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The Population Analysis of Valence Bond Wave Functions

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The population analysis of valence bond (v.b.) wave functions is shown to lead to a new way of understanding the role of the structures of valence bond theory. It also gives a detailed insight into the electronic organization in molecules as estimated by valence bond theory. Three examples, H_2, LiH and the butadiene π electrons are discussed.

Introduction

One important objective of theoretical chemistry is the provision of simple pictures of the electron distribution within molecules. Such pictures can never be precise, but they provide the only easy way of visualising the factors which govern molecular structure. To this end, various quantities have been defined[1] which are said to give such insight into the electron organization within molecules. These quantities are all derived from the concept of atoms in molecules and the resulting idea of the charge on an atom, or in a bond, in a molecule. The most thoroughgoing definitions of such quantities are the population analysis formulas proposed by Mulliken.[2] These were originally defined to apply to the results of a one determinant molecular orbital (MO) wave function, but they have since been developed further by Karo[3] to deal with many determinant MO wave functions. Since it is now feasible to carry out calculations on a valence bond basis and since it is most helpful if both MO and valence bond wave functions can be interpreted in the same way, we report in this paper a valence bond wave function population analysis which parallels that of MO wave functions already in use. Previously, the general method of interpreting valence bond wave functions[4] has been quite crude and very different from that used for MO wave functions, so it has been difficult to compare the results given by the two kinds of wave function. It turns out, furthermore, that the population analysis also leads to a helpful way of understanding the role of the structures of valence bond theory. Many earlier interpretations of the significance of these structures have been unsatisfactory since they assumed that the wave functions of the structures are orthogonal. In fact, the structure wave functions are sometimes very far from orthogonal and so one structure is in part contained in another.

This situation has been discussed a number of times,[5] and various attempts have been made to recast valence bond theory in a form which makes such concepts as the covalent and ionic structures correspond to orthogonal functions and so be mutually exclusive. The most recent and detailed effort in this direction is Shull's work[5] on the two electron homopolar bond. This approach departs rather far from the conventional ideas of valency, and it now seems likely that no simple and perfectly satisfactory solution to the non-orthogonality problem of valence bond theory will be found. Nevertheless, all the successful but qualitative ideas of the valence bond theory of the structure of large molecules, due in the main to Pauling,[4] are so useful that some method of analysing valence bond wave functions is desirable.

The procedure suggested in this paper is a population analysis method. This is a compromise between a formal analysis and the intuitive ideas of chemical valence theory. From a formal point of view, it has the disadvantage of starting out from an arbitrary form of the wave function itself and of the basis functions. Its advantages are first, its close connection with MO population analysis and with chemical thinking in general, and second, the ease with which it may be extended to deal with large molecules.

The general approach to any kind of population analysis is simple. Given a 2n electron wave function, Ψ, for a molecule, this is a function of 6n spatial coördinates (x_1, y_1, z_1, $\ldots\ldots z_{2n}$) and 2n spin coördinates ($\sigma_1 \ldots\ldots \sigma_{2n}$). If Ψ is normalized to unity, then the function

$$\begin{aligned}\rho(x,y,z) &= 2n\int\Psi^*\Psi dx_2,dy_2,dz_2\ldots dz_{2n}\,d\sigma_1\ldots d\sigma_{2n} \\ &= 2n\int\Psi^*\Psi d\tau_2\ldots d\tau_{2n}d\sigma_1 \qquad (1)\end{aligned}$$

is an electron density function in real space, describing the probability of finding an electron at the point x,y,z of real space. (It is important to notice that much of the information in the wave function (Ψ) is lost during this integration, so that ρ is much poorer in information than is Ψ. The second order density matrix, which has the disadvantage of being much more complicated than ρ, is as far as one can go while retaining all the information present in the wave function.) If Ψ is already expressed as, or can be transformed into, sums and products of the AOs of the constituent atoms (χ), then ρ can be put into the form of sums and products of AOs of the kind $\chi_a\chi_a$ and $\chi_a\chi_b$. The electron density of the molecule, then, is a superposition of a number of simpler density functions, each of which is associated with a particular AO or with a product of two different AOs. Now there is no unique way of expressing the molecular wave function in terms of the AOs of the constituent atoms, but in practice one particular way is usually clearly more sensible than others.

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[1] C. A. Coulson, *Proc. Roy. Soc.* (*London*), **169A**, 419 (1939). B. H. Chirgwin and C. A. Coulson, *ibid.*, **201A**, 196 (1950). R. McWeeney, *J. Chem. Phys.*, **19**, 1614 (1950); **20**, 920 (1951).

[2] R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

[3] A. M. Karo, *ibid.*, **31**, 182 (1959).

[4] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1960.

