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REGULAR ARTICLE

Intrinsic local constituents of molecular electronic wave functions. I. Exact representation of the density matrix in terms of chemically deformed and oriented atomic minimal basis set orbitals

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Abstract A coherent, intrinsic, basis-set-independent analysis is developed for the invariants of the first-order density matrix of an accurate molecular electronic wavefunction. From the hierarchical ordering of the natural orbitals, the zeroth-order orbital space is deduced, which generates the zeroth-order wavefunction, typically an MCSCF function in the full valence space. It is shown that intrinsically embedded in such wavefunctions are elements that are local in bond regions and elements that are local in atomic regions. Basis-set-independent methods are given that extract and exhibit the intrinsic bond orbitals and the intrinsic minimal-basis *quasi-atomic* orbitals in terms of which the wavefunction can be exactly constructed. The quasi-atomic orbitals are furthermore *oriented* by a basis-set independent method (viz. maximization of the sum of the fourth powers of all off-diagonal density matrix elements) so as to exhibit clearly the chemical interactions. The unbiased nature of the method allows for the adaptation of the localized and directed orbitals to changing geometries.

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1 Introduction

The model of matter consisting of atoms linked by bonds has been firmly established by two centuries of chemical research. So solid is this basis for the understanding of all known experimental evidence that it seems reasonable to expect a rigorous quantification by ab-initio quantum chemistry to be possible. The theoretical identification of atoms in molecules and a corresponding analysis of their interactions have however proved to be challenging. This is because the resolution of molecules in terms of atoms is not *fundamental* to rigorous physical theory. Rather, the latter is built on the many-electron-many-nuclei model and the complexities of reliable electronic wavefunctions, mainly due to electron correlations, pose nontrivial challenges for the extraction of atomic substructures.

Theoretical computations have in fact lead to the recognition and quantification of theoretical entities that characterize *atoms*. These are the *minimal basis sets (MBS)*, i.e. the 1s, 2s, 2p, 3s, 3p, 3d, etc. type atomic orbitals that are determined by the optimization of closed- or open-shell Hartree-Fock-type self-consistent-field (SCF) or multi-configuration-self-consistent-field (MCSCF) wavefunctions in atoms. The MBS concept is in fact the basis for all-qualitative as well as quantitative understanding of the electronic structures of atoms. It is this *zeroth-order model* that essentially accounts for the periodic table, which is the fundament of all chemistry. Notwithstanding the quantitative need for complementing it by terms that account for electron correlation and relativistic effects, the MBS description of atoms is the bedrock zeroth approximation on which all refinements are built.

The dominance of the atomic minimal basis sets also extends to molecules. This can be seen by taking the expansion of any reasonable molecular electronic wavefunction in terms of a high-quality atomic orbital (AO) basis and re-expressing it in terms of a new AO basis that is derived from the original one by a transformation that generates the (MC)SCF MBS orbitals of the free-atoms (determined in the original AO basis) as part of the new basis. Typically, the first order density matrix in terms of the new basis is then dominated by the optimized free-atom minimal-basis orbitals.

These observations suggest that (a) chemical bonds establish themselves at internuclear distances where atomic building blocks, though deformed, remain still identifiable, (b) molecular wavefunctions can be analyzed in terms of orbitals, and (c) there exist zeroth-order approximations to the wavefunctions that are generated from MBS-type orbitals. One would also expect, however, that the free-atom MBS orbitals are deformed by adaptations to the molecular environment via the energy minimization. We shall call such deformed MBS orbitals *quasi-atomic*.

It is indeed found that accurate electronic wavefunctions in molecules always consist of a qualitatively indispensable (single- or multi-configurational) zeroth-order component, which contains the essential chemical, i.e. bonding information but not the higher order refinements that provide the dynamic correlations needed to achieve accuracy to the millihartree level. From the preceding considerations, one would then expect that the former, "non-dynamic" component is expressible in terms of quasi-atomic MBS orbitals.

The present investigation will exhibit that this is indeed the case. Building on previous work of this group [1–10], we develop an intrinsic, i.e. basis-set-independent analysis of the first-order density matrix that will lead to quasi-atomic MBS orbitals capable of exactly expressing the zeroth-order wavefunction of a given molecule. We moreover provide a general unbiased method for the intrinsic determination of *oriented* quasi-atomic hybrid orbitals that reflect the directionality of the chemical interactions of the atoms in a molecule. These quasi-atomic orbitals furthermore generate local bonding and antibonding orbitals. When applied to computationally determined electronic wavefunctions, the conjunction of these analyses contribute to a conceptual understanding of the embedded bonding structures, as will be illustrated in the subsequent paper. We shall refer to the resulting interpretative picture as the *Intrinsic Localized Density Analysis* (*ILDA*).

We emphasize that our aim is *not* to generate an atomic partitioning of calculated molecular quantities by forcing onto an electronic wavefunction a clever apportionment based on preconceived intuitive notions. Rather, we search for the existence of internal transformations among the orbitals from which a specific wavefunction is constructed such that the wavefunction, when expressed in terms of the transformed orbitals, will naturally appear as built from atomic-like elements that exhibit bonding. Moreover, the procedure for finding such transformations should be free of any input bias and unrelated to the numerical basis sets in terms of which specific calculations are executed (be they STO-3G or cc-double-zeta or plane-waves or others). These are the characteristics of our approach that we subsume under the attribute *"intrinsic"*. It is conceivable that, for certain systems, an intrinsic atomic resolution does not exist and this in itself would then be of interest.

Historically, the idea that atomic building blocks are to some degree preserved in molecular wavefunctions is of course already embodied in the approach that Heitler and London [11] chose in dealing with the H_2 molecule as well as in the LCAO expansions of the subsequently developed molecular orbital method. In the fifties, Moffitt [12] formulated the first general approach for expressing molecular wavefunctions in terms of *antisymmetrized products of atomic state wavefunctions* ("composite atomic functions") and he explicitly created the concept and the term of *"Atoms-in-Molecules"*. Subsequently, Hurley [13] modified and successfully quantified Moffitt's approach for the calculation of numerous molecular energies and this approach was further developed by Lam, Schmidt and Ruedenberg [14,15]. Two decades later, at about the same time as the analysis to be discussed in the present paper was initiated [1–5], interesting interpretative analyses of electronic wavefunctions in molecules were also developed by Weinhold [16,17][1] as well as by Bader [21–24].[2] Bader's *Atoms-in-Molecules* analysis [21–24] is unique in that it is not based on orbitals but on an imaginative *cellular* partitioning of the total density in real three-dimensional space that is deduced from a topological analysis of its differential geometry.

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[1] Further references can be found in [18]. This *Natural Bond Orbital analysis* differs from the present approach in the following respects:

(a) It generates a set of minimal-basis-type atom-localized orbitals that do however *not* span the space of all occupied molecular orbitals. The actual wavefunction and energy can therefore not be recovered from this minimal basis set.

(b) Its *definitions depend essentially* on the atomic orbital basis sets used. Hence, it cannot extract, *e.g.*, quasi-atomic orbitals from *plane-wave-based* Bloch orbitals in crystals, whereas this has in fact been accomplished by the method described in the present paper (see Ref. [10]).

(c) It depends on the human user to *input* the location of two-center bonds, three-center-bonds, etc. and certain weight factors on the basis of his/her intuition, whereas in the method described in the present paper this quantitative information is automatically generated from the density by an unbiased intrinsic formalism.

The approach is thus not intrinsic in the sense specified in the introduction. Bachler [19,20] has skillfully used the Weinhold approach to generate a localized bonding scheme for full-valence-space wavefunctions.

[2] Further references can be found in [25].

2 Zeroth-order wavefunction and the molecular valence space

2.1 Hierarchy of natural orbitals

The first order density matrix of an electronic wavefunction is properly to be understood as the kernel of a corresponding integral operator. As such, *it is completely and most succinctly characterized by its mathematical invariants*. These invariants are its natural orbitals (NOs) and their occupation numbers [26–28].

Due to the physical nature of the molecular hamiltonian operator, the NOs of an accurate wavefunction typically fall into three categories: *Strongly occupied NOs* (*SONOs*), *moderately to weakly occupied NOs* (*MONOs*) *and very weakly occupied NOs* (*VONOs*).

The SONOs are small in number, typically only a few more than half the number of electrons at most, and they have occupations between 0.5 and 2. In many cases, the single (Hartree–Fock-like) determinant formed from the SONOs provides a serviceable zeroth-order model of the electronic structure.

At the other extreme, the VONOs are very large in number and have occupations of less than 0.1. They are needed when the *dynamical inter-electronic correlations* are represented by a configuration interaction expansion. While their aggregate effect is required for the quantitative recovery of chemical accuracy in the energy (1 mh), little chemical insight is usually associated with *individua*l VONOs beyond the fact that they provide certain correlation contributions. They are not needed when the dynamic correlations are recovered by different means.

The MONOs, finally, are a small group of orbitals, typically at most half the number of electrons, with occupations between 0.1 and 0.5. Together with the SONOs, they generate the limited multi-configurational wavefunctions that are necessary to furnish quantitatively adequate *zeroth-order approximations* whenever the single determinant of the SONOs is even qualitatively incapable of doing so.

