Chapter 7

POPULATION ANALYSIS, BOND ORDERS, AND VALENCES

When performing quantum chemical investigations, one usually concentrates on the values of the total energy and on different quantities related to the latter, like the geometrical parameters corresponding to an energy minimum, the vibrational frequencies that are determined by the shape of the potential energy surface around the energy minimum, etc. Often one wishes to get a better understanding of the system studied by utilizing not only the energetic data but also the information contained in the wave function. However, the wave function is usually defined by too big a set of numerical data to be directly used for that purpose, and one needs a sort of "data compression" to make any interpretation of the result possible.

A very important, *measurable physical quantity* is the electron density, i.e., the distribution of the electrons in the physical space. Its detailed analysis—as done e.g., in Bader's "Atoms in molecules" theory—represents an interesting field, which is, however, out of the scope of the present book. Alternately, it is also of interest to consider the distribution of the electrons between the individual basis orbitals and, especially, between the different atoms and define in this manner the resulting charge that can be attributed to the individual atoms in the molecule. One may also be interested in different parameters characterizing the valence state of an atom in a molecule as well as the chemical bonding between the individual atoms. We are going to describe here some parameters of this type. They are often very useful in interpreting the results of calculations and may even have some predictive power. Nevertheless, one has to keep in mind that neither of quantities discussed in this chapter—except the spatial electron and spin densities—are true measurable physical quantities; they merely serve the purpose of presenting the results of calculations in a relatively simple and

compact manner by using terms that may be related to the genuine chemical concepts. (Neither a basis orbital nor its population is a measurable physical quantity.)

As opposed to an analysis of the electron distribution in the physical space, the methods described in this chapter give an analysis in the Hilbert space of the basis orbitals.

1. Mulliken's population analysis

1.1. Electron density

In Section 2.1 of Chapter 2 we have already given an expression of the electron density $\varrho(\vec{r})$ that one obtains by integrating over the coordinates of all the electrons but one and summing over all the electrons. The electron density at the point $\vec{r}$ can be considered as the expectation value of the operator $\hat{\varrho}(\vec{r})$, representing the sum of one-electron operators, symmetric with respect of the individual electrons:

$$\hat{\varrho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) . \qquad (7.1)$$

As an electron has a negative charge, the electron density $\varrho(\vec{r})$ corresponds to an electrostatic charge density $-\varrho(\vec{r})$ if atomic units are used. (Otherwise one has to write $-e_0\varrho(\vec{r})$, where e_0 is the elementary charge.)

If the many-electron wave function is a Slater determinant $\Psi = \hat{\mathcal{A}}[\psi_1(1)\psi_2(2)\ldots\psi_N(N)]$ built up of orthonormalized spin orbitals, then we may use the Slater rule in (5.100), and—similarly to other one-electron quantities—the electron density $\varrho(\vec{r})$ can be presented as the sum over the individual occupied spin orbitals $\psi_i(\vec{r}, \sigma) = \varphi_i(\vec{r})\gamma(\sigma)$ as

$$\varrho(\vec{r}) = \langle \Psi | \hat{\varrho}(\vec{r}) | \Psi \rangle = \sum_{j=1}^{N} \langle \psi_j(\vec{r}_1, \sigma_1) | \delta(\vec{r} - \vec{r}_1) | \psi_j(\vec{r}_1, \sigma_1) \rangle \qquad (7.2)$$

$$= \sum_{j=1}^{N} \langle \varphi_j(\vec{r}_1) | \delta(\vec{r} - \vec{r}_1) | \varphi_j(\vec{r}_1) \rangle = \sum_{j=1}^{N} \varphi_j^*(\vec{r})\varphi_j(\vec{r}) = \sum_{j=1}^{N} |\varphi_j(\vec{r})|^2 .$$

If, in particular, Ψ contains n_a orbitals a_i occupied with spin α and n_b orbitals b_i occupied with spin β, (7.2) becomes

$$\varrho(\vec{r}) = \sum_{j=1}^{n_a} |a_j(\vec{r})|^2 + \sum_{j=1}^{n_b} |b_j(\vec{r})|^2 . \qquad (7.3)$$

Of course, the electron density is invariant under the unitary transformations of the sets of orbitals $\{a_i\}$ or $\{b_i\}$ as they leave invariant the wave function Ψ.

For instance, if

$$a_j(\vec{r}) = \sum_{k=1}^{n_a} U_{kj} a'_k(\vec{r}) , \qquad (7.4)$$

and matrix $\mathbf{U}$ is uniter ($\mathbf{U}^\dagger = \mathbf{U}^{-1}$), then

$$
\begin{aligned}
\sum_{j=1}^{n_a} |a_j(\vec{r})|^2 &= \sum_{j=1}^{n_a} a_j^*(\vec{r}) a_j(\vec{r}) = \sum_{j=1}^{n_a} \sum_{k=1}^{n_a} U_{kj}^* a_k'^*(\vec{r}) \sum_{l=1}^{n_a} U_{lj} a_l'(\vec{r}) \\
&= \sum_{j,k,l=1}^{n_a} a_k'^*(\vec{r}) a_l'(\vec{r}) U_{lj} (\mathbf{U}^\dagger)_{jk} = \sum_{k,l=1}^{n_a} a_k'^*(\vec{r}) a_l'(\vec{r}) \delta_{kl} \\
&= \sum_{k=1}^{n_a} a_k'^*(\vec{r}) a_k'(\vec{r}) = \sum_{k=1}^{n_a} |a_k'(\vec{r})|^2 .
\end{aligned}
\qquad (7.5)
$$

Q.E.D.

According to the previous results, the electron density corresponding to a determinant wave function behaves like that of a set of independent electrons occupying orthonormalized orbitals. However, we shall stress again that one should not attribute too much physical meaning to these *individual* orbitals because any set of orthonormalized orbitals spanning the given occupied subspace will exhibit the same behavior and give the same resulting electron density. (The same holds for any other one-electron property, as well.)

If one uses an LCAO expansion of the type (6.90), (6.115) then the electron density can be expressed also in terms of the basis orbitals χ_μ:

$$
\begin{aligned}
\varrho(\vec{r}) &= \sum_{j=1}^{n_a} a_j^*(\vec{r}) a_j(\vec{r}) + \sum_{j=1}^{n_b} b_j^*(\vec{r}) b_j(\vec{r}) \qquad (7.6) \\
&= \sum_{j=1}^{n_a} \sum_{\nu=1}^{m} a_\nu^{j*} \chi_\nu^*(\vec{r}) \sum_{\mu=1}^{m} a_\mu^j \chi_\mu(\vec{r}) + \sum_{j=1}^{n_b} \sum_{\nu=1}^{m} b_\nu^{j*} \chi_\nu^*(\vec{r}) \sum_{\mu=1}^{m} b_\mu^j \chi_\mu(\vec{r}) .
\end{aligned}
$$

By using the elements of the P-matrices defined in (6.116), this may be rewritten as

$$\varrho(\vec{r}) = \sum_{\mu,\nu=1}^{m} (P_{\mu\nu}^a + P_{\mu\nu}^b) \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) = \sum_{\mu,\nu=1}^{m} D_{\mu\nu} \chi_\nu^*(\vec{r}) \chi_\mu(\vec{r}) . \quad (7.7)$$

We have introduced the "spinless density matrix" $\mathbf{D}$:

$$\mathbf{D} = \mathbf{P}^a + \mathbf{P}^b . \qquad (7.8)$$

In the RHF case this definition coincides with that in (6.110). Equation (7.7) obviously gives the sum of the densities that one can assign to the electrons

with spin α and β, respectively. Analogously, one can define the spin density $\varrho_s(\vec{r})$ as the difference of these densities:

$$\varrho_s(\vec{r}) = \sum_{\mu,\nu=1}^{m} (P_{\mu\nu}^a - P_{\mu\nu}^b)\chi_\nu^*(\vec{r})\chi_\mu(\vec{r}) = \sum_{\mu,\nu=1}^{m} P_{\mu\nu}^s \chi_\nu^*(\vec{r})\chi_\mu(\vec{r}) , \quad (7.9)$$

where

$$\mathbf{P}^s = \mathbf{P}^a - \mathbf{P}^b \qquad (7.10)$$

is the "spin-density matrix."