[5] J. C. Slater, *J. Chem. Phys.*, **19**, 220 (1951). R. McWeeney, *Proc. Roy. Soc.* (*London*), **227A**, 288 (1954), and previous papers. J. Braunstein and W. T. Simpson, *J. Chem. Phys.*, **23**, 174 (1955). R. S. Berry, *ibid.*, **30**, 936 (1959). H. Shull, *J. Am. Chem. Soc.*, **82**, 1287 (1960).

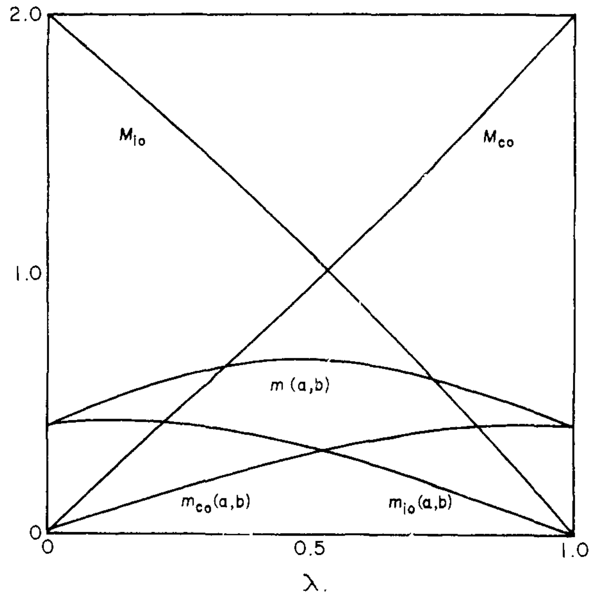

Fig. 1.—Structure populations, M_{co} and M_{io}, overlap populations, m_{co} (a,b) and m_{io} (a,b), and the total overlap population, m(a,b), in the H_2 like case: $S_{a,b} = 0.50$: see eq. 12 and Table I.

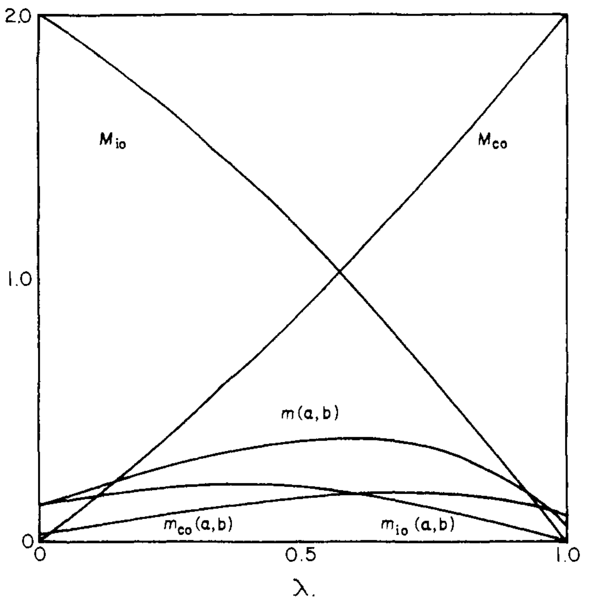

Fig. 2.—Structure populations, M_{co} and M_{io}, overlap populations, m_{co}(a,b) and m_{io}(a,b) and the total overlap population, m(a,b) in the H_2 like case: $S_{a,b} = 0.25$; see eq. 12 and Table I.

It is also true that, in the molecule, it is convenient to work with one electron functions which differ somewhat from the AOs of the free atoms, but such modified AOs can always be expressed as linear combinations of the free atom AOs and the analysis completed, in principal at least, in terms of these.

It is natural, then, to think of these different contributions to the total density function as charges, or populations, on an atom or in a bond. Further discussion of the general ideas underlying population analysis may be found in the earlier papers.[1,2]

Summary of MO Population Analysis.—From the point of view described in the preceding paragraphs, it is easily seen that the population analysis of MO and valence bond wave functions are closely related and, before discussing the valence bond analysis, it is helpful to summarize the MO treatment in a form which emphasizes the parallels. The analysis of MO wave functions in which configuration interaction is included divides into three steps. We consider in the usual way a 2n electron ground state wave function (Ψ_{MO})

$$\Psi_{MO} = \alpha\psi_0 + \sum_\beta \beta\psi_\beta \qquad (2)$$

where $\psi_0 = |\phi_a\bar{\phi}_a \ldots\ldots \phi_n\bar{\phi}_n|$ is the first approximation to the state wave function. The remaining ψ are formed by raising one or more electrons to excited MOs. As an example, suppose that one electron is raised from the ground state MO ϕ_i to the excited MO ϕ_q, then $\psi_\beta = |\phi_a\bar{\phi}_a \ldots \phi_i \ldots \phi_n\bar{\phi}_n \ldots \phi_q|$. The functions ψ_0, etc., and the MOs are normalized to unity so that[6a]