The reason for this NO hierarchy is that the nature and occupation of orbitals in molecules are influenced by two independent factors. On the one hand, there is the tendency to lower the energy by forming bonds, i.e. by sharing occupied orbitals between different atoms. On the other hand, there is the tendency to lower the energy by occupying orbitals that will generate favorable correlation interactions. While the SONOs are essentially determined by bond formation, the VONOs are essentially determined by correlation recovery. The MONOs however can serve both purposes. Sometimes they are needed during bond formation, sometimes bond formation and certain correlation interactions enhance each other, sometimes they are simple correlating orbitals. The correlations they contribute are frequently called near-degenerate or non-dynamical.

The primary objective of the present study is to identify those features of molecular electronic wavefunctions that are essential for and hence elucidate the bonding interactions. Since practically all understanding and conceptual interpretations of interatomic valence activities derive from the SONOs and MONOs, the present analysis is not concerned with the VONOs.

Since the MONOs do play a role in rearrangements of bonding structures, the multi-configurational wavefunctions they generate are indispensable as zeroth-order approximations in many instances, such as calculations along reaction paths, and they provide a basis for elucidating energy changes such as, e.g., reaction energies, transition state barriers and energy spacings between states in transition metals. They are especially important when, along a reaction path, certain reactant SONOs gradually turn into product MONOs while certain reactant MONOs turn into product SONOs. Noteworthy instances are those reactions that form the objects of the frontier orbital approach of Fukui [29–32], Woodward and Hoffman [33–35], where the LUMOs represent models of certain MONOs that are deemed pertinent for the reaction at hand.

In regions on a reaction path where MONOs and SONOs switch occupation magnitudes, the distinction between these two orbital types becomes obviously fuzzy. It is also possible that, in some regions on a reaction path, the MONO occupations become so weak that they could be considered as VONOs. Moreover, there usually exist some configurations generated by the SONOs and MONOs that have very small weights in the actual wavefunction. Such inclusions of configurations providing some dynamic correlations in some regions of the potential energy surface are often unavoidable if, in order to treat chemical reactions, larger areas of that surface are to be covered consistently.

2.2 The molecular valence space

Calculations in the full configuration space generated by the SONOs and MONOs are size-consistent and rarely yield unreasonable energies. We therefore consider the orbital space spanned by these two orbital groups together as the *zeroth-order orbital space* for a given reaction, and the *full* configuration space generated by these orbitals as its *zeroth-order configuration space*. Wavefunctions in it are prototype zeroth-order approximations of the type referred to in the Introduction.

While, in principle, the zeroth-order orbital space of a molecule is identified from the natural orbital expansion of the exact wavefunction, a close approximation to it can frequently be determined from the NOs of a wavefunction obtained from a Hartree–Fock + singles + doubles CI calculation. From these occupation numbers, SONOs and MONOs can be identified and they can then be further refined by an MCSCF optimization. Alternative determinations will be discussed below.

An important finding is that, for a particular reaction, the zeroth-order space forms a subspace of the *full optimized reaction space (FORS)* of the system [2–6]. The latter is obtained by the MCSCF calculation in the *full* configuration space of all possible determinants generated by *all N valence electrons in M orbitals, where M is the total number of minimal basis valence orbitals* in the system, i.e. the sum of the numbers of MBS valence orbitals of all atoms in it (e.g. $M = 1+1+4+4 = 10$ in H_2CO). The cores are inactive, but optimized. This definition of the *full valence orbital space* as well as the *full valence configuration space* avoids any bias in the absence of prior information on the importance of various orbitals and configurations. It should also be noted that *the orbital space as well as the configuration space defined in this manner are basis-set independent entities* in the same way that the exact SCF MOs are. In zeroth-order, all possible valence activities of a molecule are thus described in the MCSCF optimized function space of M orbitals, where M is the total number of *minimal basis set orbitals*.

Sometimes, it is expedient to enlarge this orbital space slightly by choosing the number of orbitals, M, equal to the number of electrons. Such a space typically differs from the ones considered in the preceding paragraph by including also a correlation orbital for each lone pair.

For the sake of clarity, we shall formulate the following general analysis within the framework of this full valence space. A practical problem is, of course, that the dimensions of full configurational valence spaces increase rapidly with the size of the molecule. However, up to 90% of the determinants are configurational deadwood, when appropriate orbitals are chosen [36,37] and methods to identify and eliminate this deadwood exist [38,39].

The application of the present analysis to wavefunctions containing dynamic correlations in terms of configurations outside the full valence space manifestly proceeds by first identifying those natural orbitals that lie in the full valence space and the zeroth-order part of the density matrix determined by these orbitals. The latter can then be analyzed by the present method.

In Sect. 5, we shall furthermore show how the general analysis is readily adapted for use with wavefunctions that are expressed in terms of configurations that do *not* span the full valence space.

2.3 Local bases of molecular valence spaces

To understand a molecule in terms of atoms and bonds means to construct it conceptually from local components. The object of the present analysis is therefore to examine whether there exist *local MBS-type orbitals that are capable of exactly spanning the molecular valence orbital space and of exactly generating the molecular valence configuration space.*

An essential tool for such analyses is *the invariance of full valence spaces under non-singular orbital transformations*. This fundamental property is invoked, for instance, when the orbitals that are the immediate results of an MCSCF energy minimization are transformed into the natural orbitals of a given wavefunction, because the NOs represent a standard reference basis and typically yield a stronger MC convergence. It is because of the latter attribute that the occupation numbers of the NOs in an optimized full valence space furnish the basis for separating the SONO space from the MONO space discussed above.

Atoms and bonds manifestly represent two different, though related kinds of local concepts. Correspondingly, there exist two different kinds of localization analyses for density matrices of full valence spaces:

(a) A localization that accomplishes the identification of bond and lone pair orbitals, which we call *split localization procedure*;
(b) A localization that accomplishes the identification of quasi-atomic orbitals, which we call *full localization procedure*.

3 Intrinsic bonds and lone pairs as bases of full valence spaces

3.1 Split-localized valence orbitals

The split-localized orbitals, formulated by Bytautas et al. [7], are obtained by *separate localizations* of the NOs within the SONO space and of the NOs within the MONO space, while maintaining orbital orthonormalities.

In the SONO space, one obtains the *strongly occupied localized molecular orbitals (SOLMOs).* Since the SONO space is nearly always extremely close to the standard SCF space, the SOLMOs are extremely similar to the traditional localized MOs in the occupied Hartree–Fock space. They typically have bond or lone-pair character.

In the MONO space, one obtains the *moderately occupied localized MOs (MOLMOs).* Each of the MOLMOs is typically localized in the same 3D space as one of the SOLMOs. It is apparent that the MCSCF energy minimization determines the shape and location of each MOLMO so as to provide the dominant electronic correlation for the corresponding SOLMO. As an example [7], Fig. 1 exhibits the SOLMOs and MOLMOs that span the full valence space of NCCN. calculated with Dunning's cc-pVTZ basis.

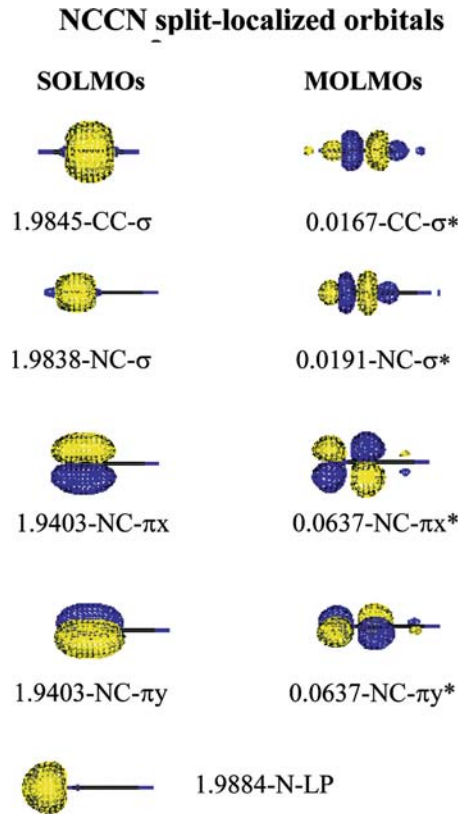

Fig. 1 Split-localized orbitals of the full valence space MCSCF wavefunction of NCCN. Only the orbitals in the *center* and on the *left side* of the molecule are displayed. The orbitals on the *right side* are mirror images of those on the *left*. CC and NC indicate bond regions, LP indicates lone pairs. For each orbital, the occupation number is listed

It is of some interest that, as shown in Ref. [7] and contrary to widely entrenched notions, determinantal expansions of full MCSCF functions in terms of split-localized orbitals typically converge somewhat *more* rapidly than the expansion in terms of natural orbitals. The analysis of such expansions moreover yields a systematic identification of configurational deadwood in full-valence-space MC expansions and an unbiased a-priori reduction of the size of these expansions [33–35]. The conceptual anticipation of such correlations is also the basis for the configuration choices of the valence-bond-type.

In the subsequent paper it will be shown that it can also be useful to form split-localized orbitals in one part of a molecule while forming atom-localized orbitals (see Sect. 4) in other parts.