If one integrates the electron density $\varrho(\vec{r})$ over the whole space, then the number of electrons $N = n_a + n_b$ is recovered. This follows from the fact that orbitals a_i and b_i are normalized, so each term in the sums in (7.3) contributes unity to the integral $\int \varrho(\vec{r})dv$. By using the expansion in (7.7), the integral of the electron density can also be expressed through the traces of matrices $\mathbf{P}^a\mathbf{S}$, $\mathbf{P}^b\mathbf{S}$, and $\mathbf{DS}$:

$$\begin{aligned}
\sum_{\mu,\nu=1}^{m} P_{\mu\nu}^a S_{\nu\mu} &= \sum_{\mu=1}^{m}(\mathbf{P}^a\mathbf{S})_{\mu\mu} = \mathrm{Tr}(\mathbf{P}^a\mathbf{S}) = n_a \\
\sum_{\mu,\nu=1}^{m} P_{\mu\nu}^b S_{\nu\mu} &= \sum_{\mu=1}^{m}(\mathbf{P}^b\mathbf{S})_{\mu\mu} = \mathrm{Tr}(\mathbf{P}^b\mathbf{S}) = n_b \qquad (7.11) \\
\sum_{\mu,\nu=1}^{m} D_{\mu\nu} S_{\nu\mu} &= \sum_{\mu=1}^{m}(\mathbf{DS})_{\mu\mu} = \mathrm{Tr}(\mathbf{DS}) = N .
\end{aligned}$$

We should note that the expansion in (7.7) and the equalities in (7.11) are valid for any N-electron wave function with n_a electrons of spin α and n_b electrons of spin β—i.e., with the resulting spin projection $S_z = \frac{1}{2}(n_a - n_b)$— because the expansion in (7.7) has the most general possible form, provided that the wave function is built up of the m basis orbitals χ_μ. However, the idempotency properties $(\mathbf{P}^a\mathbf{S})^2 = \mathbf{P}^a\mathbf{S}$; $(\mathbf{P}^b\mathbf{S})^2 = \mathbf{P}^b\mathbf{S}$ hold only if the wave function is a single determinant.

1.2. Population analysis

According to (7.11) the trace of matrix $\mathbf{DS}$ equals the number of electrons in the system, and this equation defines a distribution of the electrons between the basis orbitals χ_μ. In accord with this, the quantity

$$q_\mu = (\mathbf{DS})_{\mu\mu} = \sum_{\nu=1}^{m} D_{\mu\nu} S_{\nu\mu} \qquad (7.12)$$

is called "Mulliken's gross orbital population" of the basis orbital χ_μ, and the q_μs sum to the number of electrons.

One can consider q_μ as consisting of terms of two types:

$$q_\mu = D_{\mu\mu} + \sum_{\substack{\nu=1 \\ (\nu \neq \mu)}}^{m} D_{\mu\nu} S_{\nu\mu} \,. \tag{7.13}$$

(The basis functions are assumed normalized $S_{\mu\mu} = 1$.)

The first term is called "Mulliken's net orbital population" of orbital χ_μ; it comes from integrating the term $D_{\mu\mu}\chi_\mu^*(\vec{r})\chi_\mu(\vec{r})$ in the expansion in (7.7). The second term comes from integrating the terms $D_{\mu\nu}\chi_\nu^*(\vec{r})\chi_\mu(\vec{r})$ with $\nu \neq \mu$. It is connected with the existence of an "overlap density" $\chi_\nu^*(\vec{r})\chi_\mu(\vec{r})$ that does not integrate to 0, which would be the case if the basis set were orthogonal.

The given pair of orbitals χ_μ and χ_ν give the contribution $\chi_\nu^*(\vec{r})\chi_\mu(\vec{r}) + \chi_\mu^*(\vec{r})\chi_\nu(\vec{r})$ to the total electron density in (7.7). The first of these terms is taken into account when computing the gross orbital population q_μ, whereas the second contributes to the gross orbital population q_ν. In the case of real orbitals these two terms are equal, and this is the reason why one often speaks about the "halving" of the total overlap density $2\chi_\mu(\vec{r})\chi_\nu(\vec{r})$ and the corresponding "overlap populations" $2D_{\mu\nu}S_{\mu\nu}$ when computing Mulliken's gross populations q_μ, q_ν. (If the orbitals are real, $D_{\mu\nu} = D_{\nu\mu}$, as well.) The present author cannot agree with the opinion that this halving is "arbitrary"; it follows from (7.11) and therefore it is the only possibility that is consistent with the mathematical structure of the formalism of using overlapping basis orbitals (matrices $\mathbf{P}^a\mathbf{S}$ and $\mathbf{P}^b\mathbf{S}$ are the idempotent projection matrices).

If one applies a basis set each orbital of which is centered on a given atom (as is common), then one may sum the gross orbital populations q_μ for all the orbitals assigned to a given atom A (this assignment will be denoted as $\mu \in A$) and get Mulliken's gross atomic population of that atom:

$$Q_A = \sum_{\mu \in A} q_\mu = \sum_{\mu \in A} (\mathbf{DS})_{\mu\mu} = \sum_{\mu \in A} \sum_{\nu=1}^{m} D_{\mu\nu} S_{\nu\mu} \,. \tag{7.14}$$

The gross atomic population Q_A can naturally be decomposed as

$$Q_A = d_A + \sum_{\substack{B \\ (B \neq A)}} d_{AB} \,, \tag{7.15}$$

where the quantity d_A containing the terms in which both indices correspond to atom A

$$d_A = \sum_{\mu,\nu \in A} D_{\mu\nu} S_{\nu\mu} \tag{7.16}$$

is called Mulliken's net atomic population, whereas the quantity of diatomic nature

$$d_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} D_{\mu\nu} S_{\nu\mu} \qquad (7.17)$$

is called "Mulliken's overlap population." (Often this name is used for the quantity $d_{AB} + d_{BA}$, which is equal to $2d_{AB}$ if real orbitals are used.) It is to be stressed that the net atomic population d_A is not simply the sum of the net orbital populations but it also contains the overlap populations of all pairs of the orbitals that both are centered on the same atom.

Mulliken's overlap population is a significant positive number (say of order ~0.5) for chemically bonded pairs of atoms and reflects the accumulation of the electronic charge in the bonding region. Its value usually correlates well with the strength of the bond between the atoms involved. From the other side, a negative value of the overlap population between chemically nonbonded atoms indicates an antibonding situation and makes probable a repulsive interaction.

Invariance

In practice one usually applies basis orbitals that are centered on the given atom and are oriented according to the external "laboratory" coordinate frame—e.g., one uses orbitals p_x, p_y, p_z that are oriented along the axes x, y, and z. Obviously, if one rotates the molecule with respect to the laboratory frame, then the expansion coefficients of each molecular orbital will change, although the molecular wave function remains essentially the same. This is especially evident if one considers this process as the laboratory frame being rotated around the molecule. The change of the orbital coefficients results in the change of the matrix $\mathbf{D}$, as well, although the physical situation—the state of the molecule—remains invariant. (In particular, only the D-matrix elements between orbitals of s-type remain the same; all the others will change under rotations.)

One often uses the concept of "hybrid atomic orbitals" representing linear combinations of the basis orbitals of type s and p (sometimes also d) for the discussion of different chemical problems, in particular the directional character of the chemical bonds. Obviously, turning to such a hybrid basis will not change any relevant results of the calculations.

According to the previous discussion, one may use for interpretations only quantities that have "rotational–hybridizational invariance", i.e., remain the same if one subjects the orbitals centered on a given atom to any nonsingular linear transformation. (For that reason neither the individual D-matrix elements nor their sum for a given pair of atoms can be assigned any significance—contrary the old π-electron theories in which the off-diagonal elements $D_{\mu\nu}$ were treated as "bond orders.")