$$1 = \alpha^2 + \beta^2 \ldots \qquad (3)$$

The density function which results from (2) is

$$\rho(x,y,z) = 2n\alpha^2 \int \psi_0^* \psi_0 d\tau_2 \ldots d\tau_{2n}\, d\sigma_1 + 2n \sum_\beta \beta^2 \int \psi_\beta^* \psi_\beta\, d\tau_2 \ldots d\tau_{2n}\, d\sigma_1$$

$$= \alpha^2(2\phi_a^*\phi_a + 2\phi_b^*\phi_b \ldots) + \sum_\beta \beta^2(2\phi_a^*\phi_a \ldots) \qquad (4)$$

plus, in some cases, products of the kind $\phi_j^*\phi_q$ which individually integrate to zero. It is important to notice these latter terms which, although they make no contribution to the final numbers, do show that the electron density function itself is not quite so simple as a direct superposition of the individual density functions of the occupied MOs. Apart from these terms, ρ does appear as a sum of terms each of which is connected with a particular configuration. We call the quantities $2n\alpha^2$, etc., the configuration populations[6b] and denote them by N_α, etc.

The second step in the analysis of MO wave functions follows immediately from the second form of writing in equation 4. The configuration population $2n\alpha^2$, for example, is divided up among the MOs, $2\alpha^2$ electrons in ϕ_a, $2\alpha^2$ in ϕ_b and so on. The third step is the division of the population of an MO among the contributing AOs *via* the equations

$$1 = \int \phi_a^*\phi_a\, d\tau = \int \left(\sum_{rk} C_{ark}\chi_{rk}\right)^* \left(\sum_{sl} C_{asl}\chi_{sl}\right) d\tau$$

$$= C_{ark}^2 \int \chi_{rk}^*\chi_{rk}\, d\tau \ldots + 2S_{rk,sl}C_{rk}C_{sl} \int \frac{\chi_{rk}^*\chi_{sl}}{S_{rk,sl}}\, d\tau \ldots \qquad (5)$$

Here, the r^th AO of atom k is denoted χ_{rk}. From this point of view, the various atom and bond populations are defined in the usual way.[2,3]

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(6) (a) To simplify the treatment, we have supposed that all the ψ_β are orthogonal to ψ_0 and to each other. From a numerical point of view, more rapid convergence is obtained if the ψ_β are selected from the more general and flexible set of simple functions which are not orthogonal to ψ_0. Then configuration overlap populations arise which resemble the structure overlap populations of the valence bond theory which are discussed later. (b) Karo[3] called these quantities $N(\phi_r)$. The notation used in the present paper is that N or n denote a quantity obtained from a MO wave function while M or m denote that from a valence bond wave function.

Valence Bond Population Analysis.—Having outlined briefly the population analysis of MO wave functions, we return to valence bond wave functions. Now the analysis follows very similar lines. There are two steps, the first of which is analogous to the division of the electrons among the MO configurations. We write the normalized 2n electron ground state valence bond wave function as

$$\Psi_{\mathrm{VB}} = \lambda\psi_\lambda + \mu\psi_\mu \ldots \qquad (6)$$

where ψ_λ, etc., are the conventional bond eigenfunctions, themselves usually linear combinations of determinants which are eigenfunctions of S_z and S^2 which correspond to different ways of joining together the AOs of the atoms by single bonds. The electron density function in real space is now

$$\begin{aligned}\rho(\mathrm{x,y,z}) &= 2n\int\Psi_{\mathrm{VB}}{}^*\Psi_{\mathrm{VB}}\, \mathrm{d}\tau_2\ldots\mathrm{d}\tau_{2\mathrm{n}}\cdot\mathrm{d}\sigma_1 \\ &= 2n\lambda^2\int\psi_\lambda{}^*\psi_\lambda\, \mathrm{d}\tau_2\ldots\mathrm{d}\tau_{2\mathrm{n}}\, \mathrm{d}\sigma_1 + \\ &\quad 2n\mu^2\int\psi_\mu{}^*\psi_\mu\, \mathrm{d}\tau_2\ldots\mathrm{d}\tau_{2\mathrm{n}}\, \mathrm{d}\sigma_1\ldots + \\ &\qquad 4n\lambda\mu\int\psi_\lambda{}^*\psi_\mu\, \mathrm{d}\tau_2\ldots\mathrm{d}\tau_{2\mathrm{n}}\mathrm{d}\sigma_1\ldots \qquad (7)\end{aligned}$$

