

A Viewpoint on Population Analyses

Ernest R. Davidson^{1*} | Aurora E. Clark^{2*}

¹Department of Chemistry, University of Washington, Seattle, Wa 98195

²Department of Chemistry, Washington State University, Pullman, Wa 99164

Correspondence

Email: erdavid@uw.edu, auclark@wsu.edu

Funding information

National Science Foundation, Award No. OAC- 1934725.

Population analyses have become an indispensable tool to computational chemists. Yet implementation within popular quantum chemistry software has buried the interesting philosophical choices made when partitioning the electron density into atomic contributions. There is further historical context that has significantly influenced common conceptions of chemical bonding and reactivity. This work reviews select aspects of orbital and spatial decomposition schemes of the density matrix, pointing out essential linear algebraic considerations and associated tools of shared interest to us and Prof. Mayer.

KEYWORDS

atomic charges, electron population, wave function analysis

1 | INTRODUCTION

Population analyses (i.e., the dividing of electron density within a material or molecule into specific atomic contributions) is deeply intertwined with the Chemistry aesthetic. Partial atomic charges serve as an important rationalization of organic and inorganic reactivity. They further form the basis of understanding non-covalent interactions via permanent or induced polarization of the electron density. Beyond interpretation of chemical trends, they serve a vital role in coarse graining Hamiltonians within empirical descriptions of inter-particle interactions (i.e.

*Equally contributing authors.

force fields), where accounting for coulombic forces is essential to predictive capability. The electron distribution about an atom forms the basis for multipole expansion to determine moments associated with an atom in a molecule, which in turn affects polarizability, etc. Indeed, Pauling used this in reverse and based his electronegativity scale partially on the assumption that the observed dipole moment was due to charge transfer.[1]

The physical justification for determining an atom's properties when it is embedded within a molecule or material essentially depends upon whether you adopt a Schrödinger or Heisenberg perspective of quantum mechanics. The isolated atom does not appear in the Schrödinger equation of a molecule, and thus subsequent Hilbert space analysis of atomic properties can be thought of as a post-processing partitioning of the wave function. Alternatively, if one considers the quantum mechanically derived characteristics of the electron density of the system, then it is possible to define a bounding surface (i.e., the zero-flux in the gradient vector field) that then supports a Euclidean spatial division of the atomic properties within a molecule as defined by Heisenberg's equation of motion. Of course, Euclidean partitioning is not mandated by a Heisenberg perspective, the latter merely provides a different theoretical framework for its justification. This report discusses the historical context and relevant (but often overlooked) technical considerations of population analyses (primarily from the Schrödinger perspective). Within this theme, we note the contributions of Istvan Mayer, whose interests often overlapped with our own as it pertains to the development of chemically motivated schemes that seek to bridge experimental observation and chemical experience with quantum mechanical theories.

The spin-free first order reduced density matrix (called simply the density matrix in this paper) is defined as

$$\rho(r; r') = N \sum_{m_1, m_2, \dots, m_N} \int \psi(r m_1, r_2 m_2, \dots, r_N m_N) \psi(r' m_1, r_2 m_2, \dots, r_N m_N)^* dr_2 dr_3 dr_N \quad (1)$$

Computer programs used to generate the wave function conventionally produce this quantity as a quadratic sum over the basis functions

$$\rho(r; r') = \sum_{i,j} f_i(r) \Pi_{ij} f_j^*(r') \quad (2)$$

To simplify the equations in this paper we define Dirac kets $|f\rangle$ associated with each basis function by

$$f_i(r) = \langle r | f_i \rangle \quad (3)$$

and arrange these kets into a row matrix symbolized by

$$|f\rangle = (|f_1\rangle, \dots, |f_k\rangle) \quad (4)$$

The adjoint to $|f\rangle$ is the column matrix of the bras symbolized by $\langle f|$.

The overlap matrix of the basis functions then appears as

$$S = \langle f | f \rangle \quad (5)$$

This allows the density matrix to be written in Dirac form as

$$\begin{aligned}\rho(r; r') &= \langle r | \rho | r' \rangle \\ \rho &= |f\rangle \Pi \langle f|\end{aligned}\tag{6}$$

Partitioning ρ into atomic contributions in order to define the conventional atomic populations will be the focus of most of this paper.

$$\begin{aligned}\Pi &= \Pi_A + \Pi_B + \dots \\ \rho_A &= |f\rangle \Pi_A \langle f| \\ \rho_A(r; r') &= \langle r | \rho_A | r' \rangle \\ n_A &= \int \rho_A(r; r) dr = \text{Tr}(\Pi_A S)\end{aligned}\tag{7}$$

We begin with a modest basis set $\{f\}$ that is used to construct a wave function Ψ . The expectation value of any property operator $Z = \sum_{k=1}^N z(r_k)$ is given by

$$\langle Z \rangle = \langle \Psi | Z | \Psi \rangle = \text{Tr} \rho z = \sum_{i,j} \Pi_{ij} \langle f_j | z | f_i \rangle\tag{8}$$

and if the basis set is atom-centered, then it is trivial to divide this into single-center contributions Z_{AA} and two-center contributions Z_{AB} as

$$\begin{aligned}\langle Z \rangle &= \sum_A Z_{AA} + \sum_{A \neq B} Z_{AB} \\ Z_{AB} &= \sum_{i \in A} \sum_{j \in B} \Pi_{ij} \langle f_j | z | f_i \rangle\end{aligned}\tag{9}$$

