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Valency. I. A Quantum Chemical Definition and Properties

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A quantum chemical definition of the valency of an atom in a molecule is proposed. It is defined as the sum of the squares of the appropriate off-diagonal elements of the first-order density matrix of the system in an orthogonal basis. It is a measure of the degree of electron sharing of the given atom with the other atoms. Its properties such as invariance to rotation of the coordinate system, its limiting values as well as its relation to natural hybrids and bond orbitals are discussed.

Key words: Definition and properties of valency.

1. Introduction

Valency is a central concept in chemistry. However, like many other chemical concepts, valency is rather vaguely defined. Chemists intuitively understand it to be the degree of binding of an atom in a molecule. Thus hydrogen has a valency of 1 in compounds like HCl, H_2O, CH_4; oxygen is divalent in H_2O, Cl_2O, MgO; carbon is tetravalent in CH_4, CCl_4, C_2H_2 and so on. But this qualitative approach soon fails in many situations. For example one cannot easily decide whether the valency of the bridging H in B_2H_6 is 1, 2 or some other value. Other examples of such ambiguity are: B in B_2H_6, O in O_3 and OLi_4, C in C_2, CO, CLi_6, CH_5^+ etc.. The traditional definition of valency may be formulated as the number of "univalent" or their equivalent atoms bonded to the given atom. This means effectively the number of covalent bonds formed by the atom in the formal valence structure of the compound. Such a formulation has

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two major difficulties: (1) It is not possible to write down a single valence structure for compounds that exhibit the classical "resonance" as CO or O_3 for example. (2) If valency is computed merely from the number of covalent bonds in a formal structure, without regard for the strength of these bonds, one often obtains valencies that are abnormal in the traditional sense. Thus the bridging H in B_2H_6 would be divalent, C would be hexavalent in CLi_6 and pentavalent in CH_5^+, O and Li would both be tetravalent in OLi_4. While it is possible to postulate "hypervalency" in these compounds, such a definition of valency simply equates it to the coordination number or stoichiometry. This attributes a physical rather than chemical origin to valency and it is difficult to see how and when an atom attains "saturation" of its valency. Clearly any definition of chemical valency should have a well defined maximum that corresponds to a saturation of its bonding capacity. This does not mean that we reject hypervalency; we return to a discussion of it in Part II of this series. Here we simply comment that a definition of valency that leads to traditionally abnormal values in many situations need not be adopted unless there are other compelling reasons to do so.

The above two major difficulties may be sought to be removed if one defines the valency of an atom as the sum of its calculated bond orders to the other atoms in the molecule. This is simply a generalisation of the idea that Coulson [1] used in the definition of free valence for π electron systems in molecular orbital theory. This definition clearly takes proper account of the weak or strong nature of the bonds formed and has a maximum since most bond order definitions involve the electron density in the interatomic regions. However, here we come across problems that are usually associated with the definition of bond orders [2]. Briefly these are: (1) Most bond order definitions are not invariant to a coordinate transformation. (2) Even when invariant to a coordinate transformation, the definition of valency as the sum of bond orders often leads to abnormally high values even for the "ordinary" compounds [3]. (3) Bond order basically measures the difference between the number of "bonding" and "antibonding" pairs of electrons. Contrary to this, the traditional concept of valency seems to imply the totality of electron sharing by an atom with other atoms. Therefore it appears that a quantum chemical definition of valency may desirably have the following properties:

1) It must be invariant to coordinate transformations.
2) It must be a measure of the extent of electron sharing by the considered atom with other atoms in the molecule.
3) It must have an upper limit corresponding to the saturation of covalent bonding of the atom.
4) It may be related to the covalent chemical reactivity of the atom in the molecule.
5) It should be deduced from the density matrix of the system.