The function ρ is analogous to that from the MO wave function (equation 4) and must be interpreted in the same way. If Ψ_{VB} itself and all the ψ_λ are normalized to unity, we have

$$1 = \lambda^2 + \mu^2\ldots + 2\lambda\mu S_{\lambda\mu} \ldots \qquad (8)$$

where $S_{\lambda\mu} = \int\psi_\lambda{}^*\psi_\mu \mathrm{d}\tau_1\ldots\mathrm{d}\tau_{2\mathrm{n}}$. The important difference from the simplest MO case (equation 3) is that $S_{\lambda\mu}$ is not now zero. We call the quantities $4n\lambda\mu S_{\lambda\mu}$ the *structure overlap populations*, $\mathrm{m}_{\mu,\lambda}$. These must be distinguished clearly from the overlap populations between two AOs since the latter are localized in regions of real space while the structure overlap populations are not so localized. We call the quantities $2n\lambda^2$, etc., the *net structure populations.* These latter numbers have, in the past, frequently been used to describe or define the amount of covalentness and of ionic character of the valence bond wave function, the non-zero overlap of the structure wave function being ignored. These numbers do not add to $2n$, the total number of electrons, since the overlap terms remain to be included. Just how these overlap terms are to be divided up among the two structures which are connected with each one is in general arbitrary, although in special cases, such as the two Kekulé structures of benzene, they must clearly be divided evenly. The same situation arises[2] with the overlap terms of two AOs in an MO. If we decide, for the present, to always divide the structure overlap populations equally between the two structures, we may then define a gross structure population, M_λ, for structure λ, by

$$M_\lambda = 2n\lambda^2 + 2n \sum_{\mu(\neq\lambda)} \lambda\mu S_{\lambda\mu} \qquad (9)$$

These quantities, M_λ, now add to $2n$, the total number of electrons. They may be thought of as the weights of the structures in the final wave function.

To exemplify the idea of a structure population, we take the H_2 molecule whose ground state valence bond wave function is, apart from a singlet spin function, written as

$$\begin{aligned}\Psi_{\mathrm{VB}} &= \lambda\psi_{\mathrm{covalent}} + \mu\psi_{\mathrm{ionic}} \\ &= \lambda(a(1)b(2) + a(2)b(1))(2 + 2S_{\mathrm{ab}}{}^2)^{-1/2} + \\ &\qquad \mu(a(1)a(2) + b(1)b(2))(2 + 2S_{\mathrm{ab}}{}^2\ )^{-1/2} \qquad (10)\end{aligned}$$

To be quite specific, we suppose that we are using Weinbaum's H_2 wave function, with free atom hydrogen AOs in both the covalent and ionic wave functions.[7] These are written $a(1)$, etc., and $S_{\mathrm{ab}} = \int a(1)b(1)\mathrm{d}x_1\mathrm{d}y_1\mathrm{d}z_1$. Equation 8 is now

$$1 = \lambda^2 + \mu^2 + 2\lambda\mu S_{\lambda\mu} \qquad (11)$$

and the gross structure population of the covalent structure M_{co} is $(2\lambda^2 + 2\lambda\mu S_{\lambda\mu})$ and of the ionic structure M_{io}, $(2\mu^2 + 2\lambda\mu S_{\lambda\mu})$. Numerical values for these quantities are given in the last column of Table II.

In the extreme right hand column of Table III and in Table V are given the gross structure populations of the valence bond wave functions of LiH[8] and of the π electron system of butadiene.[9] We take up the discussion of these results later in this paper.

Hurley[10] has expressed similar ideas in a rather more complex mathematical format. Hurley's comment that the gross structure populations provide a rigorous definition of the weights of the valence bond structures in a valence bond wave function is formally correct, but it is important to notice that this is not the *only* possible definition. Others in which the structure overlap populations are not divided up equally between the contributing structures are possible. Hijikata[11a] has used the idea to discuss the results of a calculation on F_2 and Brown[11b] has used it to discuss a number of LiH wave functions.

The second step, analogous to steps 2 and 3 of the MO treatment, is the division of the gross structure populations among the AOs and the bond regions. The general formulas are complicated, and it is convenient to set out first the equations for the simplest case of H_2. Starting with the gross structure population of the covalent structure of H_2, which is $2(\lambda^2 + \lambda\mu S_{\lambda\mu})$, this may be written out in detail as

$$\begin{aligned}M_{\mathrm{co}} &= 2[\lambda^2\int(a^1b^2 + a^2b^1)^2(2 + 2S_{\mathrm{ab}}{}^2)^{-1}\, \mathrm{d}\tau_1\mathrm{d}\tau_2 + \\ &\qquad \lambda\mu\int(a^1b^2 + a^2b^1)(a^1a^2 + b^1b^2)(2 + 2S_{\mathrm{ab}}{}^2)^{-1}\, \mathrm{d}\tau_1\mathrm{d}\tau_2\} \\ &= 2[\lambda^2\int(a^1a^1 + b^1b^1 + 2S_{\mathrm{ab}}a^1b^1)(2 + 2S_{\mathrm{ab}}{}^2)^{-1}\mathrm{d}\tau_1 + \\ &\qquad \lambda\mu\int(a^1a^1S_{\mathrm{ab}} + b^1b^1S_{\mathrm{ab}} + 2a^1b^1)(2 + 2S_{\mathrm{ab}}{}^2)^{-1}\mathrm{d}\tau_1 \\ &= 2[\lambda^2(1 + 1 + 2S_{\mathrm{ab}}{}^2)(2 + 2S_{\mathrm{ab}}{}^2)^{-1} + \\ &\qquad \lambda\mu(S_{\mathrm{ab}} + S_{\mathrm{ab}} + 2S_{\mathrm{ab}}) \times (2 + 2S_{\mathrm{ab}}{}^2)^{-1}] \qquad (12)\end{aligned}$$