This supports the concept that atomic properties can be calculated when those atoms exist within a molecule; the sum of all atom contributions yield the expectation value $\langle Z \rangle = \sum_A Z_{AA}$. In the context of the observable that is the total number of electrons N , we can define the unit operator for which $\langle I \rangle = N = \text{Tr} \rho$, where

$$\begin{aligned}I_{AB} &= \sum_{i \in A} \sum_{j \in B} \Pi_{ij} S_{ji} \\ S_{ji} &= \langle f_j | f_i \rangle\end{aligned}\tag{10}$$

However, the two-center terms in Eqn. 9 and Eqn. 10 present a fundamental difficulty and decision point. How do you allocate the two-center terms to atoms? What do you do with an extended basis set that has high overlap between centers, or, functions that are not on atomic centers (as in functions on ghost atoms)?

The remainder of this paper is dedicated to select aspects of orbital and spatial decomposition schemes of the density matrix that attempt to address such questions. We note the attributes and limitations of each - in context of the method employed to create the density - and point to mathematical distinctions amongst different

methods (e.g., partitioning versus projection).

2 | ORBITAL DECOMPOSITION SCHEMES OF THE DENSITY MATRIX

The choices made when dividing N into atomic contributions are intimately related to the underlying theory employed to construct the wavefunction (and in a related manner, the type of density that is analyzed, i.e., the valence density). Starting early in the development of quantum theory, Hückel developed LCAO-MO theory to rationalize the bond lengths and bond energies of the delocalized π bonds in planar hydrocarbons.[2, 3, 4, 5] This assumed one active basis function per atomic center, an off-diagonal matrix element β between adjacent centers, and the overlap matrix being the identity matrix. This simple model has led to the common text-book picture of atomic orbitals combining to form bonding and anti-bonding molecular orbitals. This has been extended in many ways (as in Hoffmann [6]). One extension is to include all the valence orbitals and electrons of each atom, which introduces the need to approximate the off-diagonal elements H_{ij} . Wolfsberg and Helmholz[7] used the Mulliken approximation[8]

$$f_{iA}f_{jB} \approx (1/2)S_{iA,jB}(f_{iA}^2 + f_{jB}^2) \quad (11)$$

based upon the arithmetic mean of the corresponding diagonal elements H_{ii} and H_{jj} multiplied by S_{ij} , and introducing an empirical scaling factor K (typically 1.75):

$$H_{ij} = K S_{ij} (H_{ii} + H_{jj})/2. \quad (12)$$

A variety of other approximations of varying complexity have been proposed - from that of Hoffmann and Libscomb[9, 10]

$$H_{ij} = K S_{ij}. \quad (13)$$

to Cusachs approximation:[11]

$$H_{ij} = S_{ij}(2 - |S_{ij}|)(H_{ii} + H_{jj})/2. \quad (14)$$

It is understood in these equations that the basis set consists of the true orthonormal atomic orbitals with diagonal elements that obey Koopmans' theorem - i.e., equal to the negative of the atomic ionization potential. While it is simple to obtain a bond order from the original Hückel orbitals with one basis function per atom ($BO_{\pi}(A, B) = \sum_{\mu=1}^{occ} c_A^{(\mu)} c_B^{\mu}$), it is more difficult for extended Hückel. Wiberg[12] suggested using $\text{Tr} \mathbf{\Pi}_{AB} \mathbf{\Pi}_{BA}$ which gives the square of the bond order and cannot distinguish bonding from anti-bonding.

Pople in CNDO[13, 14] (complete neglect of differential overlap) and Dewar in AM1[15] have modified Hückel theory to include approximations to the electron-electron repulsion as it would appear in a true Roothaan Hartree-Fock (HF) calculation using the same atomic basis. CNDO still retains a core Hamiltonian contribution proportional to the overlap. Comparison with Roothaan HF shows that the overlap matrix should also be considered in the normalization of the orbitals. For Hückel theory, the π - π overlap of adjacent centers is only ca. 0.25 and

might be negligible. For σ bonds, the overlap is much larger (0.7 or greater) and cannot be neglected.[16] Modifying the empirical HF equation to include overlap gives simply

$$\begin{aligned}
 \phi_k &= \mathbf{f} \mathbf{c}_k \\
 \mathbf{F} \mathbf{c}_k &= \epsilon_k \mathbf{S} \mathbf{c}_k \\
 \mathbf{C} &= (\mathbf{c}_1, \dots, \mathbf{c}_N) \\
 \rho(r; r') &= \sum_{k=1}^N \phi_k(r) \phi_k^*(r') = \mathbf{f}(r) \mathbf{C} \mathbf{C}^\dagger \mathbf{f}^\dagger(r')
 \end{aligned} \tag{15}$$

where N is the number of valence electrons and ρ is the valence density matrix. This is easily solved as

$$\begin{aligned}
 \mathbf{S}^{-1/2} \mathbf{F} \mathbf{S}^{-1/2} \mathbf{x}_k &= \epsilon_k \mathbf{x}_k \\
 \mathbf{c}_k &= \mathbf{S}^{-1/2} \mathbf{x}_k \\
 \mathbf{\Pi} &= \mathbf{C} \mathbf{C}^\dagger
 \end{aligned} \tag{16}$$