The LCAO form of MO theory is particularly apt to implement these features. The MO coefficients of AO's define the density matrix and are a basis to determine the probability of electron distribution among the atoms. A lone pair should have valency zero and an electron pair equally shared between two atoms should contribute a unit of valency to each of the atoms. Since the density matrix contains pertinent information about the system and can be defined in *ab initio* as well as semiempirical MO methods, the qualitative features of the definition do not depend on a particular MO approximation. Depending on the accuracy of the density matrix, which in turn depends on the wavefunction used, quantitative changes may occur for the valency value.

2. Definition of Valency

Wiberg [4] has proposed an index for the multiplicity of bonds between two atoms. He defined the "bond index", W_{AB}, between atoms A and B as the square of the off-diagonal density matrix elements, p_{ab}, between nonorthogonal orbitals a on A and b on B, summed over all such distinct orbital pairs:

$$W_{AB} = \sum_{a}^{A} \sum_{b}^{B} p_{ab}^{2} = \sum_{a}^{A} w_{a}^{B} . \tag{2.1}$$

W_{AB} as a bond index has the disadvantage that it is always positive and hence cannot describe antibonding situations. However as Wiberg has pointed out [4], this index is a measure of the extent of electron sharing between the two atoms. This is easily seen by expanding p_{ab} in terms of the molecular orbitals. The LCAO MO's are of the form:

$$\psi_i = \sum_{a} c_{ia} \phi_a \tag{2.2}$$

where the ϕ_a's are the atomic orbitals. Throughout this article we take the set $\{\phi\}$ to be *orthonormal*; i.e.

$$\int \phi_a \phi_b \, d\tau = \delta_{ab}. \tag{2.3}$$

This simplifies the equations and makes their interpretation easier. In the numerical applications also we consistently use orthogonalised AO's. Now by definition,

$$p_{ab} = \sum_{1} n_i c_{ia} c_{ib} \tag{2.4}$$

$$p_{aa} = \sum_{1} n_i c_{ia}^{2} = q_a. \tag{2.5}$$

Here q_a is the charge or the occupancy of the orbital ϕ_a. We take all c's and ϕ's to be real without loss of generality. From the orthogonality of the MO's it follows that

$$\begin{aligned} \int \psi_i \psi_j \, d\tau &= \int \Big(\sum_{a} c_{ia}\phi_a\Big)\Big(\sum_{b} c_{jb}\phi_b\Big) \, d\tau \\ &= \sum_{a} \sum_{b} c_{ia} c_{jb} \int \phi_a \phi_b \, d\tau = \sum_{a} \sum_{b} c_{ia} c_{jb} \delta_{ab} \\ &= \sum_{b} c_{ib} c_{jb} = \delta_{ij}, \end{aligned}$$

where Eq. (2.3) has been used.

We then obtain

$$\sum_b p_{ab}^2 = \sum_b \left(\sum_i n_i c_{ia} c_{ib}\right)\left(\sum_j n_j c_{ja} c_{jb}\right)$$
$$= \sum_j \sum_i n_i n_j c_{ia} c_{ja} \sum_b c_{ib} c_{jb}$$
$$= \sum_j \sum_i n_i n_j c_{ia} c_{ja} \delta_{ij}.$$

Thus

$$\sum_b p_{ab}^2 = \sum_i n_i^2 c_{ia}^2 \tag{2.6}$$

and so

$$\sum_{b \neq a} p_{ab}^2 = \sum_i n_i^2 c_{ia}^2 - p_{aa}^2 = \sum_i n_i^2 c_{ia}^2 - q_a^2. \tag{2.7}$$

Eq. (2.7) takes a simpler form for closed shell systems, for which $n_i = 2$. For such systems,

$$\sum_{b \neq a} p_{ab}^2 = 2 \sum_i 2c_{ia}^2 - q_a^2 = 2q_a - q_a^2. \tag{2.8}$$