We are going to prove here the rotational–hybridizational invariance of Mulliken's net and gross atomic populations of a given atom and of Mulliken's

overlap population of a given pair of atoms. For that reason we consider non-singular linear transformations between the basis orbitals centered on the same atom:

$$\chi'_\mu = \sum_{\nu \in A} T^A_{\nu\mu} \chi_\nu \qquad (\mu \in A) . \tag{7.18}$$

One can treat the rotational–hybridizational transformations (7.18) of the basis orbitals of all atoms simultaneously by introducing the block-diagonal transformation matrix $\mathbf{T}$, the diagonal blocks of which are the transformation matrices $\mathbf{T}^A$ of the individual atoms:

$$\mathbf{T} = \begin{pmatrix} \mathbf{T}^1 & \mathbf{0} & \mathbf{0} & \ldots & \mathbf{0} \\ \mathbf{0} & \mathbf{T}^2 & \mathbf{0} & \ldots & \mathbf{0} \\ \vdots & \vdots & \vdots & & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \ldots & \mathbf{T}^M \end{pmatrix} \tag{7.19}$$

where M is the number of the atoms in the system. Using matrix $\mathbf{T}$, the transformation of the whole basis can compactly be defined as

$$\chi'_\mu = \sum_{\nu=1}^{m} T_{\nu\mu} \chi_\nu \qquad \mu = 1, 2, \ldots, m . \tag{7.20}$$

As every transformation $\mathbf{T}^A$ has been assumed to be nonsingular, the same holds for matrix $\mathbf{T}$; the inverse matrix $\mathbf{T}^{-1}$ is again block-diagonal and its diagonal blocks are the inverse transformation matrices $(\mathbf{T}^A)^{-1}$, corresponding to the individual atoms. The inverse matrix $\mathbf{T}^{-1}$ permits one to define the inverse of the transformation in (7.20):

$$\chi_\mu = \sum_{\nu=1}^{m} (\mathbf{T}^{-1})_{\nu\mu} \chi'_\nu . \tag{7.21}$$

Thus each molecular orbital $a_i = \sum_{\mu=1}^{m} a^i_\mu \chi_\mu$ can also be expressed in terms of the new basis orbitals:

$$\begin{aligned} a_i &= \sum_{\mu=1}^{m} a^i_\mu \chi_\mu = \sum_{\mu=1}^{m} a^i_\mu \sum_{\nu=1}^{m} (\mathbf{T}^{-1})_{\nu\mu} \chi'_\nu \\ &= \sum_{\nu=1}^{m} \left(\sum_{\mu=1}^{m} (\mathbf{T}^{-1})_{\nu\mu} a^i_\mu \right) \chi'_\nu = \sum_{\nu=1}^{m} a^{i\prime}_\nu \chi'_\nu \end{aligned} \tag{7.22}$$

i.e., the vectors of the orbital coefficients transform by the inverse of matrix $\mathbf{T}$:

$$\mathbf{a}^{i\prime} = \mathbf{T}^{-1} \mathbf{a}^i \tag{7.23}$$

and similarly for the orbitals of spin β.

According to these considerations, matrix $\mathbf{D}$ transforms as

$$
\begin{aligned}
\mathbf{D}' = \mathbf{P}^{a\,\prime} + \mathbf{P}^{b\,\prime} &= \sum_{i=1}^{n_a} \mathbf{a}^{i\,\prime}(\mathbf{a}^{i\,\prime})^\dagger + \sum_{i=1}^{n_b} \mathbf{b}^{i\,\prime}(\mathbf{b}^{i\,\prime})^\dagger \\
&= \sum_{i=1}^{n_a} \mathbf{T}^{-1}\mathbf{a}^i\mathbf{a}^{i\dagger}\mathbf{T}^{-1\dagger} + \sum_{i=1}^{n_b} \mathbf{T}^{-1}\mathbf{b}^i\mathbf{b}^{i\dagger}\mathbf{T}^{-1\dagger} \\
&= \mathbf{T}^{-1}\mathbf{D}\mathbf{T}^{-1\dagger} ,
\end{aligned}
\tag{7.24}
$$

where the identity $(\mathbf{Ab})^\dagger = \mathbf{b}^\dagger \mathbf{A}^\dagger$ has been utilized.

The overlap matrix transforms as

$$
\begin{aligned}
S'_{\mu\nu} &= \langle \chi'_\mu | \chi'_\nu \rangle = \langle \sum_{\varrho=1}^m T_{\varrho\mu}\chi_\varrho | \sum_{\tau=1}^m T_{\tau\nu}\chi_\tau \rangle \\
&= \sum_{\varrho,\tau=1}^m T^*_{\varrho\mu} S_{\varrho\tau} T_{\tau\nu} = \sum_{\varrho,\tau=1}^m (\mathbf{T}^\dagger)_{\mu\varrho} S_{\varrho\tau} T_{\tau\nu}
\end{aligned}
\tag{7.25}
$$

i.e.,

$$
\mathbf{S}' = \mathbf{T}^\dagger \mathbf{S} \mathbf{T} .
\tag{7.26}
$$

The net atomic population d_A and the interatomic overlap populations d_{AB} are invariant with respect to the rotational–hybridizational transformations described by matrix $\mathbf{T}$; consequently Mulliken's gross atomic population representing their sum according to (7.15) is invariant as well.

Proof

We have for the net atomic population in the transformed basis

$$
\begin{aligned}
d'_A &= \sum_{\mu,\nu\in A} D'_{\mu\nu} S'_{\nu\mu} = \sum_{\mu,\nu\in A} (\mathbf{T}^{-1}\mathbf{D}\mathbf{T}^{-1\dagger})_{\mu\nu}(\mathbf{T}^\dagger \mathbf{S}\mathbf{T})_{\nu\mu} \\
&= \sum_{\kappa,\lambda,\varrho,\tau=1}^m \sum_{\mu,\nu\in A} (\mathbf{T}^{-1})_{\mu\kappa} D_{\kappa\lambda}(\mathbf{T}^{-1\dagger})_{\lambda\nu}(\mathbf{T}^\dagger)_{\nu\varrho} S_{\varrho\tau} T_{\tau\mu} .
\end{aligned}
\tag{7.27}
$$

Owing to the block-diagonality of matrices $\mathbf{T}$, $\mathbf{T}^{-1}$ and $\mathbf{T}^\dagger$, $\mathbf{T}^{-1\dagger}$, one has by summing over μ and ν,

$$
\sum_{\mu\in A} T_{\tau\mu}(\mathbf{T}^{-1})_{\mu\kappa} = \begin{cases} \delta_{\tau\kappa} & \text{if } \tau,\kappa \in A \\ 0 & \text{otherwise} \end{cases}
\tag{7.28}
$$

and

$$
\sum_{\nu\in A} (\mathbf{T}^{-1\dagger})_{\lambda\nu}(\mathbf{T}^\dagger)_{\nu\varrho} = \begin{cases} \delta_{\lambda\varrho} & \text{if } \lambda,\varrho \in A \\ 0 & \text{otherwise} \end{cases}
\tag{7.29}
$$

respectively. Therefore, the summations over κ, λ, ϱ, and τ can be restricted to the indices belonging to atom A. We get accordingly

$$d'_A = \sum_{\kappa,\lambda,\varrho,\tau \in A} \delta_{\tau\kappa} D_{\kappa\lambda} \delta_{\lambda\varrho} S_{\varrho\tau} = \sum_{\tau,\varrho \in A} D_{\tau\varrho} S_{\varrho\tau} = d_A \,, \qquad (7.30)$$

i.e., the net atomic population is invariant. The overlap population between atoms A and B is invariant, as well. We have, similarly to the previous case

$$
\begin{aligned}
d'_{AB} &= \sum_{\mu \in A} \sum_{\nu \in B} D'_{\mu\nu} S'_{\nu\mu} & (7.31)\\
&= \sum_{\kappa,\lambda,\varrho,\tau=1}^{m} \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{T}^{-1})_{\mu\kappa} D_{\kappa\lambda} (\mathbf{T}^{-1\dagger})_{\lambda\nu} (\mathbf{T}^{\dagger})_{\nu\varrho} S_{\varrho\tau} T_{\tau\mu} \,.
\end{aligned}
$$

For the sum over μ we have again (7.28), whereas for the sum over ν we get (7.29) but with A being replaced by B. Thus the summation over κ and τ should be restricted to atom A whereas the sums for λ and ϱ are restricted to atom B:

$$d'_{AB} = \sum_{\kappa,\tau \in A} \sum_{\lambda,\varrho \in B} \delta_{\tau\kappa} D_{\kappa\lambda} \delta_{\lambda\varrho} S_{\varrho\tau} = \sum_{\tau \in A} \sum_{\varrho \in B} D_{\tau\varrho} S_{\varrho\tau} = d_{AB} \,. \qquad (7.32)$$

Q.E.D.

