The delocalisation energy of benzene and the non-empirical MO theory

Melvyn P. Melrose

Department of Chemistry, King's College London, Strand, London WC2R 2LS, UK

Abstract. Algebraic expressions for the vertical Delocalisation Energy (DE) of benzene are derived from non-empirical MO theory. For comparison with early work in the π-electron approximation, and ultimately with Hückel theory, the results are formulated in terms of a core resonance integral, β, and π-electronic repulsion integrals. All integral values are inferred from the results of *ab initio* SCF calculations. Two expressions are derived, which refer to two ways of forming the localised π MOs: one where three pairs of adjacent atomic orbitals are selected from a set of six orthogonalised orbitals; and another where a non-orthogonal set of atomic orbitals is used. The first expression is formally similar to an expression originally derived by Pople from a different point of view and with many approximations. This expression gives too large a magnitude for DE when used with an *ab initio* value of β. The second expression gives a result much closer to an empirical value of DE and shows that the main reason for DE being about 50% of 2β rather than 2β is the stabilising effect of overlap in the localised structure, and that the less important factor is the inclusion of electronic repulsion.

Key words: Delocalisation energy – Non-empirical MO – Resonance integral

Introduction

Ab initio studies [1 – 4] of benzene and especially recent work [1–3] analysing the influence of π electron delocalisation upon molecular geometry, have produced an interesting range of values for the vertical delocalisation energy (DE). This quantity, which is the same as the quantum mechanical resonance energy, may be defined [4] as the electronic energy of benzene *minus* the electronic energy of the non-resonating triene which has the same geometry as benzene. The definition does not say how the model wave function for the non-resonating triene should be chosen, and this choice can have a greater effect on the value of DE than the variational level of the calculation.

The VB scheme seems to provide the most natural choice of model wave function – the single Kekulé bond eigenfunction. However, it is only recently that this approach has been implemented with fully optimised wave functions. Bernardi

et al. [1] have determined a CAS-SCF wave function for benzene using a 4–31 G basis and an active space confined to the π orbitals. This wave function was then accurately transformed to a VB form which included all the Dewar and both the Kekulé bond eigenfunctions. It was found that the energy of a single Kekulé bond eigenfunction was 62.4 kcal mol^{-1} above that of the full CAS-SCF wave function, i.e. DE was -62.4 kcal mol^{-1}.

Most other determinations of DE have started with an SCF MO wave function for benzene. In this approach, the model wave function for the non-resonating molecule is obtained from the SCF wave function by replacing the three canonical π MOs with three localised MOs. The constitution of the localised MOs turns out to be critical. Glendening et al. [2] report a value of -147 kcal mol^{-1} using a 6–31 G basis. They constructed their localised MOs by first transforming their canonical MOs to a basis of symmetrically orthogonalised atomic orbitals and then combining orthogonal orbitals centred on adjacent atoms. A rather different value, -85.2 kcal mol^{-1}, was obtained by Shaik et al. [3] also using a 6–31 G basis. Their localised MOs were obtained by first determining the bonding π MO of ethylene (through an SCF calculation using a benzenoid C–C bond lengths) and then placing three such MOs on a benzene framework and orthonormalising the set. Glendening et al. [2] cited spectroscopic evidence [5] (the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition energy) in support of their value of DE. This is an unsound argument. It is only in Hückel theory [6] that the lowest π–π^* transition energy, ΔE, is the same as (minus) DE, and even then an average value of ΔE should be taken, because Hückel theory does not distinguish between energy levels arising from the same configuration. Both quantities are predicted equal to $|2\beta|$, where β is the Hückel resonance integral. This prediction is usually regarded as an artefact of the Hückel approximation, and not as a correlative definition of DE.

The method of using *ab initio* calculations on ethylene to model the localised MOs appears to have originated with Kollmar [4], who obtained a DE value of -86.4 kcal mol^{-1} using a double zeta basis. Kollmar also investigated the effect on DE of allowing the σ electron distribution to adapt to the localisation of the π electrons, and the effect of including correlation energy. The effect of σ relaxation was small, stabilising the localised structure by only 1.2 kcal mol^{-1}, but the effect of including correlation energy, through PMO-CI calculations, was more significant. The localised structure was made relatively more stable by 16.0 kcal mol^{-1} when π-electron correlation was taken into account; but σ–π correlation favoured the delocalised structure by 6.9 kcal mol^{-1}. The overall effect of including correlation was thus to reduce the magnitude of DE by about 9 kcal mol^{-1}.

The experimental determination of DE is also slightly problematic because of uncertainties in the assignment of bond enthalpies and force constants in a hypothetical molecule. A widely cited empirical value of DE is due to Parr and Mulliken [7]. These authors first determined the thermochemical resonance energy of benzene to be -41.8 kcal mol^{-1}, and then subtracted the energy, 36.6 kcal mol^{-1}, needed to distort a structure of alternating single (1.54 Å) and double-bond lengths (1.34 Å) to a structure with uniform bond lengths (1.39 Å). The distortion energy was determined from spectroscopic force constants typical of alkane and alkene carbon–carbon bonds. Thus, the empirical value of DE is around -78.4 kcal mol^{-1} – in excellent agreement with the theoretical value of Kollmar with correlation included. (Parr and Mulliken regarded the thermochemical part of their calculations as more uncertain than the distortion energy.)

