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A comprehensive analysis of molecule-intrinsic quasi-atomic, bonding, and correlating orbitals. I. Hartree-Fock wave functions

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Through a basis-set-independent web of localizing orbital-transformations, the electronic wave function of a molecule is expressed in terms of a set of orbitals that reveal the atomic structure and the bonding pattern of a molecule. The analysis is based on resolving the valence orbital space in terms of an internal space, which has minimal basis set dimensions, and an external space. In the internal space, oriented quasi-atomic orbitals and split-localized molecular orbitals are determined by new, fast localization methods. The density matrix between the oriented quasi-atomic orbitals as well as the locations of the split-localized orbitals exhibit atomic populations and inter-atomic bonding patterns. A correlation-adapted quasi-atomic basis is determined in the external orbital space. The general formulations are specified in detail for Hartree-Fock wave functions. Applications to specific molecules exemplify the general scheme. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4840776>]

I. INTRODUCTION

Even though the efficient representation of a specific molecular electronic wave function leads to specific molecular orbitals, there still remains some flexibility regarding the choice of these orbitals. This freedom does not diminish the value of the orbital concept. Rather, it makes it possible to cast a wave function in the form that is most effective for solving and elucidating a particular physical problem. Over the years, a variety of approaches have been taken to identify molecular orbitals that are useful in various contexts.

Determining orbitals that generate a given many-electron function and, at the same time, make *chemical* features manifest poses a challenge. The difficulty arises because the connection between conceptual physical reasoning, on the one hand, and the mathematical-computational methods used to find quantitative solutions, on the other hand, is not as immediate in quantum mechanics as it is in classical mechanics. In particular, the well-established¹ chemical model of molecules consisting of bonded atoms is not transparently manifest from the physics of electrons and nuclei. Coulson² famously expressed apprehension at the Boulder Conference of 1958 that the computer-generation of accurate wave functions might ruin conceptual interpretations. Indeed, the extraction of the chemical model from rigorous molecular electronic wave functions requires additional methods of analysis, as noted by Ruedenberg³ in 1962 in formulating the first comprehensive “energy decomposition analysis” for *ab initio* wave functions.

The goal of the present study is to formulate a coherent scheme for identifying, among the orbital sets that are embedded in a molecular electronic wave function, those orbitals that are useful in elucidating bonding and correlation

patterns. The approach is based on the fact that the electron distributions of the lower states in atoms and molecules are dominated by the *minimal basis set orbitals*. This insight was an essential intuitive element in the seminal conceptual models of atoms and molecules that were developed in the 1930s. Since then, minimal basis sets have remained fundamental for all qualitative chemical reasoning and rationalization as well as for all semi-empirical theories. Fukui’s frontier orbital theory⁴ and the Woodward-Hoffmann rules⁵ are notable examples of the power of this model. The role that minimal basis sets can play in understanding *ab initio* wave functions has been examined from various points of view by Mulliken,⁶ Adams,⁷ Davidson,⁸ Anderson,⁹ Roby,¹⁰ Ahlrichs and co-workers,¹¹ Weinhold and co-workers,¹² Sanchez-Portal,¹³ Mayer,¹⁴ Cioslowski,¹⁵ and others.

Implicit in Ref. 3 was the premise that any finite orbital set used for interpretative purposes should also be a set from which the wave function can be constructed. In the late 1970s, Ruedenberg, Schmidt, Gilbert, and Elbert¹⁶ showed that a set of *intrinsic minimal basis orbitals with quasi-atomic characteristics* can in fact be deduced from the multi-configuration-self-consistent-field (MCSCF) *ab initio* wave function that is optimized in the *full* configuration space generated by M orbitals, where M is the sum of the number of valence minimal basis set orbitals of all atoms in the molecule. Except for this *number* of orbitals, no explicit atomic bias is introduced through this definition. Since such wave functions are invariant under non-singular orbital transformations, the molecular orbitals can be localized by standard procedures, and it turns out that, in most cases, the localized molecular orbitals have indeed the character of deformed atomic minimal basis set orbitals, i.e., they are *quasi-atomic*. This model, termed the Full Optimized Reaction Space (FORS) model,¹⁷ was used by several of the present authors in many contexts to obtain meaningful chemical information.¹⁸ Furthermore, Ivanic,

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Atchity, and Ruedenberg¹⁹ devised an *unbiased* method for “hybridizing” these quasi-atomic minimal basis orbitals so that the resulting *oriented* quasi-atomic orbitals point along bonds and yield bond orders that exhibit the chemical interactions.

Since, even for moderately sized molecules, the full configuration space generated by all valence minimal basis orbitals is excessively large, it is desirable to be able to deduce quasi-atomic orbitals from simpler wave functions. To this end, Lee and Head-Gordon²⁰ proposed in 2000 what they termed an atomic analog of Boys’ localization criterion to deduce minimal basis orbitals from Hartree-Fock SCF wave functions. In 2004 Lu, Wang, Schmidt, Bytautas, Ho, and Ruedenberg²¹ developed a method that identified, in the *virtual Hartree-Fock space*, the subspace of those orbitals that, together with the occupied Hartree-Fock orbitals, yield extremely close approximations to the MCSCF orbitals of the full valence space. These orbitals, denoted as the *valence-virtual orbitals* (VVOs) in Ref. 21, were further improved by Schmidt, Windus, and Hull,²² who showed that at least 80% of the difference between MCSCF and HF energies is recovered by a VVO-based configuration interaction. The procedure was also generalized to MCSCF wave functions that use *parts* of the full valence space.

The authors of Ref. 21 subsequently learned that certain aspects of their approach were contained in an earlier paper by Iwata.²³ A slightly modified implementation has been given by Knizia.²⁴ An interesting novel approach and analysis has very recently been advanced by Laikov.²⁵

In the present work, the methods of Refs. 16, 19, 21 for covalent bonding are further developed and integrated into a coherent scheme. The analysis is also extended to include the external orbitals, i.e., the orbital space that is complementary to the core and the valence spaces. These orbitals are analogous to the “hard virtual orbitals” of Subotnik, Dutoi and Head-Gordon,²⁶ whose analysis is also based on the division of the orbital space into occupied Hartree-Fock orbitals, valence-virtual orbitals and external orbitals.

In the present paper, the theory is formulated for Hartree-Fock reference functions. The text is organized as follows. Section II formulates the conceptual framework on which the work is based. Section III summarizes certain mathematical tools that are used. Sections IV–VI present the analyses of core, valence, and external orbitals, respectively. A subsequent paper will deal with the generalization to MCSCF reference functions.

II. CONCEPTUAL FRAMEWORK

A. Internal and external orbital spaces

In assessing the physical factors that determine electronic distributions in atoms and molecules, it is conceptually meaningful and quantitatively justified to distinguish between (i) the primary influence of the effective one-electron potential that is generated by the nuclei and the *average* electron distribution and (ii) the secondary influence of the electron correlations that are generated by the many-electron potential that embodies the deviations of the *individual* inter-electronic in-

teractions from the average. The primary potential creates a *primary orbital space* in which the zeroth-order “stock”²⁷ of the ground state wave function takes form, which can be a single configuration or, if several configurations energetically compete, a multi-configurational expression. The secondary potential generates correlation refinements of the wave function that are “grafted” onto the primary stock, which is often called the reference wave function in this context.

