

Quantum mechanical basis for Mulliken population analysis

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Using an approach alternative to that of Mayer, this paper shows that a Hermitian operator can be found, such that, in a molecule atomic populations can be obtained as its expectation values. In this way, atomic charges can be computed within a quantum mechanical correct definition. When working within the LCAO MO framework, it is found that Mulliken populations appear as the appropriate expectation values of the charge operator.

KEY WORDS: Mulliken population analysis, atomic charge, electron density, density function, LCAO MO

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1. Introduction

An often used concept in chemical reasoning about molecular behavior and reactivity, are atomic charges and charge transfer. As a result, atomic charges continue to play an important role in quantum chemistry and much research continues to be done to refine the concept of an atomic charge. Since the description of atomic populations by Mulliken [1–4], many alternative definitions of atomic charges and populations have been presented as a natural consequence of the previous statements [5].

One of the leitmotifs of the various charge definitions can be expressed in just a few words. First of all, the question can be raised whether it is justified to consider atoms within a molecule [6]. Atomic charges, according to the usual

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quantum chemical lore, are arbitrarily defined throughout, even if they involve judicious and well founded partitions or manipulations of the quantum mechanical density function. This is so because atomic charges or populations are not quantum mechanical observables and thus, such molecular descriptors can result from some reasonable, albeit arbitrary procedure. Although electron density itself is an observable, the problem arises from the fact that there is no operator which describes how to distinguish atoms in a molecule. Since an atomic charge is not an observable in quantum mechanical sense, meaning that atomic charges are not expressed as expectation values of some Hermitian operator attached to some experimental value; it could be argued that discussions about such chemical molecular descriptors are irrelevant from the quantum mechanics point of view.

Despite this fundamental problem, the published literature shows a tremendously large number of studies where atomic charges were found to be very instructive in interpreting different aspects of molecular behavior as such. This situation warrants any effort to reconcile theoretical quantum mechanics and applied quantum chemistry. Such a task requires finding a proper reasoning to solidly establish a background for such a large number of valuable chemical researches. Put shortly, the aim of the paper is to discover a Hermitian operator that for each atom A in a molecule gives its atomic population by means of an expectation value expression:

$$\langle \Omega_A[\rho] \rangle = \int \Omega_A[\rho(\mathbf{r})] d\mathbf{r} = N_A. \quad (1)$$

As will be shown below, using an approach alternative to that of Mayer [5], application of such a Hermitian operator in the LCAO MO framework gives results equal to Mulliken's atomic populations. Accordingly, it will be shown that Mulliken's charges are expectation values of a Hermitian operator.

2. First-order density function in a LCAO MO context

Mulliken atomic populations are mainly based on first-order density functions within a LCAO MO theory approach [7], a widespread technique that Mulliken himself described for the first time. Because of this, the development of the following reasoning will be based on this well-known theoretical setup.

First a summary of the first-order density function structure will be given, employing a convenient notation, which will be also used thereafter. In LCAO MO theory, a molecular orbital (MO) is a monoelectronic function, $|i\rangle$, expressed as a linear combination of monoelectronic functions: $M = \{\chi_\mu(\mathbf{r}) \equiv |\mu\rangle\}$ considered as a basis set. Usually these basis functions are centered on the positions of the nuclei of the atoms composing the molecule, although in principle they can be centered anywhere in space. The MOs can then

be written as:

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

where the set of linear coefficients $\{c_{\mu i}\}$ can be collected into a column vector in this way

$$|c_i\rangle = \{c_{\mu i}\}. \quad (3)$$

Equation (2) can be cast in terms of the column vector (3) and a row vector collecting all the basis functions

$$\langle M| = \{|\mu\rangle\} = (\dots; |\mu\rangle; \dots), \quad (4)$$

so the MO expression becomes

$$|i\rangle = \langle M|c_i\rangle. \quad (5)$$

In such a notation, the first-order density function can be simply expressed as a bilinear form