The aim of this work is to give algebraic expressions for DE, derived without any unquantifiable approximation from SCFMO theory, which will explain why

Glendening et al. obtained such a large magnitude for DE and why the more generally accepted magnitude is considerably less than the $\pi \to \pi^*$ excitation energy. The expressions will be algebraically comparable with Hückel theory and will give results numerically comparable with *ab initio* SCF calculations.

The idea of retaining some of the structure of Hückel theory in an improved method, explicitly including π-electronic repulsion, is very old and takes us back to the historic calculations of Pariser and Parr [8] on the electronic spectrum of benzene and of Pople [9] on DE. Although these calculations are usually presented as approximate forms of MO theory, their explanatory power is compromised to some extent by the use of parameters designed to give better agreement with experimental quantities than exact MO theory could give. The presence of parameters makes the approximations which are introduced difficult to validate, and it is not clear that the underlying model really is MO theory. Indeed, so far as the Pariser–Parr calculation is concerned, it has been convincingly argued [10] that the parameters which reproduce the spectrum of benzene effectively model a CI Hamiltonian, and not an SCF Hamiltonian. For the calculation of DE, on the other hand, the inclusion of electron correlation is less critical than it is for the calculation of spectra, and it would be interesting to see what MO theory says about DE without parameters and without the approximative assumptions which Pople made in regard to the core Hamiltonian.

There was one non-empirical calculation of DE before the era of *ab initio* calculations: Parr and Mulliken [7] calculated DE using localised MOs of the ethylenic form and the core Hamiltonian of Goeppart–Mayer and Sklar [11] (GMS). This Hamiltonian is explicitly defined, but it is not the core Hamiltonian which is variationally appropriate for MO theory in benzene, being bereft of hydrogen atoms and σ–π exchange interactions. Using the GMS framework, Parr and Mulliken obtained a theoretical value of DE in better agreement with their empirical value than any subsequent *ab initio* MO calculation, for reasons which are not immediately obvious.

The first step in this paper is the formulation of the core Hamiltonian as part of the SCF Hamiltonian. The only approximation then introduced is the ZDO approximation for electronic repulsion integrals involving orthogonalised $2p\pi$ orbitals. This approximation, which should be distinguished from Pople's *formal* neglect of overlap, has been the subject of much study [12, 13] and its effect on results can be quantified. Using this approach the algebraic results of Pople can be obtained without any further approximation, and the numerical result of the Parr–Mulliken calculation can be brought into line with *ab initio* calculations.

SCF Hamiltonian, the core Hamiltonian and the total pi energy

For an electron in a closed-shell molecule the SCF Hamiltonian, $\hat{F}$, may be written

$$\hat{F} = \hat{H} + \hat{G}, \tag{1}$$

where $\hat{H}$ is the sum of the kinetic energy and bare nuclear attraction operators and $\hat{G}$ is the electron interaction operator. For molecules with a plane of symmetry $\hat{G}$ may be divided into contributions from the σ and π electrons:

$$\hat{G} = \hat{G}^{\sigma} + \hat{G}^{\pi}. \tag{2}$$

Although the operators in Eqs. (1) and (2) refer to *any* electron it is useful when considering an π electron to combine $\hat{H}$ and $\hat{G}^\sigma$ into a core Hamiltonian $\hat{H}^c$, i.e.

$$\hat{H}^c = \hat{H} + \hat{G}^\sigma, \tag{3}$$

so that

$$\hat{F} = \hat{H}^c + \hat{G}^\pi. \tag{4}$$

The π MOs are eigenfunctions of $\hat{F}$ with orbital energies ε_i:

$$\hat{F}\psi_i = \varepsilon_i \psi_i. \tag{5}$$

At this point the LCAO expansion is introduced for the π MOs, which are exclusive of the σ MOs by symmetry:

$$\psi_i = \sum_p C_{pi}\, \phi_p. \tag{6}$$

In a minimal basis ϕ_p would be a single $2p\pi$ atomic orbital on atom p and, for benzene, the summation would be from $p = 1$ to $p = 6$. The charge and bond order matrix, P, is defined by

$$P_{pq} = 2 \sum_{\text{iocc}} C_{pi}^* C_{qi}. \tag{7}$$

In parallel with Eq. (4), the elements of the Fock matrix, F, are given by

$$F_{pq} = H_{pq}^c + \sum_{rs} P_{rs}[(pq/rs) - \tfrac{1}{2}(ps/rq)]. \tag{8}$$

In the above equation the $p, q, r,$ and s refer to real $2p\pi$ AOs and

$$(pq/rs) = \iint \phi_p(1)\, \phi_q(1)\, r_{12}^{-1}\, \phi_r(2)\, \phi_s(2)\, dv_1\, dv_2. \tag{9}$$

In parallel with Eq. (3), the elements of H^c are given by

$$H_{pq}^c = H_{pq} + \sum_{\rho\sigma} P_{\rho\sigma}\,[(pq/\rho\sigma) - \tfrac{1}{2}(p\sigma/\rho q)], \tag{10}$$

where ρ and σ refer to the σ-type AOs of the core. This way of defining the core Hamiltonian is implicit in Roothaan's original paper [14], although it is not explicitly found there.