Löwdin dealt with the LCAO overlap problem by suggesting that the basis set be transformed from a locally orthonormal set to a fully orthonormal one using $\mathbf{S}^{1/2}$ as the transformation matrix and then partitioning the resulting basis among atoms just like the original LCAO basis. He justified this by showing that this transformation produced orthonormal orbitals as similar as possible to the original LCAO basis.

$$\begin{aligned}
 \mathbf{S} &= \begin{pmatrix} \mathbf{1} & \mathbf{S}_{AB} \\ \mathbf{S}_{BA} & \mathbf{1} \end{pmatrix} = \langle \mathbf{f} | \mathbf{f} \rangle \\
 |\mathbf{f}\rangle &= (|\mathbf{f}_A\rangle, |\mathbf{f}_B\rangle, \dots) = (|\mathbf{g}_A\rangle, |\mathbf{g}_B\rangle, \dots) \mathbf{S}^{1/2} \\
 \rho &= |\mathbf{f}\rangle \mathbf{\Pi} \langle \mathbf{f}| = |\mathbf{g}\rangle \mathbf{\Gamma} \langle \mathbf{g}| \\
 \mathbf{\Gamma} &= \mathbf{S}^{1/2} \mathbf{\Pi} \mathbf{S}^{1/2} \\
 \mathbf{S}^{1/2} &\approx \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} + (1/2) \begin{pmatrix} \mathbf{0} & \mathbf{S}_{AB} \\ \mathbf{S}_{BA} & \mathbf{1} \end{pmatrix} + \dots \\
 \mathbf{\Gamma}_{AA} &\approx \mathbf{\Pi}_{AA} + \mathbf{\Pi}_{AB} \mathbf{S}_{BA}/2 + \mathbf{S}_{AB} \mathbf{\Pi}_{BA}/2 + \dots \\
 \mathbf{\Gamma}_{AB} &\approx \mathbf{\Pi}_{AB}
 \end{aligned} \tag{17}$$

This gives the Löwdin population and partitioned density matrix

$$\begin{aligned}
 P &= |\mathbf{g}\rangle \mathbf{1}_A \langle \mathbf{g}| \\
 \rho &= (P_A \rho + \rho P_A)/2 = (|\mathbf{g}\rangle (\mathbf{1}_A \mathbf{\Gamma} + \mathbf{\Gamma} \mathbf{1}_A) \langle \mathbf{g}|)/2 = |\mathbf{g}\rangle \mathbf{\Gamma}_A \langle \mathbf{g}| \\
 \mathbf{\Gamma}_A &= \begin{pmatrix} \mathbf{\Gamma}_{AA} & \mathbf{\Gamma}_{AB}/2 \\ \mathbf{\Gamma}_{BA}/2 & \mathbf{0} \end{pmatrix} \\
 n_A &= \text{Tr} |\mathbf{g}\rangle \mathbf{\Gamma}_A \langle \mathbf{g}| = \text{Tr} |\mathbf{g}_A\rangle \mathbf{\Gamma}_{AA} \langle \mathbf{g}_A| = \text{Tr} \mathbf{\Gamma}_{AA}
 \end{aligned} \tag{18}$$

For LCAO wave functions with small overlap integrals, this will be nearly the same as the Mulliken population. Sigma bond overlaps can be very large however, so the difference can be substantial.[16]

It is important to note that these tools for interpreting wave functions have been developed using minimum valence-only basis sets that are meaningful atomic orbitals. The use of Gaussians (chosen to make the integrals more computationally tractable) or other function types often necessitates much larger basis sets that are not analogous to atomic orbitals and introduce new challenges to partitioning. For basis sets that are atom centered, the most common approach is to continue trying to partition these into atomic sets. The LCAO equations may then be used with the essential change of including the one center overlap matrix which is generally no longer a unit matrix. The Mulliken partition of the density matrix is invariant to separate linear transformations within each atom centered set, and thus extension of the LCAO results to general basis sets seems reasonable. The extension of the generalized Löwdin population to basis sets that are non-orthogonal within separate atoms is harder to justify. Löwdin explicitly assumed that the one center overlaps formed a unit matrix as was true for an LCAO basis. As has been pointed out by Clark and Davidson, the result is not invariant under linear transforms within the atomic basis sets if the one-center overlap is not a unit matrix.[17] Mayer has pointed out that these transforms may be induced by rigid rotation of the molecule within a space-fixed coordinate system.[18] This problem is solved by first transforming the basis sets into locally orthonormal atomic sets as Löwdin originally envisioned.[17] Even then, the Löwdin orthogonalization method for general basis sets may not give new orbitals that can be sensibly partitioned among atoms.