This quantity has the value zero when q_a, the occupancy of orbital ϕ_a is either 2 or 0; that is, when we have either a lone-pair or an empty orbital. It has its maximum value of 1 when q_a is 1. Therefore this quantity is a measure of the extent of sharing of the q_a electrons in ϕ_a with other atoms. For another instance, when we consider a free radical where the odd electron is localised in a single atomic orbital, then in Eq. (2.7) $\sum_i n_i^2 c_{ia}^2 = 1$ and $q_a = 1$ so that the valency contribution of the electron is zero. Thus the present definition of valency fulfills our requirement (2) above. It may be noted that the quantity in Eq. (2.8) includes the density matrix elements between ϕ_a and other orbitals, say ϕ_{a_1}'s on atom A. We may write

$$\sum_{b \neq a} p_{ab}^2 = \sum_{b \neq a \neq a_1} p_{ab}^2 + \sum_{a_1 \neq a} p_{aa_1}^2 = \sum_{B \neq A} w_a^B + \sum_{a_1 \neq a} p_{aa_1}^2$$
$$= w_a + \sum_{a_1 \neq a} p_{aa_1}^2 \tag{2.9}$$

with w_a^B defined by Eq. (2.1), and

$$w_a = \sum_{B \neq A} w_a^B = \sum_{B \neq A} \sum_b^B p_{ab}^2. \tag{2.10}$$

Now suppose we make an orthogonal transformation of the basis orbitals $\{\phi\}$ into a new set $\{h\}$ such that the intraatomic off-diagonal elements of the new density matrix P' are zero. The set $\{h\}$, originally proposed by McWeeny [5], are called the natural hybrid orbitals (NHO). In the NHO basis we may rewrite Eq. (2.9) as

$$\sum_{b' \neq a'} p_{a'b'}^2 = \sum_{B \neq A} w_{a'}^B = w_{a'} \tag{2.11}$$

since the intraatomic terms are zero in this basis. Here the prime denotes the

NHO basis. As we show in Sect. 4, it turns out that

$$\sum_{a'} w_{a'} = \sum_{a} w_a. \tag{2.12}$$

In other words, the sum of the orbital bond indices of an atom in an orthogonal basis, defined as the sum of the squares of the density matrix element of the orbital with all orbitals on other atoms is invariant to natural hybridisation. More generally, it can be shown that $\sum_a w_a$ is invariant to any orthogonal transformation of the basis (see Sect. 3). Further we shall prove that, in analogy with Eq. (2.8),

$$\sum_{b' \neq a'} p^2_{a'b'} = w_{a'} = 2q_{a'} - q^2_{a'} \tag{2.13}$$

for a closed shell system, where $q_{a'}$ is now the occupancy of the natural hybrid orbital a'. By virtue of these properties it appears reasonable to term w_a as the valency of orbital ϕ_a. Thus *the valency of an atomic orbital in a molecule is defined as the sum of the squares of its density matrix elements with the orbitals on all other atoms, the basis set being orthonormal.*

We further define the valency of an atom as the sum of the valencies of its atomic orbitals. Thus the valency V_A of atom A is given by

$$V_A = \sum_{a}^{A} w_a = \sum_{a}^{A} \sum_{B \neq A} \sum_{b}^{B} p^2_{ab}. \tag{2.14}$$

Equivalently, valency of an atom may be defined as the sum of the valencies of its natural hybrid orbitals. Thus

$$V_A = \sum_{a'}^{A} w_{a'} = \sum_{a'} \sum_{B \neq A} \sum_{b'}^{B} p^2_{a'b'}. \tag{2.15}$$

Also, from Eq. (2.13), for closed shell systems we can express V in terms of NHO occupancies as.