3.2 Intrinsic localization

Split-localizations are accomplished using *intrinsic* localization procedures. "Intrinsic" means that they are based on maximizing localization measures that are functionals of the total *electronic* distribution only and contain *no* quantities relating to *anticipated* localization results that would bias the functional. (Non-intrinsic is, for instance, any basis-set-dependent procedure, such as the maximization of the MO expansion coefficients corresponding to a selected set of basis AOs, or the a priori incorporation of presumptions regarding the locations of two-center bonds, three-center bonds, etc., into the procedure.)

The two most widely used intrinsic localization methods are based on maximizing localization measures of the form

$$L = \sum_{\upsilon} \int \mathrm{d}V_1 \int \mathrm{d}V_2 [\phi_\upsilon(x_1)]^2 [\phi_\upsilon(x_2)]^2 w(r_{12}) \qquad (3.1)$$

while maintaining the orthogonality of the molecular orbitals $\phi_\nu(x_1)$. The algorithm for maximizing such fourth-order functionals of the orbitals with an arbitrary monotonic weight function $w(r_{12})$ was developed by Edmiston and Ruedenberg [1]. The two localization methods differ in the weight criterion $w(\mathrm{r}_{12})$, namely

$$w_1(r_{12}) = |\mathbf{x}_1 - \mathbf{x}_2|^{-1} \quad \text{and} \quad w_2(r_{12}) = -(\mathbf{x}_1 - \mathbf{x}_2)^2, \qquad (3.2)$$

respectively. The first had been postulated by Pople and Lennard-Jones [40], the second was proposed by Edmiston and Ruedenberg [1]. Subsequently, the algorithm for w_1 was made considerably more efficient by Raffenetti [41],[3] and that for w_2 was significantly simplified by Boys [42].[4,5] For reasons beyond the control of the present authors, the procedures using criterion w_1 and w_2 mostly go by the names of Edmiston–Ruedenberg method and Boys method, respectively. A new algorithm has recently been proposed by Subotnik et al. [45].

4 Intrinsic quasi-atoms as bases of full valence spaces

4.1 Quasi-atomic localized molecular orbitals (QUALMOs)

Here, we apply the intrinsic localization procedure discussed in Sect. 3.2 to *all* SONO's and MONOs *together*. As was first shown in Ref. [2–6], such *full valence space localizations* lead to molecular orbitals that have the character of deformed MBS atomic orbitals on the atoms in the molecule. Thus, *intrinsically embedded in ab-initio wavefunctions are basis-set-independent molecular orbitals with quasi- atomic character*. That character is exhibited by the overlap integrals between these Quasi-Atomic Localized Molecular Orbitals (QUALMOs) and the corresponding optimized MBS orbitals of the *free atoms*: In all cases examined so far, their values

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[3] This method was first developed by Raffenetti in 1967.

[4] A more explicit description was given by Kleier et al. [43].

[5] A different criterion and algorithm, which Foster and Boys had proposed earlier [44], was subsequently abandoned.

exceed 0.95. A variety of examples will be exhibited in the subsequent paper.

It should be noted that, by virtue of its basis-set-independence, this approach as well as those to be discussed in Sects. 4.2 and 5 are also applicable when the molecular orbitals are originally not obtained in LCAO form. The method has in fact been used to extract good quasi-atomic orbitals in crystals from DFT orbital sets that were calculated in plane-wave bases [10].

Since the QUALMOs are molecular orbitals, the zeroth-order molecular electronic wavefunction can be *exactly* expressed in terms of the determinants formed from them. The latter manifestly have the character of valence-bond type structures, as had been illustrated, e.g., in [5].

Since the QUALMOs differ so little from the *free-atom* MBS orbitals, it is remarkable that the determinants formed from the *latter* are known to provide poor configurational bases for molecular wavefunctions. The small deformations embodied in the quasi-atomic MBS orbitals are thus essential for obtaining reasonable energy differences. R.S. Mulliken's comment[6] on relevant energetic effects often caused by slight orbital changes was: "A little bit can go a long way".

It is possible that, under certain conditions, an intrinsic localization will not yield quasi-atomic orbitals. Such a result brings to light that the electronic structure of the system deviates significantly from the standard situation.

4.2 Localization by atomic adaptation

When the intrinsic localization yields orbitals that exhibit quasi-atomic character, then it would appear desirable from an interpretative point of view to have these QUALMOs deviate *as little as possible* from free-atom orbitals. This can be achieved by localization procedures that refine the QUALMOs by making them as similar as possible to free-atom MBS orbitals, i.e. by *atomic adaptation*.

Let f_n be some set of orthogonal MOs, such as, e.g., the SONOs + MONOs, that span the full molecular valence space, and let $|\mathrm{A}\alpha\rangle$ denote the QUALMOs that are to be found. Here, atoms are indexed by capital letters A, B, ... and orbitals on a given atom by lower case letters $\alpha, \beta, \ldots$ The QUALMOs are related to the original MOs f_n by a square non-singular transformation

$$|\mathrm{A}\alpha\rangle = \sum_n f_n T_{n,\mathrm{A}\alpha} \tag{4.1}$$

that is to be determined by the localization procedure. Since, at the present stage of development, we consider only wavefunctions with inactive (though optimized) closed cores, the transformation matrix $\mathbf{T}$ is taken to be block-diagonal: The inner-shell block localizes the inner-shell MOs f_n into the inner-shell quasi-AOs $|\mathrm{A}\alpha\rangle$, and the valence-shell block localizes the valence f_n into the valence $|\mathrm{A}\alpha\rangle$. Core space and valence space are mutually orthogonal. Here and in the following, the labels α, β should not be confused with spin function labels.

A method for determining the transformation $\mathbf{T}$ by atomic adaptation was given in [3]. Let $|\mathrm{A}\alpha^*\rangle$ denote an MBS orbital *on the free atom* A, obtained by an *atomic* SCF or MCSCF calculation. The corresponding QUALMO $|\mathrm{A}\alpha\rangle$ is then obtained by minimizing the mean square deviation

$$\langle \mathrm{A}\alpha - \mathrm{A}\alpha^* | \mathrm{A}\alpha - \mathrm{A}\alpha^* \rangle = 2[1 - \langle \mathrm{A}\alpha | \mathrm{A}\alpha^* \rangle] \tag{4.2}$$

under maintenance of normalization. This yields the QUALMOs as the renormalized projections

$$|\mathrm{A}\alpha\rangle = \sum_n f_n \langle f_n | \mathrm{A}\alpha^* \rangle \bigg/ \left[\sum_n \langle f_n | \mathrm{A}\alpha^* \rangle^2 \right]^{1/2} . \tag{4.3}$$

The overlap between the quasi-atomic and the free-atom MBS orbitals is seen to be

$$\langle \mathrm{A}\alpha | \mathrm{A}\alpha^* \rangle = \left[\sum_n \langle f_n | \mathrm{A}_j^* \rangle^2 \right]^{1/2} . \tag{4.4}$$

Since the $|\mathrm{A}\alpha\rangle$ obtained in this way are not orthogonal to each other, they can be transformed into an orthonormal set by a symmetric orthogonalization using the transformation $[\langle \mathrm{A}\alpha | \mathrm{B}\beta \rangle]^{-1/2}$, or possibly a population-weighted orthogonalization. Thereby the quasi-atomic character is somewhat reduced but not lost. The described procedure is applied separately in the full valence space and in the core space.

An alternative atomic adaptation would be an *energetic* adaptation, which we explain using the CO molecule as an example. The original MOs f_n on the right-hand side of Eq. (4.1) comprise two of the inner-shell type and eight of the valence type, whereas the QUALMOs $|\mathrm{A}\alpha\rangle$ on the left-hand side of that equation are expected to comprise one inner-shell orbital and four valence orbitals on carbon, and an equal complement on oxygen. Let us denote them as $|\mathrm{C}\alpha\rangle$ and $|\mathrm{O}\beta\rangle$ respectively and take one atom at a time. From the QUALMOs $|\mathrm{C}\alpha\rangle$ to be found for carbon, we formally construct the *full* space of all *six-electron* determinants (each with a doubly occupied closed shell) and, from them, the matrix elements for the Hamiltonian operator of the free carbon atom. Since, according to Eq. (4.1), the five orbitals $|\mathrm{C}\alpha\rangle$ are linear combinations of the ten known original MOs f_n with as yet to be determined coefficients $T_{n,\mathrm{C}\alpha}$, an MCSCF calculation will yield these expansion coefficients $T_{n,\mathrm{C}\alpha}$ of the carbon QUALMOs as well as the MC mixing coefficients that express the quasi-atomic states of the chemically deformed carbon atom in terms of the determinants formed from the f_n. An analogous eight-electron MCSCF procedure is then performed with respect to the oxygen atom and it yields the

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[6] A frequent verbal remark of R.S. Mulliken.

coefficients $T_{n,\mathrm{O}\beta}$ of the five oxygen QUALMOs $|\mathrm{O}\beta\rangle$ in terms of the MOs f_n.