No approximations in the form of H^c are contemplated here, but it is useful to see how a core Hamiltonian like that of GMS could be obtained from an SCF core Hamiltonian by integral approximations. This does not seem to have been demonstrated elsewhere. The first approximation is the neglect of exchange between σ and π electrons, i.e. ignoring the integrals $(p\sigma/\rho q)$. Although the σ and π orbitals are orthogonal by symmetry, this is a much more severe approximation than the ZDO approximation within the π system. The Coulombic interactions between the σ and π electrons are then approximated by retaining only integrals of the form $(pq/\sigma\sigma)$. In the GMS method, the potential due to the charge density around each sp^2 hybridised carbon atom is treated as being effectively spherical. This could be modelled by giving the integral $(pq|\sigma\sigma)$ the same (spherically averaged) value for all σ orbitals on the same atom and with the same principal quantum number. Inner shell atomic orbitals (1s on carbon, designated κ) are ignored and carbon nuclear charges correspondingly reduced by 2, on the grounds that 1s orbitals make

a contribution to H_{pq}^c which is $P_{\kappa\kappa}$ times $(pq/\kappa\kappa)$, and this will almost exactly cancel the nuclear attraction integral 2 times (pq/r_c). A similar but much less justified approximation leads to hydrogen atoms being ignored altogether. The contribution of hydrogenic $1s$ orbitals (designated η) to H_{pq}^c is $P_{\eta\eta}$ times $(pq/\eta\eta)$, and this partially (but not entirely) cancels the nuclear attraction integral (pq/r_H).

The approximation which will be introduced – to simplify the algebra – is the neglect of π repulsion integrals (pq/rs) when either $p \neq q$ or $r \neq s$. Such integrals are known [12] to be quite small (< 0.12 eV) provided that p, q, r and s refer to the symmetrically orthogonalised $2p\pi$ atomic orbitals, i.e. Löwdin orbitals [15]. From now on it is assumed that p refers to a Löwdin orbital χ_p and not to a Slater-type orbital (STO) ϕ_p, i.e.

$$\chi = \phi S^{-1/2}, \tag{11}$$

where S is the matrix of overlap integrals between STOs. The effect of the ZDO approximation upon gross quantities like G_{pq}^π will be investigated in the next section.

Within the ZDO simplification, the formulation of the Fock matrix elements and the total π energy becomes similar to the PPP scheme, except that H_{pq}^c is now defined *ab initio*. Equation (8) becomes

$$F_{pp} = H_{pp}^c + \tfrac{1}{2}P_{pp}(pp/pp) + \sum_{q \neq p} P_{qq}(pp/qq) \tag{12}$$

and

$$F_{pq} = H_{pq}^c - \tfrac{1}{2}P_{pq}(pp/qq), \quad p \neq q. \tag{13}$$

The total energy of the π system is given by

$$E^\pi = \sum_p \sum_q [P_{pq} H_{pq}^c + \tfrac{1}{2}P_{pq} G_{pq}^\pi] \tag{14}$$

$$= \sum_p \tfrac{1}{2}P_{pp}[2H_{pp}^c + \tfrac{1}{2}P_{pp}(pp/pp) + \sum_{q \neq p} P_{qq}(pp/qq)]$$

$$+ \sum_p \sum_{q \neq p} [P_{pq} H_{pq}^c - \tfrac{1}{4}P_{pq}^2(pp/qq)]. \tag{15}$$

The above expression is still valid when the π MOs are localised, i.e. the LCAO coefficients do not have to be eigenvectors of F. Also, for an alternant hydrocarbon like benzene, $P_{pp} = 1$ for each carbon atom p, whether the MOs are localised or not. Hence, Eq. (15) becomes

$$E^\pi = \sum_p [H_{pp}^c + \tfrac{1}{4}\gamma_{pp} + \sum_{q \neq p} (\tfrac{1}{2}\gamma_{pq} + P_{pq} H_{pq}^c - \tfrac{1}{4}P_{pq}^2 \gamma_{pq})], \tag{16}$$

where (pp/qq) has been replaced by γ_{pq}. Since the carbon atoms are equivalent, a convenient form of Eq. (16), which compares with Hückel theory, is

$$E^\pi = 6\alpha + 6 \sum_{q \neq 1} (H_{1q}^c P_{1q} - \tfrac{1}{4}P_{1q}^2 \gamma_{1q}), \tag{17}$$

where

$$\alpha = H_{11}^c + \tfrac{1}{4}\gamma_{11} + \sum_{q \neq 1} \tfrac{1}{2}\gamma_{1q}.$$

The evaluation of the integrals

The required integrals could have been obtained by modification of a standard SCF package. However, given the ZDO approximation, only a very few matrix elements are required for a molecule with high symmetry like benzene, and it is possible to deduce what these must be from SCF orbital energies and from theoretical (single-configuration) energy levels already in the literature. This approach is instructive, because of the link with spectroscopy.