$$V_A = \sum_{a'} 2q_{a'} - q^2_{a'} \tag{2.15b}$$

3. The Limit of Valency

We may show generally that the requirement (3) that valency should have an upper limit is satisfied by the present definition. Eq. (2.7) may be rewritten as

$$V_A = \sum_{a} \sum_{i}^{MO} n_i(n_i c^2_{ia}) - q^2_a. \tag{3.1}$$

Since $\sum_i n_i c^2_{ia} = q_a$, the occupancy of orbital a on atom A, and $0 \leq q_a \leq 2$ together with $0 \leq n_i \leq 2$, we have the inequality

$$0 \leq \sum_{i} n_i(n_i c^2_{ia}) \leq 2q_a. \tag{3.2}$$

Hence we have, for the valency

$$0 \leq V_A \leq \sum_{a} (2q_a - q^2_a). \tag{3.3}$$

This sets the limits on valency in terms of the atomic orbital occupancies. Each term in the summation in (3.3) is positive and has a maximum of 1, which occurs when $q_a = 1$. We may also write (3.3) as

$$0 \le V_A \le \left(2Q_A - \sum_a q_a^2\right) \tag{3.4}$$

where Q_A $(=\sum_a q_a)$ is the total number of electrons on atom A. Since normally $\sum_a q_a^2 \ge \sum_a q_a$ $(=Q_A)$ (exception occuring when many q_a's are considerably less than unity), we have from (3.4), $V \le Q_A$. This simply means that valency cannot normally exceed the number of electrons on the atom. However, inner core and valence lone pairs, for which $q_a = 2$, do not contribute to valency and hence the usual limit of valency is the number of electrons on the atom minus the number of innershell electrons, lone pair electrons and single electrons localised on the atom and hence not involved in covalent bonding. This result is in agreement with the traditional view of valency. Valency can somewhat exceed the above number of electrons when, for instance, there is lone pair delocalisation on to other atoms or when an electron partly occupies several atomic orbitals as in an extended basis set. In any case, the rigorous limit on valency is given by Eqs. (3.3) or (3.4).

4. Invariance Properties of Valency

4.1. Invariance Under Coordinate Transformation

Consider the $n \times n$ first order density matrix P as divided into atomic and interatomic blocks as,

$$P = \begin{bmatrix} P_{AA} & P_{AB} & \cdots & P_{AL} \\ P_{BA} & P_{BB} & \cdots & P_{BL} \\ \vdots & & & \\ P_{LA} & P_{LB} & \cdots & P_{LL} \end{bmatrix}. \tag{4.1}$$

Here the submatrix P_{AA} of order $m \times m$ is associated with the m atomic orbitals on A. Consider further a 2×2 rotation of the orbitals on A which transforms, say the ith and jth orbitals of A. The $n \times n$ transformation matrix is

$$T = \begin{array}{c} \\ \\ \\ i \\ \\ j \\ \\ m \\ \\ \\ n \end{array} \begin{array}{c} \begin{array}{cccccccccc} & & i & & j & & m & & & n \end{array} \\ \left[\begin{array}{cccccccccc} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & x & 0 & y & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -y & 0 & x & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array}\right] \end{array} \tag{4.2}$$

where $x = \cos\alpha$ and $y = \sin\alpha$ and α is the angle of rotation. The new density matrix P' is then given by

$$P' = \tilde{T}PT. \tag{4.3}$$

In P' the off-diagonal elements that lie on the i, j rows and columns will be different from those of P, all other off-diagonal elements being unaffected. The new off-diagonal elements are given by,

$$\left.\begin{array}{l} p'_{ki} = p'_{ik} = p_{ik}\cos\alpha - p_{jk}\sin\alpha \quad \text{and} \\ p'_{kj} = p'_{jk} = p_{ik}\sin\alpha + p_{jk}\cos\alpha \end{array}\right\} i, j \neq k.$$

Therefore,

$$p'^2_{ki} + p'^2_{kj} = p^2_{ik} + p^2_{jk} = p^2_{ki} + p^2_{jk}. \tag{4.4}$$

This means that the transformation leaves the sum $P^2_{AB} + P^2_{AC} + \cdots + P^2_{AL}$ invariant, where P^2_{AB} stands for the sum of the squares of the elements of the block P_{AB}. Similarly a 2×2 orthogonal transformation of the orbitals of B would leave the sum $P^2_{BA} + P^2_{BC} + \cdots + P^2_{BL}$ invariant and so on. The transformation considered here is similar to that of the well-known Jacobi matrix diagonalisation procedure, though not identical with it. In the Jacobi procedure, (i, j) are any two indices whereas in the present case they must be indices of atomic orbitals on the same atom. Only in the latter case is the above invariance on the blocks valid. Since a general transformation of the coordinate can be generated by successive application of the transformation of the type T of Eq. (4.2) to the various atomic blocks, P_{AA}, P_{BB}, etc., we obtain the general result that the sum of the squares of the interatomic blocks of the density matrix, hence by Eq. (2.14) the valency V_A, is invariant under a coordinate transformation.