The orbitals obtained in this way are the energetically closest approximations to the free-atom orbital possible within the constraints of the molecular orbital space. They will be similar to those of Eq. (4.3) in as much as the free-atom orbitals $|\mathrm{A}\alpha^*\rangle$, which are projected in Eq. (4.3), are in fact obtained by energy minimization in the free atoms. The resulting six- and eight-electron wavefunctions represent the quasi-atoms that are embedded in the fourteen-electron molecular wavefunction of CO.

The resulting five orthogonal carbon-type QUALMOs $|\mathrm{C}\alpha\rangle$ together with the five orthogonal oxygen-type QUALMOs $|\mathrm{O}\beta\rangle$ span the same space as the ten original MOs f_n. As was the case for the orbitals of Eq. (4.3), the $|\mathrm{C}\alpha\rangle$ are not orthogonal to the $|\mathrm{O}\beta\rangle$ however, except that all valence orbitals are orthogonal to all core orbitals. As before, we can obtain an orthogonal QUALMO basis by two symmetric orthogonalizations, one between the core orbitals and the other between the valence orbitals of the sets $|\mathrm{C}\alpha\rangle$ and $|\mathrm{O}\beta\rangle$.

It is possible to formulate an analysis in terms of orthogonal as well as of non-orthogonal quasi-atomic orbitals and arguments pro and con can be advanced regarding the desirability of orthogonalizing QUALMOs associated with different atoms. Global orthogonalization has the considerable advantage that it yields a flawless definition and identification of orbital occupations and simpler energy expressions. The omission of interatomic orthogonalizations, on the other hand exhibits more dramatically the closeness of the QUALMOS to the free-atom MBS orbitals. Even in that case, *the quasi-atomic orbitals on the same atom should always be orthogonalized.*

5 Full valence space precursors from incomplete valence spaces

Many useful zeroth-order wavefunctions are not determined in full valence spaces. There are two possibilities. One case is that of a wavefunction that actually uses *a full MO basis in the valence orbital space*, but contains only a small subset of all valence *configurations*. In that case, the procedures described in the preceding sections can be applied without change. A complication will arise only if one should proceed to re-express the N-electron wavefunction in terms of the determinants generated from the localized orbitals, because one would then, in general, be forced to generate the full space. But that is not necessary for the purpose of the present analysis.

The second case is that of a wavefunction that does *not even contain a full complement of orbitals required to span the full orbital valence space*. Let us consider the most common example of such a zeroth-order wavefunction, namely the SCF approximation, which essentially contains only the SONOs but no MONOs. As is well known, localization of the SCF MOs yields bonds and lone pairs and these turn out to be very close to the SOLMOs of the full valence space discussed in Sect. 3.

To make headway in such a system, we consider [8] the problem of finding quasi-atomic orbitals with the following attributes:

(a) Their number is equal to the total number M of minimal basis orbitals of the atoms in the molecule. *Note that $M > M_o$ = the number of occupied SCF-MOs.*
(b) The $\mathrm{M_o}$ occupied Hartree–Fock orbitals can be expressed *exactly* in terms of these quasi-atomic orbitals.
(c) The quasi-atomic orbitals differ from the optimal minimal-basis orbitals of the free atoms as little as possible.

In contrast to the situation in Sect. 4, these quasi-atomic orbitals are *not* molecular orbitals of the SCF problem. We have therefore called them *quasi-atomic minimal basis orbitals* (QUAMBOs).

According to (b), the space spanned by the M QUAMBOs must contain the M_o occupied SCF MOs. It therefore must be that the QUAMBO space can be spanned by the M_o occupied SCF MOs *and* $(M - M_o)$ *orbitals in the virtual Hartree–Fock space*. According to (c), these $(M - M_o)$ virtual SCF orbitals must be those $(M - M_o)$ linear combination of *all* virtual SCF MOs that minimize the deviations of the QUAMBOs from the free-atom MBS orbitals. We have recently given a solution of this optimization problem by a simple, basis-set-independent algorithm [8,9]. The details of the mathematical formalism are elaborated in Ref. [8,9].

The QUAMBOs, that are intrinsic to the occupied Hartree–Fock MOs can thus be determined and they turn out to be close precursors of the QUALMOs of the corresponding full valence space MCSCF problem. As an example, Fig. 2 displays the QUAMBOs resulting [9] from a SCF calculation of $\mathrm{Si_4H_6}$ using Dunning's cc-pVTZ basis.

Since the QUAMBO space is the precursor of the corresponding QUALMO space, it is furthermore apparent that the projection of the QUAMBO space on the *virtual* SCF space yields a close precursor of the $(M - M_o)$ dimensional MONO space of the full valence MCSCF problem. Accordingly, split-localized orbitals can also be constructed in the QUAMBO space [8,9]. Finally, one can also determine the eigenvalue of the Fock operator in the virtual projection of the QUAMBO space and they represent basis-set-independent formulations of LUMOs.

The described method can be applied without any change to wavefunctions obtained by the DFT method. In fact, it has even been successfully applied to DFT calculations of crystals in terms of plane-wave bases [10].

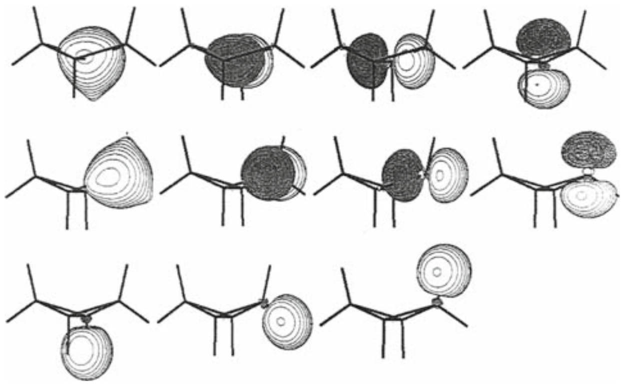

Fig. 2 The QUAMBOs deduced from the SCF wavefunction of S_4H_6. Only the eleven non-equivalent orbitals are shown. The other 11 are given by symmetry

This method, which has been described for an SCF wavefunction, can also be applied to any mutliconfigurational wavefunction that is generated from an orbital set that includes some but not all MONOs in the full valence space. No changes are required in the procedure. This capability is useful when a reaction region is treated more accurately than the spectator-remainder of a system. The method will then yield precursors to the remaining MONOs in the full valence space.

6 Populations and bond orders

Suppose that the optimized full valence space wave function is expressed in terms of some set of molecular orbitals f_n. The electronic energy can then be expressed in terms of the orbital integrals as follows:

$$E=\sum_{m,n}\langle f_m|\hbar|f_n\rangle \mathrm{p}_{nm}+\sum_{jk}\sum_{mn}[f_j f_k|f_m f_n]\mathrm{P}_{ij.nm}, \qquad (6.1)$$

where **p** and **P** are the representations of the spin-less first and second order density matrices in this orbital basis. The operator $\hbar$ is the one-electron part of the Hamiltonian and the $[f_j f_k|f_m f_n]$ are the two-electron integrals. Now, it is well known that the energy *lowering that leads to chemical binding is typically dominated by the interatomic contributions to the one-electron energy involving the valence orbitals in Eq.* (6.1). Meaningful inferences regarding binding interactions can therefore be drawn from the first-order density matrix.

Particularly useful in this context are the representations of this matrix in terms of the split-localized orbitals and of the quasi-atomic orbitals. Further elucidating insights can moreover be gained by combining these two types of density resolutions, as will be seen in the subsequent paper. It can also be instructive to use an orbital basis that is quasi-atomic in some parts of the molecule and split-localized in other parts.

Let the representation of the first order density matrix in terms of quasi-atomic orbitals (QUALMOs or QUAMBOs) be given by

$$\rho(1,2)=\sum_{\mathrm{A}\alpha}\sum_{\mathrm{B}\beta}|\mathrm{A}\alpha\rangle\pi_{\mathrm{A}\alpha,\mathrm{B}\beta}\langle\mathrm{B}\beta|. \qquad (6.2)$$

Since we have assumed inactive closed cores, we have

$$\pi_{\mathrm{A}\alpha,\mathrm{A}\alpha}=2, \quad \pi_{\mathrm{A}\alpha,\mathrm{B}\beta}=0 \quad \text{for} \quad \mathrm{A}\alpha\neq\mathrm{B}\beta, \\ \text{if } \mathrm{A}\alpha=\text{a core orbital.} \qquad (6.3)$$

When the quasiatomic orbitals are chosen to be *orthonormal*, then the diagonal elements $\pi_{\mathrm{A}\alpha,\mathrm{A}\alpha}$ represent the electron *populations* of these orbitals.

When the quasiatomic orbitals are chosen to be non-orthogonal, then Mulliken's "gross population" definition [46][7]

$$\mathrm{q}(\mathrm{A}\alpha)=\sum_{\mathrm{B}\beta}\langle\mathrm{A}\alpha|\mathrm{B}\beta\rangle\pi_{\mathrm{A}\alpha,\mathrm{B}\beta} \qquad (6.4)$$

can be expected to furnish adequate information, since these definitions tend to work rather satisfactorily in the context of minimal basis sets. Within the framework of the present approach, the contributions from the extended-basis AOs are absorbed in the "deformations" of the quasi-atomic minima basis set. Therefore, Mulliken's population analysis [47] can be used here without suffering from the erratic inconsistencies that it typically encounters in its conventional indiscriminate applications to extended AO bases.