For the determination of the electronic energy levels of benzene, the canonical MOs are most conveniently expressed in complex form:

$$\sqrt{6}\psi_j = \sum_p \chi_p \exp(2\pi i p j/6), \quad j = 0, \pm 1, \pm 2, 3.$$

The lowest $\pi \to \pi^*$ transition then corresponds to the orbital substitution $\psi_{\pm 1} \to \psi_{\pm 2}$, and gives rise to electronic states $^3B_{1u}$, $^1B_{1u}$, $^3B_{2u}$, $^1B_{2u}$, $^3E_{1u}$ and $^1E_{1u}$. From expressions for these energy levels [16], determined in the one-configuration approximation, it can be shown that the simple average of the four B_u term energies is given by

$$\Delta E(B_u) = \varepsilon_2 - \varepsilon_1 - J_{21} + K_{-21}. \tag{18}$$

The average of the $^3E_{1u}$ and $^1E_{1u}$ energies provides another useful equation for the determination of molecular integrals:

$$\Delta E(E_{1u}) = \varepsilon_2 - \varepsilon_1 - J_{21} + K_{21}. \tag{19}$$

Now the difference between the orbital energies above is readily expressed as a difference between Fock matrix elements (in the χ basis):

$$\varepsilon_2 - \varepsilon_1 = -2(F_{12} - F_{14}) = -2(H^c_{12} - H^c_{14}) - 2(G^\pi_{12} - G^\pi_{14}).$$

The subscripts of H^c and G^π refer to the atomic orbitals, those of J, K and ε refer to MOs. Expressions for molecular integrals provided by Parr et al. [17] (PCR) reveal that, in the ZDO approximation, $J_{21} - K_{-21}$ has the same value as $-2(G^\pi_{12} - G^\pi_{14})$; both integrals are equal to $(\frac{2}{3}\gamma_{12} + \frac{1}{3}\gamma_{14})$, where the γ integrals refer to the χ basis. Hence, a simple cancellation occurs, and

$$\Delta E(B_u) \approx -2(H^c_{12} - H^c_{14}). \tag{20}$$

Thus, if the ZDO approximation for repulsion integrals were accurate, and a one-configuration description of each level were adequate, the average $^1A_{1g} \to B_u$ excitation energy would be -2β, where β is $(H^c_{12} - H^c_{14})$. The same β turns out to be the main determinant of DE, so that the analogy with Hückel's β is obvious.

How accurate is Eq. (20)? Since its derivation does not depend on the nature of the core Hamiltonian, its accuracy can be tested by comparing the value of the GMS core integral, $-2(H^c_{12} - H^c_{14})$ with the GMS value of $\Delta E(B_u)$ determined with a full set of accurate repulsion integrals. Moskowitz and Barnett [28] recalculated the GMS energy levels with more accurate repulsion integrals than were available either to GMS or PCR. They found $\Delta E(B_u)$ to be 5.38 eV which is very close indeed to the value (5.358) of -2β using a GMS core. Thus, it seems that Eq. (20) is quite accurate at least if a basis of symmetrically orthogonalised STOs (orbital exponent $\zeta = 1.59$) is used. Surprisingly, the ZDO estimate of the two-electron contribution to $\Delta E(B_u)$, i.e. zero, is actually closer to the correct

theoretical value than is the estimate obtained by using the full set of PCR integrals. According to PCR the "full" value of $-2(G_{12}^{\pi} - G_{14}^{\pi})$ is 7.577 eV, while the full value of $J_{12} - K_{-21}$ is 7.443 eV. The ZDO value in each case is 7.573 eV (using values $\gamma_{12} = 8.92$ eV and $\gamma_{14} = 4.88$ eV obtained by McWeeny [19] from the PCR set of integrals).

Thus, the value of 2β for an SCF core may be deduced from a calculation of the electronic spectrum of benzene at the SCF level, provided a simple STO description of the π orbitals is used. Such a calculation has been provided by Stevens et al. [20], using orbital exponent $\zeta = 1.69$. The theoretical value of $\Delta E(B_u)$ was 7.12 eV, indicating $\beta = -3.56$ eV, assuming that Eq. (20) is not less valid at the slightly higher ζ value. The SCF orbital energy difference $(\varepsilon_2 - \varepsilon_1)$ is 14.74 eV for this calculation, which indicates from Eq. (18) that $J_{21} - K_{-21}$ is 7.61 eV. The theoretical value of the $\Delta E(E_{1u})$ transition energy is 8.82 eV, which indicates, from Eq. (19), that $J_{12} - K_{12}$ is 5.92 eV. Values of γ_{12} and γ_{14} consistent with these molecular integral values are 8.97 and 4.89 eV, respectively.