4.2. Invariance to Natural Hybridisation

Natural orbitals of a system are those for which the density matrix is diagonal [6], the diagonal elements being their occupation numbers. For a single determinantal wavefunction, the natural orbitals are the MO's themselves with occupation numbers of 2, 1 or 0. But the MO's are generally delocalised over the whole molecule and do not resemble the chemists' conventional hybrid orbitals on atoms. McWeeny has suggested [5] that such hybrids could be obtained for an atom A by simply diagonalising the atomic block P_{AA} of the density matrix. The eigenvectors of P_{AA} are called the natural hybrid orbitals (NHO) of A.

Recently Foster and Weinhold [7] have employed a modified procedure to obtain NHO's. This involves certain numerical procedures which render the resulting NHO's analytically rather intractable and we do not consider them presently. These authors have pointed out that the NHO's do not generally resemble the conventional hybrids in that the former are not directed along bond axes. The "optimum hybrids" obtained by McWeeny and Del Re [8] through a constrained variational procedure should also be distinguished from the NHO's with which we are presently concerned. Our purpose here is to show that the McWeeny

NHO's are related to the valency of the atom. We will also see that these NHO's are related to the "bond orbitals" introduced in Sect. 5.

The transformation which converts the AO basis to the NHO basis is simply a special case of the general transformation T of Eq. (4.2). Thus choosing the angle of rotation α such that $p_{ij} = p_{ji} = 0$ leads to the diagonalisation of the block P_{AA} and thus to the NHO's of A. Hence it follows that for the transformation to NHO's also Eq. (4.4) is valid and therefore we conclude that *the valency of an atom is invariant under natural hybridisation.* This is the result that we quoted earlier as Eq. (2.12).

To obtain Eq. (2.13) which relates the valency of an NHO to its occupation number for a closed shell system, we simply note that the derivation of Eq. (2.8) is equally valid for the NHO's also since the NHO's are orthonormal and we have only to remember that the occupancies and the MO coefficients now refer to the NHO basis.

We must note by comparing Eqs. (2.8), (2.9) and (2.13) that for a given AO a, the bond index is the sum of its valency and intraatomic terms whereas the bond index and valency are identical for an NHO. It may also be pointed out that it is only the total valency of the atom and not the orbital valencies that is invariant under coordinate transformations.

Interestingly, it is seen from the right hand side (rhs) of Eq. (2.13) that valency of A can be obtained from the NHO occupancy, i.e. from the atomic block P_{AA} of the density matrix; or alternatively, as is clear from the left hand side (lhs) of this equation, it can be obtained from the interatomic blocks P_{AB}, $P_{AC}, \ldots, P_{AL}$. Simultaneous use of atomic and interatomic blocks is therefore redundant for the determination of valency. In fact there exists a close relationship between valency and hybrid orbitals on the one hand and the "bond orbitals" and their eigenvalues obtained from the interatomic blocks on the other hand. We investigate these relations in the following section.

5. Relations Between Valency, NHO's and Bond Orbitals

Bond orbitals which represent a bond between two molecules were obtained earlier by Jug [9] by diagonalising the interatomic part of the density matrix involving these atoms. Thus for the A–B bond, with m AO's on A and n on B, the sub matrix

$$Q_{AB} = \begin{array}{c} m \\ n \end{array} \left[\begin{array}{c|c} 0 & P_{AB} \\ \hline P_{BA} & 0 \end{array} \right] \tag{5.1}$$

is diagonalised. The bond order between A and B was evaluated from the eigenvalues of Q_{AB}. The eigenvalues of the various submatrices involving atom A, viz. $Q_{AB}, Q_{AC}, \ldots, Q_{AL}$ are related to the valency of A as we prove now.