The primary orbital space of an *atom* is spanned by its optimized *minimal basis set orbitals*. This intuitive fundamental insight by the quantum chemical pioneers of the 1930s provided the basis for their seminal conceptual elucidations, and its fruitfulness has been confirmed by the quantitative *ab initio* work of the computer-age. In the many atoms with open valence shells, i.e., where the number of valence electrons is less than twice the number of minimal basis valence orbitals, the primary stock of atomic wave functions is frequently multi-configurational.

In *molecules*, *covalent* bonds between atomic primary stocks form when at least one atom has an open valence shell because, then, the *innate delocalization drive* causes some valence electrons to use available minimal basis set orbitals on *several* atoms to lower the *inter-atomic electronic kinetic energy* by electron sharing.²⁸ In covalent bonds, this bonding in the primary orbital space typically dominates markedly over the correlation contributions. But even when correlations play a greater or even an essential role in bonding, separating the two types of contributions greatly elucidates the analysis.

For this reason, the primary orbital space that generates the stock of a molecular wave function can, in most cases, be effectively understood as being generated from a *molecular minimal basis set*, which consists of the molecule-adapted, i.e., suitably deformed, minimal basis set orbitals on all atoms in a molecule. As in previous studies,^{19,21} such minimal basis orbitals are called *quasi-atomic*. The primary molecular orbital space that is spanned by these orbitals will be called the *internal orbital space*. The internal quasi-atomic orbitals can be manifestly divided into *chemical core orbitals* and *valence-internal* orbitals.

The part of the function space that is orthogonal to the internal space is called the *external orbital space*. The external orbitals are needed for the full recovery of electron correlation, if this problem is tackled by full configuration interaction (FCI). In the present analysis, the correlation of the chemical core is not considered. Only that part of the external space is therefore required that serves to correlate the valence part of the wave function. It is called the *valence-external* orbital space. With this restriction, it is physically meaningful and quantitatively effective to divide the full orbital space into three subspaces:

$$\begin{aligned} \text{Full orbital space} &= \text{inner shell core space} \\ &+ \text{valence-internal space} \\ &+ \text{valence-external space}. \end{aligned}$$

The corresponding orbitals are called *chemical core orbitals*, *valence-internal orbitals*, and *valence-external*

orbitals. The space spanned by the chemical core orbitals and the valence-internal orbitals is manifestly identical with the space spanned by the quasi-atomic minimal basis set orbitals.

In general, the primary stock of the wave function has multi-configurational character and can be formulated as a MCSCF wave function in terms of optimized molecular minimal basis set orbitals. Such wave functions typically require only a part of the *full* configuration space that is generated by the minimal basis orbitals. The remaining valence-internal configurations contribute therefore also to correlation, which may be called the *valence-internal correlation*.

B. Valence-internal orbital space and primary SCF reference functions

In many cases, the molecular wave function is dominated by a single determinant. In the electron density expansion,

most of the electron population is then concentrated in the natural orbitals (NOs) from that determinant, and the space these NOs span is in general well approximated by that spanned by the orbitals of the optimized single-configuration self-consistent-field (SCSCF) function, i.e., the Hartree-Fock self-consistent-field (HFSCF) approximation. While these orbitals lie in the valence-internal space, they do not span the *entire* valence-internal space. Typically, localization of the occupied valence Hartree-Fock orbitals yields certain bonding molecular orbitals as well as non-bonding quasi-atomic orbitals. But certain anti-bonding combinations between possible quasi-atomic orbitals are missing. They are Fukui's famous LUMOs (= lowest unoccupied molecular orbitals).⁴ They are embedded in the sea of all virtual (i.e., unoccupied) Hartree-Fock orbitals (HF-virtuals) and can be fished out of that sea, as will be discussed below. In the present context, they are called *valence-virtual* orbitals (VVOs).²¹ Starting from a Hartree-Fock calculation, the full valence-internal space can thus be reconstituted as

$$\text{Valence-internal space} = \text{filled HFSCF space} + \text{valence-virtual HFSCF space}.$$

In this case, the *valence-external* orbital space is manifestly that part of the virtual HFSCF space that is orthogonal to the space of the VVOs. Note that a distinction is made between the *virtual orbitals*, which are defined as *complementary to the reference function (in this case HFSCF)*, and the *external orbitals*, which are defined as *complementary to the internal orbital space*.

In studies of reactions, where some bonds are preserved while others are broken or formed, accounting for these bonding changes requires, as primary stock, a MCSCF wave function which includes certain orbitals that are optimized analogues to the local HF-VVOs in the bonds whose breakage or formation is studied. These VVO analogues in the valence-internal space are thus among the *occupied MCSCF orbitals* and not embedded among the *MCSCF virtual orbitals*. For such MCSCF functions, an appropriate division of the valence-internal space is

$$\text{Valence-internal space} = \text{occupied MCSCF space} + \text{valence-virtual MCSCF space}.$$

In this case, the occupied MCSCF valence orbitals constitute a larger part of the full valence-internal space than the occupied HFSCF orbitals, and the MCSCF-VVOs span a correspondingly smaller part of the internal space. The difference between the MCSCF wave function and the HFSCF wave function (and their energies) used to be called “non-dynamic” correlation. More recently, the terms “static” or “strong” correlation are used with similar meanings. The remaining correlation, i.e., the difference between the MCSCF and the FCI calculation, is usually denoted as “dynamic” correlation. In view of the preceding discussion, the dynamic correlation can be broken down into three kinds of contributions according to the following scheme:

$$\text{Dynamic correlation} = \text{valence-internal dynamic correlation} + \text{valence-external correlation},$$

$$\begin{aligned} \text{Valence-internal dynamic correlation} = & \text{Valence-internal dynamic correlation 1} \\ & + \text{valence-internal dynamic correlation 2,} \end{aligned}$$

$$\begin{aligned} \text{Valence-internal dynamic correlation 1} = & \text{Due to configurations that do not occur in the} \\ & \text{MCSCF function, although they contain the same} \\ & \text{orbitals as the MCSCF function,} \end{aligned}$$

$$\begin{aligned} \text{Valence-internal dynamic correlation 2} = & \text{Due to configurations generated from the valence-} \\ & \text{virtual orbitals that do not occur in the MCSCF} \\ & \text{function.} \end{aligned}$$

In some molecules, the correlation provided by the most weakly occupied internal orbitals can be comparable in magnitude to that of the most strongly occupied external orbitals. In these cases, sorting out the internal and external orbitals requires the analysis of wave functions beyond the full-valence MCSCF level. This subject will be taken up in a subsequent paper.

C. Localized orbital bases

For reasons of formal simplicity and computational practicality, molecular wave functions are often determined in terms of delocalized orbitals. By contrast, atoms are local entities, and both covalent bonds and correlation interactions have short range character. For the analysis of these phenomena, it is therefore expedient to transform electronic wave functions into expressions that are generated by orbitals with local character.