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} |\mu\rangle\langle\nu|, \quad (6)$$

where the charge and bond order matrix: $\mathbf{P} = \{P_{\mu\nu}\}$ is defined in terms of the MO coefficients (3) as:

$$\mathbf{P} = \sum_i \omega_i |c_i\rangle\langle c_i| \rightarrow \forall \mu, \nu: P_{\mu\nu} = \sum_i \omega_i c_{\mu i} c_{\nu i}, \quad (7)$$

where the parameters $\{\omega_i\}$ are the MO occupation numbers. This definition becomes the same as to write the first-order density function in terms of the MO as:

$$\rho(\mathbf{r}) = \sum_i \omega_i |i\rangle\langle i|. \quad (8)$$

Finally, it must be stated that the first-order density function integrates to the total number of electrons in the molecule, N_M ; in the following way:

$$\langle \rho \rangle = \int_D \rho(\mathbf{r}) d\mathbf{r} = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \int_D |\mu\rangle\langle\nu| d\mathbf{r} = \sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} = N_M, \quad (9)$$

where D is the appropriate integration domain, which in the usual practice refers to entire space, and the involved integrals over the basis set are the overlap integrals, the scalar products over the basis functions:

$$\int_D |\mu\rangle\langle\nu| d\mathbf{r} = S_{\nu\mu} = \langle\nu|\mu\rangle, \quad (10)$$

which in case of real functions produce a symmetric positive definite matrix:

$$\mathbf{S} = \{S_{\nu\mu}\} = \mathbf{S}^T = \{S_{\mu\nu}\}. \quad (11)$$

Knowing this, equation (9) can be simplified to

$$\sum_{\mu} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} = \sum_i \omega_i \sum_{\mu} \sum_{\nu} c_{\mu i} c_{\nu i} S_{\mu\nu} = \sum_i \omega_i \langle c_i | \mathbf{S} | c_i \rangle \quad (12)$$

and, owing to the fact that the MO coefficients can be considered without loss of generality as an orthonormalized set of vectors, one can write:

$$\forall i, j : \langle c_i | \mathbf{S} | c_j \rangle = \delta_{ij}, \quad (13)$$

so, equation (12) can finally be written as:

$$\langle \rho \rangle = \sum_i \omega_i \langle c_i | \mathbf{S} | c_i \rangle = \sum_i \omega_i = N_M. \quad (14)$$

3. Mulliken atomic populations as a quantum mechanical expectation value

The elements of the basis set M are usually centered in the sites where the atomic nuclei are in a given molecular structure. The basis function centers will be noted by capital letters: A, B, ... For example, such a convention can be expressed in the present notation as:

$$\mu \in A \rightarrow |A; \mu\rangle, \quad (15)$$

meaning that the μ th basis function is centered (or belongs) to atom or space site A . We will refer to these centers as atomic centers and will call the populations attached to them atomic populations. Naturally, nothing opposes to the use of non-atom centered basis functions, although their use is uncommon.

Keeping this in mind, the aim is now to find a Hermitian operator Ω_A , attached to center A , that, when applied to the density function (6), has as expectation value the corresponding population N_A ; that is

$$\langle \Omega_A [\rho] \rangle = \int_D \Omega_A [\rho(\mathbf{r})] \mathbf{dr} = N_A, \quad (16)$$

where D is an appropriate integration domain.

Atomic populations, defined in any way must sum up to the molecular total number of electrons, N_M , so they must fulfill

$$\sum_A N_A = N_M, \quad (17)$$

and using this necessary property over atomic population definition (16), it is found that

$$\sum_A \langle \Omega_A [\rho] \rangle = \left\langle \sum_A \Omega_A [\rho] \right\rangle = N_M. \quad (18)$$

However, the density function possesses the usual property to integrate to the number of electrons too, as shown in the previous section, so one arrives to the conclusion that

$$\left\langle \sum_A \Omega_A [\rho] \right\rangle = N_M = \langle \rho \rangle \rightarrow \sum_A \Omega_A = I. \quad (19)$$

This result suggests that atomic population operators can possess a projection nature, which allows the derivation of elegant formulae for the calculation of electron populations on atoms. Roby defined population analysis based on projector operators as projection-density population analysis [8,9]. There, use was made of atomic orbitals instead of the non-orthonormal basis functions used, and Gleason's theorem [10] was used extensively to calculate electron populations over unions of atoms. This is then used to calculate not only atomic electron populations but also shared electron density between two atoms, three atoms, ... always based on the first-order electron density. The use of projection operators in several formulations of population analysis was recently discussed by Clark et al. [11].

Equation (19) entails that

$$\Omega_A [\rho] = \rho_A \wedge \sum_A \rho_A = \rho. \quad (20)$$

This is the same as considering that population operators project the density function into an atomic or center density function, attached to the associated molecular structure.

Now, the natural way of choosing these projections, without recurring to the search of the nature of the atomic operator set, is to write:

$$\rho_A = \sum_{\mu \in A} \sum_B \sum_{\nu \in B} P_{\mu\nu}^{AB} |A; \mu\rangle \langle \nu; B|, \quad (21)$$

where the superscripts on the charge and bond order matrix elements show the belonging of the subscripts to the corresponding basis set function centers.