Papers focused on just the atomic charge have generally emphasized the partitioning of the overlap density ($P_A \rho P_B$) as a starting point. In order to deal with operators other than the unit operator, it is better to partition the density matrix. For example

$$\begin{aligned} \rho_A &= |f\rangle \Pi_A \langle f| \\ \Pi_A &= \begin{pmatrix} \Pi_{AA} & \Pi_{AB} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \end{aligned} \quad (19)$$

leads to the generalization of the Mulliken charge for any operator. Because the density matrix is Hermitian,

$$\Pi_A = \begin{pmatrix} \Pi_{AA} & \Pi_{AB}/2 \\ \Pi_{BA}/2 & \mathbf{0} \end{pmatrix} \quad (20)$$

leads to a more symmetrical form for the Mulliken population. Mayer has emphasized that these may be derived from projection operators. Following Mayer and Hamza[19] and in analogy to Clark and Davidson [20] define

$$\begin{aligned} \mathbf{1}_A &= \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \\ P_A &= |f\rangle \mathbf{1}_A S^{-1} \langle f| \\ P_A P_B &= P_A \delta_{AB}, \end{aligned} \quad (21)$$

then the non-Hermitian and Hermitian forms of the Mulliken density are

$$\rho_A = P_A \rho = |f\rangle \mathbf{1}_A S^{-1} \langle f| \rho = |f\rangle \begin{pmatrix} \Pi_{AA} & \Pi_{AB} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \langle f| \quad (22)$$

or

$$\rho_A = (P_A \rho + \rho P_A^\dagger)/2 = (|f\rangle\langle f| \Pi_A + \Pi_A |f\rangle\langle f|)/2 = |f\rangle\langle f| \begin{pmatrix} \Pi_{AA} & \Pi_{AB}/2 \\ \Pi_{BA}/2 & 0 \end{pmatrix} \langle f| \quad (23)$$

The second form, like the density matrix itself is Hermitian. Note too the difference between using the projection operator to partition the density as opposed to a projection of the density. The projection using this operator misses the overlap density $P_A \rho P_B$ and would be

$$\begin{aligned} \rho_{AA} &= P_A \rho P_A^\dagger = |f\rangle\langle f| \Pi_A \Pi_A |f\rangle\langle f| = |f\rangle\langle f| \begin{pmatrix} \Pi_{AA} & 0 \\ 0 & 0 \end{pmatrix} \langle f| = |f_A\rangle\langle f_A| \Pi_{AA} \langle f_A| \\ \rho_{BB} &= P_B \rho P_B^\dagger = |f\rangle\langle f| \Pi_B \Pi_B |f\rangle\langle f| = |f\rangle\langle f| \begin{pmatrix} 0 & 0 \\ 0 & \Pi_{BB} \end{pmatrix} \langle f| = |f_B\rangle\langle f_B| \Pi_{BB} \langle f_B| \\ \rho_{AA} + \rho_{BB} &\neq \rho \end{aligned} \quad (24)$$

Either of the atomic density matrices in Eqns. 22 - 23 would sum to the correct molecular density matrix for which $S^{1/2} \Pi S^{1/2}$ has eigenvalues between 0 and 2.

Extensions may be made to analyze a wave function that is a spin eigenfunction where the spin-orbital basis is blocked into subsets which are pure spin-up or spin-down. The density matrix will then be block diagonal on spin. The spin-free density matrix (defined in Eqn. 1) will then be the sum of the spin up and down blocks of the original matrix, provided the space parts of the up and down orbitals are identical. The natural spin-orbital occupations will be in the range from 0 to 1. For a singlet state ($S = 0$) the occupation numbers for up and down densities will each be equal to half that for the spin-free density.

As an alternative partitioning scheme, Coulson, McWeeny[21] and Mulliken all focused on partitioning the LCAO density into atomic contributions (as opposed to starting with the overlap density). A bond order definition analogous to Wiberg is not easily obtained in this case, but the Wolfsburg-Helmholz approximation suggests that bond strength should be proportional to the overlap population. The Mulliken partition of the density using the Mayer approach (Eqn. 21) leads to atomic densities with associated populations that correctly sum to the total population. Further, for any two atoms A and B the sum of the partitions is the partition for the combined $A + B$ region. These partitions are not true density matrices however. Natural orbital occupations computed for them do not lie within the allowed range from 0 to 2. The density itself may have regions where it is negative. For extended basis sets, the population assigned to an individual basis function in popular programs may be negative or may exceed unity. Even for modest basis sets, the results for transition metals are often unphysical.

The non-Hermitian form of the Mulliken populations is most easily computed as

$$\begin{aligned} n_i &= (\Pi S)_{ii} \\ n_A &= \sum_{i \in A} n_i \end{aligned} \quad (25)$$

The n_i may be interpreted as the population of the individual orbitals. For LCAO densities, these are often pointed to as indications of promotion and hybridization in the atomic orbital basis. For arbitrary Gaussian basis sets these

populations are still reported by many programs although they have little significance. It is usually possible to compute sub-sums over basis functions on a center with definite angular momentum l

$$n_{l,A} = \sum_{i \in l,A} n_i \quad (26)$$

This allows the atomic population for a general basis set to be interpreted in terms of s , p , d , etc. population.[22]