In this context, the quasi-atomic orbitals mentioned in Secs. II A and II B are manifestly valuable. The valence-internal quasi-atomic orbitals reveal molecular bonding patterns and valence-internal correlations. The valence-external quasi-atomic orbitals characterize dynamic correlation patterns. On the other hand, molecular orbitals that are localized in bonds, rather than atoms, are also useful. In the present approach, *all localized orbitals together furnish a linearly independent basis for the full orbital space. Such a complete basis is specific for the molecular electronic wave function that is being analyzed.*

In the present scheme, the valence-internal orbitals are determined first, and the valence-external orbitals are subsequently determined. The details of the procedure depend on the structure of the electronic wave function, in particular the role of the reference function. When the reference function is determined using the HFSCF approximation, then all VVOs have to be retrieved from the virtual space in order to con-

stitute the valence internal space. If, at the other extreme, the reference function is obtained as the MCSCF function in the *full* minimal basis space (which has been called FORS by the present authors¹⁷), no VVOs have to be recovered from the MCSCF virtual space.¹⁶ This is also the case for certain other reference functions that contain the full minimal basis set of orbitals. In the general situation, the reference function is such that some VVOs have to be recovered from the corresponding virtual space, but not as many as for the Hartree-Fock reference function.

The present study focuses on bonding situations that have predominantly covalent character. The analysis of strongly ionic bonds requires modifications that will be discussed in a subsequent paper.

In the interest of clarity, we find it expedient to describe the present approach first for a Hartree-Fock reference function. The generalization to more general wave functions will be presented in the subsequent paper.

III. OPERATIONAL FRAMEWORK

The quantitative implementation of the described program involves a sequence of different localizing procedures and uses a variety of algorithmic techniques. It is useful to give an overview of these aspects before developing the explicit details in Secs. IV–VI.

A. Overview of sequence of localizations

The sequence of procedures for the case of a Hartree-Fock reference function is shown in Figure 1. The numbers in this figure indicate the following sequential operational steps.

1. The canonical HF orbitals are separated into the chemical core, the valence orbitals, and the virtual orbitals.

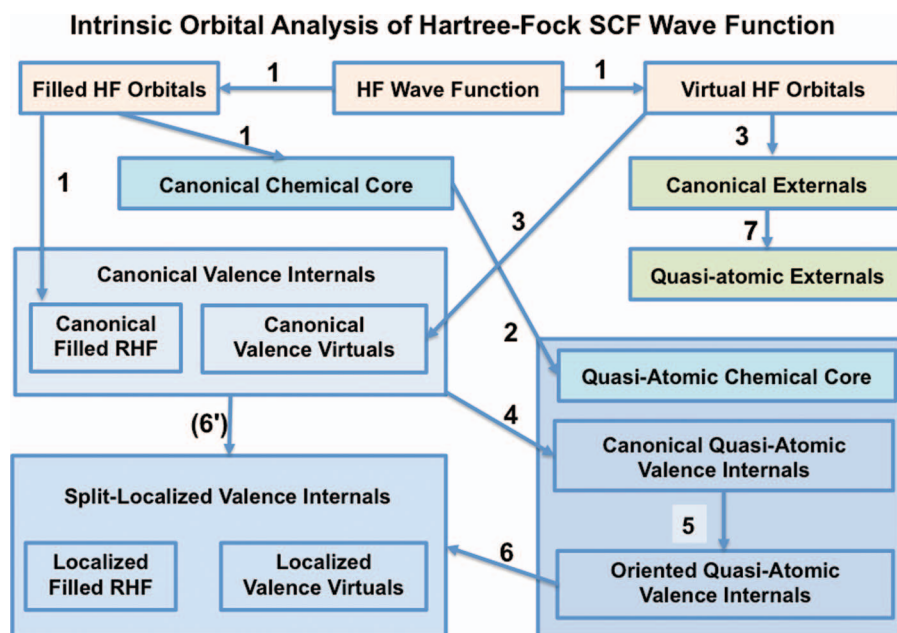


FIG. 1. Overview of molecule-intrinsic orbital sets and the sequence of their determination.

2. The quasi-atomic orbital basis for the chemical core space is determined.
3. The subspace of the valence-virtual orbitals (VVOs) is identified in the virtual HF space. Together with the filled HF orbitals, they form the canonical basis for the internal valence space. The remaining orthogonal HF virtual orbitals provide the canonical basis for the valence-external space.
4. The canonical filled HF orbitals and the valence-virtual orbitals are merged, and, from this *canonical molecular valence-internal basis*, the *canonical quasi-atomic valence minimal basis set* is generated by a single localization. The population-bond-order matrix is constructed.
5. On each atom, the quasi-atomic orbitals are hybridized so that they are oriented according to bonding interactions. These *oriented quasi-atomic orbitals* are also used to identify the location of partially delocalized orbitals.
6. Using the oriented quasi-atomic orbitals, localized orbitals are separately determined in the filled HF orbital space and in the space of the valence-virtual orbitals. Together, they provide the split-localized basis for the valence-internal space.
7. In the valence-external space found under (3), a quasi-atomic basis is determined.

The entire operational sequence of this analysis exists as a module in the GAMESS program suite.^{29,30} In a specific application, not all of these steps may be required of course.

B. Quantitative orbital bases

The explicit orbital constructions are based on the following orbital sets, which are presumed to be available.

1. Basal orbital set

The working atomic orbital basis on all atoms in the molecule, in terms of which the molecular orbitals are expressed, such as, e.g., one of Dunning's correlation consistent sets, are denoted as *basal atomic orbitals (BAOs)*:

$$|\chi_\nu\rangle \text{ when they are summarily referred to,} \quad (3.1)$$

$$|A\nu\rangle \text{ when they are specifically identified,} \\ \text{viz. as the } n\text{-th BAO on atom } A. \quad (3.2)$$

In order to avoid linear dependencies in some of the mathematical transformations, it is essential that the BAOs are used in spherical harmonic form.

Although, in molecular calculations, the basal orbitals are in general taken to be atom centered, the present analysis is also applicable when other basal orbitals are used, for instance plane waves. Such applications have in fact been made.³¹

2. Accurate atomic minimal basis sets

The physical character of each individual atom in a molecule enters into the present analysis through a *minimal*

orbital basis that is a *very* close approximation to the exact minimal basis that yields the *optimal* multi-configurational (i.e., full atomic minimal basis CI) wave function for the isolated ground state of that atom.³² These high-accuracy atomic orbitals are independent of the BAOs of Eq. (3.2). They are in fact expanded in terms of a large set of optimized uncontracted one-center Gaussian primitives that differ from those occurring in the BAOs. For all atoms up to xenon, these orbitals have been determined and will be discussed in an investigation by Schmidt, Windus, and Hull.²² They will be denoted as

$$|A^*a\rangle = \text{accurate atomic minimal basis set (AAMBS)} \\ \text{orbital } a \text{ on atom } A. \quad (3.3)$$

They are mutually orthogonal within each atom but non-orthogonal between different atoms.

3. Molecular Hartree-Fock orbitals

For a given system that is to be examined, the occupied as well as virtual canonical Hartree-Fock orbitals, expressed in terms of the BAOs, are presumed to be available.

C. Algorithms

A number of algorithms are employed for the orbital constructions described in Sec. III A. Some of these methods are standard; some were previously developed by the present authors; others are derived in the subsequent sections. All algorithms are implemented in the GAMESS²⁹ program suite.

1. Overlap integrals between Gaussian primitives

Inter-atomic overlap integrals are required (i) between the AAMBS orbitals of Eq. (3.3) as well as (ii) between the AAMBS orbitals of Eq. (3.3) and the basal atomic orbitals $|\chi_\nu\rangle$ of Eqs. (3.1) and (3.2). Since the AAMBS orbitals contain different Gaussian primitives than the BAOs, a program for calculating overlap integrals between arbitrary Gaussian orbitals must be available.

