equations,

$$\begin{vmatrix} \epsilon_1 - E & \psi_1 \sum c_i^1 \psi_i & \dots \\ \psi_2 \sum c_i^2 \psi_i & \epsilon_2 - E & \dots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

A.5

obtaining a configuration wave-function (C.W.F.).

Here

$$\epsilon_1, \dots, \epsilon_n$$

are the "orbital energies" (of the π -electrons in this case), and $\psi_1 \dots \psi_n$ are the associated wave-functions.

If the configurations are well spaced in energy, only those within a small energy range need be used for any given configuration, wave-function, as other terms will not much affect the solution of the secular equation A.5.

Having determined the appropriate configuration wave-function, it only remains to calculate the energy of the system. For both benzene and hexamethylbenzene

$$E = \int \Psi^* H \Psi d\tau + \int \Psi^* \Delta H \Psi d\tau \quad A.6$$

Here H is a limited Hamiltonian and ΔH the potential due to the benzene hydrogen (or methyl carbon) atoms and to the π -electron repulsion interaction terms.

H includes only the following:

$$H = \sum_{\nu=1}^6 W(\nu) + \sum_{\nu \neq \mu} e^2/r_{\nu\mu} \quad A.7$$

$$W(\nu) = T(\nu) + \sum_{K=1}^6 \left\{ -4e^2/r_{\nu K} + \sum_{h=1}^3 \int e^2/r_{\nu\mu} K_h^*(\nu) K_h(\mu) d\tau_\mu \right. \\ \left. + \sum_{L=1}^4 \left\{ -4e^2/r_{\nu L} + \sum_{q=1}^4 \int e^2/r_{\nu\mu} L_q^*(\nu) L_q(\mu) d\tau_\mu \right\} \right\} \quad A.8$$

$T(\nu)$ = the kinetic energy operator for the ν -th electron.

r = distance between particles.

K = serial number of a ring carbon atom.

L = serial number of a sidechain hydrogen.

p = trigonal carbon orbital.

q = tetrahedral carbon orbital (HMB) or 1s hydrogen.

The $W(\mu)$ portion of E may be expanded in the usual way as a series of one-electron integrals. These integrals are denoted by ϵ_i . This is the energy a single π -electron would have if all other π -electrons were removed from the system without any change in the electron distribution in the rest of the molecule. It should be noted that $W(\mu)$ contains terms referring to the repulsion and attraction potentials between μ and core electrons, and μ and nuclei respectively.

Terms containing $\sum e^2/r_{\mu\nu}$ are two-electron integrals. These are the V_{ij} and δ_{ij} terms of Parr, Craig and Ross.

When several determinants are included in the configuration wave-function, more terms, of "coulomb" (ξ) and "exchange" type (ζ) appear, due to the off-diagonal matrix element,

$$\int |A|H|B|d\tau$$

$$\xi = \int \phi_i(\mu) \phi_i(\mu) \frac{e^2}{r_{\mu\nu}} \phi_j(\nu) \phi_j(\nu) d\tau_\mu d\tau_\nu$$

A.9

$$\zeta = \int \phi_i(\mu) \phi_j(\mu) \frac{e^2}{r_{\mu\nu}} \phi_i(\nu) \phi_j(\nu) d\tau_\mu d\tau_\nu$$

A.10

It may be noted that the ξ and η integrals are only special cases of the more general ζ_{kl}^{ij} integral

$$\xi = \zeta_{22}'' \quad \eta = \zeta_{12}'' \quad \text{A.II}$$

where

$$\zeta_{kl}^{ij} = \iint \varphi_i(\nu) \varphi_j(\nu) \frac{e^{-1}}{r_{\nu\nu}} \varphi_k(\nu) \varphi_l(\nu) d\nu d\nu \quad \text{A.I2}$$

Additional ζ_{kl}^{ij} terms are added by configuration interaction.

In principle, configuration interaction demands an infinite number of configurations to give the optimum result. However, the small coefficients of many of the terms allow sufficient accuracy to be achieved with only a few terms. The coefficients are found by the usual variation method.

Now

$$\int \Psi_1 H \Psi_2 = 0 \quad \text{A.I3}$$

when Ψ_1, Ψ_2 contain the same irreducible representation; i.e. we get a value for ζ_{kl}^{ij} if, and only if,

$$(i + j + k + l) = 0 \bmod 6 \quad \text{A.I4}$$

It is now possible to express the total electronic energy of benzene and hexamethylbenzene as

$$E = \sum \epsilon_j + \sum \gamma_{ij} + \sum \delta_{ij} + \sum \xi + \sum \eta + \sum_{\xi+\eta} \zeta_{kl}^{ij} \quad \text{A.I5}$$

All that then remains to be done is to expand the expressions given above, to evaluate the integrals thus obtained (using ordinary Slater orbitals), and to add them together.

B. Additional Refinements Carried Out:

Many of the integrals required above had already been evaluated by Gray (1956), and the method of their evaluation is described by him. However, additional refinements had to be made.

(a) The re-evaluation of some of the three-centre integrals for which the approximations used were considered unsatisfactory.

(b) A change of axes had to be made to allow

(c) the inclusion of ionic contributions to the wave-function.

(d) All the terms had to be added up again, both as a check and to find out the effect of these ionic terms on the orbital energies.

(e) The secular equations had to be re-solved.



C. Calculation of Three-Centre Two-Electron Integrals by an Approximation Formula.

To calculate this type of integral in the past, the formulae of Mulliken (1949) and Rudenberg (1951), (which are stated below), have been used.

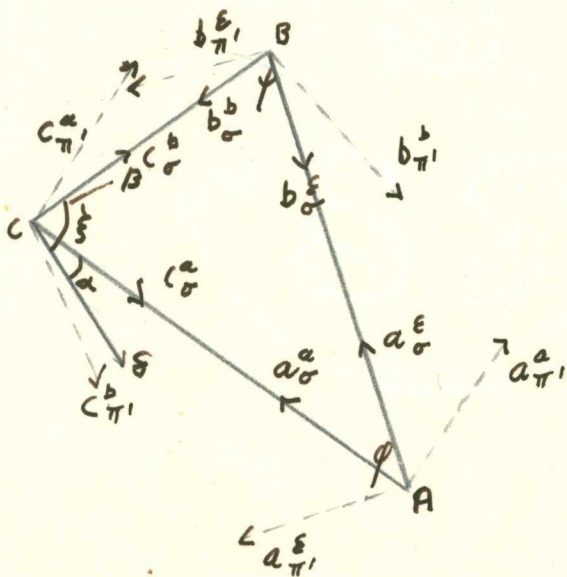
$$\begin{aligned}
 & \iint \chi_A(\mathbf{r}_1) \chi_B(\mathbf{r}_1) \frac{e^2}{r_{12}} \chi_C(\mathbf{r}_2) \chi_D(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= \frac{1}{4} S_{AB} S_{CD} \left\{ (\chi_A^2; \chi_C^2) + (\chi_A^2; \chi_D^2) + (\chi_B^2; \chi_C^2) + (\chi_B^2; \chi_D^2) + \frac{C.I.}{(\chi_A^2; \chi_D^2)} \right\} \\
 (\chi_A \chi_B; \chi_C \chi_D) &\approx \frac{1}{4} S_{AC} S_{BD} \left\{ (\chi_A \chi_B; \chi_A \chi_B) + (\chi_C \chi_D; \chi_C \chi_D) + \right. \\
 &\quad \left. (\chi_A \chi_D; \chi_A \chi_D) + (\chi_B \chi_C; \chi_B \chi_C) \right\} \tag{C.2} \\
 (\chi_A \chi_B; \chi_C \chi_D) &\approx \frac{1}{4} S_{AD} S_{BC} \left\{ (\chi_A \chi_B; \chi_A \chi_B) + (\chi_C \chi_D; \chi_C \chi_D) + \right. \\
 &\quad \left. (\chi_A \chi_C; \chi_A \chi_C) + (\chi_B \chi_D; \chi_B \chi_D) \right\}
 \end{aligned}$$

It turns out that Rudenberg's approximation is only good for acute-angled configurations (Barker and Eyring, 1954), so Mulliken's approximation was used, wherever possible. However, sometimes, when A and B or C and D were orthogonal (such as A = S, B = π), the whole integral vanished. It would be expected that the integral - in common with other simpler integrals of the type which have already been evaluated - would have some value other than zero. Thus

an approximation was made to the values of these overlaps as follows, in these cases;

$$S'(ac)^2 = \frac{4 (X_a X_c X_a X_c)}{(X_A X_A; X_a X_a) + (X_c X_c; X_c X_c) + 2(X_a X_a; X_c X_c)} \quad \text{C.3}$$

The algebra is further complicated by the fact that the σ orbitals used are not oriented at the right angles for the calculation of the integrals given above. They have to be resolved, and this can be illustrated by means of a specific example.



Take the ($c_{\sigma}a_{\pi}; c_{\sigma}b_{\pi}$) case. In the following equations c and s refer to cosine and sine, and $\underline{a}$, $\underline{b}$, $\underline{c}$ are wave-functions centred on nuclei A, B and C respectively.

Now for the geometry of the figure:

$$\xi = \beta - \alpha = \pi - \psi - \phi \quad \text{C.4}$$

By trigonometry, it follows directly that

$$\underline{c}_{\sigma}^a = \underline{c}_{\sigma}^b c + \underline{c}_{\pi'}^b s \quad \text{C.5}$$

$$\underline{c}_{\pi'}^b = \underline{c}_{\sigma}^a c + \underline{c}_{\pi'}^a s$$

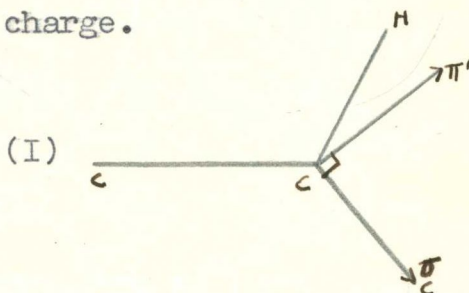
and so also for $\underline{a}$ and $\underline{b}$. These expressions may then be used directly with the Mulliken formulae. The algebra is tedious but straightforward, so the calculations were only carried out for the three largest integrals which needed modification. From the results obtained it did not appear necessary to evaluate the smaller three-centre terms in this way.

