

Charge and current densities for approximate molecular wavefunctions

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The charge and current densities for variational molecular wavefunctions in finite basis spaces are examined, and the consequences of their failure to satisfy a continuity equation, and the local charge generation and annihilation, are discussed. The current can be used to compute observables even though it might not satisfy the continuity equation. When approximate wavefunctions are used charge is not conserved locally, but is conserved globally, and the details of the structure of the charge sources and sinks are discussed in the case of benzene. A valence bond technique for the calculation of current density is described and applied to benzene. Valence bond and molecular orbital methods are compared.

This paper examines some of the aspects of the current density in molecules. It has been pointed out previously [1] that non-conservation of charge is a problem when approximate wavefunctions are used to calculate the current density, and we explore some of the consequences of this deficiency.

The formal definition of current density depends on selecting a lagrangian density functional which leads to the Maxwell and Schrödinger equations when varied with respect to the potentials \mathbf{A} , ϕ and the complex conjugate of the matter field ψ^* . If we write

$$\mathcal{L}\{\psi, \psi^*, \mathbf{A}, \phi\} = \mathcal{L}_{\text{em}}\{\mathbf{A}, \phi\} + \int dt \int d\tau \psi^* \times \left[\left(i\hbar(\partial/\partial t) + e \sum_{k=1}^n \phi_k \right) - (1/2m_e) \sum_{k=1}^n (\mathbf{p}_k + e\mathbf{A}_k)^2 - V \right] \psi, \quad (1)$$

\mathcal{L}_{em} being the electromagnetic field lagrangian, then functional differentiation with respect to ψ^* leads to the Schrödinger equation and differentiation with respect to \mathbf{A} , ϕ leads to the Maxwell equations if we make the identifications

$$\rho(r) = -e \sum_k \int d\tau \psi^* \psi \delta(\mathbf{r}_k - \mathbf{r}), \quad (2a)$$

$$\mathbf{j}(r) = \sum_k \int d\tau [(i\hbar/2m_e)(\psi^* \nabla_k \psi - \psi \nabla_k \psi^*) - (e^2/m_e) \mathbf{A}_k \psi^* \psi] \delta(\mathbf{r}_k - \mathbf{r}). \quad (2b)$$

These constitute the *canonical* charge and current densities. They are not independent because they must satisfy the continuity equation

$$\nabla \cdot \mathbf{j} + \partial \rho / \partial t = 0. \quad (3)$$

If we require ψ to have the form of an antisymmetrized product of n one-electron orthonormal functions the lagrangian density functional should be written

$$\begin{aligned} \mathcal{L}\{\{\psi_k; k=1, \dots, n\}, \{\psi_k^*; k=1, \dots, n\}, \mathbf{A}, \phi\} = & \mathcal{L}_{em}\{\mathbf{A}, \phi\} \\ & + \sum_k \int dt \{ \int d\tau_1 \psi_k^*(1) [i\hbar(\partial/\partial t) + e\phi(1)] \psi_k(1) \\ & - (1/2m_e) \int d\tau_1 \psi_k^*(1) [\mathbf{p} + e\mathbf{A}(1)]^2 \psi_k(1) - \int d\tau_1 \psi_k^*(1) V(1) \psi_k(1) \\ & - \frac{1}{2} \sum_l (e^2/4\pi\epsilon_0) \int d\tau_1 d\tau_2 \psi_k^*(1) \psi_k(1) (1/r_{12}) \psi_l^*(2) \psi_l(2) \\ & + \frac{1}{2} \sum_l (e^2/4\pi\epsilon_0) \delta(\sigma_k, \sigma_l) \int d\tau_1 d\tau_2 \psi_k^*(1) \psi_l(1) (1/r_{12}) \psi_l^*(2) \psi_k(2) \}, \quad (4) \end{aligned}$$

where the interelectronic repulsion has been extracted from the potential V , and where σ_k is the spin part of ψ_k . Functional differentiation of this expression produces Hartree-Fock equations for the ψ_k and Maxwell equations so long as we make the identifications

$$\rho(\mathbf{r}) = -e \sum_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}), \quad (5 a)$$

$$\begin{aligned} \mathbf{j}(\mathbf{r}) = \sum_k \{ i(e\hbar/2m_e) (\psi_k^*(\mathbf{r}) \nabla \psi_k(\mathbf{r}) - \psi_k(\mathbf{r}) \nabla \psi_k^*(\mathbf{r})) \\ - (e^2/m_e) \mathbf{A}(\mathbf{r}) \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}) \}. \quad (5 b) \end{aligned}$$

These quantities satisfy the continuity equation, as may be easily verified.