Then the net population on each atom in the covalent structure, $m_{\mathrm{co}}(\mathrm{a})$ is $2(\lambda^2 + \lambda\mu S_{\mathrm{ab}}{}^2)(2 + 2S_{\mathrm{ab}}{}^2)^{-1}$. The overlap population in the covalent structure, $m_{\mathrm{co}}(\mathrm{a,b})$ is $2(2\lambda^2 S_{\mathrm{ab}}{}^2 + 2\lambda\mu S_{\mathrm{ab}}{}^2)(2 + 2S_{\mathrm{ab}}{}^2)^{-1}$. The gross population of one atom in the covalent structure, $M_{\mathrm{co}}(\mathrm{a})$, is $(\lambda^2 + \lambda\mu S_{\lambda\mu})$. These definitions are consistent with those used for MO wave functions. In Table I are set out these quantities and the corresponding ones for the ionic structures, together with certain total populations

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(7) S. Weinbaum, *J. Chem. Phys.*, **1**, 593 (1933).

(8) J. Miller, L Friedmann and F. A. Matsen, *Bull. Amer. Phys. Rev.*, Ser. 11, 1, 90 (1956).

(9) J. Fain and F. A. Matsen, *J. Chem. Phys.*, **26**, 376 (1957).

(10) A. C. Hurley, *ibid.*, **28**, 539 (1958); *Proc. Roy. Soc.* (London), **248A**, 119 (1958).

(11) (a) K. Hijikata, *J. Chem. Phys.*, **34**, 230 (1961); (b) J. C. Brown, *ibid.*, in the press.

TABLE I

GENERAL POPULATION ANALYSIS OF VALENCE BOND WAVE FUNCTIONS OF H_2 LIKE SYSTEMS[a,b]

Population Structure	Net atomic $m_\lambda(a) = m_\lambda(b)$	Overlap $m_\lambda(a,b)$	Gross atomic $M_\lambda(a) = M_\lambda(b)$	Total structure M_λ
Covalent	$m_{co}(a) = m_{co}(b) = (\lambda^2 + \lambda\mu S_{ab}) \times (1 + S_{ab}^2)^{-1}$	$m_{co}(a,b) = (2\lambda^2 S_{ab}^2 + 2\lambda\mu S_{ab}) \times (1 + S_{ab}^2)^{-1}$	$M_{co}(a) = M_{co}(b) = (\lambda^2 + \lambda\mu S_{\lambda\mu})$	$M_{co} = 2(\lambda^2 + \lambda\mu S_{\lambda\mu})$
Ionic	$m_{io}(a) = m_{io}(b) = (\mu^2 + \lambda\mu S_{ab}) \times (1 + S_{ab}^2)^{-1}$	$m_{io}(a,b) = (2\mu^2 S_{ab}^2 + 2\lambda\mu S_{ab}) \times (1 + S_{ab}^2)^{-1}$	$M_{io}(a) = M_{io}(b) = (\mu^2 + \lambda\mu S_{\lambda\mu})$	$M_{io} = 2(\mu^2 + \lambda\mu S_{\lambda\mu})$
Total	$m(a) = m(b) = (\lambda^2 + \mu^2 + 2\lambda\mu S_{ab}) \times (1 + S_{ab}^2)^{-1}$	$m(a,b) = 1 - (1 - S_{ab}^2) \times (\lambda^2 + \mu^2)(1 + S_{ab}^2)^{-1}$	$M(a) = M(b) = 1$	2

[a] *Cf.* equations 10, 11 and 12. [b] $S_{\lambda\mu} = 2S_{ab}(1 + S_{ab}^2)^{-1}$.

defined below. This table is immediately applicable to any problem which can be simplified until it resembles the H_2 case. The figures illustrate the numerical values of the various populations for the two representative cases, $S_{ab} = 0.25$ and 0.50. The numerical values for H_2 itself, using Weinbaum's wave function,[6] are given in Table II.

TABLE II

POPULATION ANALYSIS OF WEINBAUM'S H_2 WAVE FUNCTION[a]

Population structure	Net atomic $m_\lambda(a) = m_\lambda(b)$	Overlap $m_\lambda(a,b)$	Gross atomic $M_\lambda(a) = M_\lambda(b)$	Total structure M_λ
Covalent	0.576	0.588	0.870	1.740
Ionic	.068	.124	0.130	0.260
Total	.644	.712	1.000	2.000

[a] Ref. 7, free atom a.o.s for both ψ_{co} and ψ_{io}.