<u>Integral</u>	<u>Value</u>	<u>Value</u> ($3.180^3/a_0$) $\times 10^7$
	<u>(recalc.)</u>	<u>(approx.)</u>
($\underline{I}_{\sigma} \underline{II}_{\pi}; \underline{IV}_{\sigma} \underline{II}_{\pi}$)	7470	9509
($\underline{I}_{\pi} \underline{II}_{\pi}; \underline{III}_{\sigma} \underline{II}_{\pi}$)	45220	50825
($\underline{I}_{\sigma} \underline{III}_{\pi}; \underline{II}_{\sigma} \underline{III}_{\pi}$)	9340	12525

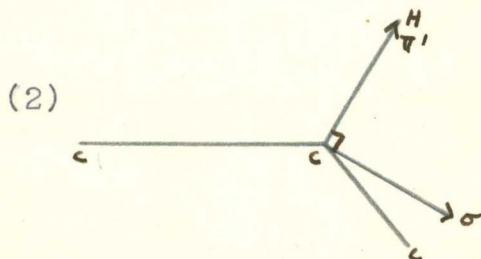
D. Change of Axes for Calculation of Ionic Terms.

The previously calculated integrals (Gray, 1956) have their axes oriented in no fixed direction, but merely in the direction most convenient for purposes of calculation. When there are no ionic terms, the same orientation is not required for each set of axes for symmetry reasons. If ionic terms are to be included in the wave-function, it is necessary to re-orientate these terms so that the axes are all pointing either along or at right-angles to the direction of transfer of charge.

For example,



in the above figure the σ axis is chosen along the C-C bond, but the π' axis is at an angle to the CH bond, along which we may assume a possible charge transfer. It is necessary to use new axes,

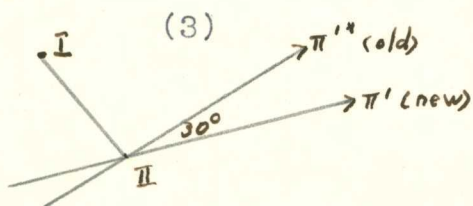


as in figure (2), to allow the easy calculation of the effect of such a charge transfer. It is found, in fact,

that thirty integrals have thus to be modified.

Take, for example, the integral $(I_{\pi} II_{\pi}; III_{\pi'}, III_{\pi'})$.

A diagram of the relevant axes is as follows:



Now, by simple trigonometry,

$$(I_{\pi} I_{\pi}; II_{\pi'}, II_{\pi'}) = 3(I_{\pi} I_{\pi}; II_{\pi'}^*, II_{\pi'}^*) / 4 + (I_{\pi} I_{\pi}; II_{\sigma}^*, II_{\sigma}^*) / 4$$

Thus the new integrals can easily be expressed as a function of those already tabulated.

E. Inclusion of Ionic Terms in Wave-Functions.

Petro (1958) has postulated from experimental evidence that the moments of $C^-(sp^2) - H^+$ and $C^-(sp^2) - C^+(sp^3)$ are respectively about $0.63 \mu D$ and $0.69 \mu D$.

Thus it seems reasonable to calculate these moments with the atomic wave-functions used in the benzene and hexamethylbenzene calculations and see what discrepancy occurs. This would give a measure of the additional polarity required to perfect the model.

Therefore, the bond moments were calculated for each case, using ordinary Heitler-London covalent wave-functions, and the following integral was evaluated:

$$\langle \psi_A(1) \psi_B(2) + \psi_B(2) \psi_A(1) | z_1 + z_2 | \psi_A(1) \psi_B(2) + \psi_B(2) \psi_A(1) \rangle \quad E.I$$

Here the usual notation is used. A and B refer to the $C(sp^2)$ and H or $C(sp^3)$ nuclei respectively. Integrals used were obtained from Kotani's tables. Logarithmic interpolation was used where necessary.

The results obtained from this calculation are $-0.8 \mu D$ for the CH case, and -0.04 for the C-C case. These results, while not exactly corresponding to the benzene and hexamethylbenzene calculations, should at least give an approximate measure of the dipoles tacitly assumed present therein. Also, it must be remembered that Petro's

experimentally obtained results do not bear a direct relation to the theoretical results. At best, the concept of bond dipole is a vague one and difficult to relate to precise theoretical quantities.

However, from the above figures, it seems reasonable to assume that the ordinary covalent bond picture does not give the correct dipolar charge distribution. The effect of this inaccuracy upon the energy values can only be determined by an actual calculation. In view of the above figures, a 10% ionic contribution ($\text{C}^- \text{H}^+$ or $\text{C}^- \text{CH}_3^+$) (about $0.6 \mu\text{D}$) was added to the bond wave-functions, by altering the coefficients of the integrals associated with these centres. It was found that this only had a small effect on the energy (see Appendix C) and it is possible to draw the conclusion that changes -- and, more especially, relative changes as one goes from benzene to hexamethylbenzene -- in assumed bond dipole matter little in energy calculations for this type of system.

F. Evaluation of Energies.

The integrals were added as indicated earlier (equation A.I5). The original secular equations of Parr, Craig, Ross were then solved in the usual manner, the A and B matrices being evaluated on the Silliac automatic computer. (Silliac Library Program M5 was used.)

Two discrepancies were noted when the PCR results were recalculated.

$3A_{2g}$: The wave-function designated as III_a by PCR was calculated as being 12.586 electron volts above the $'A_{Ig}$ state (taken as energy zero). PCR quote a value of 11.1.

$3A_{Ig}$: The energy value for the lowest wave-function i.e. "V" is calculated as 13.936 eV, while PCR give a value of 13.600 eV and apparently base their higher energy states VII, VIa, VIb on this zero.

Apart from these two small anomalies, agreement was obtained throughout with PCR.

G. Interpretation of Results:

The results are given in Tables I and II of Appendix C. The first column of Table I consists of a copy of the results of Parr, Craig and Ross, with corrections (See Part F). In column (a), the results of PCR are again stated, but with two important modifications.

(i) Mulliken's (1949) approximation for the three-centre integrals is used instead of that of London (1945). This substitution is made for the twofold reason that Mulliken's approximation is the more accurate one, and that this approximation is used in the present work. The latter reason makes it possible more readily to compare any small differences in the two methods of calculation.

(ii) For a similar reason (and also to avoid duplication of calculation), instead of the hydrogen-like carbon 2s atomic orbital wave-functions, nodeless atomic orbital wave-functions are used.

In other words, any subsequent comparison of the PCR values with the present ones will be made using column (a) instead of the first column. The large discrepancies between the direct PCR value and column (a) are noteworthy. This emphasises what a great difference can be made merely by making slightly better initial assumptions. It can be seen that the $(\epsilon_3 - \epsilon_2)$ value has increased by an amount

approximately corresponding to the decrease in $(\epsilon_1 - \epsilon_0)$ while $(\epsilon_2 - \epsilon_1)$ has remained approximately the same. This has the (probably expected) effect of making the values of $(\epsilon_3 - \epsilon_0)$ very similar. In actual fact, the divergences are mainly due to changes in only a few three-centre integrals, but, owing to the fact that the energy terms are a small difference between large quantities, the effect is magnified.

In column (b), the exchange interactions between core electrons as well as the coulomb interactions are included. The relative values of the energies seem much more reasonable in this column, but this merely emphasises the fact that agreement with the expected values is probably somewhat fortuitous in any case, and suggests that an even more refined calculation could again make these values diverge from the expected results. The physical reason for the spreading apart of these energy levels is connected with the fact that the exchange forces now included are an attractive contribution to the core potential. This means that a certain divergence of levels should occur, and that, also, $(\epsilon_3 - \epsilon_0)$ should increase (and this also happens). It is noteworthy that while, as a general rule, the direction of such effects may be predicted (i.e. divergence rather than convergence in this case),

prediction of their absolute magnitude is rather doubtful, and what might be considered to be a small refinement to the energy picture could turn out to have a major influence upon the redistribution of energy levels.

This latter statement is well illustrated by the results in column (c), which is the stage of furthest refinement of the calculation. In column (c) further exchange terms are included, and these are due to hydrogen atom exchange. Now, although both $(\epsilon_3 - \epsilon_1)$ and $(\epsilon_1 - \epsilon_0)$ have been increased slightly, and $(\epsilon_2 - \epsilon_1)$ reduced, the effect is not nearly so marked as in column (b). In fact, it would be possible to reasonably group together PCR and (a), and also (b) and (c) -- as far as $(\epsilon_3 - \epsilon_0)$ goes, that is. Contrast this with the almost anomalous differences between PCR and column (a), for the $(\epsilon_3 - \epsilon_1)$, $(\epsilon_2 - \epsilon_1)$ and $(\epsilon_1 - \epsilon_0)$ terms.

From all this it seems possible to conclude -- but only tentatively -- that in this, and in similar calculations, any given type of refinement will have one definite kind of effect on the final result, but increase in refinement after a certain point along this direction is fairly futile unless other refinements of a different kind are made. For example, as long as a certain amount of correction for this type of exchange force is made, the results will give a reasonable indication of just what

effect this force has. That is, after inclusion of the hydrogen exchange forces -- a considerable additional refinement -- there is a change in $(\epsilon_3 - \epsilon_0)$ of only 0.57 eV. On the other hand, going from PCR to column (c), there is a change of 2.9 eV.

Column (d) refers to hexamethylbenzene. Even although interactions with methyl groups are now included, the results are not spectacularly different from those in columns (b) and (c).

In Table II the values of the lower energy levels of both benzene and hexamethylbenzene are given, with and without the inclusion of configuration interaction.

When the PCR results (no configuration interaction) and the corresponding results using column (a) are compared, it can be seen that these are very close together. Naturally, the lower A states show the best agreement, but agreement is good even with the E_{2g} case. These results depend upon the value for $(\epsilon_2 - \epsilon_1)$ and (for reasons mentioned previously) this does not alter much with the inclusion of the extra terms.

In column (c) it can be seen that the excited states are actually raised in energy by about 1 eV. Now this means that these results actually agree less well with experiment than the previous ones do. If we compare with

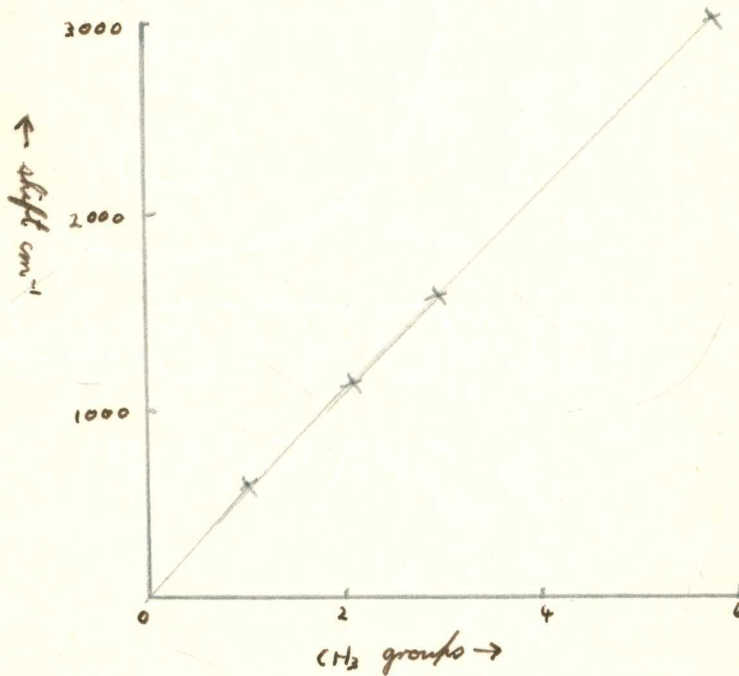
Table I, this seems anomalous, because here the column (c) results are actually better than column (a).