In view of the mentioned importance of the one-electron energy for chemical binding, it is justified to use the traditional name *bond orders* (see, e.g., [48]) for the off-diagonal elements of the first-order density matrix between quasi-atomic orbitals. It should be noted that their quantitative values for orthogonal orbitals are distinctly different from those for non-orthogonal orbitals.

The expansion of the split-localized orbitals $|\lambda_\nu\rangle$ in terms of the quasiatomic orbitals $|\mathrm{A}\alpha\rangle$, *viz.*

$$|\lambda_\nu\rangle=\sum_{\mathrm{A}\alpha}|\mathrm{A}\alpha\rangle\mathrm{L}_{\mathrm{A}\alpha,\nu} \qquad (6.5)$$

provides immediate quantitative information on the spatial nature of the bond and lone pair orbitals as well as their principal correlating orbitals. If the density matrix is expressed in terms of split-localized contributions, i.e.,

$$\rho(1,2)=\sum_{\nu,\mu}|\lambda_\nu\rangle\Lambda_{\nu\mu}\langle\lambda_\nu| \qquad (6.6)$$

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[7] A review is given in Section II.E of [47].

then the matrix $\Lambda_{\nu\mu}$ is related to the matrix $\pi_{\mathrm{A}\alpha,\mathrm{B}\beta}$ of Eq. (6.2) by

$$\pi_{\mathrm{A}\alpha,\mathrm{B}\beta} = \sum_{\nu,\mu} \mathrm{L}_{\mathrm{A}\alpha,\nu}\Lambda_{\nu\mu}\mathrm{L}_{B\beta,\mu}. \tag{6.7}$$

In Ref. [9], the application of such relations led to the identification of the quantum mechanical cause of ring strain in $\mathrm{Si_4H_6}$.

7 Orientation (“hybridization”) of quasi-atomic orbitals

7.1 Intra-atomic orientation of quasi-atomic MOs

There still remains a certain freedom in the quasi-atomic valence MOs in as much as *the localization onto atoms is preserved when the orbitals associated with any one atom are mixed among each other* by arbitrary non-singular transformations. Let us assume that

(i) the optimized free-atom atom orbitals $|\mathrm{A}\alpha^*\rangle$ that are used to generate the quasi-atomic orbitals by the projections in Eq.(4.3) are proportional to spherical harmonics, i.e., of the type s,p,d … etc,

(ii) the deduced quasi-atomic orbitals $|\mathrm{A}\alpha\rangle$ are *orthogonalized on each atom.*

We shall call these the *canonical quasi- atomic orbitals*. The mixing of the canonical quasi-atomic valence orbitals corresponds then to what traditionally is referred to as “hybridization”. We shall refer to this mixing as *orienting the quasi-atomic orbitals in certain directions*. The justification for this term will be apparent in the subsequent paper.

The method that will be derived to this end in this section is independent upon whether or not the quasi-atomic orbitals from *different* atoms are orthogonal to each other. Furthermore, the method is equally applicable to QUALMOs as well as QUAMBOs.

Let us denote the resulting oriented quasiatomic valence orbitals by $|\mathrm{Aa}\rangle$. They are obtained from the canonical quasi-atomic orbitals $|\mathrm{A}\alpha\rangle$ by an *orthogonal* transformation **D**:

$$|\mathrm{Aa}\rangle = \sum_{\alpha} |\mathrm{A}\alpha\rangle\, D_{\mathrm{A},\alpha\mathrm{a}} \tag{7.1}$$

that is block diagonal with respect to the atoms:

$$\mathbf{D} = \begin{bmatrix} \mathbf{D}_\mathrm{A} & \mathbf{0} & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{D}_\mathrm{B} & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{0} & \mathbf{D}_\mathrm{C} & \cdots \\ \cdot & \cdot & \cdot & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{bmatrix}, \tag{7.2}$$

where every non-zero block is an intra-atomic orthogonal matrix.

The relation between the density matrix elements $\pi_{\mathrm{A}\alpha,\mathrm{B}\beta}$ associated with the original canonical orbitals $|\mathrm{A}\alpha\rangle$ and the corresponding elements $\mathrm{p_{Aa,Bb}}$ associated with the oriented hybrid orbitals $|\mathrm{Aa}\rangle$ is determined by the identity

$$\sum_{\mathrm{A}\alpha}\sum_{\mathrm{B}\beta} |\mathrm{A}\alpha\rangle\, \pi_{\mathrm{A}\alpha,\mathrm{B}\beta}\, \langle \mathrm{B}\beta| = \sum_{\mathrm{Aa}}\sum_{\mathrm{Bb}} |\mathrm{Aa}\rangle\, p_{\mathrm{Aa,Bb}}\, \langle \mathrm{Bb}|. \tag{7.3}$$

In the present context, it is useful to partition the two matrix representations in terms of intra-atomic and inter-atomic blocks, viz.

$$\pi = \begin{bmatrix} \pi_\mathrm{AA} & \pi_\mathrm{AB} & \pi_\mathrm{AC} & \cdots \\ \pi_\mathrm{BA} & \pi_\mathrm{BB} & \pi_\mathrm{BC} & \cdots \\ \pi_\mathrm{CA} & \pi_\mathrm{CB} & \pi_\mathrm{CC} & \cdots \\ \cdot & \cdot & \cdot & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{bmatrix}, \quad \mathbf{p} = \begin{bmatrix} \mathbf{p}_\mathrm{AA} & \mathbf{p}_\mathrm{AB} & \mathbf{p}_\mathrm{AC} & \cdots \\ \mathbf{p}_\mathrm{BA} & \mathbf{p}_\mathrm{BB} & \mathbf{p}_\mathrm{BC} & \cdots \\ \mathbf{p}_\mathrm{CA} & \mathbf{p}_\mathrm{CB} & \mathbf{p}_\mathrm{CC} & \cdots \\ \cdot & \cdot & \cdot & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{bmatrix}. \tag{7.4}$$

The transformation between the two matrix representations is then given by

$$p_{\mathrm{AaBb}} = \sum_{\alpha}\sum_{\beta} D_{\mathrm{A},\alpha\mathrm{a}}\pi_{\mathrm{A}\alpha,\mathrm{B}\beta}D_{\mathrm{B},\beta\mathrm{b}} \tag{7.5}$$

i.e., every block transforms internally according to

$$\mathbf{p}_\mathrm{AB} = (\mathbf{D}_\mathrm{A})^{\dagger}\pi_\mathrm{AB}\mathbf{D}_\mathrm{B} \tag{7.6}$$

7.2 Orientation criterion

We now wish to determine the transformation **D** so as to adjust the quasi-atomic MOs in such a way that chemical interactions between atoms are exhibited in the most lucid manner. In view of what has been said in Sect. 6, this amounts to simplifying the one-electron part of the energy expression (6.1) as much as possible. We shall therefore determine the oriented orbitals by postulating that *the off-diagonal bond order matrix blocks between oriented quasi-atomic valence orbitals have as few quantitatively significant elements as possible*, implying that each of the oriented orbitals interacts with the smallest number of analogous orbitals on other atoms. Since these operations all take place within the valence space, we shall make no further reference to the cores.

In many instances, nonbonding orbitals, single bonds and multiple bonds can of course be anticipated on the basis of chemical intuition and these qualitative expectations could be incorporated as zeroth order approximations. The approach to be described shuns such *extrinsic* initial bias in any part of the formalism. Rather, all atoms and bonds are treated on an equal footing at each stage so that the directional bonding information that is *intrinsic* to the wavefunction will be brought to light by an unbiased mathematical formalism. The method should therefore also be applicable where intuition is no sure guide, e.g. at transition states.

The postulated conceptual criterion implies that the bond orders between the oriented orbitals should, ideally, fall into two groups: Many that are very small in absolute value and some that are large in absolute value. It must also be kept in mind that, for $i \neq j$, the elements p_{ij} can be positive or negative. For a quantitative mathematical formulation that would implement this goal, the *squares of the bond orders* furnish therefore an expedient vehicle since they apply equally to positive and negative bond orders. Moreover, one readily deduces from the transformation equation (7.6) that, *for any block* ***AB***, the conservation relation

$$\mathrm{Trace}\{(\mathbf{p}_{\mathrm{AB}})(\mathbf{p}_{\mathrm{AB}})^{\dagger}\} = \mathrm{Trace}\{(\pi_{\mathrm{AB}})(\pi_{\mathrm{AB}})^{\dagger}\} \tag{7.7a}$$

$$\sum_{\mathrm{Aa}}\sum_{\mathrm{Bb}} (p_{\mathrm{A}\alpha,\mathrm{B}\beta})^2 = \sum_{\mathrm{A}\alpha}\sum_{\mathrm{B}\beta} (\pi_{\mathrm{A}\alpha,\mathrm{B}\beta})^2, \tag{7.7b}$$

holds so that, *if a transformation* ***D*** *makes some bond orders in a block large in absolute value, then the others must necessarily become small in absolute value*.