With the general valence bond wave function, the structure populations become rather complicated if written as functions of the quantities defined below,[12] so it is easier if the equations analogous to (12) are developed for each case individually. We have, in fact, to transform equation 9 into an equation involving only AOs. The resulting equations can always be written in the form

$$M_\lambda = 2n\left[\sum_{r_k} d_{rk}{}^{\lambda}\int \chi_{rk}{}^{*}\chi_{rk}d\tau + \sum_{r_k s_l}\sum d_{rk,sl}{}^{\lambda}\int \frac{\chi_{rk}{}^{*}\chi_{sl}}{S_{rk,sl}}\,d\tau\right]$$
$$= 2n\left[\sum_{r_k} d_{rk}{}^{\lambda} + \sum_{r_k}\sum_{s_l} d_{rk,sl}{}^{\lambda}\right] \qquad (13)$$

In the double summation, $r_k = s_l$ is omitted. There are some obvious differences between this equation and the corresponding MO equation, although the latter can always be put into this form. In practice, the derivation of (13) is straightforward providing the normalization conditions are dealt with carefully.

This equation 13 can now be taken as the starting point in the definition of the various simple quantities analogous to those used for MO wave functions. Some of these are not required immediately, but they are included for completeness and to standardize the notation. To summarize the notation, k and l label atoms, r and s label AOs. Structure labels, written as subscripts, are λ and μ. M always labels a *gross* population, either of an atom or of a structure and m a *net* atomic population or an overlap population, either between two AOs, two atoms or two structures. The term 'partial' refers to a quantity of *one* structure, and the term 'total' implies that summation over all the structures has been carried out. The term 'net' implies that the overlap contributions have been omitted, and 'gross' that they have been included.

Overlap Populations.—Partial overlap population between AOs χ_{rk} and χ_{sl} in structure λ = $m_\lambda(r_k,s_l) = 4nd_{rk,sl}{}^{\lambda}$. Partial overlap population between atoms k and l in structure λ = $m_\lambda(k,l) = \sum_{r,s} m_\lambda(r_k,s_l)$. Total overlap population between AOs χ_{rk} and χ_{sl} = $m(r_k s_l) = \sum_\lambda m_\lambda(r_k,s_l)$. Total overlap population between atoms k and l = $m(k,l) = \sum_\lambda m_\lambda(k,l) = \sum_{r,s} m(r_k,s_l)$. Total overlap population = $m = \sum_{k,l} m(k,l)$.

Atom Populations.—Partial net population of AO χ_{rk} in structure λ = $m_\lambda(r_k) = 2nd_{rk}{}^{\lambda}$. Partial net population of atom k in structure λ = $m_\lambda(k) = \sum_r m_\lambda(r_k)$. Total net population of χ_{rk} = $m(r_k) = \sum_\lambda m_\lambda(r_k)$. Total net population of atom k = $m(k) = \sum_r m(r_k) = \sum_\lambda m_\lambda(k)$. Partial gross population of χ_{rk} in structure λ = $M_\lambda(r_k) = 2n(d_{rk}{}^{\lambda} + \sum_{sl} d_{rk,sl}{}^{\lambda})$, $r_k \neq s_l$. Partial gross population of atom k in structure λ = $M_\lambda(k) = \sum_r M_\lambda(r_k)$. Total gross population of χ_{rk} = $M(r_k) = \sum_\lambda M_\lambda(r_k)$. Total gross population of atom k = $M(k) = \sum_\lambda M_\lambda(k)$. Total number of electrons = $2n = \sum_k M(k)$.

Structure Populations.—Overlap population between structures λ and μ = $m_{\lambda,\mu} = 4n\lambda\mu S_{\lambda\mu}$. Net population of structure = $2n\lambda^2$. Gross population of structure λ = $M_\lambda = 2n(\lambda^2 + \sum_{\mu(\neq\lambda)} \lambda\mu S_{\lambda\mu}) = 2n(\sum_{rk} d_{rk}{}^{\lambda} + \sum_{rk \neq sl}\sum d_{rk,sl}{}^{\lambda})$. Total number of electrons = $2n = \sum_\lambda M_\lambda$.

Some of these populations have been derived for a LiH wave function[7] and these are reported in Tables III and IV. A complete valence bond wave function for the π electrons of butadiene has been reported[8] and the derived gross structure populations are reported in Table V.

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(12) Both Lowdin[13] and Hurley[10] have given formal equations for doing this.

(13) P. O. Lowdin, *Phys. Rev.*, **97**, 1474 (1955).