In some cases it is of interest to consider the one-electron decomposition of the current density. The canonical form of the current can be constructed in the same way as before, but basing the development on the appropriate one-electron lagrangian (which is virtually the same as equation (4) but lacks a sum over k). Variation with respect to the potentials leads to the identification of the canonical one-electron current density

$$\mathbf{j}_k = \mathbf{j}_k^{\text{eff}} + \mathbf{j}_k^{\text{exch}}, \quad (6)$$

where the first term is formally identical to the summand in equation (5 b). The second term, $\mathbf{j}_k^{\text{exch}}$, is the *exchange current* of electron k , and its explicit form is not easily obtained. Nevertheless, when summed over all the electrons in the system, all the individual exchange currents cancel, and so they are not needed in the calculation of molecular properties. The total current may therefore be expressed as the sum of individual one-electron effective currents:

$$\mathbf{j} = \sum_k \mathbf{j}_k^{\text{eff}}. \quad (7)$$

The origin of the exchange currents may be traced to the non-local character of the potential sampled by an individual particle when it moves in the field of others [2]. Discussions of exchange contributions to nucleons have been given by Korolev [3] and Wild [4].

In practice a *finite* basis set is normally used to expand the many-electron function ψ in equation (1) and in the Schrödinger equation derived from that lagrangian, or in the one-electron functions ψ_k in equation (4) and in the Hartree-Fock equations associated with them. Neither the Schrödinger equation nor the Hartree-Fock equations, however, can in general be satisfied exactly by

expansions of this type, and in order to determine the best set of expansion coefficients well-known techniques are used, which normally consist of a type of averaging over the whole space. An important consequence of the approximation procedure is that when the optimum expansion is used in equation (2) or (5) the canonical charge and current densities fail to satisfy the continuity equation. For any stationary system, however, the global integral of $\nabla \cdot \mathbf{j}$ is zero: this can be seen by noting that

$$\int d\tau \nabla \cdot \mathbf{j} = \mathcal{L} - \mathcal{L}^* = 0 \tag{8}$$

because \mathcal{L} is real. The significance of this result is that the charge density is conserved globally even though it might not be conserved locally. In other words, charge creation in one region must be matched by charge annihilation elsewhere.

The canonical current density should be suspected as being only an *effective* current density in the sense that, even though it does not satisfy the continuity equation in approximate calculations of the wavefunction, it can be used to calculate the energy of interaction with some external field through the conventional expression

$$\delta E = - \int d\tau \mathbf{j} \cdot \delta \mathbf{A}. \tag{9}$$

We may demonstrate the validity of this interpretation of \mathbf{j} by considering the energy of a molecule in the presence of two magnetic fields, I and II. The hamiltonian for the system is

$$= H(0) + H(I) + H(II) + H(I, I) + H(I, II) + H(II, II), \tag{10}$$

where the labels denote the order of the fields. The expansion of the wavefunction can be labelled similarly :

$$|\rangle = |0\rangle + |I\rangle + |II\rangle + |I, I\rangle + |I, II\rangle + |II, II\rangle + \dots \tag{11}$$

Perturbation up to third order with an arbitrary basis set leads to the following expressions for the energies :

$$E(I) = 2 \sum_{\text{occ}} \langle 0 | H(I) | 0 \rangle, \tag{12 a}$$

$$E(I, I) = \sum_{\text{occ}} \{ 2 \langle 0 | H(I, I) | 0 \rangle + \langle I | H(I) | 0 \rangle + \langle 0 | H(I) | I \rangle \}, \tag{12 b}$$

$$E(I, II) = 2 \sum_{\text{occ}} \{ \langle 0 | H(I, II) | 0 \rangle + \langle I | H(II) | 0 \rangle + \langle 0 | H(II) | I \rangle \}, \tag{12 c}$$

$$E(I, I, I) = \frac{2}{3} \sum_{\text{occ}} \{ \langle I, I | H(I) | 0 \rangle + \langle 0 | H(I) | I, I \rangle + \langle I | H(I) | I \rangle + 2 \langle I | H(I, I) | 0 \rangle + 2 \langle 0 | H(I, I) | I \rangle \}, \tag{12 d}$$