As is well known, a linear combination of Gaussian functions, with fixed or variable coefficients, can be a better description of a $2p\pi$ atomic orbital than a single Slater function. The present work uses the STO description in the first instance, partly because of the connection with the historic calculations and partly because Eq. (20) is not really established for χ functions which are groups of Gaussians. Nevertheless, it is interesting to see how different basis sets affect the value of $\Delta E(B_u)$, and not too daring to suggest that Table 1 indicates how β varies with basis set.

Considering Table 1, there are two calculations [21, 22] which treat the $2p\pi$ orbitals as a fixed group of Gaussian functions, and the better variational calculation [21] suggests a $|\beta|$ value of 3.37 eV. The lowest value in (3.20 eV) in Table 1 arises from an extended basis set calculation [23] where β cannot be defined uniquely and where the ZDO approximation and Eq. (20) are less likely to be accurate. The typical *ab initio* value of $|\beta|$ is larger than the GMS value (2.679 eV), which in turn is larger than the semi-empirical values of Pariser and Parr (2.39 eV) and Pople (2.13 eV). The explanation for the last value will be given in the next section.

Method I for DE

In a minimal basis, P is completely determined by symmetry and for the canonical MOs one finds

$$P_{11} = 1, \quad P_{12} = \tfrac{2}{3}, \quad P_{16} = \tfrac{2}{3}, \quad P_{13} = 0, \quad P_{14} = -\tfrac{1}{3}.$$

Substituting these values into Eq. (17) gives

$$E^{deloc} = 6\alpha + 8 H_{12}^c - 2H_{14}^c - \tfrac{4}{3}\gamma_{12} - \tfrac{1}{6}\gamma_{14}. \tag{21}$$

Table 1.

SCF calculations and basis	Description of $2p\pi$ orbital	$\Delta E (B_u)/2$ eV
Ref. [20] Minimal STO	Single STO, $\zeta = 1.69$	3.56
Ref. [22] $(7s, 3p/3s)$ GTO	One group of 3 functions	3.30
Ref. [21] $(10s, 5p/5s)$ G-lobes	One group of 5 functions	3.37
Ref. [23] $(10s, 5p/5s)$ G-lobes	Two groups, 4 functions and 1 function	3.20

For the non-resonating structure a simple way of choosing the localised MOs is to combine χ functions from adjacent atoms:

$$\psi_{56} = (\chi_5 + \chi_6)/\sqrt{2}, \qquad \psi_{12} = (\chi_1 + \chi_2)/\sqrt{2}, \qquad \psi_{34} = (\chi_3 + \chi_4)/\sqrt{2}. \tag{22}$$

A similar method seems to have been used by Glendening et al. [2] (although their basis was not minimal and therefore the choice of orthogonal hybrid orbitals on each centre was not unique). With the above MOs doubly occupied, the elements of $\boldsymbol{P}^{\text{loc}}$ are

$$P_{11}^{\text{loc}} = 1, \quad P_{12}^{\text{loc}} = 1, \quad P_{16}^{\text{loc}} = 0, \quad P_{13}^{\text{loc}} = 0, \quad P_{14}^{\text{loc}} = 0.$$

Substitution of these values into Eq. (17) gives

$$E^{\text{loc}} = 6\alpha + 6H_{12}^c - \tfrac{3}{2}\gamma_{12}. \tag{23}$$

The subtraction of Eq. (23) from Eq. (21) now yields

$$E^{\text{deloc}} - E^{\text{loc}} = \text{DE} = -2(H_{12}^c - H_{14}^c) + \tfrac{1}{6}(\gamma_{12} - \gamma_{14}). \tag{24}$$

The above expression shows that DE is dominated by the one-electron part, 2β, as might be expected from a Hückel theory. The result is formally similar to a result obtained many years ago by Pople [9], if one allows his approximations $H_{14}^c \approx 0$ (neglect of non-neighbour resonance integrals) and $\gamma_{pq} \approx d_{pq}^{-1}$, where d_{pq} is the distance between atoms p and q. However, Pople's derivation was based on more drastic approximative assumptions than these, and it is important to see how a result of the same form as Pople's has been obtained without his approximations.

In Pople's treatment the reference system is not cyclohexatriene, but consists of three separate ethylene molecules with benzenoid bond lengths. Since the σ framework of benzene is not the same as the framework(s) of the reference system, Pople introduced effective nuclear repulsions between the core atoms (effective charge $= +1$). In order to use the same core integrals in both benzene and ethylene, Pople had to assume that the monatomic part of H_{11}^c was independent of environment and that H_{12}^c was purely diatomic in character. In the present derivation the σ framework of benzene is the same as that of the non-resonating triene, and therefore the core integrals are the same in both systems, and there is no need to introduce nuclear repulsions. The localised electron pairs are not independent: each π electron interacts with the π electrons in other bonds and with the nuclear centres in other bonds.