This is another illustration of the almost random factors which enter into a calculation of this kind, and make interpretation of results difficult. In this case, however, a fairly logical reason can be given for the inaccuracy of column (c) results. The value of Z (3.18) used throughout is the old value of Zener (1931). If this value is too high, the energy levels would be brought closer together; in fact, the higher excited states would be reduced more than the lower levels and by suitable manipulation a reasonable result could be got.

H. Comparison With Experimental Results.

It is possible to compare the shift of the $'B_{2u} - 'A_{2g}$ band in hexamethylbenzene relative to benzene with the experimental value. The position of the band (2600 Å) in benzene itself is well-known from spectral measurements. However, the vapour spectrum of hexamethylbenzene shows practically no vibrational structure, probably due to internal rotation and steric hindrance of the methyl groups. The following reasonably exact data are available.

<u>Compound</u>	<u>CH₃ Groups</u>	<u>Red Shift</u>	<u>Author</u>
toluene	I CH ₃ group	610 cm ⁻¹	Ginsburg et al. 1946
m-xylene	2 CH ₃ groups	1135 cm ⁻¹ mean	Cooper, Sponer 1952
p-xylene	2 CH ₃ groups		Cooper, Sastri 1952
mesitylene	3 CH ₃ groups	1533 cm ⁻¹	Sponer, Stallcup 1948



Extrapolation graph (to find approx. red shift for 6 CH_3 groups)

From simple extrapolation it may be seen that the red shift for hexamethylbenzene is about 3000 cm^{-1} .

Now, in the calculation carried out here, we have taken the ground $'A_{1g}$ state of both benzene and hexamethylbenzene to be

$$10\bar{0}1\bar{1}-1-\bar{1}|$$

H.I

The first excited $'B_{2u}$ state has a wave-function of

$$\frac{1}{2} \{ 10\bar{0}1\bar{1}-1\bar{2}| - 10\bar{0}-1-\bar{1}1-\bar{2}| - 10\bar{0}1\bar{1}-\bar{1}2| \\ + 10\bar{0}-1-\bar{1}\bar{1}-2| \}$$

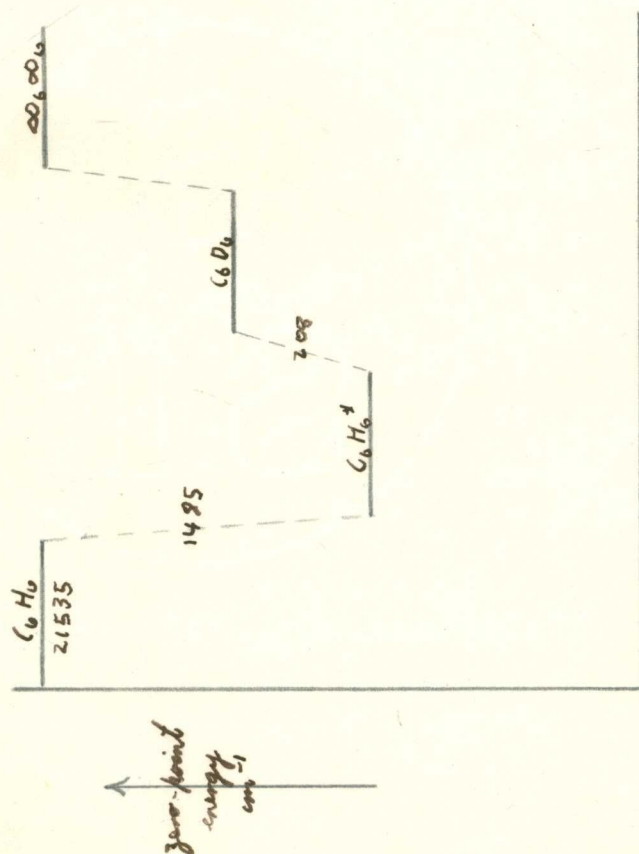
H.2

In theory, the shift in absorption due to aliphatic side-chain substitution could have a number of causes, hyperconjugation, changes in bond polarity and changes in the π -electron potential field all being possible.

The present calculations seem to show that changes in bond dipoles must be large to affect the energy, so the shift is mainly due to the two latter effects. The calculated value of the shift can be derived directly from the $\Delta(\epsilon_2 - \epsilon_1)$ values in columns (c) and (d) of Table I. The value obtained is 0.082 eV. If, in addition, the presence of configuration interaction is taken into account, a value of 0.089 eV (720 cm^{-1}) is obtained for the red shift. So many additional factors must be taken into consideration, however, that a one to one correspondence

between experimental and theoretical values cannot be expected at this stage.

Now consider the zero-point energy level diagram (data from Garforth, Ingold and Poole, 1948). An asterisk refers to the first excited level.



The ω_0 value comes from the fact that, if infinite masses replaced the benzene hydrogen atoms, the red shift due to zero-point energy would not occur at all on excitation. Assume now that the change in internal frequencies of the CH_3 group does not have much effect upon the zero-point energy change on excitation. This means that the CH_3 group can be treated as if it were a point mass, atomic weight 15.

The classical formula for a vibration is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

H.3

where

ν = the vibration frequency,

k = the force constant, and

m = the reduced mass of the system.

From equation H.3 it can be shown directly that the total shift due to zero-point energy ought to be about 800 cm^{-1} . That is, a total red shift of 3800 cm^{-1} is to be expected.

This only increases the discrepancy between the experimental and theoretical values. Now, this could be explained by saying that (allowing an optimistic 15% for polar effects, which were shown earlier to be small) the remaining 65% of the shift is due to a delocalisation

phenomenon. π electrons in the ring would only delocalise with other π orbitals, which must therefore be found in the methyl group. For the methyl carbon atom, there need only be 2p atomic orbitals, but for the hydrogen atoms it is necessary to consider H_3 as a group (the "group orbitals" mentioned by Coulson, 1953). Let the hydrogens be H_a , H_b and H_c . Then group orbitals may be formed, of the type

$$(\psi_a + \psi_b + \psi_c), (\psi_a - \frac{1}{2}(\psi_b + \psi_c))$$

H.4

The first of these is symmetrical about the C(ring) to C(methyl) bond axis -- in other words, it has σ symmetry and would take part in σ hyperconjugation. The other orbital is similar in shape to a π -orbital, having positive and negative lobes above and below a nodal plane (through the benzene ring). It is by this orbital that π -delocalisation (hyperconjugation) can take place.

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THE NON-EMPIRICAL CALCULATION

OF THE

SINGLET-TRIPLET SEPARATION

FOR THE $\frac{1}{2}$ AND $\frac{3}{2}$ COPPER BONDS

IN

BINUCLEAR COPPER ACETATE.

INTRODUCTION.

X-ray studies of crystalline copper acetate (Niekerk and Shoening, 1953) have shown it to be binuclear, the copper atoms being bridged by four acetate groups which act as bidentate chelates. There is no direct bond of any strength between the two coppers in this picture.

To help explain certain anomalous properties (such as the diamagnetic susceptibility and its variation with temperature) of copper acetate, Figgis and Martin (1950) postulated a δ -bond between the copper atoms. This implies that a "localised" triplet state is present, with energy low enough to be significantly populated thermally at modest temperatures less than the decomposition temperature of the complex. On ligand field theory, such a bond should have been between either $3d_{z^2}$ or $3d_{xy}$ orbitals, the latter being the more likely because, although the overlap of orbitals is very much less, the bond energy is also less by about 12000 cm^{-1} .

The excitation energy from the singlet state to the triplet (denoted as 3J) is only 300 cm^{-1} . However, the system affords excellent opportunity for the testing out of d--orbital bonding theory, as this is a case where an isolated d-orbital bond occurs, and first order interaction of other bonding systems is not present.

A. Theory.

Previous algebraic calculations of the energy difference (Yates, 1957) between singlet and triplet states did not include the kinetic energy terms explicitly. The procedure is therefore briefly summarised, with their inclusion.

A single Heitler-London covalent bond is used between either $3d_{\frac{5}{2}}$ or $3d_{\frac{3}{2}}$ orbitals. The notation

$$a = \psi (A 3d_{\frac{5}{2}})$$

$$b = \psi (B 3d_{\frac{5}{2}})$$

$$A = \psi (A 3d_{\frac{3}{2}})$$

$$B = \psi (B 3d_{\frac{3}{2}})$$

A.1

is used, where A, B, are the copper nuclei, and the convention of small letters for $3d_{\frac{5}{2}}$ orbitals and large letters for $3d_{\frac{3}{2}}$ orbitals is used throughout.

The singlet- $\frac{5}{2}$ state now becomes

$$\Psi_s (1,2) = \frac{1}{\sqrt{2!}} \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1+s^2}} (|a\bar{b}| - |\bar{a}b|)$$

A.2

Here s is the overlap between the orbitals, and the bars indicate + or - spin.

The total energy is now

$$w_s = \int \Psi_s (H_1 + H_2 + H_{12}) \Psi_s d\tau_1 d\tau_2$$

A.3

where

$$H_I = T_I + V_{AI} + V_{BI} \quad A.4$$

$$H_2 = T_2 + V_{A2} + V_{B2} \quad A.5$$

$$H_{I2} = e^2/r_{I2} \quad A.6$$

Now T_i is the kinetic energy operator for the i -th electron, and V_{Ai} is the potential energy of the i -th electron in the field of the atom A.

Now this integral and the corresponding triplet state wave-functions

$$\Psi_{\tau}^{\circ}(I,2) = \frac{I}{\sqrt{2}!} \cdot \frac{I}{\sqrt{2}} \cdot \frac{I}{\sqrt{1-s^2}} (|\bar{a}b| + |\bar{a}b|) \quad A.7$$

$$\Psi'_{\tau}(I,2) = \frac{I}{\sqrt{2}!} \cdot \frac{I}{\sqrt{1-s^2}} (|ab|) \quad A.8$$

have already been evaluated, with the assumption that the kinetic energy terms may be regarded as a constant. In fact, we get a set of answers (Mulliken's notation - see Appendix B).