$$\begin{aligned} E(I, II, II) &= 2 \sum_{\text{occ}} \{ \langle II, II | H(I) | II \rangle + \langle II, II | H(I) | 0 \rangle + \langle 0 | H(I) | II, II \rangle \\ &\quad + \langle 0 | H(I, II) | II \rangle + \langle II | H(I, II) | 0 \rangle \} \\ &= \sum_{\text{occ}} \{ \langle II, II | H(I) | 0 \rangle + \langle 0 | H(I) | II, II \rangle + \langle II | H(I) | II \rangle \\ &\quad + \frac{1}{2} \langle I, II | H(II) | 0 \rangle + \frac{1}{2} \langle 0 | H(II) | I, II \rangle + \langle 0 | H(II, II) | I \rangle \\ &\quad + \frac{1}{2} \langle I | H(II) | II \rangle + \frac{1}{2} \langle II | H(II) | I \rangle + \langle I | H(II, II) | 0 \rangle \\ &\quad + \frac{3}{2} \langle II | H(I, II) | 0 \rangle + \frac{3}{2} \langle 0 | H(I, II) | II \rangle \}. \end{aligned} \tag{12 e}$$

The same energy terms may also be generated by selecting the appropriate order of the expansion of the integrated form of equation (9). A difficulty in the procedure is that when two fields are present the integrated form of equation (9) depends on the way that the two fields are scaled up from zero to their full strength. It is shown in Appendix A that the energy term of order $I^p II^q$, $E(p, q)$ is in fact independent of the relation between the scaling up of I and II for a flexible class of switching functions, and is given by

$$E(p, q) = -(1/q) \int d\tau \mathbf{j}(p, q-1) \cdot \mathbf{A}(\text{II}), \quad (13)$$

where $\mathbf{j}(p, q)$ is the term of order $I^p II^q$ in the expansion of the current density. This confirms that the canonical current density may be used to compute observables even though it does not satisfy the continuity equation.

The conservation of charge is an aspect of the divergence of the current density. The extent of charge non-conservation is a measure of the incompleteness of the basis because we have seen that the equation of continuity is satisfied by exact but not, in general, by inexact wavefunctions. The conservation of charge, however, is a necessary but not sufficient condition for the exact (or Hartree-Fock) wavefunctions, and the observation that it is conserved does not necessarily entail that the wavefunction is good. It follows that local conservation of charge cannot be used alone as a reliable criterion in a minimization procedure for the local or the global improvement of a wavefunction, but it might provide a sensitive auxiliary test.

The benzene molecule provides an illuminating example of these problems. Furthermore, a detailed study of current density distribution in this molecule should throw light on the controversy about the reality of ring currents.

First we summarize the results of a calculation of the π -electron current density on the basis of conventional methods. As a consequence of the hexagonal symmetry, the $2p_z\pi$ -orbitals have a simple form totally determined by symmetry, and when gauge-invariant atomic orbitals are used, the first-order perturbed functions arise from the field-dependent parts of the orbitals because the first-order bond orders vanish identically.

Using the numerical parameters of reference [1] the general pattern of currents shown in figure 1 is found. This is analysed in more detail in figures 2 and 3. The overall current in the ring is diamagnetic, but locally there may be

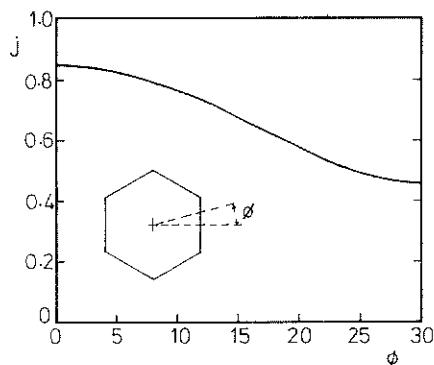


Figure 1. Current through a vertical plane in the benzene molecule at an angle ϕ , in units of $e^2 B / 2m_e$.

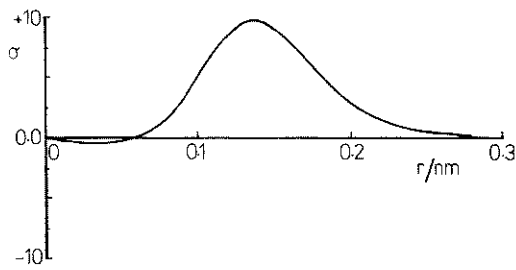


Figure 2. Plot of σ as a function of distance from the centre of the benzene ring, where $\sigma = \int_{-z}^z j dz$, at $\phi = 0$ and cylindrical coordinate r , in units of $(e^2 B / 2m_e) / \text{nm}$.