2. Singular value alignment of orbital sets

At various stages, the objective is to achieve an *optimal alignment* between the orbital bases of two different, *mutually* non-orthogonal orbital spaces of different dimensions. These alignments are accomplished by applying the singular value decomposition (SVD) to the overlap matrix between the two orbital sets and, then, choosing those transformed orbitals that correspond to the largest singular values. Here, "optimal alignment" means that the sum of the projections of the first basis into the space of the second basis is maximal and that the reverse is true as well. This simultaneous maximization of the mutual basis projections is achieved by the SVD *provided that, in each space, the original basis is chosen as orthonormal*. Since this technique is an essential part of the present

approach, it is discussed in some detail in Subsection A 1 of the Appendix.

3. Canonicalization of orbitals sets

In several contexts, an assessment of an *orbital energy* is desired when the orbital ϕ is not a solution of the Hartree-Fock equation. To this end, the expression $\langle \phi | \mathcal{F} | \phi \rangle$ is used where \mathcal{F} is the “quasi-Fock operator” that is defined by the following matrix representation in the BAO basis χ_ν of Eq. (3.1):

$$\langle \chi_\nu | \mathcal{F} | \chi_\mu \rangle = \langle \chi_\nu | h | \chi_\mu \rangle + \sum_{\kappa, \lambda} \langle \chi_\kappa | \rho | \chi_\lambda \rangle \left\{ [\chi_\nu \chi_\mu | \chi_\kappa \chi_\lambda] - \frac{1}{2} [\chi_\nu \chi_\kappa | \chi_\mu \chi_\lambda] - \frac{1}{2} [\chi_\nu \chi_\lambda | \chi_\mu \chi_\kappa] \right\}. \quad (3.4)$$

Here, h is the one-electron operator, ρ is the first-order density matrix of the actual wave function being investigated, and $[fg]$ is Mulliken’s electron repulsion integral definition,

$$[fg] = \int d1 \int d2 \frac{f(1)g(2)}{r_{12}}. \quad (3.5)$$

In the case of HF wave functions, \mathcal{F} becomes the true Fock operator. With ρ chosen as an MCSCF density, the formulation of Eq. (3.4) has been used by Roos and co-workers.³³

At some points, it is useful to transform certain molecular orbital basis sets into basis sets that diagonalize the operator \mathcal{F} . This transformation is referred to as “canonicalization.” Often this canonicalization is performed only for certain parts of the total orbital space.

4. Orbital localization

The localizations that generate quasi-atomic orbitals are achieved by using SVDs. The localizations that generate split-localized orbitals are performed with a new fast method, which is based on quasi-atomic orbitals rather than using standard localization procedures. This new localization algorithm is described in Subsection A 2 of the Appendix.

The computational effort involved in all of the described operations represents only a very small fraction of the effort required for the Hartree-Fock calculations. All of the mentioned operations are contained in the above mentioned module in GAMESS.²⁹

IV. CHEMICAL CORE SPACE

As mentioned towards the end of Sec. II A, the present analysis is formulated for wave functions in which the chemical cores of the atoms are kept closed (“inactive”) and orthogonal to the valence and the external space. In all wave functions of this type, the core orbitals are readily identified as part of the occupied canonical molecular orbitals, and the following analysis of the core orbitals for the Hartree-Fock case is therefore generally valid.

The first step of our analysis, indicated by 1 in Figure 1, implies the separation of the canonical core, valence,

and virtual orbitals. This separation is self-evident from the wave function structure.

The second step of the analysis, indicated by 2 in Figure 1, consists of determining the *quasi-atomic* chemical core orbitals. To this end, one forms the overlap matrix

$\langle Cn | A^*a \rangle$, where $|Cn\rangle$ runs through all Hartree-Fock core orbitals in the molecule and $|A^*a\rangle$ runs through all core orbitals of the accurate atomic minimal basis set (AAMBS) orbitals, discussed in Sec. III B 2, on a given atom A.

For this rectangular overlap matrix, the SVD is performed. The number of non-zero singular values is manifestly equal to the dimension N_{CA} of the core space on atom A. One chooses the singular vectors *in the HF core space* that correspond to these non-zero singular values.

By determining the analogous local core contributions on each atom in the molecule in this manner, a set of localized orbitals is found that spans the entire Hartree-Fock core space. In case that an atom has more than one core orbital, these localized core orbitals are orthogonal within each local atomic set. In general, the local core orbitals of different atoms are mutually nonorthogonal. Whereas the intra-atomic blocks of the overlap matrix S between all these local core orbitals in the molecule are identity matrices, the off-diagonal inter-atomic blocks do not vanish. Symmetric orthogonalization, i.e., transformation by $S^{-1/2}$, generates an orthogonal set of deformed core orbitals on all atoms. These orbitals are the quasi-atomic core orbitals on the various atoms in the molecule.

There are molecules in which bonding effects are to some degree influenced by correlations with inner shells. These effects have to be accounted for in the analysis of *correlated* wave functions.

V. VALENCE-INTERNAL SPACE

A. Canonical valence-internal orbital basis

1. Determination of valence-virtual orbitals

In the next step of our procedure, indicated by 3 in Figure 1, the valence-virtual orbitals (VVOs) are extracted from the total virtual space that is generated by the Hartree-Fock calculation on the molecule. To this end, all *accurate atomic minimal basis sets (AAMBS) on all atoms in the molecule* [denoted as $|A^*a\rangle$ in Eq. (3.3) of Sec. III B 2] are symmetrically orthogonalized. Let $|A^\#a\rangle$ denote these orthogonalized AAMBS orbitals. Then, the following overlap matrix is calculated:

$\langle Vn | A^\#a \rangle$, where $|Vn\rangle$ runs through *all* (orthogonal) virtual Hartree-Fock orbitals of the molecule and $|A^\#a\rangle$ runs through *all* orthogonalized AAMBS orbitals *on all atoms*.

For this rectangular matrix, the SVD is performed. Since the number of rows (Vn) is typically greater than or equal to the number of columns ($A^\#a$), the number of non-zero singular values is equal to the number of columns, which is the dimension of the valence-internal space of the molecule.

One then chooses those N_{VVO} singular vectors *in the virtual HF space* that correspond to the *maximal singular values*.

Here N_{VVO} is the number of valence-virtual orbitals that are needed to complement the filled HF orbitals to form a basis for the full valence-internal space. Hence, N_{VVO} equals the total number of molecular minimal basis set orbitals minus the number of filled HF orbitals.

The chosen set of orbitals is canonicalized as described in Sec. III C 3. The resulting orbitals are the canonical valence-virtual orbitals. The canonical valence-virtual orbitals and the canonical filled HF orbitals, together, form the canonical basis for the valence-internal orbital space in the HF approximation. The Fock matrix is diagonal for this internal basis.

Since all singular vectors of the SVD are mutually orthogonal, those singular vectors that are *not* selected as VVOs for the valence-internal space generate an orthogonal basis for the *valence-external* virtual space. This orbital set is also canonicalized as described in Sec. III C 3, and it provides the *canonical valence-external basis*. Note that the block of the Fock matrix between the canonical valence-external orbitals and the canonical valence-internal VVOs does not vanish.