One may conclude that Mulliken's overlap population is the simplest quantity that is linear in the interatomic D-matrix elements and has the correct rotational–hybridizational invariance.

2.   Bond orders and valences

2.1.   Bond order index

Although Mulliken's overlap population is a parameter that permits one to identify chemically bonded atoms, it cannot be put directly into correspondence with such a chemical notion as the bond order (multiplicity) of a chemical bond—it does not have the value of (about) 1, 2, and 3 for a single, double, and triple chemical bond, respectively. Classically the bond order between the atoms of a diatomic molecule can be defined as $\frac{1}{2}(N_{\text{bonding}} - N_{\text{antibonding}})$, where N_{bonding} and $N_{\text{antibonding}}$ are the number of electrons occupying bonding and antibonding orbitals, respectively. Thus the molecular ion H_2^+ is characterized by a bond order of $\frac{1}{2}$ (one electron on a bonding orbital) and molecule H_2 has a bond order of 1 (2 electrons on a bonding MO), whereas the helium dimer has a zero bond order. One can describe He_2 either by using two doubly occupied localized atomic $1s$ orbitals or by using the sum and difference of them, representing delocalized MOs of bonding and antibonding character,

respectively. As both are doubly occupied, $N_{\text{bonding}} = N_{\text{antibonding}} = 2$ and one gets a bond order 0 between the two atoms, in full accord with the chemical expectations. Similarly, one gets, for instance, a bond order 3 for N_2 and 1 for F_2. Obviously, such a counting of electrons is strictly possible for a diatomics only.

In the framework of the simple Hückel theory (and, in general, in the π-electron theories) the off-diagonal elements of the matrix $\mathbf{D}$ were called (Coulson's) bond order. This definition, however, could not be generalized for theories in which a given atom bears more than one basis orbital. The first quantum chemical quantity that could be put in correspondence with the classical chemical notion of the bond multiplicity for a multiatomic molecule and is computable from the wave function was the so-called Wiberg index. It was originally introduced in the framework of the semiempirical CNDO theory and is applicable only if the basis orbitals are orthonormalized.

The Wiberg index between atoms A and B of a closed shell-system is defined as

$$W_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} |D_{\mu\nu}|^2 . \tag{7.33}$$

The adequate generalization of this formula for an open-shell system treated at the single-determinant UHF level is

$$\begin{aligned} W_{AB} &= 2 \sum_{\mu \in A} \sum_{\nu \in B} (|P_{\mu\nu}^a|^2 + |P_{\mu\nu}^b|^2) \\ &= \sum_{\mu \in A} \sum_{\nu \in B} (|D_{\mu\nu}|^2 + |P_{\mu\nu}^s|^2) , \end{aligned} \tag{7.34}$$

where matrices $\mathbf{D}$, $\mathbf{P}^a$, $\mathbf{P}^b$, and $\mathbf{P}^s$ are defined by (7.8), (6.116) and (7.10). The equivalence of the two forms given in (7.34) can be checked trivially by using the equalities $\mathbf{D} = \mathbf{P}^a + \mathbf{P}^b$; $\mathbf{P}^s = \mathbf{P}^a - \mathbf{P}^b$.

By writing $|D_{\mu\nu}|^2$ as $D_{\mu\nu}D_{\nu\mu}$, etc., and using (7.24), one can easily see that the Wiberg index is invariant with respect to unitary transformations between the orbitals centered on the same atom—as those induced by the rotations of the coordinate frame (then $\mathbf{T}^{-1\dagger} = \mathbf{T}$)—but not with respect to a general (nonsingular but nonunitary) transformation. Therefore the Wiberg index as defined previously is not applicable in the *ab initio* theory, in which invariance with respect to such transformations should be required, as well. (The basis orbitals may be nonorthogonal.) The proper generalization of the Wiberg index for the *ab initio* theory has been introduced by the present author. (An analogous definition was proposed by Giambiagi in the framework of the semiempirical "extended Hückel theory" also applying overlapping basis sets.)

The respective definitions of the bond order index are

$$B_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{DS})_{\mu\nu} (\mathbf{DS})_{\nu\mu} \qquad (7.35)$$

for the closed-shell (RHF) case and

$$
\begin{aligned}
B_{AB} &= 2 \sum_{\mu \in A} \sum_{\nu \in B} [(\mathbf{P}^a \mathbf{S})_{\mu\nu} (\mathbf{P}^a \mathbf{S})_{\nu\mu} + (\mathbf{P}^b \mathbf{S})_{\mu\nu} (\mathbf{P}^b \mathbf{S})_{\nu\mu}] \\
&= \sum_{\mu \in A} \sum_{\nu \in B} [(\mathbf{DS})_{\mu\nu} (\mathbf{DS})_{\nu\mu} + (\mathbf{P}^s \mathbf{S})_{\mu\nu} (\mathbf{P}^s \mathbf{S})_{\nu\mu}]
\end{aligned}
\qquad (7.36)
$$

for the open-shell (UHF) one. Again, the equivalence of the two forms in (7.36) can be checked by using the definitions $\mathbf{D} = \mathbf{P}^a + \mathbf{P}^b$, $\mathbf{P}^s = \mathbf{P}^a - \mathbf{P}^b$. Obviously, definition (7.36) reduces to the previous one if applied to a closed-shell RHF wave function ($\mathbf{P}^s = \mathbf{0}$). Furthermore, if the basis set is orthonormalized ($\mathbf{S} = \mathbf{1}$), then one has $B_{AB} = W_{AB}$. We shall also note that these definitions remain valid also for correlated wave functions. In that case the definition of matrices $\mathbf{P}^a$ and $\mathbf{P}^b$ or $\mathbf{D}$ and $\mathbf{P}^s$ via the orbital coefficients is not applicable, of course, but these matrices may be identified as the matrices of expansion coefficients of electron density and spin density in (7.7) and (7.9).

Invariance

The bond order index defined by (7.35) for the closed-shell RHF case is the simplest quantity that is quadratic in the interatomic elements of matrix $\mathbf{D}$ and has the correct rotational–hybridizational invariance. Similar considerations hold for definition (7.36) applicable in the UHF case involving two matrices $\mathbf{P}^a$ and $\mathbf{P}^b$ or $\mathbf{D}$ and $\mathbf{P}^s$. We shall prove the invariance of definition (7.35); the matrices in (7.36) behave in exactly the same manner.

Thus we have to study the bond order index in (7.35) and establish its invariance under the transformation in (7.18) involving the block-diagonal matrix in (7.19). We have after the transformation

$$B'_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{D}'\mathbf{S}')_{\mu\nu} (\mathbf{D}'\mathbf{S}')_{\nu\mu} , \qquad (7.37)$$

where the transformed matrices $\mathbf{D}'$ and $\mathbf{S}'$ are given by (7.24) and (7.26), respectively. Accordingly, we have for their product

$$\mathbf{D}'\mathbf{S}' = \mathbf{T}^{-1}\mathbf{D}\mathbf{T}^{-1\dagger}\mathbf{T}^{\dagger}\mathbf{S}\mathbf{T} = \mathbf{T}^{-1}\mathbf{D}\mathbf{S}\mathbf{T} \qquad (7.38)$$

and

$$B'_{AB} = \sum_{\kappa,\lambda,\varrho,\tau=1}^{m} \sum_{\mu \in A} \sum_{\nu \in B} (\mathbf{T}^{-1})_{\mu\kappa} (\mathbf{DS})_{\kappa\lambda} T_{\lambda\nu} (\mathbf{T}^{-1})_{\nu\varrho} (\mathbf{DS})_{\varrho\tau} T_{\tau\mu} . \qquad (7.39)$$

Similar to the case of the overlap population d_{AB}, we again should use (7.28) and (7.29), replacing in the latter A with B. The sums over κ and τ should again be restricted to atom A, and those for λ and ϱ to atom B:

$$
\begin{aligned}
B'_{AB} &= \sum_{\kappa,\tau \in A} \sum_{\lambda,\varrho \in B} \delta_{\tau\kappa} (\mathbf{DS})_{\kappa\lambda} \delta_{\lambda\varrho} (\mathbf{DS})_{\varrho\tau} \\
&= \sum_{\tau \in A} \sum_{\varrho \in B} (\mathbf{DS})_{\tau\varrho} (\mathbf{DS})_{\varrho\tau} = B_{AB}
\end{aligned}
\tag{7.40}
$$

Q.E.D.