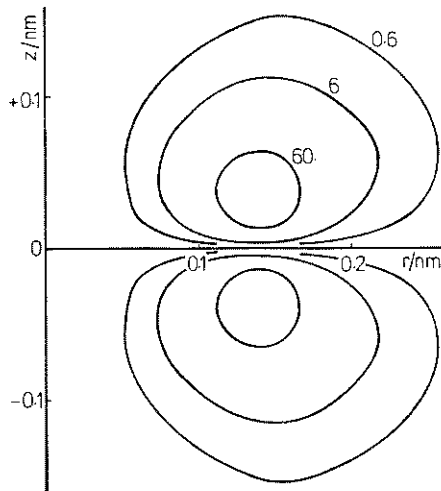


Figure 3. Creation of charge in the semi-plane $\phi = 17.5^\circ$ in units of $(e^2 B / 2m_e) / \text{nm}^2$.

paramagnetic contributions. For example, figure 2 reveals that there is a small paramagnetic flow close to the ring centre (within a radius of 60 pm). Figure 1 shows that the current through a half-plane varies significantly as it is moved from an angle that bisects a carbon-carbon bond to one that passes through a carbon atom. This variation of current indicates the charge creation going on in that sector of the molecule: the slope of the curve in the figure gives the rate of annihilation of charge in the region. The distribution of charge sources and sinks in a plane perpendicular to the ring is shown in figure 4. This reflects, of course, the structure of the amplitude of the π -bond.

The remarkably poor local behaviour of the charge and current densities for the present system comes from the restricted arbitrary choice of the $2p_z\pi$ -G.I.A.O.'s as basis. There is, in fact, no function satisfying the general requirements of a basis function which, when substituted for guarantees local charge conservation. Other functions might improve conservation, but their use

cannot be justified on this ground alone, without also invoking some energy minimization procedure.

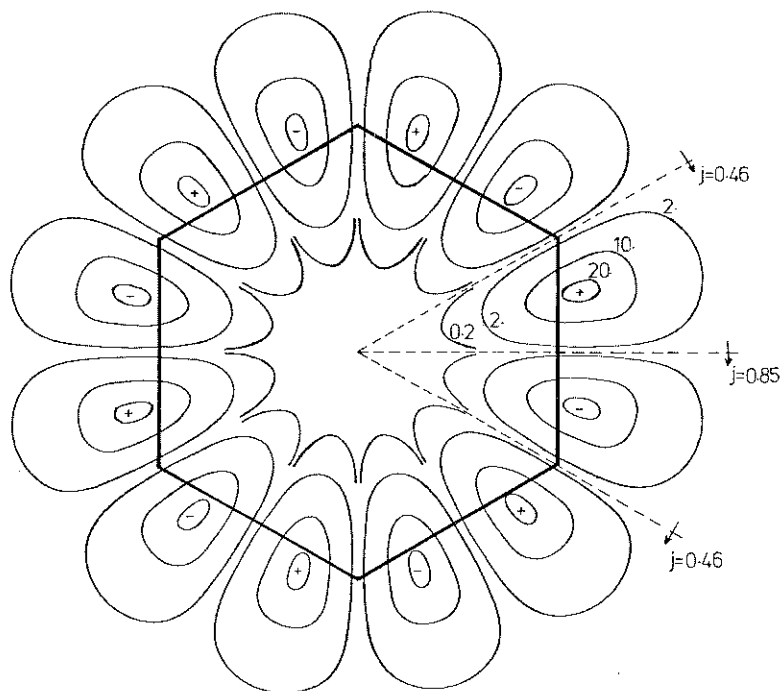


Figure 4. Pattern of charge creation and current in the benzene ring (obtained by projecting figure 3, and its analogues, on to the horizontal plane). The magnetic field lies along z , perpendicular to the ring.

The final resolution of the problem of knowing whether the current pattern depicted in figure 1 is purely a consequence of the choice of G.I.A.O.'s as a basis cannot be obtained until a full *ab initio* calculation becomes feasible. Nevertheless, some clarification might be expected if a commensurate distribution of currents could be obtained on the basis of an entirely different calculation. With this in mind we have carried out an entirely exploratory *valence-bond* (V.B.) calculation of currents in the benzene molecule.