As noted by Davidson and Roby, there is an alternative approach to defining atomic populations that is mathematically correct but leads to double counting of the overlap population.[16, 23] The density matrix is positive definite with eigenvalues between 0 and 2 and has trace N . If we view this as an operator, we may approximate its spectrum by representing it in some smaller basis. This approximate matrix may be generated by using a projection operator. As was done for the partitioning of the density, the basis can be partitioned into subsets associated with atoms

$$\begin{aligned} |f\rangle &= (|f_A\rangle, |f_B\rangle) \\ P_A &= |f_A\rangle(S_{AA})^{-1}\langle f_A| \\ \text{Tr}\langle f_A|f_A\rangle &= S_{AA} \\ \rho_A &= P_A \rho P_A \\ \rho_A &= |f_A\rangle(1, S_{AA}^{-1} S_{AB}) \Pi \begin{pmatrix} 1 \\ S_{BA} S_{AA}^{-1} \end{pmatrix} \langle f_A| \\ n_A &= \text{Tr}\{(S_{AA}^{1/2}, S_{AA}^{-1/2} S_{AB} \Pi) \begin{pmatrix} S_{AA}^{1/2} \\ S_{BA} S_{AA}^{-1/2} \end{pmatrix}\} \\ &= \text{Tr}\{\Pi_{AA} S_{AA} + \Pi_{BA} S_{AB} + S_{AB} \Pi_{BA} + S_{AB} \Pi_{BB} S_{BA} S_{AA}^{-1}\} \end{aligned} \quad (27)$$

Because this ρ_A is the matrix representation of the density operator in an incomplete sub-basis it will have many of the properties of a true density matrix. It will be Hermitian with eigenvalues between the lowest and highest eigenvalues of the full density matrix. The total occupation includes the full overlap population rather than splitting it between atoms. In addition there is a term that picks up the contributed density from a coordinate covalent bond defined when all of the coefficients in the orbital are for basis functions on other atoms. Note however, that the sum of the projections onto centers A and B is not the projection onto the combined region. A consequence of this is that the sum of these atomic populations over all atoms will over count the electrons and will exceed N . Roby has exploited this difference to interpret the bond strength.[23, 24] This makes sense for a basis of atomic orbitals but loses meaning for extended basis sets. This over-counting problem disappears if the projected orthonormal Löwdin basis is used,

$$\begin{aligned} P_A &= |g_A\rangle\langle g_A| \\ P_A |g\rangle &= (|g_A\rangle, 0) \\ P_A(|g\rangle\Gamma\langle g|)P_A &= |g_A\rangle\Gamma_{AA}\langle g_A| \\ n_A &= \text{Tr}\Gamma_{AA} \end{aligned} \quad (28)$$

Thus, the partitioned density differs from the projected density, but they give the same population. The sum of these

Löwdin populations will equal N . The projected density matrices for each atom will correctly have all eigenvalues within the range of the eigenvalues of the full density matrix. The sum of the Löwdin projected density matrices, unlike the partitioned densities, will not equal the total density matrix.

A problem with both the Mulliken and Löwdin definition is that the results fail to converge to a well-defined limit as the basis set is augmented. Staying within the current theoretical framework, Reed and Weinhold[25, 26] introduced the Natural Population Analysis method (NPA). This consists of a sequence of orthogonalization steps that concludes with an occupancy weighting scheme to include contributions of the highly occupied orbitals to the resulting atomic populations while diminishing the contributions of orbitals with low occupancy that have a small role in describing the electron density. The latter is highly sensitive to the extension of basis set and as such, removing their contributions to the atomic populations leads to well-defined limits for NPA atomic charges.[26]

Beginning with the density matrix within a basis $\{ f_i \}$, sub-blocks associated with an atom and different angular symmetries are orthogonalized to obtain their associated electron populations, yielding the orthonormal set $\{ \phi_i \}$. Using these occupancies, the orbitals are sorted into two groups: (1) a set that corresponds to all atomic (n,l) subshells of nonzero occupancy in the atomic ground state electronic configuration, and (2) a set of nominally unoccupied orbitals labelled the "Rydberg" set. The occupied set are subjected to an occupancy weighted symmetric orthogonalization, while the unoccupied set are Schmidt orthogonalized. The former minimizes

$$\sum_i^{occ} w_i ||\phi_i^w - \phi_i||^2 \quad (29)$$

where

$$w_i = \langle \phi_i | \rho | \phi_i \rangle \quad (30)$$

The consequence of the occupancy weighted orthogonalization is that orbitals that have high occupancy are minimally perturbed while those orbitals that have lower occupancy are more distorted. The natural atomic orbital orthogonalization procedure is rotationally invariant because the basis set is transformed into locally orthonormal atomic sets as described above.

3 | SPATIAL DECOMPOSITION APPROACHES

Overcoming the challenge of the complete basis set limit may also be obtained by analysing the electron density, which does approach a well-defined limit for complete basis sets. Here, a number of methods have been developed. For example, the electrostatic potential

$$V(r) = \sum_A \frac{Z_A}{|r - R_A|} - \sum_i \sum_j \Pi_{ij} \int \frac{f_i^*(r') f_j(r')}{|r - r'|} dr', \quad (31)$$

where Z_A is the nuclear charge on atom A centered at R_A , and Π_{ij} are the elements of the density matrix. Various spatial sampling approaches have been developed where atomic charges are fit (via least squares or more complicated schemes) to the discretized $V(r)$, generally referred to as electrostatic surface potential (ESP) derived