2.2. Valence indices

Following Wiberg, it is worthwhile to define the quantity $b_\mu = 2q_\mu - q_\mu^2$, where q_μ is Mulliken's gross orbital population of the basis orbital χ_μ. This quantity can be considered as a measure of the actual bonding ability of orbital χ_μ in the molecule: it has a maximum for $q_\mu = 1$, characterizing an orbital participating in a pure covalent bond and vanishes for both an empty orbital having no role in the molecule ($q_\mu = 0$) and for a doubly filled one ($q_\mu = 2$) having no chemical significance (e.g., a core orbital). If one sums the quantities b_μ for all the basis orbitals centered on a given atom, but subtracts the chemically irrelevant intra-atomic partial bond orders, then one gets the definition of the actual *valence* of an atom in the molecule:

$$
V_A = 2Q_a - \sum_{\mu,\nu \in A} (\mathbf{DS})_{\mu\nu} (\mathbf{DS})_{\nu\mu} \, ,
\tag{7.41}
$$

where Q_A is Mulliken's gross atomic population of atom A.

In the closed-shell RHF case one has for matrix $\mathbf{P}$ the idempotency property $(\mathbf{PS})^2 = \mathbf{PS}$, which leads to the equality $(\mathbf{DS})^2 = 2\mathbf{DS}$ for the matrix $\mathbf{D} = 2\mathbf{P}$. As a consequence, one obtains the equality

$$
V_A = \sum_{\substack{B \\ (B \neq A)}} B_{AB} \, ,
\tag{7.42}
$$

i.e., if a closed-shell determinant wave function is used, then the valence of an atom is equal to the sum of its bond orders formed with all the other atoms.

In fact, by substituting $Q_A = \sum_{\mu \in A} q_\mu = \sum_{\mu \in A} (\mathbf{DS})_{\mu\mu}$, one gets

$$
V_A = \sum_{\mu \in A} 2(\mathbf{DS})_{\mu\mu} - \sum_{\mu,\nu \in A} (\mathbf{DS})_{\mu\nu} (\mathbf{DS})_{\nu\mu} \, .
\tag{7.43}
$$

It follows from the idempotency property mentioned previously that

$$2(\mathbf{DS})_{\mu\mu} = [(\mathbf{DS})^2]_{\mu\mu} = \sum_{\nu=1}^{m}(\mathbf{DS})_{\mu\nu}(\mathbf{DS})_{\nu\mu} . \tag{7.44}$$

Substituting this into Eq. (7.43) we have, separating out terms with $\nu \in A$ and grouping the remaining ones by the respective atoms,

$$\begin{aligned}
V_A &= \sum_{\mu\in A}\left[\sum_{\nu\in A}(\mathbf{DS})_{\mu\nu}(\mathbf{DS})_{\nu\mu} + \sum_{\substack{B\\B\neq A}}\sum_{\nu\in B}(\mathbf{DS})_{\mu\nu}(\mathbf{DS})_{\nu\mu}\right]\\
&\quad - \sum_{\mu,\nu\in A}(\mathbf{DS})_{\mu\nu}(\mathbf{DS})_{\nu\mu} = \sum_{\substack{B\\B\neq A}}\sum_{\mu\in A}\sum_{\nu\in B}(\mathbf{DS})_{\mu\nu}(\mathbf{DS})_{\nu\mu}\\
&= \sum_{\substack{B\\(B\neq A)}} B_{AB} . \tag{7.45}
\end{aligned}$$

Q.E.D.

Equality (7.45) does not hold for an open-shell (UHF) wave function or if a correlated wave function is used. In these cases the difference between the actual total valence of the atom and the sum of its bond orders is defined as the *free valence* of the atom

$$F_A = V_A - \sum_{\substack{B\\(B\neq A)}} B_{AB} . \tag{7.46}$$

The valence index V_A may be considered as a quantum chemical counterpart of the chemist's concept of the actual covalent valence of an atom, and it usually gives values close to the integer numbers corresponding to the classical chemical picture of molecules. In the case of free radicals, biradicals, etc., the free valence index can be put in a close correspondence to the "dots" used by chemists to denote the radical centers on the chemical formulae. (More generally, significant values of the free valence index indicate the atoms where radical attack may be expected in the molecule.)

The previous interpretation of the free valence index is supported by the fact that in the UHF case the free valence index can be expressed through the spin-density matrix $\mathbf{P}^s$ as

$$F_A = \sum_{\mu,\nu\in A}(\mathbf{P}^s\mathbf{S})_{\mu\nu}(\mathbf{P}^s\mathbf{S})_{\nu\mu} . \tag{7.47}$$

To derive (7.47), first we shall get a transformed expression for the quantity $2Q_A$ occurring in the definition (7.41) of V_A, by using the equality $\mathbf{D} = \mathbf{P}^a + \mathbf{P}^b$ and the idempotency properties $(\mathbf{P}^a\mathbf{S})^2 = \mathbf{P}^a\mathbf{S}$, $(\mathbf{P}^b\mathbf{S})^2 = \mathbf{P}^b\mathbf{S}$:

$$
\begin{aligned}
2Q_A &= 2\sum_{\mu \in A} (\mathbf{DS})_{\mu\mu} = 2\sum_{\mu \in A}[(\mathbf{P}^a\mathbf{S})_{\mu\mu} + (\mathbf{P}^b\mathbf{S})_{\mu\mu}] \\
&= 2\sum_{\mu \in A}\left\{[(\mathbf{P}^a\mathbf{S})^2]_{\mu\mu} + [(\mathbf{P}^b\mathbf{S})^2]_{\mu\mu}\right\} \\
&= 2\sum_{\mu \in A}\sum_{\nu=1}^{m}[(\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + (\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu}] \qquad (7.48) \\
&= 2\sum_{\mu,\nu \in A}[(\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + (\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu}] \\
&\quad + 2\sum_{\mu \in A}\sum_{\substack{B \\ (B \neq A)}}\sum_{\nu \in B}[(\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + (\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu}] \\
&= 2\sum_{\mu,\nu \in A}[(\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + (\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu}] + \sum_{\substack{B \\ (B \neq A)}} B_{AB},
\end{aligned}
$$

where the definition in (7.36) of the bond order index B_{AB} has also been utilized. By substituting the definition in (7.41) into (7.46), we have for the free valence index

$$
\begin{aligned}
F_A &= V_A - \sum_{\substack{B \\ (B \neq A)}} B_{AB} = 2Q_A - \sum_{\mu,\nu \in A}(\mathbf{DS})_{\mu\nu}(\mathbf{DS})_{\nu\mu} - \sum_{\substack{B \\ (B \neq A)}} B_{AB} \\
&= 2Q_A - \sum_{\mu,\nu \in A}[(\mathbf{P}^a + \mathbf{P}^b)\mathbf{S}]_{\mu\nu}[(\mathbf{P}^a + \mathbf{P}^b)\mathbf{S}]_{\nu\mu} - \sum_{\substack{B \\ (B \neq A)}} B_{AB}.
\end{aligned}
$$

$$(7.49)$$

Substituting here expression (7.48) we get (terms containing B_{AB} cancel):

$$
\begin{aligned}
F_A &= \sum_{\mu,\nu \in A}\{2(\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + 2(\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu} \\
&\quad -[(\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + (\mathbf{P}^a\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu} \qquad (7.50) \\
&\quad +(\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^a\mathbf{S})_{\nu\mu} + (\mathbf{P}^b\mathbf{S})_{\mu\nu}(\mathbf{P}^b\mathbf{S})_{\nu\mu}]\} \\
&= \sum_{\mu,\nu \in A}[(\mathbf{P}^a - \mathbf{P}^b)\mathbf{S}]_{\mu\nu}[(\mathbf{P}^a - \mathbf{P}^b)\mathbf{S}]_{\nu\mu} = \sum_{\mu,\nu \in A}(\mathbf{P}^s\mathbf{S})_{\mu\nu}(\mathbf{P}^s\mathbf{S})_{\nu\mu}
\end{aligned}
$$

Q.E.D.