We decided to examine the V.B. current density on the basis of the *ab initio* V.B. calculation of the structure of benzene reported by Norbeck and Gallup [5]. They took into account the 175 different bonding diagrams that can be arranged into 22 ${}^1A_{1g}$ -functions. Unfortunately, no calculation of comparable quality is available for the excited states, and yet these must be available for the computation of the paramagnetic current. In order to obtain an indication of the V.B. current density, we have taken one of the Norbeck and Gallup ground-state functions (using as a basis only the five covalent and the 12 ortho-polar structures (figure 5), and have constructed crude excited states by one of the standard approximate procedures [6]. (The ground-state energy calculated on this covalent/ortho-polar basis lies only 0.0421 hartree above the full 175-structure calculation.) On the presence of a homogeneous, constant, magnetic

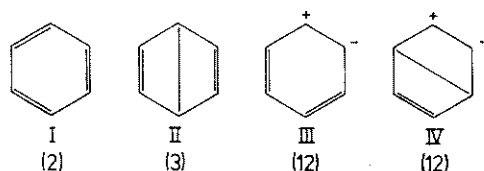


Figure 5. Representative Rumer diagrams considered in the VB calculation; the numbers in brackets indicate the number of equivalent diagrams of each type.

field B , functions of ${}^1A_{2g}$ symmetry are mixed into the ground state, in first-order perturbation theory. As there are no non-polar A_{2g} functions, the perturbed function depends on the presence of the ortho-polar structures of Types III, IV. The calculation of the approximate excited state function is outlined in Appendix B: only the function $\Phi_1 = 0.1667\Phi(\text{III}) + 0.0610\Phi(\text{IV})$ makes a significant contribution to the current, and so we confine attention to it.

Method	Reference	Molar susceptibility/ $10^{-9} \text{ m}^3 \text{ mol}^{-1}$		
		χ_n^d	χ_n^p	χ_π
VB estimate	This work	-0.726	+0.297	-0.429
MO, <i>ab initio</i>	(7)	-0.748		
MO, <i>ab initio</i>	(8)	-0.698		
MO, semi-empirical	(1)†	-0.709	+0.278	-0.431

† Corrected for the normalization of the wavefunction to non Z.D.O. π electron magnetic susceptibility.

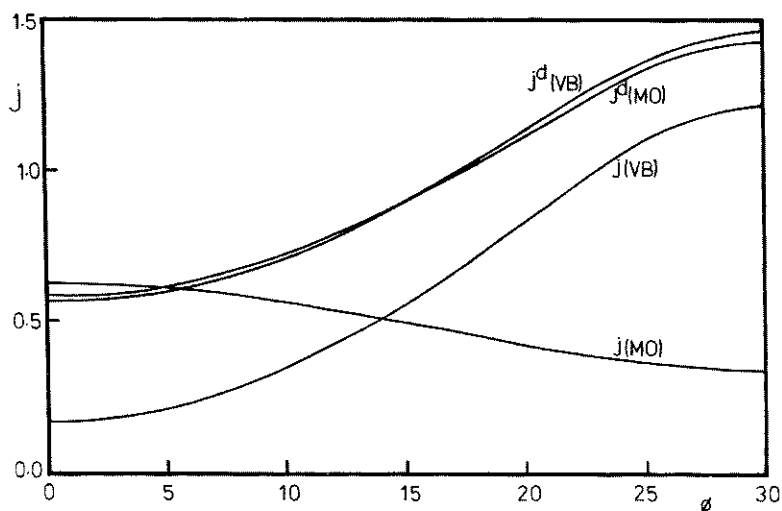


Figure 6. Current through a vertical plane in the benzene molecule at angle ϕ , in units of $e^2 B / 2m_e c$. The results of VB and of normalized semi-empirical M.O. calculation and their respective diamagnetic parts are shown.

The V.B. current density and V.B. magnetic susceptibility were calculated by the method summarized in Appendix C. Magnetic susceptibilities estimated in this way are reported in the table, together with various types of M.O. results. The V.B. current density distribution is shown in figures 6–9. In figure 6 the currents across half-planes extending from the centre of the molecule are plotted, together with the same quantity calculated on the basis of the semi-empirical M.O. method mentioned before (but after a correction for the non-ZDO normalization). Their diamagnetic contributions are also shown. The average V.B. ring current is 30 per cent greater than the M.O. current, and this shows itself in the paramagnetic part of the magnetic susceptibility. The diagrams show that there is a large charge non-conservation in the V.B. description, and this must be an indication of the poor quality of at least the excited state functions. In figures 7–9 the radial distribution of the current (integrated along the z -axis) is shown for three different planes. For comparison, the equivalent semi-empirical M.O. result is shown, as well as the two diamagnetic parts.