The object of the algorithm to be described is therefore to determine the transformations $\mathbf{D}_{\mathrm{A}}$, $\mathbf{D}_{\mathrm{B}}$, $\mathbf{D}_{\mathrm{C}}, \ldots$ in such a way that the squares of as *few* bond orders as possible will be as *large* as possible, and that the squares of as *many* bond orders as possible will be as *small* as possible. In view of Eq. (7.7), such a "disproportionation" within all inter-atomic bond order blocks can be achieved by maximizing the sum of the *fourth* powers of *all* inter-atomic density matrix elements, i.e. by maximizing the *hybridization-orientation sum*

$$\begin{aligned} \mathrm{HOS} &= \sum_{\mathrm{A<B}}\sum_{\mathrm{a,b}} (p_{\mathrm{Aa,Bb}})^4 \\ &= \sum_{\mathrm{A<B}}\sum_{\mathrm{a,b}} \left(\sum_{\alpha,\beta} \pi_{\mathrm{A}\alpha,\mathrm{B}\beta} \mathrm{D}_{\mathrm{A},\alpha\mathrm{a}} \mathrm{D}_{\mathrm{B},\beta\mathrm{b}} \right)^4, \end{aligned} \tag{7.8}$$

with respect to the elements of $\mathbf{D}$.

In order to accomplish this maximization, we proceed in two steps: First, we determine quasi-atomic hybrid orbitals with optimal chemical adaptation *for each atom separately*. Then, the bond orders between *all* atoms will be considered *collectively*.

7.3 Optimal orbital orientation for individual atoms

In order to assess the interactions of a particular atom A with the rest of the molecule, we consider the bond orders of its orbitals with *all* other atoms in the initial quasi-atomic basis. They form the rectangular matrix

$$\boldsymbol{\pi}_{\mathrm{A}\neq} = [\boldsymbol{\pi}_{\mathrm{AB}} \quad \boldsymbol{\pi}_{\mathrm{AC}} \quad \cdot \quad \cdot]. \tag{7.9}$$

We now perform a s*ingular value decomposition (SVD)* of this matrix, i.e., we find the two orthogonal square matrices $\mathbf{U}_{\mathrm{A}}$ and $\mathbf{V}_{\mathrm{A}}$ that diagonalize $\boldsymbol{\pi}_{\mathrm{A}\neq}$ as follows:

$$(\mathbf{U}_{\mathrm{A}})^{\dagger}\pi_{\mathrm{A}\neq}(\mathbf{V}_{\mathrm{A}}) = \begin{bmatrix} \tilde{\pi}_1 & 0 & 0 & .. & 0 & 0 & 0 \ldots 0 \\ 0 & \tilde{\pi}_2 & 0 & .. & 0 & 0 & 0 \ldots 0 \\ 0 & 0 & \tilde{\pi}_3 & .. & 0 & 0 & 0 \ldots 0 \\ . & . & . & .. & . & . & ..... \\ . & . & . & .. & . & . & ..... \\ . & . & . & .. & . & . & ..... \\ 0 & 0 & 0 & .. & 0 & \tilde{\pi}_{\mathrm{NA}} & 0 \ldots 0 \end{bmatrix}, \tag{7.10}$$

where NA denotes the number of quasi-atomic orbitals on atom A. Such a decomposition is always possible and standard programs exist [49].

The transformation $\mathbf{U}_{\mathrm{A}}$ manifestly generates a new set of NA orbitals on atom A,

$$|\mathrm{A}\tilde{\alpha}\rangle = \sum_{\alpha} |\mathrm{A}\alpha\rangle\, U_{\mathrm{A}}(\alpha, \tilde{\alpha}), \quad \alpha, \tilde{\alpha} = 1, 2, 3, \ldots (\mathrm{NA}), \tag{7.11}$$

whereas the transformation $\mathbf{V}_{\mathrm{A}}$ generates $(N - \mathrm{NA})$ *molecular orbitals* ϕ_{j} that are linear combinations of the orbitals on *all other atoms* (N = total number of orbitals). These orbitals are manifestly constructed in such a way that one-electron interactions occur *only* between the $|\mathrm{A}\tilde{\alpha}\rangle$ and the ϕ_{α} for $\alpha = 1, 2, \ldots \mathrm{NA}$, and that the MOs ϕ_{j} with $j = (\mathrm{NA} + 1)$ to N do not interact at all with atom A. These transformations can therefore be viewed as furnishing an optimal orbital adaptation of atom A to its entire molecular environment and an optimal orbital adaptation of the rest of the molecule with respect to interactions with atom A.

Having performed the SVD separately for each atom in the molecule, we disregard the molecular orbitals ϕ generated by the $\mathbf{V}$ matrices and keep only the atomic orbitals generated by the $\mathbf{U}$ matrices. Thus, we obtain an intermediate set of quasi-atomic orbitals $|\mathrm{A}\tilde{\alpha}\rangle$, $|\mathrm{B}\tilde{\beta}\rangle, \ldots$ by applying the block diagonal orthogonal transformation

$$\mathbf{U} = \begin{bmatrix} \mathbf{U}_{\mathrm{A}} & \mathbf{0} & \mathbf{0} & \ldots \\ \mathbf{0} & \mathbf{U}_{\mathrm{B}} & \mathbf{0} & \ldots \\ \mathbf{0} & \mathbf{0} & \mathbf{U}_{\mathrm{C}} & \ldots \\ . & . & . & \ldots \\ . & . & . & \ldots \end{bmatrix} \tag{7.12}$$

to the initial quasi-atomic orbital set $|\mathrm{A}\alpha\rangle$, $|\mathrm{B}\beta\rangle \ldots$ We then obtain the density matrix $\tilde{\mathbf{p}}$ in this intermediate basis by the transformations

$$\tilde{\mathbf{p}}_{\mathrm{AB}} = (\mathbf{U}_{\mathrm{A}})^{\dagger}\boldsymbol{\pi}_{\mathrm{AB}}\mathbf{U}_{\mathrm{B}}. \tag{7.13}$$

While the matrix $\tilde{\mathbf{p}}$ will not have as many zeros as the diagonal matrices of the various singular value decompositions, it will still exhibit a pronounced "disproportionation" of the bond orders into large and small ones. The $|\mathrm{A}\tilde{\alpha}\rangle$ orbitals represent therefore a reasonable starting point towards the orbitals satisfying the postulated criterion.

7.4 Collective orbital orientation

The preliminary orbitals $|\mathrm{A}\tilde{\alpha}\rangle$ found in the preceding section are now chosen as the initial guess for the maximization of the hybridization-orientation sum formulated in Eq. (7.8). The resulting oriented quasi-atomic hybrid orbitals $|\mathrm{Aa}\rangle$ will thus be expressed as

$$|Aa\rangle = \sum_{\tilde{\alpha}} |\mathrm{A}\tilde{\alpha}\rangle\, \mathrm{R}_{\mathrm{A},\tilde{\alpha}a} \tag{7.14}$$

so that the transformations $\mathbf{D_A}$ of Eqs. (7.1) and (7.6) are obtained as the products

$$\mathbf{D_A} = \mathbf{U_A R_A}. \tag{7.14a}$$

In accordance with Eq. (7.8), the matrix $\mathbf{R}$ is to be determined by maximizing

$$\mathrm{HOS} = \sum_{\mathrm{A<B}} \sum_{\mathrm{a,b}} \left(\sum_{\tilde{\alpha}} \sum_{\tilde{\beta}} \tilde{p}_{\mathrm{A}\tilde{\alpha},\mathrm{B}\tilde{\beta}} R_{\mathrm{A},\tilde{\alpha}\mathrm{a}} R_{\mathrm{B},\tilde{\beta}b} \right)^4 . \tag{7.15}$$

This maximization will be accomplished by building up the orthogonal matrix $\mathbf{R}$ through an iterative sequence of smaller transformations. Namely we maximize only with respect to the orbitals of one atom at a time and repeatedly cycle through all atoms. Furthermore, the optimization of the orbitals on a given atom is achieved by a sequence of 2×2 Jacobi rotations between all orbital pairs on that atom. Thus, the total transformation $\mathbf{R}$ is built up from an iterative sequence of intra-atomic orthogonal 2×2 transformations.