2.3. Exchange density and bond order

The expectation value $\varrho(\vec{r}) = \langle\Psi|\sum_{i=1}^{N}\delta(\vec{r}_i - \vec{r})|\Psi\rangle$ of the operator $\hat{\varrho} = \sum_{i=1}^{N}\delta(\vec{r}_i - \vec{r})$ gives the electron density, i.e., the probability density of finding an electron in the vicinity of the point with the radius-vector $\vec{r}$. Similarly to this, we can define the pair density $\varrho_2(\vec{r},\vec{r}')$ giving the probability of finding one electron around the point $\vec{r}$ and another electron around the point $\vec{r}'$. It is, obviously, given by the expectation value of the operator

$$\hat{\varrho}_2(\vec{r},\vec{r}') = \sum_{\substack{i,j \\ (i \neq j)}} \delta(\vec{r}_i - \vec{r})\delta(\vec{r}_j - \vec{r}') \,. \tag{7.51}$$

One can easily transform this operator as

$$\begin{aligned}
\hat{\varrho}_2(\vec{r},\vec{r}') &= \sum_{i<j}\delta(\vec{r}_i - \vec{r})\delta(\vec{r}_j - \vec{r}') + \sum_{j<i}\delta(\vec{r}_i - \vec{r})\delta(\vec{r}_j - \vec{r}') \\
&= \sum_{i<j}\left[\delta(\vec{r}_i - \vec{r})\delta(\vec{r}_j - \vec{r}') + \delta(\vec{r}_j - \vec{r})\delta(\vec{r}_i - \vec{r}')\right] \,.
\end{aligned} \tag{7.52}$$

(We have interchanged the summation indices i and j in the second term.) Now, operator $\hat{\varrho}_2(\vec{r},\vec{r}')$ is a symmetric two-electron operator of the type considered in Section 6.3 of Chapter 5 with the definition

$$\hat{g}(i,j) = \delta(\vec{r}_i - \vec{r})\delta(\vec{r}_j - \vec{r}') + \delta(\vec{r}_i - \vec{r}')\delta(\vec{r}_j - \vec{r}) \,. \tag{7.53}$$

If Ψ is a single-determinant wave function built up of the *orthonormalized* spin orbitals $\psi_i(\vec{r},\sigma) = \varphi_i(\vec{r})\gamma_i(\sigma)$, then the expectation value of $\hat{\varrho}_2(\vec{r},\vec{r}')$ can be computed by using (5.116) as

$$\begin{aligned}
&\varrho_2(\vec{r},\vec{r}') \\
&= \frac{1}{2}\sum_{i,j=1}^{N}\Big[\langle\varphi_i(1)\varphi_j(2)|\delta(\vec{r}_1-\vec{r})\delta(\vec{r}_2-\vec{r}')+\delta(\vec{r}_1-\vec{r}')\delta(\vec{r}_2-\vec{r})|\varphi_i(1)\varphi_j(2)\rangle \\
&\quad -\langle\varphi_i(1)\varphi_j(2)|\delta(\vec{r}_1-\vec{r})\delta(\vec{r}_2-\vec{r}')+\delta(\vec{r}_1-\vec{r}')\delta(\vec{r}_2-\vec{r})|\varphi_j(1)\varphi_i(2)\rangle\delta_{\gamma_i\gamma_j}\Big] \\
&= \frac{1}{2}\sum_{i,j=1}^{N}\Big[|\varphi_i(\vec{r})|^2|\varphi_j(\vec{r}')|^2 + |\varphi_i(\vec{r}')|^2|\varphi_j(\vec{r})|^2 \\
&\quad -\Big(\varphi_i^*(\vec{r})\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_i(\vec{r}') + \varphi_i^*(\vec{r}')\varphi_j(\vec{r}')\varphi_j^*(\vec{r})\varphi_i(\vec{r})\Big)\delta_{\gamma_i\gamma_j}\Big] \,.
\end{aligned} \tag{7.54}$$

After interchanging the summation indices i and j in the second and fourth term, one gets

$$\varrho_2(\vec{r}, \vec{r}') = \sum_{i,j=1}^{N} \left(|\varphi_i(\vec{r})|^2 |\varphi_j(\vec{r}')|^2 - \varphi_i^*(\vec{r})\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_i(\vec{r}')\delta_{\gamma_i\gamma_j} \right) . \quad (7.55)$$

As $\displaystyle\sum_{i=1}^{N} |\varphi_i(\vec{r})|^2 = \varrho(\vec{r})$, one can write

$$\varrho_2(\vec{r}, \vec{r}') = \varrho(\vec{r})\varrho(\vec{r}') - \varrho_2^x(\vec{r}, \vec{r}') , \quad (7.56)$$

where the first term (it may be called "direct" or "Coulomb type") is the product of the electron densities in points $\vec{r}$ and $\vec{r}\,'$, whereas the second is the two-electron "exchange pair density." The exchange pair density originates from the antisymmetry of the wave function; it contains the compensation for the "self-interaction" of the electrons (*vide infra*) as well.

According to (7.55) we have

$$\varrho_2^x(\vec{r}, \vec{r}') = \sum_{i,j=1}^{N} \varphi_i^*(\vec{r})\varphi_j(\vec{r})\varphi_j^*(\vec{r}')\varphi_i(\vec{r}')\delta_{\gamma_i\gamma_j} . \quad (7.57)$$

If Ψ is a determinant built up of n_a orbitals a_i filled with spin α and n_b orbitals b_i filled with spin β, then

$$\varrho_2^x(\vec{r}, \vec{r}') = \sum_{i,j=1}^{n_a} a_i^*(\vec{r})a_j(\vec{r})a_j^*(\vec{r}')a_i(\vec{r}') + \sum_{i,j=1}^{n_b} b_i^*(\vec{r})b_j(\vec{r})b_j^*(\vec{r}')b_i(\vec{r}') . $$
$$(7.58)$$

Now we integrate $\varrho_2^x(\vec{r}, \vec{r}')$ over both variables $\vec{r}$ and $\vec{r}'$, by taking into account that both sets of orbitals $\{a_i\}$ and $\{b_i\}$ are orthonormalized, and obtain

$$
\begin{aligned}
\int \varrho_2^x(\vec{r}, \vec{r}')dv dv' &= \sum_{i,j=1}^{n_a} \langle a_i|a_j\rangle\langle a_j|a_i\rangle + \sum_{i,j=1}^{n_b} \langle b_i|b_j\rangle\langle b_j|b_i\rangle \\
&= \sum_{i,j=1}^{n_a} \delta_{ij} + \sum_{i,j=1}^{n_b} \delta_{ij} = n_a + n_b = N . \quad (7.59)
\end{aligned}
$$

We substitute the LCAO expansion in (6.115) of the orbitals into (7.59):

$$\sum_{i,j=1}^{n_a} \langle \sum_{\mu=1}^{m} a_\mu^i \chi_\mu | \sum_{\nu=1}^{m} a_\nu^j \chi_\nu \rangle \langle \sum_{\varrho=1}^{m} a_\varrho^j \chi_\varrho | \sum_{\tau=1}^{m} a_\tau^i \chi_\tau \rangle$$
$$(7.60)$$
$$+ \sum_{i,j=1}^{n_b} \langle \sum_{\mu=1}^{m} b_\mu^i \chi_\mu | \sum_{\nu=1}^{m} b_\nu^j \chi_\nu \rangle \langle \sum_{\varrho=1}^{m} b_\varrho^j \chi_\varrho | \sum_{\tau=1}^{m} b_\tau^i \chi_\tau \rangle = N$$

i.e.,

$$\sum_{i,j=1}^{n_a} \sum_{\mu,\nu,\varrho,\tau=1}^{m} a_\tau^i a_\mu^{i*} S_{\mu\nu} a_\nu^j a_\varrho^{j*} S_{\varrho\tau} + \sum_{i,j=1}^{n_b} \sum_{\mu,\nu,\varrho,\tau=1}^{m} b_\tau^i b_\mu^{i*} S_{\mu\nu} b_\nu^j b_\varrho^{j*} S_{\varrho\tau} = N \ .$$

(7.61)

By using the definitions in (6.116) this can be rewritten as

$$\sum_{\nu,\tau=1}^{m} [(\mathbf{P}^a \mathbf{S})_{\tau\nu}(\mathbf{P}^a \mathbf{S})_{\nu\tau} + (\mathbf{P}^b \mathbf{S})_{\tau\nu}(\mathbf{P}^b \mathbf{S})_{\nu\tau}] = N \ .$$

(7.62)

We can group the terms on the left-hand side according to the atoms on which the basis orbitals are centered. We get

$$\sum_{A,B} \sum_{\nu \in A} \sum_{\tau \in B} [(\mathbf{P}^a \mathbf{S})_{\tau\nu}(\mathbf{P}^a \mathbf{S})_{\nu\tau} + (\mathbf{P}^b \mathbf{S})_{\tau\nu}(\mathbf{P}^b \mathbf{S})_{\nu\tau}] = N \ .$$

(7.63)

Comparing this expression with the definition in (7.36), we see that the bond order B_{AB} between atoms A and B is the diatomic contribution to the integral of the exchange pair density $\varrho^x(\vec{r}, \vec{r}')$. (The factor 2 present in the definition in (7.36) is also recovered, because the sum for A and B in expansion (7.63) runs over all the atoms independently.)