charges.[27, 28, 29] A variety of ESP-based schemes have been developed that differ in the spatial sampling, whether the points are associated with spherical shells around each atom[30] or nested Connolly surfaces[31] or on cubic grids.[32] However it is important to note that these sampled points always lie outside the van der Waals atomic radii, and as such are challenging to apply to large molecules that may have "buried" atoms. Charges derived from fits to electrostatic potentials have an intuitive appeal; in principle they could be derived from either theoretical or experimental data. It has been noted, however, that such potential derived charges can be conformationally dependent in ways that do not appear to reflect the changes in the molecular wave function. Further, these methods must be mindful of the typical issues of all fitting - for example the fit being overdetermined or the sampled points being linearly dependent which leads to the system being underdetermined. Nevertheless, ESP-derived charges have become incredibly popular for estimating atomic charges that are employed within analytical expressions of intra- and intermolecular interactions (i.e., force field representations in classical systems).

One approach toward Euclidean partitioning is to employ weights associated with each atom that may be assigned to each point in space and used to apportion the charge density to atoms. A number of different weighting schemes have been developed, largely inspired by the stockholder scheme of Hirshfeld[33] where the weight is based upon the relative density of the isolated atom (pro-atomic density, ρ_A^0) in relation to the sum of all isolated atoms that comprise the molecule (pro-molecular density) $w_A(r) = \rho_A^0(r) / \sum_B \rho_B^0(r)$. [34, 35, 36, 37] An alternative approach is to partition the density (or a related surface) based upon its topology. The well-known method of Bader posits that an atom in a molecule is an open system that is bounded by zero flux surface of the gradient vector field of the charge density $\nabla\rho(r)$. [38, 39, 40] This gives a local charge density from which atomic populations and moments may be computed. However neither of these approaches partition the density matrix, a topic amended by Li and Parr [41] who developed a partitioning consistent with Bader.

Clark and Davidson,[20] as reviewed by Mayer and Hamza,[19] have discussed one approach to partitioning the density matrix based on assigning each point in space a weighted contribution for each atom. In this approach,

the basis set is enlarged to form a new basis where each function has a clear association with an atom.

$$\begin{aligned}
 \mathbf{g} &= (\langle \mathbf{r} | \mathbf{g}_A, \langle \mathbf{r} | \mathbf{g}_B \rangle) = (\langle \mathbf{r} | \mathbf{w}_A | \mathbf{f} \rangle, \langle \mathbf{r} | \mathbf{w}_B | \mathbf{f} \rangle) \\
 w_A(r) + w_B(r) &= 1 \\
 w_A(r) &\geq 0 \\
 w_B(r) &\geq 0 \\
 \mathbf{f} &= \mathbf{g} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\
 \rho &= |\mathbf{f}\rangle \mathbf{\Pi}_f \langle \mathbf{f}| = |\mathbf{g}\rangle \mathbf{\Pi}_g \langle \mathbf{g}| \\
 \mathbf{\Pi}_g &= \begin{pmatrix} \mathbf{\Pi} & \mathbf{\Pi} \\ \mathbf{\Pi} & \mathbf{\Pi} \end{pmatrix} \\
 \mathbf{P}_A &= |\mathbf{g}\rangle \mathbf{1}_A \mathbf{S}_A^{-1} \langle \mathbf{g}| \\
 \rho_A &= (\mathbf{P}_A \rho + \rho \mathbf{P}_A) / 2 = (|\mathbf{g}\rangle (\mathbf{1}_A \mathbf{\Pi}_g + \mathbf{\Pi}_g \mathbf{1}_A) \langle \mathbf{g}|) / 2 \\
 \rho_A(r; r') &= \rho(r; r') [w_A(r) w_A(r') + w_A(r) w_B(r') / 2 + w_B(r) w_A(r') / 2] \\
 \rho_A(r; r') &= (\rho(r; r') [w_A(r) + w_A(r')]) / 2 \\
 n_A &= \int \rho_A(r; r) d\tau = \int \rho(r) w_A(r) d\tau = \text{Tr} \mathbf{\Pi} \langle \mathbf{f} | \mathbf{w}_A | \mathbf{f} \rangle
 \end{aligned} \tag{32}$$

For a partition into "hard" atoms, the weight would be zero outside of the atomic basin associated with the nucleus. For 'fuzzy', the weight could be prorated by some scheme which seemed reasonable to the user. Irrespective, w_A should be chosen so that they have a well-defined limiting value for a complete basis. They should be basis set independent so that they apply equally well to plane-wave basis sets, distributed Gaussian basis sets, and numerical basis sets as well as the usual Dunning-type contracted Gaussian sets.

As one changes approaches from Hartree-Fock to density functional theory (DFT) it is important to recall that DFT produces a charge density but no density matrix. This may be analyzed in atomic contributions. If positive weights are assigned which sum to unity are assigned to each point in space then atomic populations may be defined as

$$\begin{aligned}
 w_A(r) &\geq 0 \\
 \sum_A w_A(r) &= 1 \\
 n_A &= \int \rho(r) w_A(r) d\tau.
 \end{aligned} \tag{33}$$

Kohn-Sham calculations produce the density in the form of a quadratic sum over basis functions

$$\begin{aligned}\rho(r) &= \sum_{k=1}^N |\phi_k(r)|^2 \\ &= \sum_{i,j} \Pi_{ij} f_i(r) f_j^*(r)\end{aligned}\tag{34}$$

In this form the atomic population becomes

$$n_A = \sum_{i,j} \Pi_{ij} \int f_i(r) f_j^*(r) w_A(r) d\tau\tag{35}$$

The density from any of the methods which actually produce a density matrix could also be used in this form to produce atomic populations. The weights could be hard-sphere weights for space partitions or fuzzy weights for shared space.