(a) $3d_3$ state

(i) singlet

$$w_s = 2e + \frac{I}{I + s^2} \{2(A:bb) + 2S(A:ab) + (aa;bb) + (ab;ab)\} \quad A.9$$

(ii) triplet

$$w_t = 2e + \frac{I}{I - s^2} \{2(A:bb) - 2S(A:ab) + (aa;bb) - (ab;ab)\} \quad A.10$$

(b) $3d_3$ state

(i) singlet

$$W_S = 2E + \frac{I}{I + S^2} \{2(A:AA) + 2S(A:AB) + (AA;BB) + (AB;AB)\} \quad A.II$$

(ii) triplet

$$W_T = 2E + \frac{I}{I - S^2} \{2(A:AA) - 2S(A:AB) + (AA;BB) - (AB;AB)\} \quad A.I2$$

However, the kinetic energy terms ought to be evaluated, and this is readily done as follows:

Consider the singlet $3d_3$:

$$T'_S = \frac{I}{2(I + S^2)} \int (a\bar{b} - \bar{a}b)(T_I + T_2)(|a\bar{b}| - |\bar{a}b|) d\tau_a \quad A.I3$$

Here T'_S is the singlet kinetic energy integral, whilst

T_I, T_2 are kinetic energy operators.

Expanding equation A.I3 gives

$$\begin{aligned}
 T'_S &= \frac{I}{2(I + S^2)} \int (\bar{a}\bar{b} - \bar{a}b)(T_I + T_2)(\bar{a}\bar{b} - \bar{b}a - \bar{a}b + b\bar{a}) d\tau_{12} \\
 &= \frac{I}{2(I + S^2)} \left\{ (\bar{a}\bar{b}|T_I + T_2|\bar{a}\bar{b}) + (\bar{a}\bar{b}|T_I + T_2|b\bar{a}) \right. \\
 &\quad \left. + (\bar{a}b|T_I + T_2|\bar{b}a) + (\bar{a}b|T_I + T_2|\bar{a}b) \right\} \\
 &= \frac{2}{I + S^2} \left\{ (a|T|a) + S(b|T|a) \right\} \tag{A.I4}
 \end{aligned}$$

Put

$$(a|T|a) = T^0$$

$$(b|T|a) = T \tag{A.I5}$$

Then equation A.I4 becomes

$$T'_S = \frac{2(T^0 + ST)}{I + S^2} \tag{A.I6}$$

In a similar way the triplet state wave-function may be determined.

$$T'_T = \frac{I}{2(I - S^2)} \int (\bar{a}\bar{b} + \bar{a}b)(T_I + T_2)(\bar{a}\bar{b} - \bar{b}a + \bar{a}b - b\bar{a}) d\tau_{12}$$

$$= 2(T^0 - ST) / (I - S^2) \quad \text{A.I7}$$

This then gives the separation between singlet and triplet states due to the kinetic energy part of the Hamiltonian as

$$T_T - T_S = \frac{4S}{I - S^4} \{ST^0 - T + S(A:AA) - (A:AB)\} \quad \text{A.I8}$$

Here the nuclear potential terms (which may be evaluated as above) have also been included.

$$t_T - t_S = \frac{4s}{I - s^4} \{st^0 - t + s(A:aa) - (A:ab)\} \quad \text{A.I9}$$

Equation A.I9 is the corresponding form for the $3d_{\frac{3}{2}}$ integral.

It turns out, however, that the potential V_A (in the terms $(A:aa)$ and $(A:ab)$) includes contributions from the ligand field of unknown magnitude but, by calculation, of great importance. Hence we must revert to the assumption that in evaluating these terms, $\underline{a}$, $\underline{b}$ can be regarded as eigenfunctions of V_A , V_B .

B. Calculation.

The equations used for the actual calculations are (notation as in Appendix B):

Energy separation for covalent states:

$$-J = \frac{2}{I - S^4} \{ 2S(zK - SG) + S^2C - E \} \quad \text{B.I}$$

Ionic-covalent secular equation:

$$\begin{vmatrix} -W & (-zK + SG + L - SC - SE - SW) / 2(I + S^2) \\ \text{symmetric} & (\overline{M - C}) / (I + S^2) - W \end{vmatrix} = 0 \quad \text{B.2}$$

The method of integral evaluation is straightforward and is given in Appendix B.

As antisymmetrised products of Slater orbitals are used throughout, it is necessary to determine the best value for the exponential Slater parameter. Slater's rules give a value $Z(\text{eff}) = 8.5$, but this is only true for the free atom. A self-consistent field orbital should give a more nearly correct answer, but the integration of an analytic function corresponding to such an orbital would be too difficult in this case.

Accordingly, the self-consistent field orbital for Cu^+ was plotted (Hartree, 1957), and a family of Slater curves also plotted on the same graph. The Slater curves which

corresponded most closely to the Hartree function at the points of maximum interaction were considered to be the best approximation.

An alternative procedure was then applied, the $Z(\text{eff})$ value in the overlap integral between Slater orbitals on the copper atoms which gave the same value of overlap as self-consistent field orbitals being obtained. Values of self-consistent field overlap of 0.00278 (δ -orbitals) and 0.0403 (σ -orbitals) were obtained.

The calculations were performed on Cu^+ orbitals and not Cu^{++} , as no self-consistent field wave-functions were obtainable (0.35 being then added to the values obtained), and the results obtained by the two methods, which are almost equivalent, gave fairly good agreement, results being

$$Z(\text{eff}) \approx 7.5 (3d_\delta) \text{ or } 7.7 (3d_\sigma).$$

This close agreement with the Slater values is probably not significant, and, in any case, a series of values for the energy was computed over the range $\alpha = 0$ to $\alpha = 20$.

Next consider the parameter z included in the above equations. To calculate G and K , we should use a potential function of the form (the notation is, again, that of Mulliken - see Appendix B)

$$-V_{AI} = \frac{29ze^2}{r_{AI}} - \sum_q (A_q A_q;) + \frac{1}{2} \sum_q (A_q; A_q) \quad B.3$$

occupied *occupied*

The above is, in effect, the potential due to a Cu^{++} ion, minus the potential due to the bonding electron. Indeed, for an accurate evaluation, extra terms for the ligands must also be included. The integration of these terms is too complicated, so some approximation must be used.

Consider the one-electron coulomb integral, G. The potential V, as far as G is concerned, will be slightly greater than unity, due to:

(i) the imperfect shielding of the nucleus by the inner electrons;

(ii) the even less effective shielding by the electrons used for bonding with the oxygen atoms.

The resonance integral K is equally distributed between both nuclei. If it had been totally on nucleus A, it would have been multiplied by 8.5 approximately (i.e. the Slater charge) and if totally on B, by the same factor as G. So it probably takes a mean value (perhaps about 4).

The term containing G has been found to be of small arithmetical magnitude, so instead of using two parameters (which would have to be approximated to very roughly, in any case,) only one parameter, z, is used, and this part of

the expression is given the form

$$2S (zK - SG).$$

From the above considerations the value of z might be expected to be about 3, and, in fact, values of the expression for $z = 1, 2$, and 3 have been tabulated.

C. Analysis of Results Obtained.

The values obtained for the energy difference are 4 cm^{-1} (δ -bond) and 1600 cm^{-1} (σ -bond), using the self-consistent field value for $Z(\text{eff})$ and a value of 3.0 for z .

Even large alterations in these parameters would not bring about agreement with experiment (the highest reasonable value that can be taken for the δ -bond is 60 cm^{-1}) but agreement can be achieved on other grounds (Ross and Yates, 1959). These will be mentioned briefly.

(I) The calculations refer to a non-vibrating molecule. Averaging $-J$ over vibrational wave-functions would increase it.

(II) The $3d_\delta$ orbitals possibly hybridise with 4 orbitals. This assumption could increase $-J$ to 20 cm^{-1} (δ -bond) or 5600 cm^{-1} (σ -bond).

(III) Interconfigurational resonance between δ , σ and a π state could occur.

(IV) Even after the modifications (I) -- (III), for reasonable agreement, it is necessary to reduce $Z(\text{eff})$ to about 6.3.

This value of $Z(\text{eff})$ (6.3) agrees well with previous predictions made by Craig and Magnusson (1958) and Brown (1958).

THEORY OF THE METHODS

OF

CALCULATION OF MOLECULAR

POLARISABILITY.

INTRODUCTION.

Quantum-mechanical calculations have been carried out on atomic and simple molecular systems by many workers, notable among whom are Buckingham (1937), Kirkwood (1932) and Hellmann (1933). The methods which have so far been successful are either of the perturbation or variation type. In fact, the reduction of the methods to a few equations, in which atomic or molecular orbitals may be substituted, is discussed here. The method thus obtained (Rahman, 1953) is presently restricted to systems of well-known wave-function (owing to the sensitivity of polarisability to charge distribution) if accurate results are required.

Even when the wave-functions of the ground and all the excited states are known, there is certainly a contribution (Guy and Tillieu, 1953) due to transitions to continuous levels. This means that some kind of approximate calculation needs to be employed, preferably only using groundstate wave-functions. It turns out that a reasonably easy formula can be deduced, but it is only good, in general, for systems with a symmetry property such that the matrix elements of their wave-functions with respect to the applied field vanish. It is also found (Guy and Harrand, 1952) that polarisabilities

obtained in this way are not strictly additive, the criterion of additivity being that the "bond" polarisabilities. considered can be represented accurately by localised wave-functions. When the method is applied to conjugated systems, apparently (Coulson and Davies, 1952) a fairly accurate result can be obtained if an accurate delocalised wave-function for the whole system is known.