One may observe that equality (7.62) can also be obtained as a consequence of the idempotency of matrices $\mathbf{P}^a \mathbf{S}$ and $\mathbf{P}^b \mathbf{S}$ and of using the equalities (Appendix VII) $\mathrm{Tr}(\mathbf{P}^a \mathbf{S}) = n_a$ and $\mathrm{Tr}(\mathbf{P}^b \mathbf{S}) = n_b$. Accordingly, by using these idempotency relations one can define also higher order bond indices, considering for instance the three-center contributions present in the quantity $\mathrm{Tr}(\mathbf{P}^a \mathbf{S} \mathbf{P}^a \mathbf{S} \mathbf{P}^a \mathbf{S} + \mathbf{P}^b \mathbf{S} \mathbf{P}^b \mathbf{S} \mathbf{P}^b \mathbf{S}) = N$, and so on.

We have to add a few more remarks concerning the close connection between exchange and chemical bonding. One may observe that the electron–electron repulsion energy $\langle \Psi | \sum_{i<j} \frac{1}{r_{ij}} | \Psi \rangle$ can be expressed by the pair density $\varrho_2(\vec{r}, \vec{r}')$ as

$$E_{el-el} = \langle \Psi | \sum_{i<j} \frac{1}{r_{ij}} | \Psi \rangle = \iint \frac{\varrho_2(\vec{r}, \vec{r}')}{\vec{r} - \vec{r}'} \, dv dv' \ .$$

(7.64)

This follows from the possibility of writing $\frac{1}{r_{ij}}$ in the form of the integral

$$\frac{1}{r_{ij}} = \frac{1}{|\vec{r}_i - \vec{r}_j|} = \frac{1}{2} \iint \frac{\delta(\vec{r}_i - \vec{r})\delta(\vec{r}_j - \vec{r}') + \delta(\vec{r}_i - \vec{r}')\delta(\vec{r}_j - \vec{r})}{|\vec{r} - \vec{r}'|} \, dv dv' \ .$$

(7.65)

Then, when computing $\langle \Psi | \sum_{i<j} \frac{1}{r_{ij}} | \Psi \rangle$ one may change the order of integrations and complete all of them except those over $\vec{r}$ and $\vec{r}'$. For a single-determinant

wave function, (7.64) can further be written by using (7.56) as

$$E_{el-el} = \iint \frac{\varrho(\vec{r})\varrho(\vec{r}')}{|\vec{r} - \vec{r}'|} \, dv dv' - \iint \frac{\varrho_2^x(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \, dv dv' . \qquad (7.66)$$

As $\varrho(\vec{r})$ is a density obtained by summing for all the electrons, the first term on the right-hand side contains the electrostatic interaction of each electron with each electron—including the interaction of a given electron in point $\vec{r}$ with its own charge density in point $\vec{r}'$. This is the case because we have included the self-repulsion terms $\hat{J}_i - \hat{K}_i$ in the Fock operator and the Hartree–Fock energy. The necessary compensation of this self-interaction is contained in the second term on the right-hand side (the exchange energy).

Obviously, a similar representation of E_{el-el} is also possible for correlated wave functions, but in that case the exchange part $\varrho_2^x(\vec{r}, \vec{r}')$ of the pair density should be replaced by the "exchange-correlation" one, which may be (formally) defined as the difference $\varrho_2^{xc}(\vec{r}, \vec{r}') = \varrho_2(\vec{r}, \vec{r}') - \varrho(\vec{r})\varrho(\vec{r}')$. In practice it can be computed by using the actual correlated wave function.

In the single-determinant case, by substituting (7.55) into (7.66) one immediately obtains the two-electron part of the Hartree–Fock energy expression (6.44). Its exchange component is

$$\begin{aligned} E^x &= -\iint \frac{\varrho_2^x(\vec{r}, \vec{r}')}{\vec{r} - \vec{r}'} \, dv dv' = -\sum_{i,j=1}^{N} [\varphi_i \varphi_j | \varphi_j \varphi_i] \delta_{\gamma_i \gamma_j} \\ &= -\sum_{i,j=1}^{n_a} [a_i a_j | a_j a_i] - \sum_{i,j=1}^{n_b} [b_i b_j | b_j b_i] . \end{aligned} \qquad (7.67)$$

This equality shows a close connection between the exchange pair density $\varrho_2^x(\vec{r}, \vec{r}')$ and the exchange part E^x of the total Hartree–Fock energy. It is to be pointed out that the exchange energy is negative. In fact, each integral $[\varphi_i \varphi_j | \varphi_j \varphi_i]$ is positive—at least if real orbitals are used—as it represents the electrostatic self-repulsion of the respective density $\varphi_i(\vec{r})\varphi_j(\vec{r})$. (This is in accord with the fact that exchange energy contains the correction for the self-interaction.)

As we have seen previously, the integral $\iint \varrho_2^x(\vec{r}, \vec{r}') dv dv'$ of the exchange pair density can be decomposed into one- and two-center components if atom-centered one-electron basis functions are used. This cannot be performed for the exchange energy (7.67) because the expansion of the two-electron integrals over the MOs will contain, in general, three- and four-center integrals over the basis orbitals, as well.

Such a decomposition is, however, possible—and rather instructive—in the simplest case of the CNDO-type model theories using the "zero differential

overlap" approximation:

$$[\chi_\mu\chi_\nu|\chi_\varrho\chi_\tau] = \gamma_{AB}\delta_{\mu\varrho}\delta_{\nu\tau} \qquad \mu \in A; \ \nu \in B . \tag{7.68}$$

Here A and B are the atoms on which the basis orbitals χ_μ and χ_ν, respectively, are centered. Using the approximation in (7.68), one obtains by substituting the LCAO expansion (6.115) of the orbitals a_i and b_i into the expression (7.67) and using the definitions (6.116) of matrices $\mathbf{P}^a, \mathbf{P}^b$:

$$
\begin{aligned}
E^x(CNDO) &= -\sum_{i,j=1}^{n_a} \sum_{\mu,\nu,\varrho,\tau=1}^{m} a_\mu^{i*} a_\nu^{j*} a_\varrho^j a_\tau^i [\chi_\mu\chi_\nu|\chi_\varrho\chi_\tau] \\
&\quad - \sum_{i,j=1}^{n_b} \sum_{\mu,\nu,\varrho,\tau=1}^{m} b_\mu^{i*} b_\nu^{j*} b_\varrho^j b_\tau^i [\chi_\mu\chi_\nu|\chi_\varrho\chi_\tau] \\
&= -\sum_{A,B} \sum_{\mu\in A} \sum_{\nu\in B} \sum_{\varrho,\tau=1}^{m} (P_{\tau\mu}^a P_{\varrho\nu}^a + P_{\tau\mu}^b P_{\varrho\nu}^b)\gamma_{AB}\delta_{\mu\varrho}\delta_{\nu\tau} \\
&= -\sum_{A,B} \sum_{\mu\in A} \sum_{\nu\in B} (|P_{\mu\nu}^a|^2 + |P_{\mu\nu}^b|^2)\gamma_{AB} .
\end{aligned}
\tag{7.69}
$$

Comparing this expression with (7.34) and taking into account that the sum for A and B runs over all the atoms independently, we arrive to the conclusion that the diatomic contribution to the exchange energy is proportional to the respective Wiberg index:

$$E_{AB}^x = -\frac{1}{2}\gamma_{AB}W_{AB} . \tag{7.70}$$

The author introduced the *ab initio* bond order index in (7.36) by considering an approximate *ab initio* generalization of this important relationship.