4 | LOOKING FORWARD

New and more elaborate methods of extracting information from the density matrix continue to appear. Some still focus on population, while more elaborate extensions of bond order and energy decomposition continue to be developed. The Wiberg bond order $\text{Tr}(\mathbf{\Pi S})_{AB}(\mathbf{\Pi S})_{BA}$ gives the square of the bond order. Similarly, the effectively unpaired electron density $2\mathbf{\Pi} - \mathbf{\Pi S \Pi}$, introduced by Yamaguchi[42] and discussed by Staroverov and Davidson[43] measures the extent of local unpairing of electrons. This is closely related to Mayer's free valence.[44, 45] Alcoba,[46] Vantfleteren,[47] and Mayer[48] have also suggested an energy decomposition scheme. Extensions have also been made to transform basis set into sets into eigenfunctions of other relevant operators, as in the energy density operator.[49]

These methods would all produce a unique interpretation of any Hermitian matrix with eigenvalues in the range 0 to 1. The number of free coefficients in a CI expansion of a wave function is much larger than the number of free numbers in the density matrix. Consequently, many linear combinations of Slater determinants will produce the same density matrix and each combination may have a different interpretation of bonding. In the spirit of DFT, we should follow Levy and associate with the corresponding density the one wave function with that density which has the minimum average energy.[50] With this interpretation, there is a one-to-one mapping between the density and a local potential in the Hamiltonian. Clearly the potential must be considered in interpreting the density. Usually this is implicit in the recognition that there are "atomic" regions dominated by the Coulomb potential produced by the nuclei – that is, the Coulomb potential is implicit in all interpretations.

Acknowledgements

We thank Professors Surjan, Szabados and Lendvai for organizing this special issue in commemoration of Prof. Mayer and for inviting our contribution.

Funding Information

AEC was supported by National Science Foundation, Award No. OAC- 1934725.

references

- [1] Pauling L. Electron Transfer in Intermetallic Compounds 1950;36(10):533–538.
- [2] Hückel E. Zeitschrift für Physik 1931;70:204.
- [3] Hückel E. Zeitschrift für Physik 1931;72:310.
- [4] Hückel E. Zeitschrift für Physik 1932;72:628.
- [5] Hückel E. Zeitschrift für Physik 1933;83:632.
- [6] Hoffmann R. An Extended Hückel Theory. I. Hydrocarbons. The Journal of Chemical Physics 1963;39(6):1397–1412.
- [7] Wolfsberg M, Helmholz L. The Spectra and Electronic Structure of the Tetrahedral Ions MnO_4 , CrO_4 , and ClO_4 . The Journal of Chemical Physics 1952;20(5):837–843.
- [8] Mulliken, Robert S . Quelques aspects de la théorie des orbitales moléculaires (suite et fin);.
- [9] Hoffmann R, Lipscomb WN. Theory of Polyhedral Molecules. I. Physical Factorizations of the Secular Equation. The Journal of Chemical Physics 1962;36(8):2179–2189.
- [10] Hoffmann R, Lipscomb WN. Boron Hydrides: LCAO—MO and Resonance Studies. The Journal of Chemical Physics 1962;37(12):2872–2883.
- [11] Cusachs LC. Semiempirical Molecular Orbitals for General Polyatomic Molecules. II. One-Electron Model Prediction of the H–O–H Angle. The Journal of Chemical Physics 1965;43(10):S157–S159.
- [12] Wiberg KB. Application of the pople-santry-segal CNDO method to the cyclopropylcarbanyl and cyclobutyl cation and to bicyclobutane. Tetrahedron 1968;24:1083–1096.
- [13] Pople JA, Santry DP, Segal GA. Approximate Self-Consistent Molecular Orbital Theory. I. Invariant Procedures. The Journal of Chemical Physics 1965;43(10):S129–S135.
- [14] Pople JA, Segal GA. Approximate Self-Consistent Molecular Orbital Theory. II. Calculations with Complete Neglect of Differential Overlap. The Journal of Chemical Physics 1965;43(10):S136–S151.
- [15] Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP. Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model. Journal of the American Chemical Society 1985;107(13):3902–3909.
- [16] Davidson ER. Electronic Population Analysis of Molecular Wavefunctions. The Journal of Chemical Physics 1967;46(9):3320–3324.
- [17] Bruhn G, Davidson ER, Mayer I, Clark AE. Löwdin population analysis with and without rotational invariance. International Journal of Quantum Chemistry;106(9):2065–2072.
- [18] Mayer I. Löwdin population analysis is not rotationally invariant. Chemical Physics Letters 2004;393:209–212.