The latest calculations (Weisliger, 1958) which utilise the formulae of Barriol and Regnier (1953) indicate that the direct theoretical approach, even when applied with precision, does not give as good an answer at this stage in the theory as one which utilises some empirical constants. The inclusion of any empirical parameters alters the character of his calculations to such an extent as to dominate completely the final result, or, on the contrary, (Buckingham, 1937, and references) to increase the accuracy by such a small amount as to be superfluous. This is mainly because the result depends, as far as parameters go, very directly upon the initial wave-functions used. Now, Slater orbitals, with only one parameter, usually have to be used for a manageable calculation to result, and these just depend upon the atomic screening parameter. The importance of this factor is seen by the

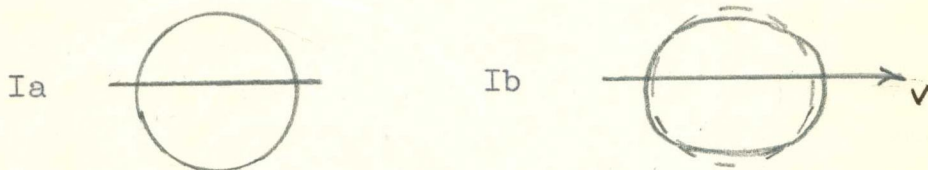
calculations of Rahman (1953), who evaluated the polarisability of the hydrogen molecule, using a very precise wave-function. This gave a result probably accurate to $\pm 3\%$. Valence-bond wave-functions, using Slater atomic orbitals (Bell and Long, 1950), give a value of $\pm 25\%$ for the hydrogen molecule, and, unfortunately, only types of wave-functions of equal simplicity can normally be used in the more complex systems which it is desired to investigate.

H However, the formulae given here may be used for a consideration of simple and symmetrical systems; for larger systems it appears impossible to perform anything but comparative calculations at the present state of the theory.

CALCULATION OF POLARISABILITY.

A. Perturbation Methods.

In the calculation of the polarisability of an atom or molecule by quantum-mechanics, it is usually assumed that, on the application of a uniform electric field, V say, in some direction a , that the original wave-function, (e.g. figure Ia), is distorted in some way (figure Ib) and that this new, distorted wave-function may be represented by a sum of wave-functions, the original wave-function Ia being the largest contributor to the new wave-function, while the remaining contributions are considered to be given by a known set of wave-functions, whose coefficients in the series can be mathematically determined (Eyring, Walter and Kimball, 1954).



It can readily be seen that this is reasonable physically, provided that the perturbing potential is small.

Now let the perturbed Hamiltonian in an electronic system with an exact wave-function be given by

$$H = E + V$$

A.I

Here E is the unperturbed Hamiltonian and V is some perturbing potential (in this case, the electric field).

Now, let the exact eigenvector of H be $|H'\rangle$ and its corresponding eigenvalue be H' . In other words, H' refers to the energy of the perturbed system.

Then

$$H|H'\rangle = H'|H'\rangle \quad A.2$$

or

$$(H' - E)|H'\rangle = V|H'\rangle \quad A.3$$

$|H'\rangle$ may then be expanded as a series of eigenvectors in the following manner:

$$|H'\rangle = |0\rangle + |1\rangle + |2\rangle + \dots \quad A.4$$

Also,

$$H' = E' + a_1 + a_2 + \dots \quad A.5$$

This merely corresponds to substituting the undistorted wave-function (or, in mathematical terms, the eigenvector $|0\rangle$) plus a sum of other wave-functions (the eigenvectors $|1\rangle$, $|2\rangle$,) for the perturbed wave-function. It is possible then to make the additional statement, (equation A.5), that the perturbed energy is a linear sum of the unperturbed energy and some other energies of perturbation, a , referring to the "first order perturbation energy" and so on.

Standard perturbation theory (Dirac, 1956a) gives results for a_1 and a_2 directly.

$$a_1 = \langle E' | V | E \rangle \quad A.6$$

$$a_2 = \sum_{E'' \neq E'} \langle E' | V | E'' \rangle \langle E'' | V | E \rangle / (E'' - E') \quad A.7$$

Equation A.6 is the first order perturbation term, and, by symmetry, can be seen to be other than zero only for atoms with a permanent dipole moment, because the potential V is of odd parity in the cases we consider (Coulson, 1952).

If the system contains n electrons, it would be reasonable to assume to a first approximation, that the potential may be split into a series of potential functions acting individually on each electron (second order interactions between electrons could be taken into account at a later stage in the calculations). The classical expression for such a potential is

$$V = f \sum_i X_i = fX, \text{ say.} \quad A.8$$

Here f is a constant (in this case the applied field) and X_i is some function (as yet unspecified) of the co-ordinates of the i -th electron. X is then the sum of the X_i functions.

Now we must assume

$$a_2 = \alpha f^2/2$$

A.9

Coulson et al. (1952) have carried out trial calculations which tend to shew that, at low field strengths, the above is accurate enough for practical purposes, if an electric field is applied to a molecule; higher terms in the series only become important at very high field strengths, such as would occur in the neighbourhood of an ion.

This gives the polarisability, α , as

$$\alpha = 2 \sum_{E'' \neq E'} \frac{\langle E' | X | E'' \rangle \langle E'' | X | E \rangle}{E'' - E'} \quad \text{A.I0}$$

According to the Kuhn-Thomas sum rule (Kauzmann, 1957a), a system containing n electrons obeys the following relation:

$$\sum_{E'' \neq E'} (E'' - E') \langle E' | X | E'' \rangle \langle E'' | X | E' \rangle = n \quad \text{A.II}$$

This just amounts to the statement that the sum of the oscillator strengths of every possible transition in a system of n electrons is equal to the number of electrons, n , in the system.

We may now define two average E'' values, e and ξ , as follows:

$$(e - E') \sum_{E'' \neq E'} \langle E' | X | E'' \rangle \langle E'' | X | E' \rangle = n \quad \text{A.I2}$$

$$\frac{I}{(\mathcal{E} - E')} \sum_{E'' \neq E'} \langle E' | X | E'' \rangle \langle E'' | X | E' \rangle$$

$$= \sum_{E'' \neq E'} \frac{\langle E' | X | E'' \rangle \langle E'' | X | E' \rangle}{(E'' - E')} \quad \text{A.I3}$$

Now, if these two averages exist and are meaningful -- and there appears to be no mathematical or physical reason why this should not be so -- then, after Vinti (1933), we can equate them as a first approximation.

$$\mathcal{E} = e \quad \text{A.I4}$$

The accuracy of any equations then deduced will depend to a large extent upon how true equation A.I4 is. In fact, the result of Kirkwood (1932) follows directly from equations A.I0, A.I2, A.I3 and A.I4.

$$\alpha = \frac{2}{n} \left\{ \sum_{E'' \neq E'} \langle E' | X | E'' \rangle \langle E'' | X | E' \rangle \right\}^2 \quad \text{A.I5}$$

Using the usual laws of matrix multiplication (Dirac, 1956b), the squared terms in equation A.I5 may be expanded as

$$\sum_{E'' \neq E'} \langle E' | X | E'' \rangle \langle E'' | X | E' \rangle = \langle E' | X^2 | E' \rangle -$$

$$\langle E' | X | E' \rangle \langle E' | X | E' \rangle \quad \text{A.I6}$$

The second term on the right hand side of this equation often vanishes. This will be so if there is a plane of symmetry perpendicular to the applied field, and, in general, if the amounts of wave-function above and below a plane perpendicular to the field have equal weights with respect to X . This means that equation A.I7 is good for atoms, homonuclear diatomics, transverse polarisability calculations on heteronuclear diatomics, and large symmetrical molecules (such as benzene).

Then

$$\alpha = \frac{2}{n} \langle E' | X^2 | E' \rangle^2 \quad \text{A.I7}$$

ensues, this being Kirkwood's (1932) original result.

Up to this point we have not specified the type of wave-function to be used. If this is of the direct product variety, equation A.I7 may immediately be written in the form used by Abbott and Bolton (1953)

$$\alpha = \frac{2}{n} \left\{ \sum_i \langle i | X^2 | i \rangle \right\}^2 \quad \text{A.I8}$$

Now, ~~if~~ instead of a direct product wave-function of the type

$$|E\rangle = |1\rangle, |2\rangle, |3\rangle \dots |i\rangle \dots |n\rangle \quad \text{A.I9}$$

where $|i\rangle$ are atomic orbital wave-functions, we use an

antisymmetrised product wave-function. This is defined as follows

$$|E\rangle = \sum_P \pm P |1.2.3.....i.....n\rangle \quad A.20$$

where P is a permutation operator. This means that the wave-function $|E\rangle$ is now a (suitably normalised) sum of all the possible permutations of the simple product wave-function A.I9, with the proviso that odd permutations have a negative sign.

Substitution of equation A.20 in equation A.I8 gives

$$\alpha = \frac{2}{n} \left\{ \sum_i (\langle i|X^2|i\rangle - \langle i|X|j\rangle \langle j|X|i\rangle) \right\}^2 \quad A.21$$

If it is desired to use some other form of wave-function (as, for example, where it is impossible to express the eigenfunction as a direct product), expansion can be carried out directly from equation A.I7.

The additional terms in equation A.21, which are not present in equation A.I8, correspond to the "electron exchange" terms obtained by Buckingham (1937) in his similar treatment. This is predictable, for electron exchange terms would not be expected to result from direct product wave-functions.

It would be expected that polarisabilities could be assigned to each individual electron, with allowance possible for electron interaction terms, but this treatment gives a mean polarisability over the system.

To illustrate, write equation A.I7 as

$$\alpha = \frac{1}{n} \left[\sum_i p_i \right]^2 \quad \text{A.22}$$

where p_i is a function of the polarisability of a given electron (or at least we may assume it to be, as the summation allots terms to each electron which seem to behave in this manner: e.g., if all terms but one are taken as zero, the final result is the polarisability of a single electron).

Equation A.22 expands as

$$\alpha = \frac{1}{n} \left[\sum_i p_i^2 + \sum_i \sum_{j \neq i} p_i p_j \right] \quad \text{A.23}$$

This indicates that, using this mathematical model, the polarisabilities of the electrons are more interdependent than one would expect intuitively from physical evidence.

Now the main approximation made in the above treatment occurs in equation A.I4, so consider again the Kuhn-Thomas sum rule.

Kauzmann (1957) proves that

$$\sum_i f_i = \langle E' | PX - XP | E' \rangle \quad A.24$$

where f_i are oscillator strengths and X and P are the total non-commuting position and momentum operators for the whole system.