Consider the following similarity transformation that diagonalises Q_{AB}:

$$C^{-1} Q_{AB} C = D \tag{5.2}$$

where D is diagonal with diagonal elements $\lambda_1, \lambda_2, \ldots, \lambda_{m+n}$. We have then

$$\begin{aligned} &\operatorname{tr} D = \operatorname{tr} Q_{AB} \quad \text{and} \\ &\operatorname{tr}(\tilde{D}D) = \operatorname{tr}(\tilde{Q}_{AB}Q_{AB}) \end{aligned} \tag{5.3}$$

But for any general matrix R

$$\operatorname{tr}(\tilde{R}R) = \sum_{i,j} R_{ij}^2.$$

Therefore

$$\operatorname{tr}(\tilde{D}D) = \sum_{i}^{m+n} \lambda_i^2 \tag{5.4}$$

$$\operatorname{tr}(\tilde{Q}_{AB}Q_{AB}) = 2\sum_{a,b} p_{ab}^2 \text{ with } a \text{ on } A \text{ and } b \text{ on } B, \tag{5.5}$$

where p_{ab} are the elements of the block P_{AB} and we have used $p_{ab} = p_{ba}$. Thus from Eqs. (5.3) and (5.5) we have,

$$\sum_{i}^{m+n} \lambda_{i(AB)}^2 = 2\sum_{a,b} p_{ab}^2. \tag{5.6}$$

As shown by Jug earlier [3], the λ's occur in pairs ($\pm\lambda_i$) with $|m-n|$ zeroes. Thus we can write

$$\sum_{i}^{m+n} \lambda_{i(AB)}^2 = 2\sum_{i}^{+ve} \lambda_{i(AB)}^2 \tag{5.7}$$

where the sum on the lhs is only over the positive λ's. From Eqs. (5.6) and (5.7),

$$\sum_{i}^{+ve} \lambda_{i(AB)}^2 = \sum_{a,b} p_{ab}^2 \equiv p_{AB}^2. \tag{5.8}$$

Now if we form the sum $P_{AB}^2 + P_{AC}^2 + \cdots + P_{AL}^2$ we have,

$$\sum_{B \neq A} P_{AB}^2 = \sum_{B \neq A} \sum_{i}^{+ve} \lambda_{i(AB)}^2. \tag{5.9}$$

The lhs of this equation is the valency of atom A by our definition Eq. (2.14). Hence

$$V_A = \sum_{B \neq A} \sum_{i}^{+ve} \lambda_{i(AB)}^2. \tag{5.10}$$

Thus the valency of an atom is also given by the sum of the squares of the positive eigenvalues of the bond orbitals of the atom with another atom, summed over all the distinct atomic pairs formed by the given atom in the molecule.

We recall that the valency of an atom may be expressed in terms of the NHO occupancies (Eq. (2.15b)), which is obtained from the *atomic* block P_{AA} of the density matrix, as well as in terms of the λ's which are obtained purely from the *interatomic* blocks $P_{AB}, \ldots, P_{AL}$ (Eq. (5.10)). It is therefore interesting to seek the connection between the bond orbitals (BO's) and the NHO's. Since the NHO's of an atom determine the valence pairing of the atom with *all* other atoms, it is apparent that the NHO's will be related not just to the eigenvectors of the matrices of the type Q_{AB} of Eq. (5.1), but to those of the complete off-diagonal submatrix $Q_{AB\ldots L}$ defined by

$$Q_{AB\ldots L}=\begin{bmatrix} 0 & P_{AB} & P_{AC} & \ldots & P_{AL} \\ P_{BA} & 0 & 0 & ..0.. & 0 \\ P_{CA} & 0 & 0 & ..0.. & 0 \\ \ldots & ..0.. & 0 & ..0.. & 0 \\ P_{LA} & 0 & 0 & ..0.. & 0 \end{bmatrix} \tag{5.11}$$

We may call the eigenvectors of $Q_{AB\ldots L}$ as the natural bond orbitals (NBO's).