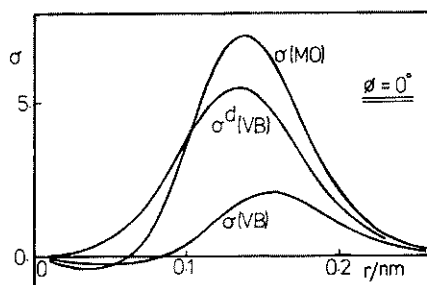


Figure 7. Plot of σ as a function of distance from the centre of the benzene ring at $\phi = 0^\circ$ and cylindrical coordinate z , in units of $(e^2 B / 2m_e) / \text{nm}$.

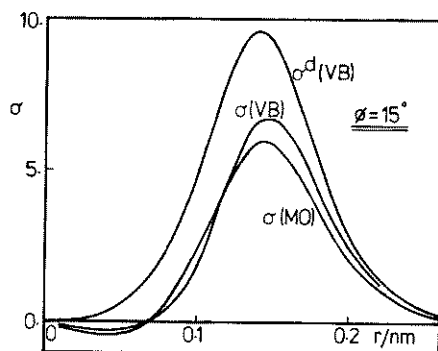


Figure 8. As in figure 7, but for $\phi = 15^\circ$.

The V.B. work points out the feasibility of *ab initio* calculations of magnetic properties. The dominating problem is the calculation of excited states of the appropriate symmetry, and if the V.B. technique is to be developed, that must

be the centre of attention. The immediate conclusion as far the aim of the present calculation is concerned, is, however, somewhat ambiguous. A sanguine view would be that since the V.B. calculation gives a ring current not less than (and in fact, 30 per cent more than) the ring current estimated in the framework of the semi-empirical M.O. theory with basis set, its existence is supported and is not simply a manifestation of some approximation.

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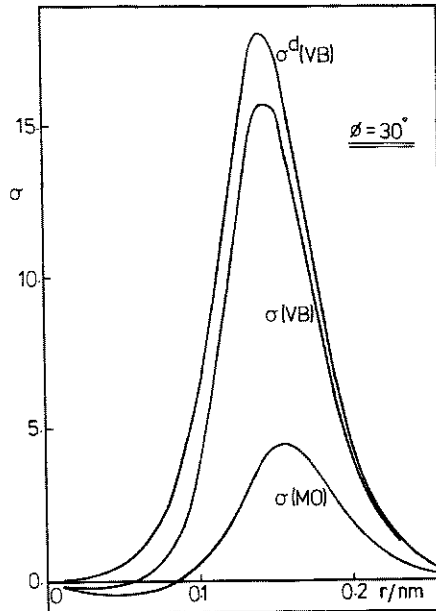


Figure 9. As in figure 7, but for $\phi = 30^\circ$.

APPENDIX A

In this Appendix we prove the following theorem.

Theorem. The interaction energy $E(p, q)$ of order $I^p II^q$ is independent of the manner of scaling the two fields from zero to their final value so long as the wavefunction is variationally determined.

We consider the case of two magnetic fields I, II which are switched from zero to their full strengths as $\lambda \mathbf{A}(I), \mu \mathbf{A}(II)$ with $\lambda, \mu : 0 \rightarrow 1$ and assume these scaling functions to be such that λ and μ are regular in all their domains. λ may be expressed as a power series in μ :

$$\lambda = \sum_s c_s \mu^s \tag{A 1}$$

with

$$\sum_s c_s = 1. \tag{A 2}$$

The interaction energy is given by the conventional expression

$$\delta E = - \int d\tau \mathbf{j} \cdot \delta \mathbf{A}. \tag{A 3}$$

The contribution of order $I^p II^q$ is determined by

$$\delta E(p, q) = - \int d\tau \{ \mathbf{j}(p-1, q) \cdot \delta \mathbf{A}(I) + \mathbf{j}(p, q-1) \cdot \delta \mathbf{A}(II) \} \tag{A 4}$$

and so

$$\begin{aligned} E(p, q) &= - \int d\tau \{ \int d\lambda \lambda^{p-1} \mu^q \mathbf{j}(p-1, q) \cdot \mathbf{A}(I) \\ &\quad + \int d\mu \lambda^p \mu^{q-1} \mathbf{j}(p, q-1) \cdot \mathbf{A}(II) \} \\ &= \sum_s c_s \frac{1}{ps+q} \{ -s \int d\tau \mathbf{j}(p-1, q) \cdot \mathbf{A}(I) \\ &\quad - \int d\tau \mathbf{j}(p, q-1) \cdot \mathbf{A}(II) \}, \end{aligned} \tag{A 5}$$