Consider first the simplest case, that of a simple product wave-function. The eigenvector $|E'\rangle$ is then represented by a product of eigenfunctions $|I'\rangle, |2'\rangle, \dots$

$$|E'\rangle = |I'\rangle |2'\rangle \dots \dots |n'\rangle \quad A.25$$

By the usual methods (Dirac, 1956b), from equations A.24 and A.25 we can get

$$f_i = n = \sum_{b'=1}^n E_I(b') \left[\sum_{b''=n+1}^{\infty} \langle b' | X | b'' \rangle \langle b'' | X | b' \rangle \right] \quad A.26$$

Here $E_I(b')$ is defined by

$$\begin{aligned} E_I(b') \sum_{b''=n+1}^{\infty} \langle b' | X | b'' \rangle \langle b'' | X | b' \rangle \\ = \sum_{b''=n+1}^{\infty} (E''(b') - E) \langle b' | X | b'' \rangle \langle b'' | X | b' \rangle \end{aligned} \quad A.27$$

If we promote the k -th electron in equation A.25 to some higher level, the l -th, say, the summation will become (where E_2 is a new average, defined like E_I)

$$\begin{aligned} f_i = n = \sum_{b'=1}^n E_2(b') \sum_{b''=n+1}^{\infty} \langle b' | X | b'' \rangle^2 - \\ \sum_{b'=1}^n E_2(b') \langle b' | X | l \rangle \langle l | X | b' \rangle - E_2(k) \sum_{k=n+1}^{\infty} \langle k | X | b'' \rangle \langle b'' | X | k \rangle \end{aligned}$$

$$\begin{aligned}
& + E_2(k) \langle k|X|1 \rangle \langle 1|X|k \rangle + E_2(1) \sum_{b''=n+1}^{\infty} \langle 1|X|b'' \rangle \langle b''|X|1 \rangle \\
& - E_2(1) \langle k|X|1 \rangle \langle 1|X|k \rangle + E_2(b') \langle b'|X|k \rangle \langle k|X|b' \rangle \quad \text{A.28} \\
& = A + B + C + D + E + F + G
\end{aligned}$$

A : Original sum with newly defined E.

B : Removes all transitions to 1-th level (including k-th transition).

C : Removes all transitions of k-th electron (and the $1 \rightarrow k$ transition the second time).

D : Replaces transition to 1-th level from k-th.

E : All transitions of 1-th above $(n+1)$ -th.

F : Transition of $1 \rightarrow k$ -th.

G : Transition of all electrons except 1-th to k-th.

It is now necessary to make assumptions about the energy.

$$\text{Put } E_I = E_2$$

A.29

This gives

$$\begin{aligned}
& \sum_1^n E_2 \langle b'|X|1 \rangle \langle 1|X|b' \rangle - \langle b'|X|k \rangle \langle k|X|b' \rangle \\
& + E_2 \sum_{b''=n+1}^{\infty} \langle k|X|b'' \rangle \langle b''|X|k \rangle - \langle 1|X|b'' \rangle \langle b''|X|1 \rangle = 0 \quad \text{A.30}
\end{aligned}$$

That is

$$\begin{aligned}
& \langle k|X^2|k \rangle - 2 \sum_1^n \langle b'|X|k \rangle \langle k|X|b' \rangle \\
& = \langle 1|X^2|1 \rangle - 2 \sum_1^n \langle b'|X|1 \rangle \langle 1|X|b' \rangle \quad \text{A.3I}
\end{aligned}$$

Thus approximately all terms in equation A.26 must be equal. Equation A.32 follows directly.

$$\sum_{E'' \neq E'} (E'' - E') \langle i' | X | i'' \rangle \langle i'' | X | i' \rangle = I \quad A.32$$

($i = 1, \dots, n$)

This set of equations still is precisely the same as equation A.II, except for the assumption that simple product molecular orbitals are being used, and each equation shows the fate of each respective electron under the set of transitions $E' \rightarrow E''$. The form of these equations is only so simple because electron interaction is not considered.

On physical grounds, then, it would be reasonable to expect a more accurate equation if the average in equation A.I4 were subdivided into one average energy for each electron. Now equation A.32 becomes

$$(E - E') \sum_{E'' \neq E'} \langle i' | X | i'' \rangle \langle i'' | X | i' \rangle = I \quad A.33$$

($i = 1, \dots, n$)

$(E - E')$ is not a constant throughout the n equations, because the calculated values of the matrix elements are different for each electron.

We can now give another set of average values for $(E'' - E')$, proceeding as before.

$$\frac{1}{I - i'} \sum_{E'' \neq E'} \langle i' | X | i'' \rangle \langle i'' | X | i' \rangle$$

$$= \sum_{E'' \neq E'} \frac{\langle i' | X | i'' \rangle \langle i'' | X | i' \rangle}{E'' - E'}$$
A.34

(i = I,n)

Then put

$$I = \mathcal{I}$$

A.35

It would be expected that equation A.35 would be a more appropriate average as, in effect, it reduces the amount of averaging to be performed.

Equation A.10, on the simple product notation, becomes

$$\alpha = 2 \sum_{i=1}^A \sum_{E'' \neq E'} \frac{\langle i' | X | i'' \rangle \langle i'' | X | i' \rangle}{E'' - E'}$$
A.36

From this it follows directly that

$$\alpha = 2 \sum_i \langle i' | X^2 | i' \rangle^2$$
A.37

This is the expected result and corresponds to Buckingham's (1937) equation using one parameter for each electron (electrons being considered individually here) and no electron interaction terms. (Simple product wave-functions were used throughout.)

A better result (Hellmann, 1935) is obtained assuming the wave-function of equation A.10 to be an antisymmetrised product.

$$\alpha = 2 \sum_{\substack{E'' \neq E' \\ i'' = i'}} \frac{1}{i'' - i'} \left[\langle i | X^2 | i \rangle - \sum_{j \neq i} \langle i | X | j \rangle \langle j | X | i \rangle \right] \quad \text{A.38}$$

This gives yet another set of equations

$$\alpha_i = 2 \frac{1}{i - i'} \sum_{\substack{E'' \neq E' \\ i'' = i'}} \left\{ \langle i | X^2 | i \rangle - \sum_{j \neq i} \langle i | X | j \rangle \langle j | X | i \rangle \right\} \quad \text{A.39}$$

($i, j = 1, \dots, n$)

For the same reasons as in equation A.35, put

$$\underline{g} = g \quad \text{A.40}$$

This gives the somewhat hybrid result of Hellmann (1935).

$$\alpha = 2 \left[\sum_i \langle i | X^2 | i \rangle \left[\langle i | X^2 | i \rangle - \sum_{j \neq i} \langle i | X | j \rangle \langle j | X | i \rangle \right] \right] \quad \text{A.41}$$

The result is unusual-looking ; and this is because, in effect, antisymmetrised product orbitals were used to get equation A.39, while simple product orbitals were used to get equation A.32.

In exactly the same manner as the above, it can be shown that, if antisymmetrised product molecular orbitals are used throughout, the final result is

$$\alpha = 2 \sum_i \left[\langle i | X^2 | i \rangle - \sum_{j \neq i} \langle i | X | j \rangle \langle j | X | i \rangle \right]^2 \quad \text{A.42}$$

This is the final, and most accurate, form of the polarisability equation, and is that eventually derived by Buckingham (1937).

It should be noted, however, that this method is a perturbation one and the method of Buckingham and Kirkwood

is variational. It is still necessary to show why the results are similar in the two types of method, and this is what the following section sets out to do.

B. Variation Methods.

When the variation method is used in polarisability theory, it assumes, in general, that the expression

$$|H'\rangle = |0\rangle + |1\rangle + |2\rangle + \dots \quad \text{B.1}$$

may be represented as

$$|H'\rangle = |0\rangle + f(r)V(r)|0\rangle \quad \text{B.2}$$

Here $f(r)$ is some function of the co-ordinates, as is $V(r)$, the applied potential; the above follows immediately from classical theory.

First try

$$f(r) = \lambda \quad \text{B.3}$$

where λ is a constant.

$$|H'\rangle = |0\rangle + \lambda V|0\rangle \quad \text{B.4}$$

Now perturbation theory (Eyring, Walter and Kimball, 1954a) gives the expression

$$|H'\rangle = |0\rangle + \sum_{Z \neq 0} |Z\rangle \frac{\langle Z|V|0\rangle}{Z'' - Z'} \quad \text{B.5}$$

In the above derivation $|Z\rangle$ is an eigenvector of a similar kind to $|H'\rangle$ (a type as yet unspecified); the treatment is, in fact, just the expansion of a single eigenvector into an orthogonal set. The primes have the usual meaning.

Following Dirac (1956a), we can once again write, using equation B.4

$$(E'' - E')|2\rangle + a_I \{ \lambda V|0\rangle - \dots \} + a_2|0\rangle$$

$$= V \{ \lambda V|0\rangle - |2\rangle \dots \} \quad \text{B.6}$$

Write equation B.6 in terms of representatives.

$$(E'' - E') \langle E''|2\rangle + a_I [\langle E''|\lambda V|E'\rangle - \langle E''|2\rangle - \dots$$

$$+ \delta_{E''E'} a_2 = V [\langle E''|\lambda V|E'\rangle - \langle E''|2\rangle \dots] \quad \text{B.7}$$

Here $\delta_{E''E'}$ is the Dirac delta.

$$(E'' - E') \langle E''|2\rangle + a_I [\langle E''|\lambda V|E'\rangle - \delta_{E''2} - \delta_{E''3} - \dots$$

$$\dots] + \delta_{E''E'} a_2 = V [\langle E''|\lambda V|E'\rangle - \delta_{E''2} - \delta_{E''3} \dots] \quad \text{B.8}$$

Put $E'' = E'$ in equation B.8, giving

$$\lambda a_I \langle E'|V|E'\rangle + a_2 = \lambda \langle E'|X^2|E'\rangle \quad \text{B.9}$$

$$a_2 = \lambda [\langle E'|V^2|E'\rangle - \langle E'|V|E'\rangle \langle E'|V|E'\rangle] \quad \text{B.10}$$

$$\text{i.e. } a_2 = \langle E'|V^2|E'\rangle \quad \text{B.11}$$

The result for simple product or antisymmetrised

product wave-functions follows directly. The above serves to show how closely the two methods of calculation are allied.

$$\lambda V|0\rangle = \sum_{Z \neq 0} |Z\rangle \frac{\langle Z|V|0\rangle}{Z'' - Z'} \quad \text{B.I2}$$

$$\begin{aligned} \text{i.e. } \lambda V &= \sum_{Z \neq 0} \frac{|Z\rangle \langle Z|V}{Z'' - Z'} \\ &= \sum_{Z \neq 0} \frac{|Z\rangle \langle Z|\lambda_z X}{Z'' - Z'} \quad \text{B.I3} \end{aligned}$$

$$\lambda_z = \langle Z|X|Z\rangle \quad \text{B.I4}$$

From equation B.I2, it can be seen that, again, exactly the same assumption has been made, namely that an "inverse average" has been taken as equal to a "product average".

Equation B.II was derived using

$$f(r) = \lambda.$$

This amounts to the expression of Buckingham where only one parameter altogether was used in the variation (the form of the perturbed wave-function is exactly that of Buckingham, 1937). The averaging process is seen to be carried on in exactly the same way as for the perturbation method, and so this lets us see that Vinti's (1933) method and Buckingham's are, in fact, the same. From this, it is

possible to draw the important conclusion that, for polarisability calculations, if the same type of wave-function is used, perturbation and variation methods ought to give exactly the same equation.