It is not difficult to show that Pople would have obtained precisely the same result even if his model for the non-resonating molecule had been cyclohexatriene, because of the approximations that he used. Pople assumed, in effect, that the electron–nucleus attraction integral, (pp/r_q), had the same magnitude as the electron–electron repulsion integral, γ_{pq} and that both integrals were equal to d_{pq}^{-1}, the repulsion between core atoms p and q. These approximations ensure that terms which should otherwise be added to E^{loc}, to change the reference system from three ethylenes to cyclohextriene, actually sum to zero. Given the same reference system as in this work, Pople's derivation then differs from the foregoing only in the formulation of diagonal matrix elements and through the inclusion of nuclear repulsions. Since these terms vanish when E^{loc} is subtracted

from E^{deloc}, the same result will be obtained by either derivation, but the interpretation of the β and γ integrals will be different. All the integrals in this work refer to explicitly orthogonalised orbitals, and the β integral involves all the centres of force.

There are obvious advantages to the non-empirical treatment. In the semi-empirical approach, the assumption that effective nuclear charges are $+1$ is somewhat arbitrary, and is really part of the parametrisation of H_{pq}^c. Moreover, in the presence of nuclear repulsions, it is not clear that the terms which "correct" the simple Hückel result are due to electronic repulsion. In the non-empirical approach, there is no need to assume that core matrix elements are transferable, or that non-neighbour core matrix elements are negligible, to get a neat result for benzene. Because of the symmetry of benzene, H_{13}^c does not appear and H_{14}^c is found within the β integral $(H_{12}^c - H_{14}^c,)$ just as it is for the expression for $\Delta E(B_u)$.

The apparent disadvantage of the more rigorous derivation is its numerical result. With the values of β, γ_{12} and γ_{14} determined in the previous section for STOs ($\zeta = 1.69$) one finds DE $= -148\ \text{kcal mol}^{-1}$. (As will be shown in the next section, the ZDO approximation overestimates the two electron contribution to DE, whose value for this wave function is nearer to $-155\ \text{kcal mol}^{-1}$.) This is similar to the result obtained by Glendening et al. and is about twice the empirical value of Parr and Mulliken. Pople found that he could reproduce the empirical value with $\beta = -2.13\ \text{eV}$, but such a low magnitude is unacceptable in a non-empirical calculation. Table 1 suggests that improving the basis set will not give a β of this magnitude. Whether a CI treatment, with or without excitations from the core, would explain such a low magnitude of β is questionable; and anyway is simpler explanation is available. There is something wrong with the localisation procedure of method I.

Method II for DE

The method of combining adjacent OAOs to make localised MOs has the appeal of simplicity because π bond orders are 1 between π-bonded atoms and zero elsewhere. However, bond orders in an orthogonal basis can give a deceptive picture of the actual charge distribution. The model wave function of method I actually contains *too much orthogonality*. It is not necessary that the AOs in each π bond should be orthogonal to each other and to the other AOs. This creates small amounts of negative overlap density between adjacent atoms which are not π-bonded.

A better route to localised MOs is to follow Kollmar [4] and Parr and Mulliken [7]: ethylenic MOs are formed from non-orthogonal AOs and then the MOs are orthogonalised on a benzene framework. Firstly, it is necessary to reconstitute the STO basis by reversing the transformation of Eq (11), i.e.

$$\phi = \chi\, S^{1/2}.$$

With $\zeta = 1.69$, the overlap integrals are

$$S_{12} = 0.226, \quad S_{13} = 0.0286, \quad S_{14} = 0.0122.$$

These values lead to the following expression for the STO on atom 1 in terms of the χ basis:

$$\phi_1 = 0.9869\chi_1 + 0.1136(\chi_2 + \chi_6) + 0.0074(\chi_3 + \chi_5) + 0.0045\chi_4. \tag{25}$$

The other ϕ's can be deduced by symmetry. The localised MOs take the following (unnormalised) form after symmetric orthogonalisation:

$$\psi_{12} \sim (\phi_1 + \phi_2) - \lambda(\phi_3 + \phi_4) - \lambda(\phi_5 + \phi_6),$$

$$\psi_{34} \sim (\phi_3 + \phi_4) - \lambda(\phi_1 + \phi_2) - \lambda(\phi_5 + \phi_6),$$

$$\psi_{56} \sim (\phi_5 + \phi_6) - \lambda(\phi_1 + \phi_2) - \lambda(\phi_3 + \phi_4). \tag{26}$$

With the given overlap integrals, λ is 0.0556, and in the χ basis the localised MOs are

$$\sqrt{N}\psi_{12} = 1.0931(\chi_1 + \chi_2) + 0.0591(\chi_3 + \chi_6) - 0.0560(\chi_4 + \chi_5),$$

$$\sqrt{N}\psi_{34} = 1.0931(\chi_3 + \chi_4) + 0.0591(\chi_2 + \chi_5) - 0.0560(\chi_1 + \chi_6),$$

$$\sqrt{N}\psi_{56} = 1.0931(\chi_5 + \chi_6) + 0.0591(\chi_1 + \chi_4) - 0.0560(\chi_2 + \chi_3). \tag{27}$$