Now it is easily proved that the squares of the positive eigenvalues of $Q_{AB..L}$ gives the valency of the atom. The proof is identical to that used in deriving Eq. (5.10). The matrix Q_{AB} has only to be replaced by $Q_{AB..L}$. The eigenvalues ξ_i of $Q_{AB..L}$ have the same pairing properties as those of Q_{AB}. We may thus write,

$$V_A=\sum_i^{+ve}\xi_i^2. \tag{5.12}$$

Thus it is immaterial whether the valency of an atom is calculated by any of the following four methods:

1) From the squares of the appropriate off-diagonal elements of the original density matrix in the orthogonalised AO basis, Eq. (2.14),
2) from the occupancies of the natural hybrids, Eq. (2.15b),
3) from the squares of the eigenvalues of the diatomic blocks Q_{AB}, $Q_{AC}, \ldots, Q_{AL}$, Eq. (5.10), or
4) from the squares of the eigenvalues of the polyatomic block $Q_{AB..L}$.

All these methods lead to the same value for valency. It is also important to note that the valency of an atom may be factored into a sum of its valencies towards every other atom in the molecule, as is obvious from Eq. (2.14) or Eq. (5.10). We shall make use of these properties when we consider numerical applications in the following article.

It is highly interesting that the NHO's and the NBO's are intimately related. If there are m AO's in the basis set for atom A, then in general there will be m positive eigenvalues for $Q_{AB..L}$. An exception occurs if there are lone-pair NHO's on A (of occupancy 2), in which case the NBO eigenvalue will be zero for each such lone-pair. If we denote the NBO's of atom A as $\chi_1^A, \chi_2^A, \ldots, \chi_m^A$, it turns out that the "A component" of each χ is an NHO of A. In fact, χ_i^A is of the form

$$\chi_i^A=(1/\sqrt{2})\ (\mathrm{NHO})_i^A+\text{function of orbitals on } B, C, \ldots, L. \tag{5.13}$$

In the case of degeneracy of the NHO's and consequently of NBO's, one must take the appropriate linear combinations to obtain this relation. It is remarkable that the NHO's obtained from the atomic block P_{AA} reappear as such in the NBO's obtained from the interatomic block $Q_{AB..L}$. This points perhaps to the fundamental role of the NHO's in describing molecular binding. However, such relations require further investigations and are beyond the scope of the present article.

6. An Illustrative Example of Valency Relations

In this section we shall illustrate the above relations on valency in the simple case of LiH. These relations are of course valid for the exact as well as approximate wavefunctions, which use an orthogonal AO basis. Here we employ the semiempirical SINDO1 wavefunctions [10].

The orthogonalised basis set of AO's used consists of $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals on Li and $1s$ on H. The x-axis is along the internuclear axis. The density matrix is:

$$\begin{array}{cc} & \begin{array}{ccccc} 2s & 2p_x & 2p_y & 2p_z & 1s \end{array} \\ \begin{array}{c} 2s \\ 2p_x \\ 2p_y \\ 2p_z \\ 1s \end{array} & \begin{bmatrix} 0.5157 & 0.3211 & 0.00 & 0.00 & 0.8139 \\ 0.3211 & 0.1999 & 0.00 & 0.00 & 0.5067 \\ 0.0000 & 0.0000 & 0.00 & 0.00 & 0.0000 \\ 0.0000 & 0.0000 & 0.00 & 0.00 & 0.0000 \\ 0.8139 & 0.5067 & 0.00 & 0.00 & 1.2844 \end{bmatrix} \end{array}.$$