Expression (21) of the atomic density, upon integration over some appropriate domain D , provides the same expression which Mulliken originally

employed in the definition of atomic population:

$$\begin{aligned} N_A &= \int_D \rho_A(\mathbf{r}) \, d\mathbf{r} = \sum_{\mu \in A} \sum_B \sum_{v \in B} P_{\mu\nu}^{AB} \int_D |A; \mu\rangle \langle v; B| \, d\mathbf{r} \\ &= \sum_{\mu \in A} \sum_B \sum_{v \in B} P_{\mu\nu}^{AB} S_{\mu\nu}^{AB}, \end{aligned} \quad (22)$$

where in the overlap elements the same superscript notation has been employed, as in the one used in the charge and bond order matrix elements, to stress the centers of the involved basis functions.

This reasoning provides an intuitive background about the fact that Mulliken atomic populations could be associated to the expectation values of some Hermitian operator. Such an operator, in turn, can be considered taking the form of a projector that, acting over the first-order density function, provides the atomic density parts corresponding to some known molecular structure.

In this sense, such a result, if possible, will permit to confirm that Mulliken atomic populations may be considered correctly defined from the quantum mechanical point of view.

4. Quantum mechanically defined atomic population definition

Mulliken atomic population can be considered as the summation of AO population contributions $\{N_\mu^A\}$, or

$$N_A = \sum_{\mu \in A} N_\mu^A. \quad (23)$$

And the basis set function populations are defined in turn by

$$N_\mu^A = \sum_B \sum_{v \in B} P_{\mu\nu}^{AB} S_{\mu\nu}^{AB}, \quad (24)$$

being the result of integrating the basis function μ density fragment, easily defined as

$$\rho_\mu^A = \sum_B \sum_{v \in B} P_{\mu\nu}^{AB} |A; \mu\rangle \langle v; B|, \quad (25)$$

which in turn can be considered the projection of the first-order density upon an operator Ω_μ^A :

$$\Omega_\mu^A[\rho] = \rho_\mu^A. \quad (26)$$

But this picture remains unsatisfactory, as the nature of the projection operators remains undefined.

In order to define unambiguously such an operator set, suppose that any basis function $|\alpha\rangle$ is chosen and the corresponding projector constructed

$$\Pi_\alpha = \sum_\lambda S_{\lambda\alpha}^{(-1)} |\alpha\rangle \langle\lambda|, \quad (27)$$

where $\mathbf{S}^{-1} = \{S_{\lambda\alpha}^{(-1)} \equiv S_{\alpha\lambda}^{(-1)}\}$ are the elements of the symmetric inverse basis set metric or overlap matrix. The above defined projector permits to write:

$$\Pi_\alpha [|\alpha\rangle] = \sum_\lambda S_{\lambda\alpha}^{(-1)} |\alpha\rangle \langle\lambda| \alpha = \sum_\lambda S_{\lambda\alpha}^{(-1)} |\alpha\rangle S_{\lambda\alpha} = \left(\sum_\lambda S_{\lambda\alpha}^{(-1)} S_{\lambda\alpha} \right) |\alpha\rangle = |\alpha\rangle. \quad (28)$$

It is interesting to compare this approach to that of Roby et al. as equation (27) allows a straightforward extension to introduce an atomic projector by summation over all basis functions centered on that atom

$$\mathbf{P}_A = \sum_{\alpha \in A} \Pi_\alpha = \sum_{\alpha \in A} \sum_\lambda S_{\lambda\alpha}^{(-1)} |\alpha\rangle \langle\lambda|, \quad (29)$$

Note that the summation in basis functions λ runs over all basis functions, irrespective of where they are centered. This is an important difference with respect to Roby's atomic projector:

$$\mathbf{P}_A = \sum_{\alpha \in A} |\alpha\rangle \langle\alpha|, \quad (30)$$

where α are the orthonormal AO's centered on atom A. Clearly one cannot suppose orthogonality with respect to the atomic orbitals of other atoms in the given molecule. Equation (30) effectively means that in Roby's formula the other basis functions are not considered in the atomic projector. This also means that when Roby's projectors are extended to unions of atoms, for every union of atoms a new overlap matrix inverse needs to be calculated [8].