2.4. Bond orders in three-center bonds

Most chemical bonds can be considered as being formed by a pair of electrons occupying a two-center localized molecular orbital. (For multiply bonded atoms a few such bonding electron pairs should be assumed.) Conjugation and aromaticity can also be discussed on this basis, assuming that the wave function is a linear combination of several components, describing "resonance" between different "Kekulé-structures," each of which is characterized by two-electron two-center bonds. There are, however, systems in which one has to postulate the existence of *three-center bonds*. The probably most known example is the diborane molecule B_2H_6 in which the two boron atoms are bridged by two symmetrically positioned hydrogen atoms. The electronic structure of this molecule is usually described in terms of two three-center two-electron bonds

each of which is built up in first approximation of appropriate hybrid atomic orbitals of the two boron atom and the $1s$ orbital of the "bridging" hydrogen. This means that the hydrogen is bonded by partial bonds to both borons symmetrically. (There is a conceptual difference with the usual hydrogen bonds in which hydrogen has only a secondary bonding with one of the partners.) The significant distance between the boron atoms seemingly would indicate that there should be no significant interaction between them. This is, however, not the case: as we shall see, the formation of three-center two-electron bonds leads to the appearance of a partial bond order between the boron atoms as well. The attractive exchange interaction corresponding to these partial bond orders can be of significant importance as far as the energetics (stability) of the diborane molecule (or similar systems) is concerned.

Let us consider the simple model in which two electrons occupy a molecular orbital formed as a linear combination of three normalized basis orbitals χ_1 to χ_3. χ_1 and χ_3 are the boron orbitals directed to the hydrogenic orbital χ_2. We assume that the overlap of the boron and hydrogenic orbitals $\langle \chi_1 | \chi_2 \rangle = \langle \chi_2 | \chi_3 \rangle = S$ whereas the overlap of the two boron orbitals is negligible. The overlap matrix $\mathbf{S}$ is, accordingly,

$$\mathbf{S} = \begin{pmatrix} 1 & S & 0 \\ S & 1 & S \\ 0 & S & 1 \end{pmatrix} . \tag{7.71}$$

We construct the simplest symmetric unpolarized three-center orbital as

$$\psi = \frac{1}{\sqrt{2(1 + \sqrt{2}S)}} \left[\chi_2 + \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \right] , \tag{7.72}$$

i.e., the vector of the LCAO coefficients is

$$\mathbf{c} = \frac{1}{\sqrt{2(1 + \sqrt{2}S)}} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ 1 \\ \frac{1}{\sqrt{2}} \end{pmatrix} . \tag{7.73}$$

The trivial evaluation of matrices $\mathbf{D} = 2\mathbf{c}\mathbf{c}^\dagger$ and $\mathbf{DS}$ gives

$$\mathbf{D} = \frac{1}{2(1 + \sqrt{2}S)} \begin{pmatrix} 1 & \sqrt{2} & 1 \\ \sqrt{2} & 2 & \sqrt{2} \\ 1 & \sqrt{2} & 1 \end{pmatrix} ; \tag{7.74}$$

$$\mathbf{DS} = \frac{1}{2} \begin{pmatrix} 1 & \sqrt{2} & 1 \\ \sqrt{2} & 2 & \sqrt{2} \\ 1 & \sqrt{2} & 1 \end{pmatrix} , \tag{7.75}$$

respectively. This means that one obtains bond orders $B_{12} = B_{23} = \frac{1}{2}$; $B_{13} = \frac{1}{4}$. (When using the definition in (7.35) one has to take into account that each center bears a single basis orbital in our simplified model.)

These results mean that in the diborane molecule there should be bond orders of about $\frac{1}{2}$ between the bridging hydrogens and each boron atom, as well as between the two boron atoms: because the diborane molecule contains two independent two-electron three-center bonds, the boron–boron bond order should be doubled as compared with the value $\frac{1}{4}$ obtained previously. These values are in very good agreement with those obtained in the actual *ab initio* calculations.

Similar derivations can be performed for the case of three-center four-electron bonds, in which a nonbonding orbital is also doubly occupied. A typical example is the axial bonding system of a hypervalent sulphur atom. In that case one has to assume that the central orbital χ_2 located on the sulphur is of p-type, thus $\langle \chi_1 | \chi_2 \rangle = S$ and $\langle \chi_2 | \chi_3 \rangle = -S$. The bonding and nonbonding orbitals are in this case

$$\psi_b = \frac{1}{\sqrt{2(1 + \sqrt{2}S)}} \left[\chi_2 + \frac{1}{\sqrt{2}}(\chi_1 - \chi_3) \right] \qquad (7.76)$$

and

$$\psi_n = \frac{1}{\sqrt{2}}(\chi_1 + \chi_3) \, , \qquad (7.77)$$

respectively. As it is trivial to check, this difference, however, does not influence the results obtained for the bond orders: $B_{12} = B_{23} = \frac{1}{2}$ and $B_{13} = \frac{1}{4}$. (It is not surprising that the presence of the electrons on the nonbonding orbital ψ_n does not influence the bond order values.) These relatively small values of the bond orders can be used to explain why the axial bonds of the hypervalent sulphur compounds like SF_4 are longer than the conventional two-electron two-center equatorial bonds.

Notes

The importance of distinguishing between population analyses performed with respect to the three-dimensional physical space and with respect to the Hilbert space of the basis orbitals was stressed by Hall [1].

Section 1.

Mulliken's population analysis [2] is discussed in most textbooks of quantum chemistry (e.g., [3]). The requirement of the rotational-hybridizational invariance was first studied systematically in connection with the parametrization of the semiempirical CNDO method [4]. Despite its fundamental importance, the rotational-hybridizational importance of Mulliken's net and overlap population is not discussed explicitly in any sources known to the author.

A disadvantage of Mulliken's populations is that the gross orbital population q_μ of orbital χ_μ is not strictly limited by the numbers 0 and 2, as would be the case for an orthonormalized basis set. This may cause problems if large basis sets are used, containing several "diffuse" functions which decay slowly and hence are not really of atomic character [5]. (They are significantly populated for negative ions.) In such a case one has to turn to the Löwdin-orthogonalized counterpart (Section 2.3 of Chapter 3) of the basis applied, and perform the population (and bond order) analysis in terms of this auxiliary orthonormalized basis set.

Section 2.1.

Wiberg introduced his index in [6] for closed-shell systems. The proper generalization for the open-shell systems was given by Borisova and Semenov [7]. They also proved [8] that the Wiberg index is equal to $\frac{1}{2}(N_{\text{bonding}} - N_{\text{antibonding}})$ for first row homonuclear diatomics—except C_2 which has a very peculiar electronic structure [9].

The general bond order index Eq. (7.35) was proposed on intuitive grounds by Giambiagi *et al.* [10] for the semiempirical extended Hückel method. Being unaware of that, the present author introduced it for the *ab initio* case [11] on the basis of analyzing the exchange energy contribution obtained in an energy decomposition scheme [12]. The correct form Eq. (7.36) for the open-shell case was given in [13] as an *ab initio* generalization of the results of Borisova and Semenov [7]. (Also see [14,15].)

The invariance of bond order index with respect to rotational-hybridizational transformations has been established in [16].

Section 2.2.

The concept of the valence index was introduced in the CNDO framework independently by Borisova and Semenov [7] and Armstrong *al.* [17]; it was generalized for the *ab initio* case by the present author [11], who also introduced the free valence index. (Also see [13, 14, 15].)

Section 2.3.

The present derivation has a close relationship to the analysis of the connections between the bond order index and the normalization of the exchange part of the "second order density matrix $\rho_2(x_1, x_2; x_1', x_2')$ [13, 14, 15].

Section 2.3.

The material is based on [18].

Suggested readings

The survey papers [19, 20] are recommended.

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