This procedure is related to the one described by Lu, Wang, Schmidt, Bytautas, Ho, and Ruedenberg,²¹ as modified by Schmidt, Windus, and Hull.²² That approach failed, however, to account for the necessary orthogonalities, which are identified in Subsection A 1 of the Appendix.

2. Properties

As was already observed in Refs. 21, the valence-virtual orbitals have several noteworthy properties, which were confirmed in a variety of applications.

- (i) In all molecules examined to date, the first N_{VVO} singular values are all very close to unity whereas the remaining non-zero singular values are an order of magnitude smaller. The remarkably sudden drop in the magnitude in the singular values of the overlap matrix $\langle \text{Vn} | \text{A}^\# | \text{a} \rangle$ (see Sec. V A 1) beyond the first the N_{VVO} singular values is illustrated in Table I for eight molecules of various

types and sizes, containing between one and ten VVOs. The implication is that, in many molecules, the valence-virtual orbitals clearly form a distinct subspace of the HF virtual space.

- (ii) *The valence-virtual orbitals are basis set independent*, i.e., the canonical valence-virtual orbitals converge rapidly to a complete basis set limit. This invariance is illustrated in Figure 2 which exhibits the orbital energies of the *canonical valence-virtual* orbitals in the sea of the orbital energies of *all standard canonical virtual* Hartree-Fock orbitals for the HNO molecule, using five basis sets of various sizes. As the number of *all* positive virtual Hartree-Fock orbital energies (shown in colors) proliferates from 32 to over 300 with increasing basis set size, the lowest virtual orbital energies predictably become smaller and smaller and the corresponding orbitals more and more diffuse. Even the symmetry (in C_s) of the lowest virtual orbital is basis set dependent, as indicated. By contrast, the positive valence-virtual orbital energies (shown in black) hardly change and approach their limiting values as rapidly as the negative energies of the occupied Hartree-Fock orbitals, which are also shown in the figure.
- (iii) The canonical valence-virtual orbitals are typically as delocalized as the canonical filled RHF orbitals. This delocalization is illustrated in Figure 3 by the contours of the seven highest occupied orbitals (the HOMOs) and the seven lowest VVOs (the LUMOs) of the 1,4-benzoquinone molecule. The orbitals for the quinone molecule that are shown in Figure 3 as well as those in several subsequent figures were obtained from a Hartree-Fock calculation with the cc-pVDZ basis set³⁴ at the HF-optimized geometry. (All internuclear distances are within 0.03 Å, all bond angles are within 1° of the experimental values.)
- (iv) The internal orbital space spanned by the valence-virtual orbitals plus that of the filled Hartree-Fock orbitals typically represents a close approximation to the *optimal* full valence-internal orbital space, i.e., the orbital space that

TABLE I. Smallest singular SVD value retained and largest singular value not retained in applying the VVO selection procedure to various molecules.^a

| Molecule | No. of inner shell orbitals | No. of filled valence orbitals | No. of valence virtual orbitals | N_{mbs}^b | $\lambda(N_{\text{mbs}})^c$ | $\lambda(N_{\text{mbs}} + 1)^c$ |
|--|-----------------------------|--------------------------------|---------------------------------|--------------------|-----------------------------|---------------------------------|
| HNO, nitroxyl | 2 | 6 | 3 | 11 | 0.999995 | 0.185919 |
| NaCl, table salt | 10 | 4 | 1 | 15 | 0.999996 | 0.105702 |
| HNCO, isocyanic acid | 3 | 8 | 5 | 16 | 0.999995 | 0.186137 |
| HOCH=O, formic acid | 3 | 9 | 5 | 17 | 0.999933 | 0.190360 |
| H ₂ Si=CH ₂ , silene | 6 | 6 | 6 | 18 | 0.999909 | 0.176907 |
| SO ₂ , sulfur dioxide | 7 | 9 | 3 | 19 | 0.999993 | 0.272371 |
| MnO ₄ ⁻ , permanganate | 13 | 16 | 6 | 35 | 0.999997 | 0.146642 |
| As ₄ S ₄ , realgar | 76 | 22 | 10 | 108 | 0.999997 | 0.186473 |

^aRHF calculations with aug-cc-pVQZ bases at optimized geometries. For the permanganate ion, the geometry obtained with the aug-cc-pVTZ basis was used.

^bThe number N_{mbs} is the sum of the second, third, and fourth column. It is the total number of minimal basis set orbitals in each molecule, which is equal to the sum of the number of AAMBS orbitals on all atoms.

^cThe symbol $\lambda(n)$ denotes the singular value of the n th SVD orbital, based on the ordering of the singular values by decreasing magnitudes.

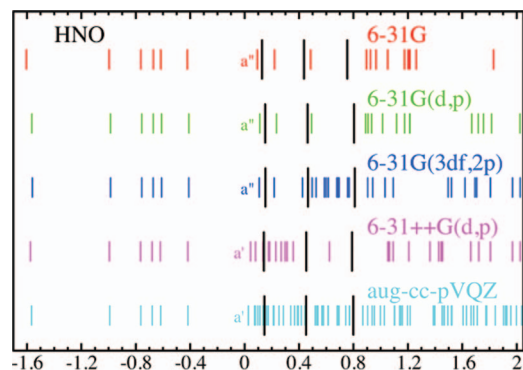


FIG. 2. Orbital energies of occupied and virtual canonical HF orbitals of HNO, calculated with five different basis sets as indicated. The canonical standard orbital energies are shown in color. The symmetry of the lowest standard virtual orbital in each set is indicated in front of the respective orbital marker. The symmetries a'' and a' correspond to π - and σ -orbitals, respectively. The canonical valence-virtual orbital energies are shown in black.

results from the FORS-MCSCF calculation in which the number of orbitals is equal to the total number of minimal basis orbitals. Specifically, the natural orbitals (NOs) of these MCSCF calculations in the full valence-internal space typically fall into two groups: the *strongly occupied* NOs (occupation $> \sim 0.9$) and the *weakly occupied*

NOs (occupation $< \sim 0.4$). The space spanned by the *strongly* occupied MCSCF-NOs is found to be very close to that of the *occupied* HF orbital space, and the space of the *weakly* occupied MCSCF-NOs is found to be very close to that of the space spanned by the *HF-VVOs*. These similarities are documented in Table II for the valence spaces of the molecules H_2CO , H_2SiCH_2 , and the $^3\Sigma_g^-$ ground state of the open-shell NCN biradical. Listed are the projections of the *occupied* canonical HF orbitals on the space of the *strongly* occupied MCSCF-NOs and the projections of the *HF-VVOs* on the space of the *weakly* occupied MCSCF-NOs. For the core spaces, the corresponding numbers are all larger than 0.999.

- (v) By virtue of these strong overlaps, the HF-VVOs are in fact the most effective starting orbitals for FORS-MCSCF optimization iterations that we have found so far. This observation is documented for four molecules in Table III, which shows that the full valence CI calculations using the VVOs yield between 80% and 90% of the valence-internal correlation energies that are obtained by the full valence MCSCF optimizations.
- (vi) The weakly occupied full valence MCSCF-NOs represent the most rigorous *ab initio* implementation of the LUMO concept that Fukui conceived sixty years ago. *The HF-VVOs furnish therefore the best ab initio approximation to the LUMO space that can be deduced from a Hartree-Fock wave function.* The effort of determining the HF-VVOs is manifestly minuscule compared to the work that is required to calculate the full valence space MCSCF NOs.