From Eq. (2.14), the valency of Li is

$$\begin{aligned} V_{\text{Li}} &= w_{2s} + w_{2p_x} + w_{2p_y} + w_{2p_z} \\ &= 0.8139^2 + 0.5067^2 + 0 + 0 \\ &= 0.919. \end{aligned}$$

It is easily seen that Eq. (2.14) gives V_{H} also as 0.919. Now we verify Eq. (2.15b) which gives valency in terms of the NHO occupancies. For H, the NHO is the $1s$ orbital itself which has occupancy 1.2844. Therefore, from Eq. (2.15b),

$$V_{\text{H}} = 2 \times 1.2844 - 1.2844^2 = 0.919.$$

For Li, the NHO's are the eigenvectors of the matrix

$$\begin{array}{c} \begin{array}{cc} 2s & 2p_x \end{array} \\ \begin{bmatrix} 0.5157 & 0.3211 \\ 0.3211 & 0.1999 \end{bmatrix} \end{array}$$

since we need not consider the empty p_y and p_z orbitals. The eigenvalues of this matrix are 0.7156 and zero. The natural hybrid orbital corresponding to the eigenvalue 0.7156 is

$$(\text{NHO})_{\text{Li}} = 0.8489\ (2\text{s}) + 0.5285\ (2p_x). \qquad (5.14)$$

From Eq. (2.15b) we now have,

$$V_{\text{Li}} = 2 \times 0.7156 - 0.7156^2 = 0.919.$$

This verifies the invariance of valency to natural hybridisation. It may be noted that the appreciable departure of the occupation number of the NHO's of Li and H, viz. 0.7156 and 1.2844 from the ideal value of unity reduces the covalency from the maximum of 1 to 0.919.

The natural bond orbitals of Li, which are identical to those of H in this diatomic case, are, by definition, the eigenvectors of the partial density matrix:

$$\begin{array}{c} \begin{array}{ccccc} 2s & 2p_x & 2p_y & 2p_z & 1s \end{array} \\ \begin{bmatrix} 0.0 & 0.0 & 0.0 & 0.0 & 0.8139 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.5067 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.8139 & 0.5067 & 0.0 & 0.0 & 0.0 \end{bmatrix} \end{array}$$

The eigenvalues are

$$-0.9587,\ 0.0,\ 0.0,\ 0.0,\ +0.9587$$

The eigenvector corresponding to the positive eigenvalue with which we are concerned is

$$0.6003\ (2s)+0.3737\ (2p_x)+0.7071\ (1s).$$

It is readily seen that the Li part of this orbital is simply $1/\sqrt{2}$ times the NHO on Li given by Eq. (5.14), thus verifying the relation Eq. (5.13). Valency of Li is calculated from the eigenvalue 0.9587 using Eq. (5.12),

$$V_{\mathrm{Li}} = 0.9587^2 = 0.919$$

which is identical to the value obtained by the other methods above.

7. Conclusions

In an attempt to quantify the chemists' concept of valency, we have formulated a definition of valency so that its value can be calculated from the density matrix of the system. As will be shown in the subsequent article, this definition reproduces in most cases the chemical "common sense" values of valency. According to this definition, valency is a measure of the degree of electron sharing between atoms. We have demonstrated the invariance of this definition to coordinate transformations. We have also seen that valency has a limit generally equal to the number of electrons on the atom minus its inner shell, lone pair and localised odd electrons. We have also established the relation of valency to the natural hybrid orbitals and natural bond orbitals of the atom in a molecule. Molecular binding may be viewed as a reorganisation by the atoms of the occupancies of their natural hybrids from the atomic values so as to attain increased valency. Thus effects such as lone-pair donation or delocalisation, d-orbital participation in second-row atoms, charge transfer, etc. could be quantitatively discussed in terms of the valency changes accompanying these effects.

Since the present definition of valency is general in the sense that it depends only on the density matrix, we have the possibility of generalising the π-electron concept of free valence to sigma systems also and of relating the reactivity properties of molecules to their free valences. Such problems are taken up in the following article.

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