It may readily be seen that equations can be derived using one parameter per electron (as Buckingham did for his more accurate equation). These would involve a series of λ values and a series of summations. Again, a direct parallel can be drawn with the perturbation method.

It may be shewn that, by solving a differential equation, an exact value for $f(r)$ may be obtained. However, the equation becomes insoluble for all but the simplest cases (Guy, Tillieu and Harrand, 1954).

C. Assumptions Made in Derivation and Application.

At this point the assumptions leading to equation A. 42 may be reviewed. These are of two kinds:

(i) Assumptions inherent in the mathematical processes used.

(ii) Physical assumptions about such things as the actual algebraic form of the one electron wave-functions, etc. Some class (ii) assumptions would have to be made no matter what mathematical technique is used.

PART I.

(a) It is assumed that antisymmetrised molecular orbital wave-functions are to be used. This is no limitation in practice, as, in fact, these are normally required.

However, this is just a matter of convenience and it may readily be shown that most wave-functions which can be separated into portions representing each electron may be arranged in a similar manner, giving, for example,

$$\alpha = 2 \sum_i f(i)^2 \quad \text{C.I}$$

where $f(i)$ is a function of the chosen wave-function.

(b) The technique is only good for non-polar systems.

Extra terms (which are hard to work out) must be introduced when it is desired to deal with polar systems.

(c) Assumptions made in the averaging process: In the first approximation made (equation A.I7), the average is taken (after Vinti) over the complete n-electronic wave-functions;

i.e.

$$\sum_{i=1}^n E_i t_i = n \quad \text{C.2}$$

E_i = electronic energy of the i-th electron.

t_i = transition probability of the i-th electron.

Put

$$E \sum_{i=1}^n t_i = n \quad \text{C.3}$$

Now this is equated to another (reciprocal) average. However, it is obvious that one transition should be greater by far in oscillator strength than the others if equation C.3 is to be valid.

The second, more accurate approximation, equation A.37, gives a similar sum, except that this time the summation is taken over all the possible transitions of an electron, k, say, to a series of upper levels $l(n + 1 \dots \infty)$.

Now

$$\sum_l E_{kl} t_l = I \quad \text{C.4}$$

Put

$$E_k \sum_l t_l = I \quad \text{C.5}$$

This time it seems that there can be one big transition for each electron. This allows a total of n transitions (one per electron), of any strength whatever (assuming these are the only important ones). This is a great advance on equation A.17 with only one transition for the system. In this approximation we have also taken $E_I = E_2$ (equation A.29). This means that :

- (i) There are many electrons in the system (in which case transition of one electron to a higher level does not change the average energy much). or
- (ii) There are only a few important transitions.

Oscillator strengths and transition moments (Bates and Poots, 1953; Bates et al., 1953, 1954; Bates and Damgaard, 1950; Bacher and Goudsmit, 1932) may be substituted in these equations, and they show that the above statements are correct.

PART II.(a) Variation of Polarisability with Internuclear Distance:

If this variation is great, and internuclear distance is an important parameter (as it is in the above formulae), bond length must be known accurately for a good polarisability value. In fact, there is usually a rapid increase in ionic terms with increasing internuclear distance (Bell and Long, 1950); thus, if possible, ionic terms should be included in the wave-functions used and not merely added afterwards as a correction factor.

(b) Charge Distribution in Orbitals;

It has been shewn (Abbott and Bolton, 1953; Guy, Tillieu and Harrand, 1954; Pople and Schofield, 1957) that most of the polarisability comes from the outer regions of the orbitals; for atomic orbitals, it takes about 90% of the charge to contribute 50% of the polarisability (this is because induced dipole increases with distance as well as charge). All that this means is that it is hard to choose the correct parameter for the atomic orbital wave-functions. For example, Slater parameters which are intended to describe the inner portions of the wave-function cannot be expected to be accurate for the outer regions as well.

(c) Number of Parameters used in the Perturbation:

If the wave-functions are perfect, accuracy would increase with the number of parameters used. However, with the imperfect wave-functions available, if too many parameters are used (Pople and Schofield, 1957; Guy, Tillieu, 1952, 1953), accuracy can actually decrease. The equation A.42 cited above is probably the best for most purposes.

(d) The Energy Requirement:

Rahman (1953b) has pointed out that a relationship may be derived between the accuracy of an unperturbed wave-function and the accuracy of the corresponding perturbed wave-function, perturbation being caused by an electric field F .

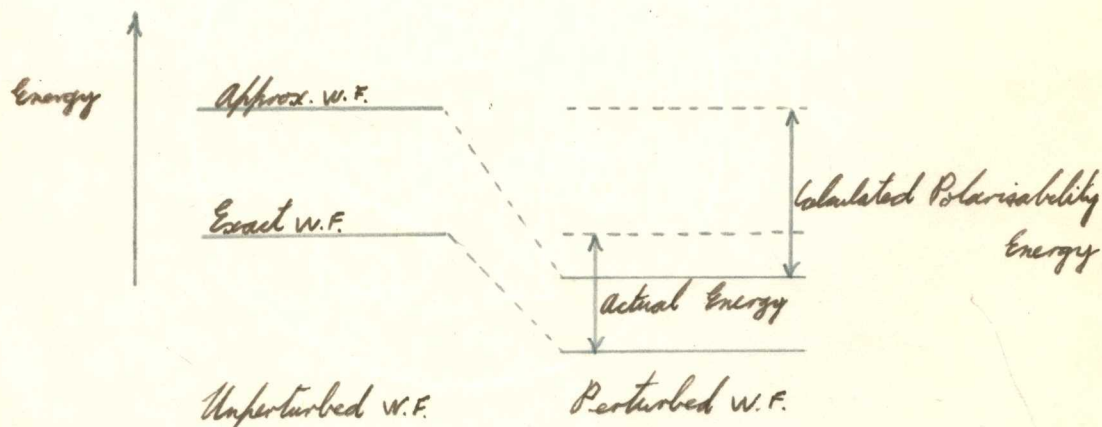
He found three cases could be considered.

(i) If the exact eigenfunctions are known for the whole system, including the continuum: The Schrodinger perturbation method can be used and the accuracy is absolute in principle (depending in fact on how hard the integrations are). However, all these eigenfunctions are known in only a very few cases.

(ii) If the exact eigenfunction is known only for the groundstate: The variation method gives the energy of

perturbation to any desired accuracy. The calculated value of polarisability will always be less than the true value. In practice, if an exact eigenfunction is known for the groundstate, some excited state eigenfunctions are probably known as well. However, these can be neglected as a theoretically exact result can be obtained without their use.

(iii) If no exact eigenfunction is known, but only approximate wave-functions for one or more of the energy levels: In most cases to be dealt with in practice, only approximate wave-functions are available. The energy calculated from such a wave-function is higher than the true value as the following diagram shows.



The actual magnitude of this effect is calculated as follows:

Consider a perturbed wave-function (usual notation)

$$\Psi = \Psi_0 + c\Psi' \quad \text{D.I}$$

The variation method gives for the energy

$$E = -B^2 F^2 / 2A + B^4 F^4 / 8A^3 \quad \text{D.2}$$

$$A = \frac{1}{2(\Psi'|\Psi')} \{ (\Psi'|H|\Psi') - E (\Psi'|\Psi') \} \quad \text{D.3}$$

$$B^2 = (\Psi'|h|\Psi')^2 / (\Psi'|\Psi') \quad \text{D.4}$$

E = approximate groundstate energy.

H_0 = unperturbed Hamiltonian.

$H_0 + h$ = perturbed Hamiltonian.

If we want the first term in the expansion of to predominate (which it must do for the polarisability equations to hold), then for an accuracy of 1 in N , Rahman claims

$$\frac{1}{N} \gg B^4 F^4 / 8A^3 \div B^2 F^2 / 2A \quad \text{D.5}$$

$$\frac{1}{N} \gg B^2 F^2 / 4A^2$$

D.6

We consider that a less rigorous criterion may suffice.

Let E_0 be the accurate groundstate energy, and ΔE be the error in the calculated energy.

$$\text{i.e. } \Delta E + E_0 = E$$

D.7

Substituting for E in equation D.3, for an accuracy of I in N in the A portion of the polarisability energy

$$\frac{1}{N} \gg \Delta E / 2A$$

D.8

However, inaccuracies occur in B^2 as well as in A , but B^2 has no obvious relation to ΔE , so neither method really gives a complete picture as far as accuracy is concerned.

Both criteria are roughly valid in general, however, and seem to lead to the result that, with simple wave-functions, such as ordinary linear combinations of Slater orbitals, accuracy will be about 20%, while more accurate wave-functions containing ten to twelve parameters (Rahman, 1953b) can give polarisabilities accurate to $I - 3\%$.

Appendix A.REFERENCES:

The following references (while not all mentioned in the text) include all the important work which has so far been done on quantum mechanical polarisability calculations. A few references to current popular books on chemical quantum mechanics containing information on the subject are also given.

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Appendix B.(i) Notation for Copper Calculations:

overlap

$$S = \int \psi_a(I) \psi_b(I) d\tau_1 = S$$

one electron

coulomb

$$G = \int \psi_a(I) V_{BI} \psi_a(I) d\tau_1 = (B:aa)$$

resonance

$$K = \int \psi_a(I) \psi_b(I) V_{BI} d\tau_1 = (B:ab)$$

two electron

mononuclear

$$M = \int \psi_a^2(I) V_{I2} \psi_a^2(2) d\tau_2 = (aa;aa)$$

coulomb

$$C = \int \psi_a^2(I) V_{I2} \psi_b^2(2) d\tau_2 = (aa;bb)$$

hybrid

$$L = \int \psi_a^2(I) V_{I2} \psi_a(2) \psi_b(2) d\tau_2 = (aa;ab)$$

exchange

$$E = \int \psi_a(I) \psi_b(I) V_{I2} \psi_a(2) \psi_b(2) d\tau_2 = (ab;ab)$$

For the integrals S, G the potential V is taken as the repulsive or attractive potential between two unit charges.

(ii) Integrals Used in the Copper Calculations:

Formulae for most of these integrals are given in Kotani; they were all corrected and checked. The mistakes are as follows:

Kotani (1955);

(1) Page 100, top table, line } } : coefficients j_m should be (in order) 0, 27, 0, -22, 0, 3.

(2) Page 101, line 14: coefficients of $[\eta\tau\eta\tau]$ and $[\eta\tau'\eta\tau']$ should both be 10, and not 20 and 2.

S: self-consistent field overlap.

M: not given in Kotani, but evaluated in the usual manner (Yates, 1958).