Canonical HOMOs and LUMOs of quinone
Orbital energies in mh

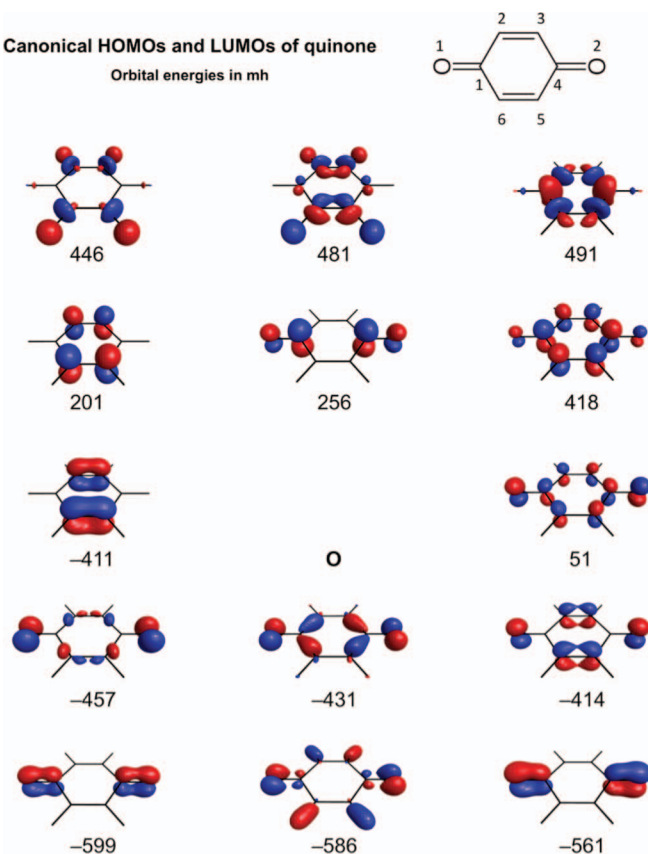


FIG. 3. The seven highest occupied canonical orbitals (HOMOs) and the seven lowest unoccupied canonical valence-virtual orbitals (LUMOs) of the HFSCF calculation of 1,4-benzoquinone. The orbital energies are given in millihartree under the orbital contours, which correspond to $0.1 \text{ bohr}^{-3/2}$. The geometry is HFSCF optimized. The basis set is cc-pVDZ.

B. Quasi-atomic valence-internal orbital basis

1. Atomic localization: Canonical quasi-atomic orbitals

The next task, indicated as 4 in Figure 1, is to find a quasi-atomic orbital (QUAO) basis in the full valence-internal orbital (VI) space, i.e., orbitals that have the character of deformed minimal basis orbitals on the various atoms in the molecule.

In this process, the physical character of each individual atom should be taken into account. This information is brought into the analysis by means of the accurate atomic minimal basis set (AAMBS) orbitals $|A^*a\rangle$, which are defined in Sec. III B 2. As mentioned after that equation, these orbitals form an orthogonal set within any one atom. The following overlap matrix is separately calculated for each atom:

$\langle VIn | A^*a \rangle$, where the orbital index n in $|VIn\rangle$ runs over the *full*, orthogonal, canonical (occupied and VVO) basis in the valence-internal space of the *entire molecule* and $|A^*a\rangle$ runs over all AAMBS valence orbitals on *one specific atom* (see Eq. (3.2)).

The SVD is then performed for this rectangular overlap matrix. Since the number of rows is larger than the number of columns, the number of non-zero singular values is exactly equal to the number of valence minimal basis orbitals on atom A. The corresponding singular vectors in the *molecular* valence-internal space are taken to be the local contributions

TABLE II. Projections of the canonical occupied HFSCF-MOs and the HFSCF-VVOs onto the spaces of the strongly and weakly occupied FORS-MCSCF NOs, respectively, in H_2CO , H_2SiCH_2 , and NCN .

| H_2CO^a | | $\text{H}_2\text{SiCH}_2^a$ | | $\text{NCN } (^3\Sigma_g^-)^b$ | |
|---|--------------------|-----------------------------|-------------|--------------------------------|-------------|
| ϵ^c | Projections | ϵ^c | Projections | ϵ^c | Projections |
| Projections of canonical <i>HF-VVOs</i> on the space of the <i>weakly</i> occupied FORS NOs | | | | | |
| | | 0.705 | 0.966 | | |
| | | 0.634 | 0.956 | | |
| 0.842 | 0.916 | 0.431 | 0.947 | 1.140 | 0.953 |
| 0.642 | 0.851 ^d | 0.388 | 0.955 | 0.503 | 0.986 |
| 0.469 | 0.974 | 0.324 | 0.980 | 0.159 | 0.997 |
| 0.198 | 0.973 | 0.141 | 0.970 | 0.159 | 0.997 |
| Projections of canonical <i>occupied HF-MOs</i> on the space of the <i>strongly</i> occupied FORS NOs | | | | | |
| | | | | −0.251 | 0.999 |
| | | | | −0.251 | 0.999 |
| −0.438 | 0.999 | −0.316 | 0.999 | −0.416 | 1.000 |
| −0.547 | 1.000 | −0.495 | 1.000 | −0.416 | 1.000 |
| −0.658 | 1.000 | −0.502 | 1.000 | −0.572 | 1.000 |
| −0.701 | 1.000 | −0.577 | 1.000 | −0.616 | 1.000 |
| −0.867 | 1.000 | −0.684 | 1.000 | −1.082 | 1.000 |
| −1.422 | 0.999 | −0.912 | 1.000 | −1.215 | 1.000 |

^aRHF optimized geometry using cc-pVTZ basis.^bFORS-MCSCF optimized geometry using cc-pVTZ basis.^cOrbital energies of canonical occupied HF orbitals and HF-VVOs in hartree.^dThis orbital has the largest number of inter-atomic nodes in H_2CO .

of atom A to that valence-internal space. By determining the analogous local contributions on *each* atom in the molecule using the same procedure, a complete set of local basis orbitals is determined for the valence-internal space.

This basis is orthogonal within each local atomic set. The local orbitals from different atoms are however in general mutually nonorthogonal. Symmetric orthogonalization, i.e., transformation by $S^{-1/2}$, generates an orthogonal set of deformed valence orbitals on all atoms. These orbitals are the *canonical quasi-atomic valence orbitals* on the various atoms in the molecule. In this context, “canonical” implies that the orbitals are lined up, as much as possible, with the spherical harmonics on each atom. (Note that the coordinate systems on different atoms differ only by parallel displacements.) This near-alignment with the $x/y/z$ axes is apparent from the contours of the canonical quasi-atomic orbitals of quinone, which are shown in Figure 4.

The question can be raised whether an analysis in terms of non-orthogonal quasi-atomic orbitals might be more physical. Such an analysis is presumably possible, but it would be considerably more complex.³ The resolution in terms of or-

thogonal orbitals exhibits more clearly the intrinsic structure of the molecular wave function and its densities.