TABLE III

GROSS POPULATIONS OF LITHIUM HYDRIDE[a,b]

Structure	$M_\lambda(1s_{Li})$	$M_\lambda(2s_{Li})$	$M_\lambda(2p_{Li})$	$M_\lambda(H)$	$M_\lambda(Li)$	M_λ
Li-H 2s 1s	1.166	0.492	0.020	0.654	1.678	2.332
Li-H 2p 1s	0.576	.025	.220	.330	0.820	1.152
$Li^+ H^-$ $(1s)^2$	.398	.041	.028	.329	.467	0.796
$Li^- H^+$ $(2s)^2$	− .055	− .038	0	− .018	− .092	− .108
$Li^- H^+$ $(2s)(2p)$	− .064	− .024	−0.020	− .020	− .108	− .128
$Li^- H^+$ $(2p)^2$	− .020	0	− .014	− .007	− .034	− .040
$M(r_k)$	2.001	0.496	.234	$M(H) = 1.268$	$M(Li) = 2.731$	$2n = 4.00$

[a] In the structure formulas, the $(1s)^2$ electrons of Li are omitted. [b] The valence bond wave function from which these results were obtained is reported in ref. 8.

TABLE IV[a]

OVERLAP POPULATIONS OF LITHIUM HYDRIDE

Structure	$m_\lambda(1s_{Li}, 1s_H)$	$m_\lambda(2s_{Li}, 1s_H)$	$m_\lambda(2p_{Li}, 1s_H)$	m_λ
Li-H 2s 1s	−0.020	+0.308	+0.040	+0.328
Li-H 2p 1s	− .004	+ .052	+ .204	+ .252
$Li^+ H^-$ $(1s)^2$	− .008	+ .084	+ .056	+ .132
$Li^- H^+$ $(2s)^2$	0	− .036	0	− .036
$Li^- H^+$ $(2s)(2p)$	0	− .016	−0.024	− .040
$Li^- H^+$ $(2p)^2$	0	0	− .012	− .012
$m(r_{Li}, 1s_H)$	−0.032	+0.392	+ .264	$m = +0.624$

[a] See footnote to Tables III.

TABLE V[a]

GROSS STRUCTURE POPULATIONS M_λ OF A BUTADIENE π ELECTRON WAVE FUNCTION

Structure	$\mathrm{C{-}C\ C{-}C}$	$\overparen{\mathrm{C\ C{-}C\ C}}$	$\mathrm{C{-}C}\ \overset{+}{\mathrm{C}}\ \overset{-}{\mathrm{C}}$	$\mathrm{C{-}C}\ \overset{-}{\mathrm{C}}\ \overset{+}{\mathrm{C}}$
Population	2.152	0.284	0.571	0.681
Structure	$\underparen{\mathrm{C}\ \overset{+}{\mathrm{C}}\ \overset{-}{\mathrm{C}}\ \mathrm{C}}$	$\overset{-}{\mathrm{C}}\ \overset{+}{\mathrm{C}}\ \overset{-}{\mathrm{C}}\ \overset{+}{\mathrm{C}}$	$\underparen{\mathrm{C}\ \overset{-}{\mathrm{C}}\ \mathrm{C}}\ \overset{+}{\mathrm{C}}$	$\overset{+}{\mathrm{C}}\ \overset{-}{\mathrm{C}}\ \overset{-}{\mathrm{C}}\ \overset{+}{\mathrm{C}}$
Population	0.120	0.089	0.034	0.032

[a] The wave function is recorded in ref. 9. The σ electron lines have been omitted from the structural formulas. All structures with a population of less than 0.02 have been neglected. The listed structures account for 3.96 electrons.

Discussion

The results reported in the tables provide some further insight into the behavior of valence bond wave functions, but they emphasize how complicated these wave functions are when examined quantitatively.

In H_2 (Table II) the structure populations are remarkable for the large size of the ionic population, $M_{io} = 0.26$. The numbers usually quoted[4] as the relative weights of the ionic and covalent forms are 0.08 and 1.92, respectively. These are simply λ^2 and μ^2 (renormalized to unity) of equation 10, the net structure populations. In fact, H_2 is a particularly bad case in which to ignore the overlap contribution since the covalent and ionic Heitler–London wave functions are much more nearly identical than orthogonal (the overlap integral between the normalized structure wave functions is 0.929). It is interesting to notice that, had we decided to divide up the overlap contribution in the proportion of $\lambda^2:\mu^2$, we would also have obtained the populations 1.92 and 0.08. So the actual decision to divide up the structure overlap population equally leads directly to the large ionic population. There seems no reason, other than familiarity, to prefer the older numbers, but it is helpful to bear in mind the origin of the large ionic populations.