- [19] Mayer I, Hamza A. Atomic decomposition of identity: General formalism for population analysis and energy decomposition. *International Journal of Quantum Chemistry*;103(6):798–807.
- [20] Clark AE, Davidson ER. Population analyses that utilize projection operators. *International Journal of Quantum Chemistry*;93(6):384–394.
- [21] McWeeny R. Charge Densities in Conjugated Systems. *The Journal of Chemical Physics* 1951;19(12):1614–1615.
- [22] Martin RL, Davidson ER. Electronic structure of the sodium trimer. *Molecular Physics* 1978;35(6):1713–1729.
- [23] Roby KR. Quantum theory of chemical valence concepts I. *Molecular Physics* 1974;27(1):81–104.
- [24] Roby KR. Quantum theory of chemical valence concepts II. *Molecular Physics* 1974;28(6):1441–1456.
- [25] Reed AE, Weinstock RB, Weinhold F. Natural population analysis. *The Journal of Chemical Physics* 1985;83(2):735–746.
- [26] Reed AE, Weinhold F. Natural bond orbital analysis of near-Hartree–Fock water dimer. *The Journal of Chemical Physics* 1983;78(6):4066–4073.
- [27] Momany FA. Determination of partial atomic charges from ab initio molecular electrostatic potentials. Application to formamide, methanol, and formic acid. *The Journal of Physical Chemistry* 1978;82(5):592–601.
- [28] Smith PH, Derissen JL, van Duijneveldt FB. Intermolecular interactions in crystals of carboxylic acids. *Molecular Physics* 1979;37(2):521–539.
- [29] Cox SR, Williams DE. Representation of the molecular electrostatic potential by a net atomic charge model. *Journal of Computational Chemistry*;2(3):304–323.
- [30] Chipot C, Maigret B, Rivail JL, Scheraga HA. Modeling amino acid side chains. 1. Determination of net atomic charges from ab initio self-consistent-field molecular electrostatic properties. *The Journal of Physical Chemistry* 1992;96(25):10276–10284.
- [31] Singh UC, Kollman PA. An approach to computing electrostatic charges for molecules. *Journal of Computational Chemistry*;5(2):129–145.
- [32] Breneman CM, Wiberg KB. Determining atom-centered monopoles from molecular electrostatic potentials. The need for high sampling density in formamide conformational analysis. *Journal of Computational Chemistry*;11(3):361–373.
- [33] Hirshfeld FL. Bonded-Atom Fragments for Describing Molecular Charge Densities. *Theroetical Chimica Acta (Berl)* 1977;44:129–138.
- [34] Bultinck P, Van Alsenoy C, Ayers PW, Carbó-Dorca R. Critical analysis and extension of the Hirshfeld atoms in molecules. *The Journal of Chemical Physics* 2007;126(14):144111.
- [35] Lillestolen TC, Wheatley RJ. Redefining the atom: atomic charge densities produced by an iterative stockholder approach. *Chem Commun* 2008;p. 5909–5911.
- [36] Ayers PW. Atoms in molecules, an axiomatic approach. I. Maximum transferability. *The Journal of Chemical Physics* 2000;113(24):10886–10898.
- [37] Parr RG, Ayers PW, Nalewajski RF. What Is an Atom in a Molecule? *The Journal of Physical Chemistry A* 2005;109(17):3957–3959. PMID: 16833715.
- [38] Bader RFW, Beddall PM, Cade PE. Partitioning and characterization of molecular charge distributions. *Journal of the American Chemical Society* 1971;93(13):3095–3107.

- [39] Bader RFW, Beddall PM. Virial Field Relationship for Molecular Charge Distributions and the Spatial Partitioning of Molecular Properties. *The Journal of Chemical Physics* 1972;56(7):3320–3329.
- [40] Bader RFW. The zero-flux surface and the topological and quantum definitions of an atom in a molecule. *Theor Chem Acc* 2001;105:276–283.
- [41] Li L, Parr RG. The atom in a molecule: A density matrix approach. *The Journal of Chemical Physics* 1986;84(3):1704–1711.
- [42] Takatsuka K, Fueno T, Yamaguchi K. Distribution of odd electrons in ground-state molecules. *Theoret Chim Acta* 1978;48:175–183.
- [43] Staroverov V, Davidson E. Distribution of effectively unpaired electrons. *Chemical Physics Letters* 2000 11;330:161–168.
- [44] Mayer I. *Bond Orders and Energy Components: Extracting Chemical Information from Molecular Wave Functions*. 1st ed. ed. CRC Press ; Boca Raton, FL; 2017.
- [45] Mayer I. Improved definition of bond orders for correlated wave functions. *Chem Phys Lett* 2012;544:83–85.
- [46] Alcoba DR, Torre A, Lain L, Bochicchio RC. Energy decompositions according to physical space partitioning schemes. *The Journal of Chemical Physics* 2005;122(7):074102.
- [47] Vanfleteren D, Ghillemijn D, Van Neck D, Bultinck P, Waroquier M, Ayers PW. Fast density matrix-based partitioning of the energy over the atoms in a molecule consistent with the hirshfeld-I partitioning of the electron density. *Journal of Computational Chemistry*;32(16):3485–3496.
- [48] Mayer I. A Chemical Energy Component Analysis. *Chemical Physics Letters* 2000;332:381–388.
- [49] Takatsuka K, Arasaki Y. Energy natural orbitals. *The Journal of Chemical Physics* 2021;154(9):094103.
- [50] Levy M. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem 1979;76(12):6062–6065.