2. Exhibition of bonding patterns: Oriented quasi-atomic orbitals

Covalent binding is driven by the *one-electron* interactions that result from individual electrons being shared

TABLE III. Comparison of correlation energies recovered at the full valence level (i) by using a VVO-based CI and (ii) by full valence MCSCF (FORS) calculations.^a

| Molecule | VVO-CI (mh) | FORS (mh) | VVO/FORS (%) |
|---------------------------|----------------|--------------|-----------------|
| HNO | 113.62 | 126.86 | 89.6 |
| HNCO | 161.49 | 181.88 | 88.8 |
| H_2SiCH_2 | 109.95 | 126.03 | 87.2 |
| SO_2 | 101.00 | 121.21 | 83.3 |

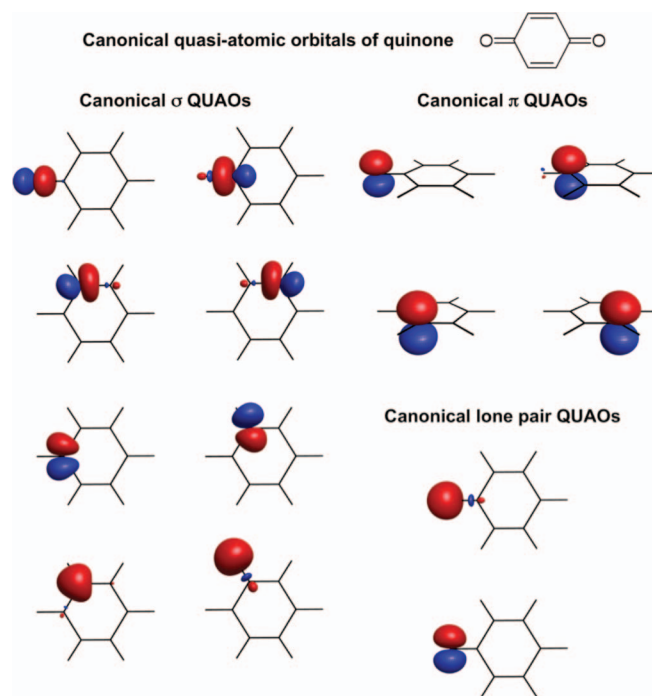
^aCalculated at the RHF optimized geometries with aug-cc-pVQZ bases.

FIG. 4. Canonical quasi-atomic orbitals of 1,4-benzoquinone.

between atoms. Consequently, essential information regarding bonding patterns in molecules is embedded in the *first-order* density matrix. The recognition of these bonding patterns is contingent on finding orbitals that lead to first-order density matrices in which the bonding patterns are clearly recognizable. The first step towards making this information manifest consists of expressing the first-order density matrix in terms of quasi-atomic orbitals.

In the basis of the delocalized canonical *molecular* valence-internal orbitals of Sec. V A, say ϕ_k , and their occupation numbers n_k , the first-order density is given by

$$\rho(1, 2) = \sum_k |\phi_k(1)\rangle n_k \langle\phi_k(2)|, \quad \text{where } n_k = 0, 1, \text{ or } 2. \quad (5.1)$$

By inserting into this expansion the transformation between the ϕ_k and the canonical *quasi-atomic* orbitals, which are determined by the procedure described in Sec. V B 1, one obtains the density expansion in terms of the canonical quasi-atomic minimal basis set orbitals:

$$\rho(1, 2) = \sum_{A\alpha} \sum_{B\beta} |A\alpha(1)\rangle p_{A\alpha, B\beta} \langle B\beta(2)|, \quad (5.2)$$

where $|A\alpha\rangle$ denotes the α th canonical QUAO on atom A. The representation matrix $p_{A\alpha, B\beta}$ is called the population-bond-order matrix³⁵ because its diagonal elements are the electron populations of the QUAOs and the inter-atomic elements represent “bond orders,” which are related to bonding interactions between the QUAOs.

The bonding interactions around each atom can be exhibited even more clearly. This sharpening is possible because there still remains a certain freedom in the QUAOs in as much as the localization onto atoms is preserved when the QUAOs associated with any one atom are mixed with each other by an arbitrary orthogonal transformation. This freedom can be exploited to manifest the intrinsic bonding patterns by *compacting distinct bonding interactions into distinct orbitals*. This objective is achieved by determining those linear combinations $|A\alpha\rangle$ of the canonical QUAOs $|A\alpha\rangle$ on the same atom for which the *off-diagonal blocks of the transformed bond order matrix* $p_{A\alpha, B\beta}$ in the density expansion,

$$\rho(1, 2) = \sum_{Aa} \sum_{Bb} |Aa(1)\rangle p_{Aa, Bb} \langle Bb(2)|, \quad (5.3)$$

have as few quantitatively significant elements as possible, which implies that each transformed orbital $|Aa\rangle$ interacts with the smallest number of orbitals on other atoms. For reasons that will become apparent presently, these QUAOs are called *oriented quasi-atomic orbitals*.

The determination of the oriented QUAOs is the next step of the analysis, which is indicated as 5 in Figure 1. The algorithm will be described in Sec. V B 3.

The elucidation that is achieved by the orientation transformation is illustrated by Figure 5, which displays the oriented QUAOs of quinone that are obtained from the canonical QUAOs of Figure 4. On each atom, oriented σ -QUAOs point in the directions of the specific bonds. On each oxygen, there is a σ -lone-pair QUAO and an in-plane p-lone pair. The π -QUAOs are not mixed with the σ -QUAOs. The oriented

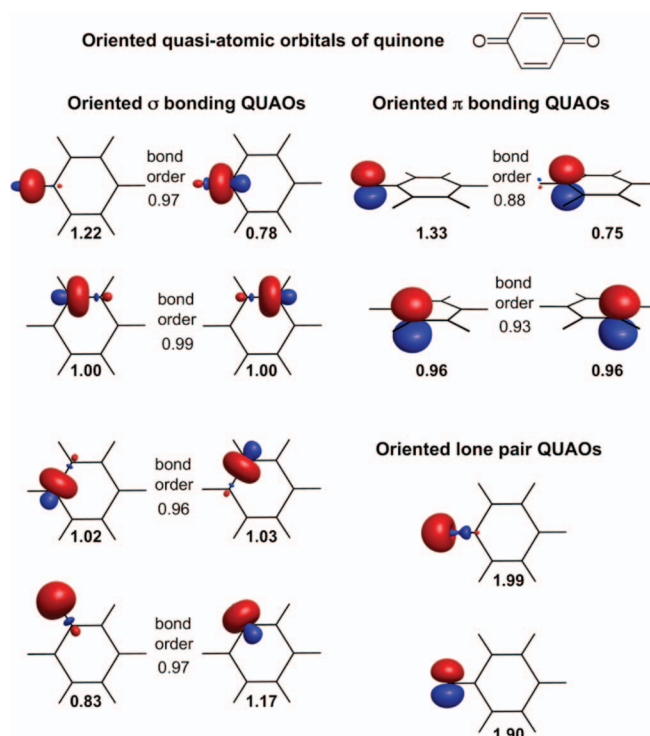


FIG. 5. Oriented quasi-atomic orbitals of quinone. Occupations are indicated below each orbital. Strong bonding is indicated by the word “bond order” between the bonded orbitals. The respective bond orders are listed below “bond order.” Additional weak bond orders are discussed in the text.

quasi-atomic orbitals manifestly are the *ab initio* counterparts to the early qualitative concept of “hybridized atomic bond orbitals.”