The overlap population between the two atoms in H_2 in the ionic structure is 0.124 as compared with 0.588 for the same quantity in the covalent structure. If the overlap population is proportional to the binding, this means that some 20% of the total binding occurs in the ionic structure. This again is large and is a direct result of the equal division of the structure overlap population discussed in the last paragraph. The total overlap population in both structures is 0.712 which is close to that[2] found with a one determinant MO wave function, 0.858. That the total overlap population in the valence bond wave function for H_2 should be smaller than that for the one determinant MO wave function is to be expected. The valence bond wave function is identical with a configuration interacted MO wave function in which only the configurations which arise from 1s AOs on hydrogen are used. The latter wave function includes, with small weight, the configuration made from two electrons in the antibonding MO and this MO has a negative overlap population between the AOs. This will reduce the total overlap population in the configuration interacted MO wave function compared with that found with a single determinant, in agreement with the results from the valence bond wave function.

The two figures show how the various populations depend on the value of λ and μ in the H_2 like situation. The gross structure populations, M_{co} and M_{io}, are close to linear in λ, becoming more so as the value of S_{ab} increases. For the usual values of S_{ab} in a two electron bond, it is better to think of $|\lambda|$ and $|\mu|$ as guides to the structure populations, rather than the conventional λ^2 and μ^2. It is also noticeable from the figures that the structure population, M_λ, may be quite small (10 to 20%), but some 20 to 50% of the total binding may occur in this structure, judging from the size of the overlap population, m_λ(a,b), in it. Furthermore, the total overlap population, m(a,b), is rather insensitive to λ, particularly in the range $\lambda = 0.3$ to 0.7.

The LiH results (Tables III and IV) show negative gross populations, M_λ, for the three Li$^-$H$^+$ structures. These are quite small, but far from negligible and their existence may be due either to the inadequacies of the wave functions themselves or to the approximate nature of the population analysis formulas. A similar, but rather smaller, effect is found in the MO population analysis.[2]

An interesting point about the LiH results is their similarity to those of H_2, particularly in the gross structure populations. In both cases, the covalent structure accounts for 87% of the total population. Conventional ideas would say that the ionic structures are more important in LiH which has a large dipole moment and ionic crystal.[14]

From the various overlap populations in LiH (Table IV), it seems that a substantial amount of the binding occurs in the ionic structures. The total overlap population in the molecule, 0.624, is quite similar to that found in other small molecules[2] and agrees with that (0.741) for LiH from the population analysis[15] of a MO wave function. The gross atomic populations also agree rather well with those found from the MO wave function,[15] and this suggests that despite the imperfections of the population analysis method, there is significant agreement in its results for both MO and valence bond wave functions.

Table IV reveals the expected small repulsions between the lithium 1s electrons and that of the hydrogen atom by the small negative values of the appropriate overlap populations. The total gross atomic populations, given in the last row of Table III, show the expected 2.00 electrons in the lithium 1s AOs. The lithium atom as a whole, however, has lost 0.27 electrons to the hydrogen atom. This over-all loss is made up of a loss of 0.50 electron from the 2sAO and a gain of 0.23 electron by the 2pσAO. More than this it is impossible to say without making further assumptions, since the amounts of promotion and charge transfer are formally inseparable. It has been suggested[2] that charge transfer be thought of as involving only the 2pσAO, and if this is so, we can describe the lithium atom as 50% promoted to the $(1s)^2(2s)(2p)$ configuration. This agrees well with Karo's results[3] from the population analysis of the LiH MO wave function in which configuration interaction is included.

The butadiene results (Table V) are rather as expected on classical ideas of resonance between valence bond structures. After the non-resonating structures, the long bonded structure is the most important contributor to the ground state wave function and this conclusion differs from that of Berry.[5] He rejected the wave function used here on the grounds that the ionic structures are underweighted in it, and this is a reasonable point of view since the basis functions of the 2p$_\pi$ AOs were represented by Slater AOs. Perhaps it would be valuable to repeat the calculations with SCF AOs for the 2p$_\pi$ basis functions, although there are some serious questions as to the behavior of the σ electrons in butadiene. For the present, it seems sufficient to say that the calculation based on Slater AOs does not contradict the classical ideas of resonance in butadiene.

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The Validity of Frequency Shift-Enthalpy Correlations. I. Adducts of Phenol with Nitrogen and Oxygen Donors

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The correlation between frequency shift and enthalpy is tested by examining thermodynamic and infrared data for the interaction of phenol with thirty-three bases in carbon tetrachloride. Contrary to literature reports a plot of enthalpy *vs.* $\Delta\nu_{O-H}$ is linear for phenol adducts. The relationship holds within ±0.5 kcal./mole. The general equation derived for predicting enthalpy values for phenol-base association from frequency shift data is $-\Delta H$ (kcal./mole) $= 0.016\ \Delta\nu_{O-H} + 0.63$. The log K *vs.* $\Delta\nu_{O-H}$ relationship is found to be limited to similar bases where no unusual entropy effects are observed and where the entropy change is a linear function of the enthalpy.

Introduction

In 1937 Badger and Bauer[2] proposed that the shift in the infrared stretching frequency of a group, X–H, upon complexation to a base was linearly related to the enthalpy for hydrogen bond formation. Until recent years, there has been little reliable enthalpy work available to test this pro-

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