

A general procedure to obtain quantum mechanical charge and bond order molecular parameters

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In an approach alternative to that of Mayer, a Hermitian operator is defined within the LCAO MO framework, which allows to obtain molecular charges and bond orders as expectation values of the first and second-order densities respectively. Such expectation values result to be nothing else than Mulliken's atom and bond populations. Thus, Mulliken populations appear to be non arbitrary condensed electron density partitions, obtained according to quantum mechanical usual procedures for molecular one and two electron observables. The theoretical simplicity of the outlined procedure can be easily extended in order to obtain the expectation values for higher-order electronic chemical bonds.

KEY WORDS: Density analysis, Mulliken populations, atomic charges, bond orders, second order density, projection operators, expectation values

1. Introduction

In a previous work [1] using an approach alternative to that of Mayer, it has been demonstrated that Mulliken atomic populations [2–5] can be deduced not as the result of an arbitrary partition of the first-order density function, but as expectation values of a Hermitian projection operator over the basis set functions, possessing in this way the required structure to be considered, even if not as observables, quantum mechanical well defined quantities.

However, this initial finding even if it connects chemical intuitive though with theoretical proceedings, as a result divides the whole density function into atomic density parts, it does not provide information at all about the chemical bond idea, which apparently still has not been explicitly linked up to date with the quantum mechanical logical structure.

The aim of the present study is the description of a similar development, as the one used in quantum chemical charge definition, but leading to the calculation of chemical bond information by the way of the quantum mechanical expectation value concept of an Hermitian operator.

For this purpose, first a résumé of the technique previously developed will be given, an extension to the concept of charge definition will be given afterwards and in second term the analysis of second-order density function will provide the adequate and equivalent tools to describe bond orders as a consequence of non-classical exchange density projection and expectation value construction.

2. Molecular atomic charges as mono-electronic operator expectation values

Suppose known the first-order density function for a given molecular structure within the LCAO MO formalism [6]. The mono-electronic density function can be written as

$$\rho(\mathbf{r}) = \sum_i \omega_i |i\rangle \langle i|, \quad (1)$$

where $\{\omega_i\}$ are the MO occupation numbers, and the MO set is expressed as: $\{|i\rangle\}$. Choosing a basis set of mono-electronic functions: $B = \{|\mu\rangle\}$, every MO can be described as a linear combination:

$$|i\rangle = \sum_{\mu} c_{\mu i} |\mu\rangle, \quad (2)$$

where $|c_i\rangle = \{c_{\mu i}\}$ are the variationally computed linear MO coefficients, which can be arranged in turn as a set of column vectors: $\{|c_i\rangle\}$. In doing so, whenever the basis set B is ordered in a row vector: $\langle M| = (\dots |\mu\rangle; \dots)$, then the i -th MO can be also written as the linear functional product:

$$|i\rangle = \langle M|c_i\rangle.$$

At the same time, the first-order density function, using definition (2) into equation (1), can be rewritten as

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} |\mu\rangle \langle \nu| \quad (3)$$

with the symmetric matrix $\mathbf{P} = \{P_{\mu\nu}\}$ being the so called charge and bond-order matrix, constructed as it is well known with the MO coefficients, supposedly defined into the real field, as

$$\mathbf{P} = \sum_i \omega_i |c_i\rangle \langle c_i| \rightarrow P_{\mu\nu} = \sum_i \omega_i c_{\mu i} c_{\nu i}. \quad (4)$$

Knowing this, then there is possible to define the metric or overlap matrix of the basis set B , by means of the scalar products of its elements:

$$\mathbf{S} = \{S_{\mu\nu} = \langle \mu | \nu \rangle\},$$

which is a positive definite, non-singular, matrix, whose inverse will be noted as

$$\mathbf{S}^{-1} = \{S_{\mu\nu}^{(-1)}\}.$$

2.1. Projectors over basis functions and atomic populations

With the inverse overlap elements it is possible to construct a projector operator over any function of the basis set B . Choosing the function: $|\alpha\rangle \in B$, for instance, then the projector has the form:

$$\begin{aligned} \Pi_\alpha &= \sum_\beta S_{\alpha\beta}^{(-1)} |\alpha\rangle \langle \beta| \rightarrow \forall |\mu\rangle \in B : \Pi_\alpha |\mu\rangle \\ &= \sum_\beta S_{\alpha\beta}^{(-1)} |\alpha\rangle \langle \beta | \mu \rangle = \left(\sum_\beta S_{\alpha\beta}^{(-1)} S_{\beta\mu} \right) |\alpha\rangle = \delta_{\alpha\mu} |\alpha\rangle \end{aligned} \quad (5)$$

and with such a projector, a new projector operator acting over the density function can be constructed as a tensor product:

$$\begin{aligned} \Pi_{\alpha\beta}^{(2)} &= \Pi_\alpha \otimes \Pi_\beta \rightarrow \Pi_{\alpha\beta}^{(2)} [\rho] = \Pi_\alpha [\rho] \Pi_\beta \\ &= \sum_\mu \sum_\nu P_{\mu\nu} \Pi_\alpha [|\mu\rangle \langle \nu|] \Pi_\beta = \sum_\mu \sum_\nu P_{\mu\nu} [\Pi_\alpha |\mu\rangle] [\langle \nu| \Pi_\beta] \\ &= \sum_\mu \sum_\nu P_{\mu\nu} [\delta_{\alpha\mu} |\alpha\rangle] [\langle \beta| \delta_{\nu\beta}] = P_{\alpha\beta} |\alpha\rangle \langle \beta| \end{aligned} \quad (6)$$

and from this it is easy to construct an Hermitian operator attached to a center A , such that:

$$\Omega_A = \sum_{\alpha \in A} \sum_\beta \Pi_{\alpha\beta}^{(2)} \rightarrow \Omega_A [\rho] = \rho_A = \sum_{\alpha \in A} \sum_\beta P_{\alpha\beta} |\alpha\rangle \langle \beta|. \quad (7)$$

The sum over all the molecular centers of the operators above described produce the unit operator as

$$\sum_A \Omega_A [\rho] = \sum_A \rho_A = \sum_A \sum_{\alpha \in A} \sum_\beta P_{\alpha\beta} |\alpha\rangle \langle \beta| = \rho \rightarrow \sum_A \Omega_A = I.$$

Then, the expectation values of the operator set $\{\Omega_A\}$ are just the Mulliken atomic populations, because:

$$\langle \Omega_A [\rho] \rangle = \langle \rho_A \rangle = \sum_{\alpha \in A} \sum_{\beta} P_{\alpha\beta} \langle \alpha\beta \rangle = \sum_{\alpha \in A} \sum_{\beta} P_{\alpha\beta} S_{\alpha\beta} = N_A \quad (8)$$

and the sum over all the centers produces:

$$\sum_A N_A = \sum_A \langle \rho_A \rangle = \sum_A \langle \Omega_A [\rho] \rangle = \left\langle \sum_A \Omega_A [\rho] \right\rangle = \langle \rho \rangle = N_M,$$

where N_M is the total number of electrons in the molecule.

In this manner, the Mulliken atomic population set: $\{N_A\}$ can be seen as an expectation value collection of the operator set $\{\Omega_A\}$ over the first-order molecular density function $\rho(\mathbf{r})$. Therefore, Mulliken populations can be considered well defined as conforming to the quantum mechanical requirements of being expectation values of a well-defined Hermitian operator.

2.2. Atomic charges as expectation values

From the atomic population set definition provided in equation (8), the atomic charges can be easily constructed as observables too. If the total first-order electronic and nuclear density function $P(\mathbf{r})$, including point-like nuclear charges $\{Z_A\}$, is made in the following way:

$$P(\mathbf{r}) = -\rho(\mathbf{r}) + \sum_A Z_A \delta(\mathbf{r} - \mathbf{r}_A), \quad (9)$$

where $\{\mathbf{r}_A\}$ are the nuclear positions and $\delta(\mathbf{r} - \mathbf{r}_A)$ Dirac's delta functions, then one can take into account a provisional form of an Hermitian operator:

$$\Upsilon_A = \Omega_A + \Theta_A, \quad (10)$$

where the first term is already defined in equation (7) and acts over the electronic density, and the second term over the nuclear charge density. The action of the operator (10) over the total density (9) can be naturally defined in the form of a Hadamard product [7], such as