$$\text{If } (1/p) \int d\tau \mathbf{j}(p-1, q) \cdot \mathbf{A}(I) = (1/q) \int d\tau \mathbf{j}(p, q-1) \cdot \mathbf{A}(II) \tag{A 6}$$

and using equation (A 2), the expression equation (A 5) for $E(p, q)$ becomes independent of the set of c_s used and the energy may be calculated for any convenient choice. In particular we may take all c_s except $c_n = 1$ to be zero. For $n=0$ we obtain

$$E(p, q) = -(1/q) \int d\tau \mathbf{j}(p, q-1) \cdot \mathbf{A}(II) \tag{A 7a}$$

and in the limit of very large n ,

$$E(p, q) = -(1/p) \int d\tau \mathbf{j}(p-1, q) \cdot \mathbf{A}(I), \tag{A 7b}$$

results used in the text.

Consider the lagrangian

$$\mathcal{L}(x, y) = \mathcal{L}\{\psi, \psi^*, \phi, \mathbf{A}(I), \mathbf{A}(II)\} \tag{A 8}$$

with $\mathbf{A}(I) = x\mathbf{a}(I)$ and $\mathbf{A}(II) = y\mathbf{a}(II)$ and let it be decomposed into a power series in x and y :

$$\mathcal{L}(x, y) = \sum_{p, q} \mathcal{L}(p, q|x, y) \tag{A 9}$$

with

$$\mathcal{L}(p, q|\alpha x, \beta y) = x^p \beta^q \mathcal{L}(p, q|x, y).$$

For the homogeneous function $\mathcal{L}(p, q)$ we can write

$$\mathcal{L}(p, q|x, y) = (x/p)(\partial/\partial x) \mathcal{L}(p, q|x, y) \tag{A 10a}$$

$$= (y/q)(\partial/\partial y) \mathcal{L}(p, q|x, y). \tag{A 10b}$$

$\mathcal{L}(p, q, x, y)$ depends on x, y explicitly through $\mathbf{A}(I)$ and $\mathbf{A}(II)$, and implicitly through ψ, ψ^* :

$$\begin{aligned} x(\partial/\partial x) \mathcal{L}(p, q, x, y) &= \int d\tau x\mathbf{a}(I) \cdot \{ \delta \mathcal{L}(p, q|\psi, \psi^*, \phi, \mathbf{A}(I), \mathbf{A}(II)) / \delta \mathbf{A}(I) \} \\ &\quad + x \int d\tau (\delta \mathcal{L} / \delta \psi) (\partial \psi / \partial x) + x \int d\tau (\mathcal{L} / \delta \psi^*) (\partial \psi^* / \partial x) \\ &= \int d\tau \mathbf{A}(I) \cdot \mathbf{j}(p-1, q), \end{aligned} \tag{A 11}$$

because $\partial \psi / \partial x$ and $\partial \psi^* / \partial x$ are in the subspace where ψ is varied, and the coefficients of the expansion in the basis $\{\psi_k\}$ are found by making

$$\int d\tau (\delta \mathcal{L} / \delta \psi^*) \psi_k^* = 0, \tag{A 12}$$

etc. The combination of equations (A 11) with (A 10a) and (A 10b) completes the proof of equation (A 6) and hence of the theorem.

APPENDIX B

In this Appendix we indicate the method used to construct the ${}^1A_{2g}$ excited V.B. states of benzene, using as a basis the covalent and ortho-polar structures.

The Kekulé (I, in figure 5) and Dewar (II) covalent structures give no contribution to A_{2g} states. From the ortho-polar structures (III, IV) we can form two combinations of A_{2g} symmetry: these we denote $\Phi(\text{III})$ and $\Phi(\text{IV})$, the coefficients being ± 1 for each individual bonding diagram. Using the rules set out by Craig [6] for calculating matrix elements between polar structures, we arrive at the following secular equation:

$$\begin{vmatrix} 24x + 62.40 & 12x - 3.36 \\ 12x - 3.36 & 24x - 131.52 \end{vmatrix} = 0.$$

The corresponding eigenbases are

$$\Phi_1 = 0.1667 \Phi(\text{III}) + 0.0610 \Phi(\text{IV}), \quad E_1 = Q + 207 \text{ kJ mol}^{-1},$$

$$\Phi_2 = 0.1667 \Phi(\text{III}) - 0.2277 \Phi(\text{IV}), \quad E_2 = Q + 849 \text{ kJ mol}^{-1}.$$

In terms of the same parameter Q , the energy of the ground state on the same covalent ortho-polar basis is $E_0 = Q - 550 \text{ kJ mol}^{-1}$. The energy gap to the first excited state is therefore $\sim 757 \text{ kJ mol}^{-1}$.