L: obtained from Mulliken's (1949) approximation and calculated values of M, C, S.

E: obtained from Kotani's W and Z functions. W functions up to 11.5 are given by Kotani. The E value for $\alpha = 20$ was calculated directly and intermediate values were taken from the almost linear logarithmic plot of E against α .

Energies are all cm^{-1} and distances in A.U. except where explicitly stated otherwise.

Cu-Cu distance was taken throughout as 2.64 Å.

α is defined as $Z(\text{eff}) R / 3a_0$.

(iii) Evaluation of Overlap Integral:

Write the overlap integral as

$$S = \int R(r_a) R(r_b) \Theta(\theta_a) \Theta(\theta_b) \bar{\Phi}^2(\varphi) r_a^2 \sin \theta_a d\theta_a d\varphi dr_a \quad \text{B.I}$$

The φ integral is trivial and must go to unity (since it is assumed that

$$\int \bar{\Phi}^2(\varphi) d\varphi = 1 \quad \text{B.2}$$

Then transform into elliptic co-ordinates.

$$r_a = (\lambda + \mu) R/2 \quad \cos \theta_a = \frac{1 \pm \lambda \mu}{\lambda \pm \mu} \quad \text{B.3}$$

$$r_b = (\lambda - \mu) R/2$$

$$r_a^2 \sin \theta_a d\theta_a dr_a = \left(\frac{R}{2}\right)^3 (\lambda^2 - \mu^2) d\lambda d\mu \quad \text{B.4}$$

and set also

$$R(r_a) = P(r_a) / r_a \text{ etc} \quad (\text{after Hartree, 1957}) \quad \text{B.5}$$

where

$$P(r) = R(r) r \quad \text{B.6}$$

and

$$\int_0^\infty P(r) dr = \int_0^\infty R^2(r) r^2 dr = 1 \quad \text{B.7}$$

Then

$$S = 2 \int_{\lambda=0}^1 \int_{\mu=0}^1 P[(\lambda + \mu) \frac{R}{2}] P[(\lambda - \mu) \frac{R}{2}] f(\lambda, \mu) \frac{R}{2} d\lambda d\mu \quad \text{B.8}$$

The values of P are tabulated by Hartree.

N.B. (1) $\int_{\mu=-1}^{+1} \dots = 2 \int_{\mu=0}^{+1} \dots$ as the integrand on the A side of the AB axis is a mirror image of that on the B side.

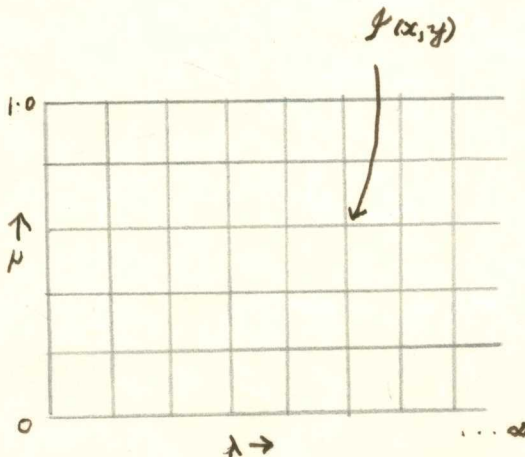
(2) $f_{(w)}(\lambda, \mu)$ depends upon $\Theta(\theta_a)$, $\Theta(\theta_b)$.

To carry out the integration, the integrand was evaluated at the mesh points of a grid in (λ, μ) space.

The following formula was used for this trapezoidal integration

$$\begin{aligned}
 S &= \iint g d\lambda d\mu \\
 &= \frac{1}{4} g(I, 0) + \frac{1}{4} g(I, I) + \frac{1}{2} \left[\sum_i g(i, 0) + \sum_i g(0, i) \right] \\
 &\quad + \sum_{i,j \neq 0} g(i, j)
 \end{aligned}$$

B.9



NUMERICAL VALUES OF INTEGRALS

	S	C	E	G	K
6.50	10338^{-1}	37953^0	64871^{-2}	40207^0	61218^{-1}
7.50	56922^{-2}	39134	21702	41083	35974
8.25	35536	39818	90067^{-3}	41560	23366
8.75	25701	40202	48928	41817	17294
11.50	38555^{-3}	41628	12987^{-4}	42711	28501^{-2}
14.00	60386^{-4}	42342	54100^{-6}	43123	47185^{-3}
16.00	12840	42709	24200^{-7}	43326	10365
18.00	26090^{-5}	42968	91100^{-9}	43467	21609^{-4}
20.00	51077^{-6}	43157	30350^{-10}	43568	43193^{-5}

IN § -TYPE BOND CALCULATION.

	M	L	J(1)	J(2)	J(3)
6.50	7909I ⁰	6I534 ^{-I}	33030 ⁺²	58796 ⁺³	I665I ⁺⁴
7.50	9I259	37III	I0965	2I824	52587 ⁺³
8.25	I0038 ^{+I}	249II	45637 ^{+I}	669I6 ⁺²	I99I8
8.75	I0647	I8848	24867	34I54	I0I39
II.50	I3993	35000 ⁻²	63230 ^{-I}	6799I ⁰	I9565 ^{+I}
I4.00	I7035	642I8 ⁻³	II0I9 ⁻²	30664 ⁻²	I9342 ^{-I}
I6.00	I9469	I524I	I6I00 ⁻³	5I200 ⁻³	I6200 ⁻²
I8.00	2I902	34I77 ⁻⁴	20200 ⁻⁵	22700 ⁻⁴	64800 ⁻⁴
20.00	24336	73I7I ⁻⁵	228I0 ⁻⁶	I0083 ⁻⁵	2442I ⁻⁵

J, the separation between singlet and triplet levels,
is given as a function of the parameter z (see section B).

NUMERICAL VALUES OF INTEGRALS

	S	C	E	G	K
6.50	13830^{-1}	49121^0	65619^{-1}	49746^0	13911^0
7.50	16072	50577	63973	48231	15092
8.25	15333	50421	51876	47394	14116
8.75	14121	50047	41945	46954	12914
11.50	56771^{-2}	47533	61641^{-2}	45561	51770^{-1}
14.00	16465	46191	66010^{-3}	45005	15168
16.00	51626^{-3}	45598	43100^{-4}	44752	47973^{-2}
18.00	14547	45183	19800^{-5}	44585	13627
20.00	37766^{-4}	44969	77839^{-7}	44469	35626^{-3}

IN } -TYPE BOND CALCULATION.

	M	L	J(I)	J(2)	J(3)
6.50	7909I ⁰	88659 ^{-I}	-36386 ⁺³	30I84 ⁺⁴	754I2 ⁺⁴
7.50	9I259	II398 ⁰	-33092	28329	7IIII2
8.25	I0038 ^{+I}	II56I	-27605	22439	5893I
8.75	I0647	II05I	-22940	I7704	48409
II.50	I3993	532I0 ^{-I}	-33820 ⁺²	I9667 ⁺³	64I82 ⁺³
I4.00	I7035	I7827	-53950 ^{+I}	960II ^{+I}	39359 ⁺²
I6.00	I9468	62024 ⁻²	-50I00 ^{-I}	II850	36548 ^{+I}
I8.00	2I902	I92I7	46460	I3382 ⁰	30703 ⁰
20.00	24336	54444 ⁻³	3259I ⁻²	85355 ⁻²	I8636 ^{-I}

J, the separation between singlet and triplet levels,
is given as a function of the parameter z (see section B).

Appendix C.

The energy units used are electron-volts, and length units are atomic units, except where explicitly stated otherwise.

Bond lengths:

C-H 1.09 A

C-CH₃ 1.54 A

C-C(ring) 1.39 A

Effect of ionic terms:

Entries in column (c) of Table I were decreased by 0.238, 0.668, 0.002, (and 0.248) eV in order downwards, and column (d) entries by 0.238, 0.064, 0.026, (and 0.328) eV.

TABLE I
ORBITAL ENERGIES (e.v.)

	PCR	(a)	(b)	(c)	(d)
Core	C ₆	C ₆	C ₆	C ₆ H ₆	C ₆ Me ₆
Exchange included	No	No	Yes	Yes	Yes
$\epsilon_3 - \epsilon_2$	2.754	4.792	3.670	4.405	4.348
$\epsilon_2 - \epsilon_I$	5.358	5.444	6.582	6.242	6.160
$\epsilon_I - \epsilon_0$	2.932	1.688	3.010	3.286	3.220
$\epsilon_3 - \epsilon_0$	11.044	11.924	13.262	13.933	13.728

TABLE II

Level and dominant configuration	NoCl	PCR ^a	Cl	NoCl
<u>Singlets</u>				
A _{Ig}	0		0(-2.72) ^b	0
*A _{2g} (I-2) ²	II.I		12.5	II.2
*B _{Iu} (I-2)	7.3		9.0	7.3
B _{2u} (I-2)	5.9		4.4	6.0
*E _{Iu} (I-2)	9.8		9.9	9.9
E _{2g} (I-3) or E _{2g} (0-2)	10.9		7.6	9.7
<u>Triplets</u>				
A _{Ig} (I-2) ²				
A _{Ig} (I-2) ²	12.6		11.5	12.8
B _{Iu} (I-2)	3.1		3.6	3.2
*B _{2u} (I-2)	5.8		8.2	5.8
E _{Iu} (I-2)	4.4		4.5	4.5
E _{2u} (I-3) or E _{2u} (0-2)	8.3		6.3	7.1

* Denotes state incompatible with non-polar valence bond structures.

a Notation of Table I.

b Figures in parentheses is the depression of the ground state energy due to Cl.

RELATIVE ENERGY LEVELS OF BENZENE (e.v.)

(a) ^a		(c) ^a			
Cl	NoCl	Cl		Expt.	
0(-2.6)	0	0(-2.4)	(13%) ^a	0.0	
12.6	12.8	14.0		-	
9.1	8.1	9.7		(6.2) ^d	
4.5	6.8	5.3	(19%)	4.9	
9.9	10.7	10.6	(12%)	7.0	
7.5	12.1	9.2	(12%)	(6.2) ^d	
11.4	13.4	13.2		-	
3.7	4.0	4.3	(9%)	3.8	
8.3	6.6	8.8		-	
4.5	5.3	5.4	(17%)	-	
6.3	9.5	7.8		-	

c Percentage of higher energy configurations in complete state wave-functions.

d Alternative assignments.

In conclusion, I should like to thank sincerely Dr I.G. Ross, under whose guidance this work was carried out, for the advice and encouragement he has given and the generosity with which he has made available time for helpful discussions.

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School of Chemistry,

University of Sydney.

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