$$\begin{aligned} \langle \Upsilon_A * [P(\mathbf{r})] \rangle &= [\Omega_A + \Theta_A] * \left[-\rho(\mathbf{r}) + \sum_A Z_A \delta(\mathbf{r} - \mathbf{r}_A) \right] \\ &= -\langle \Omega_A [\rho(\mathbf{r})] \rangle + Z_A \langle \Theta_A [\delta(\mathbf{r} - \mathbf{r}_A)] \rangle = -N_A + Z_A = Q_A, \end{aligned}$$

and there is no need in principle to specify the nature of Θ_A , the nuclear part of the operator (10), but solely to admit the additional property for the whole atomic nuclear charge operator set $\{\theta_A\}$ holds:

$$\langle \Theta_A [\delta(\mathbf{r} - \mathbf{r}_A)] \rangle = 1.$$

However, precisely Dirac's functions have the same property:

$$\forall A : \langle \delta(\mathbf{r} - \mathbf{r}_A) \rangle = 1,$$

then it is obvious that one should consider:

$$\forall A : \Theta_A \equiv I,$$

consequently, the Hermitian atomic charge operator (10) can be defined as

$$\forall A : \Upsilon_A = \Omega_A + I.$$

3. Molecular bond orders as two electron expectation values of an Hermitian operator

In the previous work on this subject the atomic populations had been discussed in the way as resumed in the previous paragraph, but it is important to find out if the so called Mulliken bond orders can be obtained in the same way.

3.1. Preliminary considerations

The previous results seem to indicate that nothing more can be extracted from the first order density function. However, second-order density, even if approximately defined, can be used to test whenever an operator can be constructed in the same way as it has been previously explained in order to describe atomic populations as expectation values.

Using the previous notation, a second-order density can be written by means of the expression:

$$\rho(\mathbf{r}_1; \mathbf{r}_2) = \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} (|\mu\rangle \langle \nu| \otimes |\lambda\rangle \langle \sigma| - \frac{1}{2} |\mu\rangle \langle \sigma| \otimes |\nu\rangle \langle \lambda|), \quad (11)$$

where in every tensor product symbol: \otimes , the first projector refers to the coordinates of the first electron and the right hand one is associated to the coordinates of the second electron. For example, when considering the first term of equation (11), which corresponds to the Coulomb contribution, it can be written

$$|\mu\rangle \langle \nu| \otimes |\lambda\rangle \langle \sigma| \equiv [|\mu\rangle \langle \nu|(\mathbf{r}_1)][|\lambda\rangle \langle \sigma|(\mathbf{r}_2)]$$

and the same for the exchange contribution appearing in the second term of equation (11) with a negative coefficient.

3.2. Two-electron projectors and bond order operators

It is easy to form the two electron projection operator, equivalent to the one used into first order density functions and described in equation (6). Such a composite operator can be constructed as

$$\Pi_{\alpha\beta\gamma\delta}^{(4)} = \Pi_{\alpha\beta}^{(2)}(\mathbf{r}_1) \otimes \Pi_{\gamma\delta}^{(2)}(\mathbf{r}_2),$$

which can act over the second-order density (11) in the following manner

$$\begin{aligned} \Pi_{\alpha\beta\gamma\delta}^{(4)}[\rho^{(2)}] &= \Pi_{\alpha\beta}^{(2)}(\mathbf{r}_1)[\rho^{(2)}(\mathbf{r}_1; \mathbf{r}_2)] \Pi_{\gamma\delta}^{(2)}(\mathbf{r}_2) \\ &= \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} \\ &\quad \times \left(\left[\Pi_{\alpha\beta}^{(2)} |\mu\rangle \langle \nu| \right] \left[|\lambda\rangle \langle \sigma| \Pi_{\gamma\delta}^{(2)} \right] - \frac{1}{2} \left[\Pi_{\alpha\delta}^{(2)} |\mu\rangle \langle \sigma| \right] \left[|\nu\rangle \langle \lambda| \Pi_{\beta\gamma}^{(2)} \right] \right) \end{aligned}$$

in such a way that the associated bond order operator may be formally written as

$$\Omega_{AB}(\mathbf{r}_1; \mathbf{r}_2) = \sum_{\alpha \in A} \sum_{\gamma} \sum_{\beta \in B} \sum_{\delta} \Pi_{\alpha\gamma\beta\delta}^{(4)}.$$