This calculation is based on a zero differential overlap (Z.D.O.) approximation. All the calculations of current density are evaluated to second order in the overlap integral between two neighbouring p_z -orbitals. The coefficients in Φ_1 were corrected accordingly, keeping the constraint that their ratio should be the same as above.

APPENDIX C

In this Appendix we outline the method of calculating the current density in a V.B. framework.

When the wavefunction in the canonical expression for the current density is written in the form of a perturbation expansion

$$\Psi = \Phi_0 + iC\Phi_1 + \dots,$$

$$C = -\{ehB/2m_e(E_0 - E_1)\}L_{10},$$

$$L = \sum_i \mathbf{k} \wedge \mathbf{r}_i \cdot \nabla_i,$$

the first-order term in the current density may be written as a sum of the paramagnetic and diamagnetic parts, $\mathbf{j} = \mathbf{j}^p + \mathbf{j}^d$ with

$$\mathbf{j}^p(\mathbf{r}) = \{e^2 \hbar^2 B / m_e^2 (E_0 - E_1)\} L_{10} D_{01}(\mathbf{r}),$$

$$\mathbf{j}^d(\mathbf{r}) = -\{e^2 B / 2m_e\} \mathbf{k} \wedge \mathbf{r} \rho(\mathbf{r}),$$

where

$$D_{01}(\mathbf{r}) = \frac{1}{2} \sum_i \int d\tau \int d\sigma (\Phi_0 \nabla_i \Phi_1 - \Phi_1 \nabla_i \Phi_0) \delta(\mathbf{r} - \mathbf{r}_i),$$

$$\rho(\mathbf{r}) = \sum_i \int d\tau \int d\sigma \Phi_0 \Phi_0 \delta(\mathbf{r} - \mathbf{r}_i).$$

τ and σ denote space and spin coordinates.

The paramagnetic and diamagnetic components of the magnetic susceptibility can be obtained at once from

$$\chi^p = -\{N\mu_0 e^2 \hbar^2 / 2m_e^2 (E_0 - E_1)\} |L_{01}|^2,$$

$$\chi^d = -\{N\mu_0 e^2 / 4m_e\} \int d\tau d\sigma |\mathbf{k} \wedge \mathbf{r}|^2 \Phi_0 \Phi_0.$$

The calculation of $D_{01}(\mathbf{r})$ is difficult because Φ_0 and Φ_1 are linear combinations of determinantal functions, but we have carried out the calculation up to second order in the overlap integral S_{ab} between pairs of neighbouring p_z -orbitals, and considering $d_{ab} = \frac{1}{2}(p_{za} \nabla p_{zb} - p_{zb} \nabla p_{za})$ to be of the same order as S_{ab} . The expansion of $D_{01}(\mathbf{r})$ involves the following terms between symmetrical functions with coefficients ± 1 of A_{1g} (subscript 1) and A_{2g} (subscript 2) symmetry :

$$D(N_1, N_2) = A(N_1, N_2) \Delta \{S(N_1, N_1) S(N_2, N_2)\}^{-1/2}$$

with $S(N_i, N_j)$ the overlap integral, Δ the mean of the d_{ij} functions

$$\Delta = \frac{1}{6}(d_{ab} + d_{bc} + d_{cd} + d_{de} + d_{ef} + d_{fa}),$$

and $A(N_1, N_2)$ the set of numbers

	N_1	I	II	III	IV
$N_2 :$	III ₂	30	36	288 S_{ab}	216 S_{ab}
	IV ₂	24	36	216 S_{ab}	288 S_{ab}

a, b, \dots, f denote the six $2p\pi_z$ -orbitals.

These expressions were used to calculate $D_{01}(\mathbf{r})$ and then $\mathbf{j}^p(\mathbf{r})$. Integration then leads directly to L_{01} and χ^p . For the diamagnetic contributions we used the bond-order matrix given by Norbeck and Gallup [5] for their covalent singly-polar calculation. This part is far less dependent on the quality of the wavefunctions.

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