The projector Π_α can be used on the electron density such that

$$\begin{aligned} \Pi_\alpha [\rho] &= \sum_{v\mu} P_{v\mu} \sum_\lambda S_{\lambda\alpha}^{(-1)} |\alpha\rangle \langle\lambda|\mu\rangle \langle v| \\ &= \sum_{v\mu} P_{v\mu} |\alpha\rangle \langle v| \sum_\lambda S_{\lambda\alpha}^{(-1)} S_{\lambda\mu} \\ &= \sum_v P_{v\alpha} |\alpha\rangle \langle v|, \end{aligned} \quad (31)$$

and so the projectors possess the necessary property that

$$\sum_\alpha \Pi_\alpha [\rho] = \rho. \quad (32)$$

The projectors can also be extended to higher order by means of a tensor product

$$\Pi_{\alpha\beta}^{(2)} = \Pi_{\alpha} \otimes \Pi_{\beta}. \quad (33)$$

This allows the definition of multicenter electron occupation numbers when using higher order electron densities. Defining the action of the operator $\Pi_{\alpha\beta}^{(2)}$ as

$$\begin{aligned} \Pi_{\alpha\beta}^{(2)} &= \sum_{\mu} \sum_{\nu} P_{\mu\nu} \Pi_{\alpha\beta}^{(2)} [|\mu\rangle\langle\nu|] \\ &= \sum_{\mu} \sum_{\nu} P_{\mu\nu} \Pi_{\alpha} [|\mu\rangle\langle\nu|] \Pi_{\beta} \end{aligned} \quad (34)$$

one finds that the action of the projector (33) over the density function is easily described in terms of the corresponding overlap integrals between basis functions

$$\begin{aligned} \Pi_{\alpha\beta}^{(2)}[\rho] &= \sum_{\mu} \sum_{\nu} P_{\mu\nu} \sum_{\lambda} S_{\lambda\alpha}^{(-1)} |\alpha\rangle\langle\lambda| [|\mu\rangle\langle\nu|] \sum_{\kappa} S_{\kappa\beta}^{(-1)} |\kappa\rangle\langle\beta| \\ &= \sum_{\mu} \sum_{\nu} P_{\mu\nu} \sum_{\lambda} \sum_{\kappa} S_{\lambda\alpha}^{(-1)} S_{\kappa\beta}^{(-1)} |\alpha\rangle\langle\lambda|\mu\rangle\langle\nu|\kappa\rangle\langle\beta| \\ &= \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left(\sum_{\lambda} S_{\lambda\alpha}^{(-1)} S_{\lambda\mu} \right) \left(\sum_{\kappa} S_{\kappa\beta}^{(-1)} S_{\nu\kappa} \right) |\alpha\rangle\langle\beta| \\ &= \left(\sum_{\mu} \sum_{\nu} P_{\mu\nu} \delta_{\alpha\mu} \delta_{\nu\beta} \right) |\alpha\rangle\langle\beta| = P_{\alpha\beta} |\alpha\rangle\langle\beta|. \end{aligned} \quad (35)$$

Equation (35) shows how the projector (33) retrieves the $|\alpha\rangle\langle\beta|$ component of the density function; the coefficient at the left can be interpreted as the corresponding charge and bond order matrix element.

Again the necessary condition for the projector, or a tensor product of such projectors is fulfilled, that is:

$$\sum_{\alpha} \sum_{\beta} \Pi_{\alpha\beta}^{(2)} [\rho] = \sum_{\alpha} \sum_{\beta} P_{\alpha\beta} |\alpha\rangle\langle\beta| = \rho. \quad (36)$$

As a consequence, using definitions (27) and (33), the appropriate operator producing as an expectation value Mulliken's atomic population can be written as:

$$\Omega_A = \sum_{\alpha \in A} \sum_B \sum_{\beta \in B} \Pi_{\alpha\beta}^{(2)}, \quad (37)$$

as the former expression (20) is fulfilled by the Hermitian operator (37).

This proves that Mulliken orbital and atomic populations can be attached to the expectation values of Hermitian projection operators. In consequence,

Mulliken's populations can be considered soundly defined from the quantum mechanical point of view, even if they remain not observable molecular properties.

Of course, the description of the adequate projection operators giving rise to Mulliken's populations does not alleviate the well-known problems associated with Mulliken population analysis. These problems concern the relatively large basis set dependence, the occurrence of inappropriate occupation numbers and the issue of diffuse functions [12]. Many of these topics, however, pervade all quantum chemistry application fields.

Finally, one should point out that the defined Hermitian operator (37), providing the atomic populations for a molecule within a LCAO MO context, can be easily generalized to obtain bond orders, when adequately applied to second order density functions. In the same way, its application to multiple bond order definition is a matter of a natural extension of the procedure to higher order density functions. Results associated to these issues will be provided in forthcoming work.

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