Such an operator will produce a partition of the second-order density function (11) into the second order diatomic terms

$$\begin{aligned} \Omega_{AB}[\rho^{(2)}] &= \rho_{AB}^{(2)} = \sum_{\alpha \in A} \sum_{\gamma} \sum_{\beta \in B} \sum_{\delta} P_{\alpha\gamma} P_{\beta\delta} \\ &\quad \times (|\alpha\rangle \langle \gamma| \otimes |\beta\rangle \langle \delta| - \frac{1}{2} |\alpha\rangle \langle \delta| \otimes |\beta\rangle \langle \gamma|), \end{aligned} \quad (12)$$

which will generate, upon a two-electron expectation value calculation, the following condensed density result:

$$\begin{aligned} N_{AB} &= \langle \Omega_{AB}[\rho^{(2)}] \rangle = \langle \rho_{AB}^{(2)} \rangle = \sum_{\alpha \in A} \sum_{\gamma} \sum_{\beta \in B} \sum_{\delta} P_{\alpha\gamma} P_{\beta\delta} (S_{\alpha\gamma} S_{\beta\delta} - \frac{1}{2} S_{\alpha\delta} S_{\beta\gamma}) \\ &= \sum_{\alpha \in A} \sum_{\gamma} P_{\alpha\gamma} S_{\alpha\gamma} \sum_{\beta \in B} \sum_{\delta} P_{\beta\delta} S_{\beta\delta} \\ &\quad - \frac{1}{2} \sum_{\alpha \in A} \sum_{\gamma} \sum_{\beta \in B} \sum_{\delta} P_{\alpha\gamma} P_{\beta\delta} S_{\alpha\delta} S_{\beta\gamma} \\ &= N_A N_B - \frac{1}{2} \sum_{\alpha \in A} \sum_{\gamma} \sum_{\beta \in B} \sum_{\delta} P_{\alpha\gamma} P_{\beta\delta} S_{\alpha\delta} S_{\beta\gamma} \\ &= N_A N_B - \frac{1}{2} \sum_{\alpha \in A} \sum_{\beta \in B} [\mathbf{PS}]_{\alpha\beta} [\mathbf{PS}]_{\beta\alpha}. \end{aligned} \quad (13)$$

In the expression of the expectation value forming the condensed diatomic density terms, it can be perfectly seen the importance of the exchange contribution leading to the second order Mulliken populations or two center bond orders.

In fact, this last result proves that the adequate bond order definition shall be found in the exchange terms, because Coulomb contribution appears to be just a product of the atomic population pair, associated to the involved atoms.

Consequently, it seems that bond orders can be related to the expectation value of the exchange part of the second-order density function attached to a composite Hermitian projection operator. Thus, this seems to indicate that chemical bonding can be measured in this way as a non-classical, quantum mechanical expectation value effect over the exchange part of the second order density function. This is consistent with the subtleties of the elusive nature of chemical bonds.

3.3. Overall sum or Minkowski norm of two-electron density function

The sums over the two center expectation values provided by the second-order condensed densities furnish the result:

$$\begin{aligned}
 \langle \rho^{(2)} \rangle &= \sum_A \sum_B N_{AB} = N_M^2 - \frac{1}{2} \sum_A \sum_{\alpha \in A} \sum_B \sum_{\beta \in B} \left[\sum_{\gamma} (P_{\alpha\gamma} S_{\gamma\beta}) \sum_{\delta} (P_{\beta\delta} S_{\delta\alpha}) \right] \\
 &= N_M^2 - \frac{1}{2} \sum_A \sum_{\alpha \in A} \sum_B \sum_{\beta \in B} [\mathbf{PS}]_{\alpha\beta} [\mathbf{PS}]_{\beta\alpha} \\
 &= N_M^2 - \frac{1}{2} \text{Tr} [(\mathbf{PS})^2] \tag{14}
 \end{aligned}$$

furthermore, it can be written:

$$\frac{1}{2} \text{Tr} [(\mathbf{PS})^2] = \frac{1}{2} \text{Tr} [\mathbf{PSPS}] = \text{Tr} [\mathbf{PS}] = N_M,$$

because the following property is fulfilled

$$\mathbf{PSP} = 4 \sum_i \sum_j |c_i\rangle \langle c_i | \mathbf{S} |c_j\rangle \langle c_j| = \sum_{\sum_j |c_i\rangle} \langle c_j | \delta_{ij} = 4 \sum_i |c_i\rangle \langle c_i| = 2\mathbf{P}.$$