Let us consider the maximization of HOS with respect to *one* such Jacobi rotation, say on atom A. Let the initial orbitals be denoted by $|\mathrm{A}j_1\rangle$, $|\mathrm{A}j_2\rangle$ and the improved orbitals by $|\mathrm{A}v_1\rangle$, $|\mathrm{A}v_2\rangle$, where $\mathrm{j}_1 < \mathrm{j}_2$ and $\mathrm{v}_1 < \mathrm{v}_2$. Then the Jacobi rotation is given by

$$\begin{aligned} |\mathrm{A}v_1\rangle &= |\mathrm{A}j_1\rangle J_{11} + |\mathrm{A}j_2\rangle J_{21} \\ |\mathrm{A}v_2\rangle &= |\mathrm{A}j_1\rangle J_{12} + |\mathrm{A}j_2\rangle J_{22} \end{aligned} \tag{7.16}$$

where

$$\begin{aligned} &J_{11} = \cos\gamma,\ \ J_{12} = -\sin\gamma, \\ &J_{21} = \sin\gamma,\ J_{22} = \cos\gamma, \end{aligned} \tag{7.17}$$

with all other orbitals remaining the same. Furthermore, let $\mathbf{p}'$ and $\mathbf{p}''$ denote the corresponding initial and final density matrices respectively. The inter-atomic blocks of these two matrices manifestly *differ* only if one atom is A and if, moreover, the matrix-element orbital-index referring to A is $\mathrm{A}j_1$ or $\mathrm{A}j_2$ for $\mathbf{p}'$, and $\mathrm{A}v_1$ or $\mathrm{A}v_2$ for $\mathbf{p}''$. To keep the notation simple, we shall denote these density matrix elements as $p'_{\mathrm{A1,Bb}}$, $p'_{\mathrm{A2,Bb}}$ and as $p''_{\mathrm{A1,Bb}}$, $p''_{\mathrm{A2,Bb}}$ respectively. The part of the hybridization–orientation sum that actually changes due to this Jacobi rotation can then be written as

$$\begin{aligned} \mathrm{HOS}^* &= \sum_v \sum_{\mathrm{Bb}}^{*} [p''_{\mathrm{A}v,\mathrm{Bb}}]^4 \\ &= \sum_v \sum_{\mathrm{Bb}}^{*} \left(\sum_j p'_{\mathrm{A}j,\mathrm{Bb}} J_{jv} \right)^4 , \end{aligned} \tag{7.18}$$

where $\sum_v$ runs over $v = 1, 2$ and $\sum_j$ runs over $j = 1, 2$. Furthermore, $\sum_{Bb}{}^*$ excludes the terms with $\mathrm{B = A}$. Eq. (7.18) can be rewritten as

$$\mathrm{HOS}^* = \sum_{i,j,k,l} P_{ijkl} J_{ijkl} \tag{7.19}$$

with

$$P_{ijkl} = \sum_{\mathrm{Bb}}{}^{*} (p'_{\mathrm{A}i,\mathrm{Bb}} p'_{\mathrm{A}j,\mathrm{Bb}} p'_{\mathrm{A}k,\mathrm{Bb}} p'_{\mathrm{A}l,\mathrm{Bb}}) \tag{7.20}$$

$$J_{ijkl} = \sum_v J_{iv} J_{jv} J_{kv} J_{lv} \tag{7.21}$$

where the indices i, j, k, l and v all run over 1,2. The 16 terms on the right-hand side of Eq. (7.19) can be reduced to essentially one term as follows.

Since the quantities P_{ijkl} as well as the quantities J_{ijkl} are manifestly invariant under all index permutations, Eq. (7.19) can be simplified to

$$\begin{aligned} \mathrm{HOS}^* = {} & P_{1111} J_{1111} + P_{2222} J_{2222} + 6 P_{1122} J_{1122} \\ & + 4 P_{1112} J_{1112} + 4 P_{2221} J_{2221}. \end{aligned} \tag{7.22}$$

According to Eq. (7.20) the P_{ijkl} in this equation are explicitly given by

$$P_{1111} = \sum_{\mathrm{Bb}}{}^{*} (p'_{\mathrm{A1,Bb}})^4 \tag{7.23a}$$

$$P_{2222} = \sum_{\mathrm{Bb}}{}^{*} (p'_{\mathrm{A2,Bb}})^4 \tag{7.23b}$$

$$P_{1122} = \sum_{\mathrm{Bb}}{}^{*} (p'_{\mathrm{A1,Bb}} p'_{\mathrm{A2,Bb}})^2 \tag{7.23c}$$

$$P_{1112} = \sum_{\mathrm{Bb}}{}^{*} (p'_{\mathrm{A1,Bb}})^3 p'_{\mathrm{A2,Bb}} \tag{7.23d}$$

$$P_{2221} = \sum_{\mathrm{Bb}}{}^{*} (p'_{\mathrm{A2,Bb}})^3 p'_{\mathrm{A1,Bb}}. \tag{7.23e}$$

For the J_{ijkl} on the other hand, insertion of the formulas of Eq. (7.17) into the definition (7.21) yields the explicit expressions

$$J_{1111} = J_{2222} = 1 - \tfrac{1}{2}(\sin 2\gamma)^2 = \tfrac{1}{4}(3 + \cos 4\gamma), \tag{7.24a}$$

$$J_{1122} = \tfrac{1}{2}(\sin 2\gamma)^2 = \tfrac{1}{4}(1 - \cos 4\gamma), \tag{7.24b}$$

$$J_{1112} = -J_{2221} = \tfrac{1}{2}\sin 2\gamma \cos 2\gamma = \tfrac{1}{4}(\sin 4\gamma). \tag{7.24c}$$

Insertion of these equations into the right-hand side of Eq. (7.22) shows that the hybridization–orientation sum of

Eq. (7.19) can be written in the form

$$\mathrm{HOS}^* = P + P_c \cos 4\gamma + P_s \sin 4\gamma, \tag{7.25}$$

where

$$P = \tfrac{3}{4}[P_{1111} + P_{2222} + 2P_{1122}], \tag{7.26a}$$

$$P_c = \tfrac{1}{4}[P_{1111} + P_{2222} - 6P_{1122}], \tag{7.26b}$$

$$P_s = P_{1112} - P_{2221}. \tag{7.26c}$$

Eq. (7.25) can then be expressed as

$$\mathrm{HOS}^* = P + Q\cos(4\gamma - \theta), \tag{7.27}$$

where

$$Q = +[P_c^2 + P_s^2]^{\frac{1}{2}} \tag{7.28}$$

and the angle θ is determined by

$$\cos\theta = P_c/Q, \quad \sin\theta = P_s/Q, \quad -\pi < \theta \le \pi. \tag{7.29}$$

It is apparent from Eq. (7.27) that the single-Jacobi-rotation hybridization–orientation function HOS* assumes the identical maximum value $(P + Q)$ for all angles $\gamma = \theta/4 + n\pi/2$, where n is any positive or negative integer. Even though four of these angles lie in the acceptable range $-\pi < \gamma \le \pi$, one can nonetheless limit the choice of γ without loss of generality to the one value

$$\gamma_0 = \theta/4, \quad \text{with} \quad -\pi/4 < \gamma_0 \le \pi/4, \tag{7.30}$$

since it is readily seen that the orbitals resulting from using the other angles differ from those obtained with γ_0 only by possible multiplications with (−1) or by a possible interchange of the two orbitals.

There exist several possibilities of skipping ineffectual Jacobi rotations. First, one can *predict* from Eqs. (7.25) and (7.27) that the increase of HOS through a particular Jacobi rotation is exactly $(Q - P_c)$. If this value is too small, then θ does not have to be calculated and the density matrix does not have to be transformed. Secondly, the invariance of the sum-of-bond-order-squares for each inter-atomic block, as expressed by Eq. (7.7), implies that the total interaction between two atoms, as measured by this criterion, is independent of the orbital orientations. If this sum is smaller than a given threshold, as may be the case for atoms at sufficiently large distances from each other, then these blocks have little relevance for the orientation algorithm. In large systems, one can therefore check all interatomic blocks first and include only those for which the sum-of-bond-order-squares exceeds a certain minimum value. An interatomic block should not be excluded, of course, when studying a reaction path along which noninteracting atoms become interacting.

In case that more than one non-bonding orbital is found on an atom, one can diagonalize the density matrix block between them to generate nonbonding orbitals with largest and smallest occupation numbers such as lone pairs. This may be of interest in some contexts. It may however also be useful to allow for more flexibility in order to account for orbital modifications along reaction paths when the orbital character changes from nonbonding to chemically interacting.

8 Magnitudes of bond orders

8.1 Bond orders between two orthogonal orbitals

A meaningful quantitative assessment of bond order values presupposes rigorous information regarding their possible ranges. Consider a first-order density matrix generated from two *orthogonal* quasi-atomic orbitals χ_1, χ_2 from different atoms

$$p_{11}\chi_1\chi_1 + p_{12}\chi_1\chi_2 + p_{21}\chi_2\chi_1 + p_{22}\chi_2\chi_2. \tag{8.1}$$

Its elements are related to its eigenvalues n_1, n_2 by

$$p_{11} + p_{22} = n_1 + n_2, \tag{8.2}$$

$$p_{11}p_{22} - (p_{12})^2 = n_1 n_2, \tag{8.3}$$

whence also follows:

$$(2 - p_{11})(2 - p_{22}) - (p_{12})^2 = (2 - n_1)(2 - n_2). \tag{8.4}$$

Since the density matrix is derived from an antisymmetric wavefunction, all eigenvalues lie between 0 and 2. In conjunction with Eqs. (8.3), (8.4), this intrinsic range limitation entails that, *for given populations* p_{11}, p_{22}, the bond order p_{12} is constrained by the inequality

$$\begin{aligned}(p_{12})^2 &\le (p_{12,\max})^2 \\ &= \text{Minimum of}[p_{11}p_{22}] \text{ and } [(2 - p_{11})(2 - p_{22})].\end{aligned} \tag{8.5}$$