These functions are rendered orthogonal by each having a small negative "tail" on the opposite side of the molecule. Normalisation gives $N = 2.403$, and the new elements of $\boldsymbol{P}^{\mathrm{loc}}$ are

$$P_{11}^{\mathrm{loc}} = 1, \quad P_{12}^{\mathrm{loc}} = 0.9890, \quad P_{16}^{\mathrm{loc}} = 0.1102, \quad P_{13}^{\mathrm{loc}} = 0.0, \quad P_{14}^{\mathrm{loc}} = -0.09912.$$

The new method has created a small positive π-bond order between adjacent atoms (e.g. 1 and 6) where none existed before, and a small negative bond order between opposite atoms. The localised structure is made more stable by the existence of the new bond orders between adjacent atoms. Useful relationships exist between the bond orders which mean that, upon substituting them into Eq. (17), a very simple result for E^{loc} is obtained. Because the total bond order is fixed, the sum of the above elements is 2. Because $\frac{1}{2}\boldsymbol{P}$ is idempotent, the sum of the squares of the above elements is also 2. Hence, on substitution into Eq. (17) one obtains

$$E^{\mathrm{loc}} = 6\alpha + 6H_{12}^{C}(1 - P) + 6H_{14}^{C}P - \tfrac{3}{2}\gamma_{12}(1 - P^2) - \tfrac{3}{2}\gamma_{14}P^2, \tag{28}$$

where $P = -P_{14}^{\mathrm{loc}}$. Subtraction of Eq. (28) from Eq. (21) then yields

$$\mathrm{DE} = E^{\mathrm{deloc}} - E^{\mathrm{loc}} = -2(H_{12}^{c} - H_{14}^{c})(1 - 3P) + \tfrac{1}{6}(\gamma_{12} - \gamma_{14})(1 - 9P^2). \tag{29}$$

Clearly, Eq. (24) is a special case of Eq. (29) above, with $P = 0$. Substituting $P = 0.0991$ gives a value of $-101\ \mathrm{kcal\,mol}^{-1}$ for DE which corresponds to a reduction of about 32% on the previous magnitude for DE. This reduction is almost entirely due to the one-electron contribution: the positive part of DE changes only by 10%. The empirical value $(-78.4\ \mathrm{kcal\,mol}^{-1})$ is still far off, but before considering how to improve the result it will be demonstrated that the transformations leading to Eq. (27) are accurate, and the error introduced by the ZDO approximation will be estimated.

Parr and Mulliken [7], in their non-empirical calculation, built their localised MOs as follows:

$$\psi_{12} \sim (\phi_1 + \phi_2), \quad \psi_{34} \sim (\phi_3 + \phi_4), \quad \psi_{56} \sim (\phi_5 + \phi_6). \tag{30}$$

These MOs are not orthogonal, but, apart from the STO exponent used ($\zeta = 1.59$), they describe the localised structure in exactly the same way as the MOs of Eq. (26), because the two sets of MOs are formally connected by a linear transformation.

Therefore the method of this section should give exactly the same DE as Parr and Mulliken provided that the same overlap and energy integrals are used. Their overlap integrals were

$$S_{12} = 0.260, \quad S_{13} = 0.0389, \quad S_{14} = 0.0177.$$

With these overlap integrals, the above procedure leads to $P_{14}^{loc} = -0.112$. Substituting this value into Eq. (29), together with the GMS value of $\beta(-2.679 \text{ eV})$, exactly reproduces the one-electron contribution to DE $(-82.1 \text{ kcal mol}^{-1})$ found by Parr and Mulliken. This confirms that the linear transformations are accurate.

However, the two-electron contribution is found to be 13.8 kcal mol^{-1} (using $\gamma_{12} - \gamma_{14} = 4.04$ eV), whereas Parr and Mulliken obtained 9.0 kcal mol^{-1}. The difference, about 4.8 kcal mol^{-1}, is caused by using the ZDO approximation instead of the full set of (PCR) repulsion integrals. It seems that the cancellation of errors which favours the ZDO estimation of the two-electron contribution to $\Delta E(B_u)$ does not apply in the calculation of DE. In particular, the diagonal elements of G^{loc} and G^{deloc} do not cancel exactly in a calculation using a full set of repulsion integrals. The largest source of ZDO error is the neglect of integrals of the form $(12/qq)$. Such integrals are multiplied in energy calculations by P_{12}, not by P_{12}^2. Thus, the main part of the ZDO correction behaves like a one-electron term; and it can be shown that if the error by method I is δ, then the error by method II is $\delta(1 - 3P)$. These considerations suggest that the error in method I for the STO basis is $4.8/(1 - 3P)$, or about 7 kcal mol^{-1}.