The result appearing in equation (14), for the Minkowski norm of the second-order density function looks almost as a variance changed of sign. As using the Minkowski norm of the first-order density function:

$$\langle \rho \rangle = N_M$$

and also taking into account that one can easily compute the Minkowski norm of the square of the first-order density function, which could be written as

$$\begin{aligned} \langle \rho^2 \rangle &= \left\langle \left| \sum_{\mu} \sum_{\nu} P_{\mu\nu} |\mu\rangle \langle \nu| \right|^2 \right\rangle = \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} S_{\mu\sigma} S_{\nu\lambda} \\ &= \sum_{\mu} \sum_{\lambda} [\mathbf{PS}]_{\mu\lambda} [\mathbf{PS}]_{\lambda\mu} = \text{Tr}[(\mathbf{PS})^2] = 2N_M \end{aligned}$$

then:

$$\langle \rho^{(2)} \rangle = N_M^2 - N_M = \langle \rho \rangle^2 - \frac{1}{2} \langle \rho^2 \rangle. \quad (15)$$

Perhaps is also worthwhile to compute the variance of the first-order density function, because it is related with the last result provided by equation (15) :

$$\text{Var}(\rho) = \langle |\rho - \langle \rho \rangle|^2 \rangle = \langle \rho^2 \rangle - \langle \rho \rangle^2 = \langle \rho^2 \rangle - N_M^2 = 2N_M - N_M^2.$$

Owing to the variance expression, there can be finally written:

$$\langle \rho^{(2)} \rangle = \frac{1}{2} \langle \rho^2 \rangle - \text{Var}(\rho). \quad (16)$$

3.4. Diagonal terms of bond order matrix

Another intriguing question can be posed about which meaning can be associated to the diagonal terms of the second-order population matrix:

$$N_{AA} = \langle \Omega_{AA} [\rho^{(2)}] \rangle = \langle \rho_{AA}^{(2)} \rangle = N_A^2 - \frac{1}{2} \sum_{\alpha \in A} \sum_{\beta \in A} [\mathbf{PS}]_{\alpha\beta} [\mathbf{PS}]_{\beta\alpha},$$

which according to the Minkowski norm of the second-order density function (16) can be also expressed as

$$\langle \rho_{AA}^{(2)} \rangle = \frac{1}{2} \langle \rho_A^2 \rangle - \text{Var}(\rho_A),$$

using the atomic projections of the first-order density function. That is the same as to say that the second-order atomic populations can be related to the variance of the first-order atomic density functions. In fact, these diagonal second-order population terms at first glance seem to do not introduce more relevant information than first-order Mulliken charges. However, somehow [8] such diagonal contributions have been called valence indices.

3.5. Mulliken bond orders as expectation values of the exchange part of the second-order density function

When analyzing the exchange part of the bond order, as defined before in equation (13):

$$N_{AB}^{Ex} = \frac{1}{2} \sum_{\alpha \in A} \sum_{\beta \in B} [\mathbf{PS}]_{\alpha\beta} [\mathbf{PS}]_{\beta\alpha},$$

one can arrive to the same expression proposed by Mulliken for diatomic populations, as already commented.

4. Conclusions

Using, previous to all other considerations, the result consisting into that Mulliken atomic populations appear as expectation values of the first-order density function, then, the extension of the procedure to two electron density functions can be shown to lead to find out that Mulliken bond orders are naturally described as two electron expectation values of the second-order density function exchange part.

A similarly based argument is also provided to show how the atomic charge concept can also be defined as an expectation value of a Hermitian operator.

According to the present theoretical findings, atomic populations and bond orders can be correctly defined within the quantum mechanical formalism as expectation values of some Hermitian operator constructed as a projector. Moreover, using the described theoretical development, the chemical bond appears to be a non-classical, exchange condensed density, conceptual consequence of the quantum mechanical electronic nature of molecules.

Owing to the procedures outlined above, the term *condensed density* is employed in the present work to also rename, in this way, Mulliken populations. The reason is simple. The old original Mulliken definitions can be shown to be easily extended up to any reduced density order, being first and second-order condensed densities just coincident with Mulliken populations. In a forthcoming paper it will be shown how to set up the straightforward procedure to extend the present theory to easily computable third and higher-order condensed density values, corresponding to bond orders involving an arbitrary number of atoms in a given molecule.

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