Since moreover

$$0 \le p_{11} \le 2, \quad 0 \le p_{22} \le 2, \tag{8.6}$$

it follows that

$$(p_{12,\max})^2 = p_{11}p_{22} = p_{\text{ave}}^2 - d^2, \text{ if } 0 \le p_{\text{ave}} \le 1, \tag{8.7a}$$

$$\begin{aligned}(p_{12,\max})^2 &= (2 - p_{11})(2 - p_{22}) \\ &= (2 - p_{\text{ave}})^2 - d^2, \quad \text{if } 1 \le p_{\text{ave}} \le 2.\end{aligned} \tag{8.7b}$$

where

$$p_{\text{ave}} = (p_{11} + p_{22})/2, \ d = (p_{11} - p_{22})/2. \tag{8.8}$$

This dependence of the maximum bond order value on the populations is illustrated in Fig. 3 by displaying contours of constant $|p_{12}|_{\max}$ in the $p_{11} - p_{22}$-plane. It shows that the maximum value possible is $|p_{12}| = 1$ and that it occurs for $p_{11} = p_{22} = 1$. The maximum value possible is seen to become less than 1 when the values of the two populations become different from each other $(d \ne 0)$ and/or when at least one of the two populations approaches 0 or

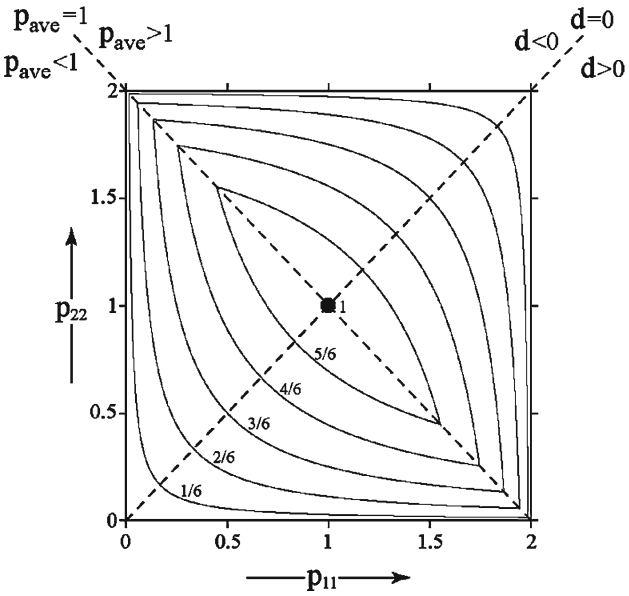

Fig. 3 Contours of the values of $|p_{12,\mathrm{max}}|$ in the p_{11}/p_{22} plane. The numbers 1/6, 2/6, …. 5/6, 1 denote the values of $|p_{12,\mathrm{max}}|$

2 ($p_{\mathrm{ave}} < 1$). These mathematical inferences are in agreement with the conventional expectation that maximal covalent bonding can occur when each atomic orbital is singly occupied and when the bond is not polarized. These two conditions are not sufficient, of course, as is apparent, e.g., from the valence-bond wavefunction of two hydrogen atoms at large distances. The ratio of the *actual* bond order to the maximum value possible can be considered as the *bond order efficacy for the given population values*. It is readily seen that the maximum value of 1 is also valid for bond orders in larger density matrices.

8.2 Covalent activity of a quasi-atomic orbital

We want to use the results of the preceding section to assess the total covalent bonding activity associated with a specific quasi-atomic orbital on atom A, say $|\mathrm{Ax}\rangle$, when the density matrix is given by

$$\rho = \sum_{\mathrm{Aa}}\sum_{\mathrm{Bb}} |\mathrm{Aa}\rangle\, \mathrm{p}_{\mathrm{AaBb}}\, \langle \mathrm{Bb}|. \tag{8.9}$$

To this end, we replace the orbitals $\langle \mathrm{Bb}|$, for $\mathrm{B} \neq \mathrm{A}$, by the orthogonal multi-center MOs

$$\langle w| = \sum_{\mathrm{Bb}}{}^{*} \langle \mathrm{Bb}|\, W_{\mathrm{Bb},w}, \quad \mathbf{W}^{\dagger}\mathbf{W} = \mathbf{I}, \tag{8.10}$$

where $\sum_{\mathrm{Bb}}{}^{*}$ implies B≠A, and the coefficient $W_{\mathrm{Bb},1}$ is defined as

$$W_{\mathrm{Bb},1} = p_{\mathrm{Bb,Ax}}/\bar{p}_{\mathrm{Ax}} \quad \text{with } (\bar{p}_{\mathrm{Ax}})^2 = \sum_{\mathrm{Bb}}^{*} (p_{\mathrm{Bb,Ax}})^2. \tag{8.11}$$

In terms of the new orbitals, which are specific for the examination of $|\mathrm{Ax}\rangle$, the density matrix has the form

$$\rho = \sum_{\mathrm{a}}\sum_{\mathrm{a}'} |\mathrm{Aa}\rangle\, p_{\mathrm{Aa,Aa}'}\, \langle \mathrm{Aa}'| + \sum_{w}\sum_{w'} |w\rangle\, \bar{p}_{w,w'}\, \langle w'| + \sum_{\mathrm{a}}\sum_{w} \{|\mathrm{Aa}\rangle\, \bar{p}_{\mathrm{Aa},w}\, \langle w| + |w\rangle\, \bar{p}_{w,\mathrm{Aa}}\, \langle \mathrm{Aa}|\}. \tag{8.12}$$

and it is readily seen that, the interatomic bond orders involving the orbital $|\mathrm{Ax}\rangle$ are given by

$$\bar{p}_{\mathrm{Ax},w} = \bar{p}_{w,\mathrm{Ax}} = \bar{p}_{\mathrm{Ax}} \quad \text{for } w = 1, \tag{8.13a}$$

$$\bar{p}_{\mathrm{Ax},w} = \bar{p}_{w,\mathrm{Ax}} = 0 \quad \text{for } w > 1. \tag{8.13b}$$

where $\bar{p}_{\mathrm{Ax}}$ is defined in Eq. (8.11).

All interatomic interactions involving $|\mathrm{Ax}\rangle$ are thus collected in the orbital $|w = 1\rangle$ and the bond order $\bar{p}_{\mathrm{Ax},1}$. Hence, we apply the results of the preceding section to the 2 × 2 submatrix

$$\begin{bmatrix} p_{\mathrm{Ax,Ax}} & \bar{p}_{\mathrm{Ax},w=1} \\ \bar{p}_{w=1,\mathrm{Ax}} & \bar{p}_{w=1,w=1} \end{bmatrix} \tag{8.14}$$

where it is readily shown that

$$\bar{p}_{w=1,w=1} = \sum_{\mathrm{Bb}}^{*}\sum_{\mathrm{Cc}}^{*} p_{\mathrm{Ax,Bb}}\, p_{\mathrm{Bb,Cc}}\, p_{\mathrm{Cc,Ax}} \Big/ \sum_{\mathrm{Bb}}^{*} (p_{\mathrm{Bb,Ax}})^2. \tag{8.15}$$

The total covalent activity of the quasi-atomic orbital $|\mathrm{Ax}\rangle$ is then given by the bond order $\bar{p}_{\mathrm{Ax}}$ and its covalent efficacy is given by $(\bar{p}_{\mathrm{Ax}}/\bar{p}_{\mathrm{Ax,max}})$, where $\bar{p}_{\mathrm{Ax,max}}$ is defined by Eq. (8.7) with the elements p_{11}, p_{22}, p_{12} being replaced by the corresponding elements of the matrix (8.14).

9 Summary

An examination of the invariants of the first-order density matrix of accurate molecular electronic wavefunctions reveals a hierarchy of three types of natural orbitals. The two most important groups provide the orbitals that generate the chemically essential zeroth-order configuration space for the wavefunction, which is contained in the full valence space and reflects the bonding structures in molecules.

It is shown that embedded in full-valence-space MCSCF wavefunctions are intrinsic building elements that are localized in the bond regions (called split-localized MOs) and building elements that are localized in the atomic regions (called quasi-atomic MOs).

Methods are developed to extract and exhibit these features without using preconceived notions regarding what they should be. The resulting local orbitals satisfy the following desiderata:

- They are determined by intrinsic, basis-set-independent criteria and algorithms.
- They can therefore change their shapes and directions along reaction paths.
- In the case of the quasi-atomic orbitals, they are of the minimal basis set type.
- They nonetheless generate determinants in terms of which the wavefunction can be *exactly* expanded. They are thus intrinsically embedded in ab-initio wavefunctions.
- Notably, a basis-set independent method has been developed for extracting *oriented* ("hybridized") intrinsic quasi-atomic hybrid orbitals from the density matrix.

The subsequent paper will illustrate how this collection of various localized orbitals provides a tool kit for generating interpretations of electronic structures that are compatible with chemical thinking. As mentioned in the introduction, we shall call this method the *Intrinsic Localized Density Analysis (ILDA)*.

While the analysis has been formulated in terms of full valence spaces, it has also been shown to apply to wavefunctions that do not use the full valence space basis, including the SCF approximation. There are also reasons to believe that complementary analyses for the dynamic correlations can be developed as well.

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