The effect of an improved AO basis upon DE may now be investigated. The best variational calculation [21] in Table 1 which uses a single group of functions to describe the $2p\pi$ orbital suggests a $|\beta|$ value of 3.37 eV. Calculations on butadiene [24] using the same AOs indicate the following overlap integrals at interatomic distances appropriate to benzene:

$$S_{12} = 0.322, \quad S_{13} = 0.0789, \quad S_{14} = 0.0479.$$

After forming localised MOs with these overlaps one finds $P_{14}^{loc} = -0.129$, which gives a one-electron part to DE which is 61% of 2β, or -95.1 kcal mol^{-1}. Estimates of the repulsion integrals for this basis, consistent with the theoretical spectrum at the one-configuration level, are $\gamma_{12} = 8.61$ eV and $\gamma_{14} = 4.81$ eV. Thus, the value of DE for the fixed Gaussian-lobe basis [21] is estimated to be about -82.7 kcal mol^{-1}. The improvement over the minimal STO result comes partly from the smaller magnitude of β, but mainly from the larger overlap integral. The result compares well with the value $(-85.2$ kcal mol$^{-1})$ obtained by Shaik et al. [3]. If method I and Eq. (24) had been used with the same integrals, a DE value -142 kcal mol^{-1} would have been obtained, which compares well with the value $(-147$ kcal mol$^{-1})$ of Glendening et al. [2]. In each case the ZDO error has made the results of this work look slightly better than they are. It is the results of the extended basis set calculations which should be closer to the empirical value.

Discussion

The fact that two methods of calculating DE give such widely separated results, underlines the problem of describing the non-resonating triene with an MO wave

function. Using non-orthogonal atomic orbitals (method II) to make the localised MOs clearly gives results which are closer to the empirical value, the improvement over method I being approximately proportional to the near-neighbour overlap integral. Methods which formally ignore the overlap integral – like those of Hückel and Pople – cannot account for this improvement and therefore assume a smaller magnitude of β in order to reproduce the empirical result. This explanation of the magnitude of β used in the semi-empirical calculations of resonance energies appears to be novel.

An answer can now be given to the old question, originally raised by Hückel theory, as to why the $\pi \to \pi^*$ excitation energy is greater than (minus) DE and why neither quantity is equal to $|2\beta|$. The excitation energy would indeed be $|2\beta|$ provided that a simple average of $^1B_{1u}$, $^3B_{1u}$, $^1B_{2u}$, and $^1B_{2u}$ excitation energies is taken, and each excitation energy is determined theoretically in a one-configuration approximation. The experimental value of $\Delta E(B_u)$ is about 70% of the SCF value [25] of $|2\beta|$, because the one-configuration approximation is inadequate. By contrast, the empirical value of DE is about 50% of 2β *for reasons which lie mainly within MO theory itself.* The one-electron contribution would be 2β if pairs of OAOs were used to form the two-centre MOs. Using non-orthogonal AOs changes the one-electron contribution by about 39% of 2β. The remaining reduction, or about 11% of 2β, is due in almost equal measure to the electronic repulsion between the π MOs and the combined effects of σ–π and π–π correlation.

The better variational calculations favour the localised structure, and reduce the magnitude of DE. A value of $-85\,\text{kcal mol}^{-1}$ probably represents the limit of exact MO calculations using method II. Parr and Mulliken obtained $-73.1\,\text{kcal mol}^{-1}$ using a simple STO description of the π MOs. This small magnitude comes from using the GMS core Hamiltonian ($\beta = -2.679\,\text{eV}$). If the core Hamiltonian appropriate to a minimal basis SCF calculation ($\beta = -3.5\,\text{eV}$) had been used, Parr and Mulliken would have obtained a value around $-100\,\text{kcal mol}^{-1}$.

Origin of the delocalisation energy

Ever since the work of Parr and Mulliken it has been known that the contribution of the π-electronic repulsion to DE is relatively small and in favour of the localised structure (i.e. positive). The main part of DE is calculated from an effective one-electron Hamiltonian, and to this extent the Hückel theory was roughly correct. The π electrons delocalise because β is negative. But why is β negative? It is easy to show that the part of β which is associated with the kinetic energy operator is about $-7.2\,\text{eV}$, so that the potential energy part is actually positive. Thus, in sofar as π-delocalisation can be considered in a fixed σ framework, its origin lies in the lowering of kinetic energy.

The role of the kinetic energy in binding, and its relation to potential energy, was originally investigated by Ruedenberg and his school. Ruedenberg [26] has also given the correct interpretation of the resonance integral. The wrong interpretation, in terms of a negative total contribution from potential energy, comes from visualising the attraction of a nuclear centre for an overlap charge distribution in terms of conventional, non-orthogonal AOs, and then turning a blind eye to the presence of overlap integrals in the MO normalisation factors. Thus, the formal neglect of the overlap integral, where this does not imply an orthogonalisation of

the basis, is not just one approximation amongst others. It actually suggests a wrong physical model.

To sum up, the overlap integral is implicitly involved twice in the expression for DE: once, in the interpretation of β, and again in accounting for the additional stability which non-orthogonal AOs give to the localised structure. Both factors must be borne in mind if a Hückel type of formalism is to be associated with a qualitatively correct model of π delocalisation.

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