Also shown in Figure 5 are the *occupations* of the quasi-atomic orbitals as well as the *bond-orders* between those orbitals that are strongly bonded. These bond orders are all larger than 0.93 except one that is 0.88. There are also bond orders of 0.25 between the in-plane p-lone pair orbitals on oxygen and the vicinal CC- σ -bonds, indicating hyperconjugation, and there are bond orders of 0.25 between the CO- π -bonds and the CC- π -bonds, showing that quinone is only very weakly aromatic. *All remaining bond orders are less than 0.1*. The sum of the orbital populations $p_{Aa, Aa}$ on any given atom A yields the total electron populations on that atom. Table IV lists the atomic populations that are obtained for quinone from working with different BAOs. It shows that the values resulting from the present population definition are *basis set independent*. The implications for the binding pattern in quinone will be discussed in a subsequent paper.

3. Determination of oriented quasi-atomic orbitals

In many instances, bonding patterns can be intuitively anticipated. *However, no such qualitative expectations are used here as input in determining the oriented orbitals.* Rather, all atoms and bonds are treated on an equal footing so that the bonding information that is *intrinsic to the wave function* is brought to light by an unbiased formalism. The method is therefore applicable where intuition is no sure guide, e.g., at transition states.

TABLE IV. Total atomic populations of the symmetry-unique atoms in quinone based on the quasi-atomic orbitals obtained for different working bases.^a

| Basis | O ₁ | C ₁ | C ₂ | H ₁ |
|-------------|----------------|----------------|----------------|----------------|
| cc-pVDZ | 8.442 | 5.568 | 6.163 | 0.832 |
| aug-cc-pVDZ | 8.460 | 5.558 | 6.162 | 0.829 |
| cc-pVTZ | 8.459 | 5.556 | 6.163 | 0.830 |
| aug-cc-pVTZ | 8.463 | 5.554 | 6.162 | 0.829 |
| cc-pVQZ | 8.462 | 5.554 | 6.162 | 0.830 |

^aThe atoms are numbered as indicated on the molecular diagram in Figure 3.

The algorithmic implementation is based on the criterion that the bond orders between the oriented orbitals of different atoms should fall into two groups: many bond orders that are very small in absolute value and a few that are large in absolute value (bond orders can be positive or negative). In this context, the following observation is relevant: By virtue of the orthogonality of the intra-atomic transformations from canonical to the oriented QUAOs, the *sum of the squares of the bond orders within any one inter-atomic bond order block that connects atoms A and B remains invariant*:

$$\sum_{\alpha} \sum_{\beta} (p_{A\alpha, B\beta})^2 = \sum_a \sum_b (p_{Aa, Bb})^2, \quad (5.4)$$

where, as in Sec. V B 2, $|A\alpha\rangle$, $|B\beta\rangle$ = canonical QUAOs; $p_{A\alpha, B\beta}$ = bond orders between canonical QUAOs; $|Aa\rangle$, $|Bb\rangle$ = oriented QUAOs; $p_{Aa, Bb}$ = bond orders between oriented QUAOs. Consequently, simultaneous orthogonal *intra-atomic* QUAO transformations on atoms A and B will change the bond orders of the inter-atomic AB block in such a way that, if some of the bond orders become larger in absolute value, then others must become smaller. The objective is thus to make the squares of a *few* bond orders as *large* as possible and the squares of as *many* bond orders as possible *small*.

Such a “disproportionation” within all inter-atomic bond order blocks is manifestly achieved by maximizing the sum of the *fourth* powers of *all* inter-atomic density matrix elements, i.e., by maximizing the *orientation sum*,

$$\begin{aligned} & \sum_{A < B} \sum_a \sum_b (p_{Aa, Bb})^4 \\ &= \sum_{A < B} \sum_a \sum_b \left(\sum_{\alpha} \sum_{\beta} p_{A\alpha, B\beta} T_{A, \alpha a} T_{B, \beta b} \right)^4, \end{aligned} \quad (5.5)$$

with respect to the matrix elements $T_{A, \alpha a}$ and $T_{B, \beta b}$, which represent the intra-atomic orthogonal transformations between canonical and oriented QUAOs on the various atoms in the molecule. An efficient algorithm to accomplish this maximization has been developed, discussed and used by Ivanic, Atchity, and Ruedenberg.¹⁹

Since the QUAOs are mutually orthogonal, they contain small contributions from the BAOs on neighboring atoms. Table V documents the magnitude of these tails for the oriented QUAOs in quinone by listing the quantities $\sum_v (c_{Av})^2 / \sum_A \sum_v (c_{Av})^2$, where c_{Av} denotes the expansion

TABLE V. Contributions from the basal atomic orbitals (BAOs) to the oriented quasi-atomic orbitals (QUAOs) of quinone. Not shown are all contributions less than 0.02.^a

| Oriented QUAOs | O ₁ atom | C ₁ atom | C ₂ atom | C ₃ atom | H atom |
|-----------------------------|---------------------|---------------------|---------------------|---------------------|--------|
| O ₁ $\sigma\ell$ | 0.88 | 0.07 | | | |
| O ₁ $p\ell$ | 0.88 | 0.06 | | | |
| O ₁ $c_1\sigma$ | 0.75 | 0.20 | | | |
| C ₁ $o_1\sigma$ | 0.17 | 0.80 | | | |
| O ₁ $c_1\pi$ | 0.97 | 0.03 | | | |
| C ₁ $o_1\pi$ | 0.02 | 0.94 | | | |
| C ₁ $c_2\sigma$ | | 0.80 | 0.17 | | |
| C ₂ $c_1\sigma$ | | 0.17 | 0.80 | 0.02 | |
| C ₂ $c_3\sigma$ | | | 0.77 | 0.21 | |
| C ₃ $c_2\sigma$ | | | 0.21 | 0.77 | |
| C ₂ $c_3\pi$ | | | 0.94 | 0.03 | |
| C ₃ $c_2\pi$ | | | 0.03 | 0.94 | |
| C ₂ $h\sigma$ | | | 0.84 | | 0.13 |
| H _{c2} σ | | | 0.20 | | 0.79 |

^aThe oriented quasi-atomic orbitals are labeled by the atom on which they are located (capital roman letters), the atom to which they point (small roman letters), and the symmetry labels σ and π . As illustrated in Figure 2, C₁ is neighbor to O₁. C₂ is neighbor to C₁ and C₃. The calculation of the contributions is described in the text.

coefficients of a given oriented orbital in terms of the BAOs $|A\nu\rangle$ on atom A.

4. Analysis of molecular orbitals in terms of quasi-atomic orbitals

The conceptual understanding of quantitative results of electronic structure calculations in molecules nearly always requires a knowledge of where in the molecule various orbitals are located, be they localized or delocalized. While the visual examination of orbital plots is very valuable to this end, a quantitative measure is often desirable as well. In some contexts, it is moreover necessary that the program is able to identify automatically which atoms are covered by specific molecular orbitals.

These objectives can be achieved by expanding the molecular orbitals in terms of the (non-orthogonal or orthogonal) quasi-atomic orbitals. If the expansion of an arbitrary orbital λ in terms of the quasi-atomic orbitals $|Aa\rangle$ is given by

$$\lambda = \sum_A \sum_a |Aa\rangle C_{Aa}, \quad (5.6)$$

then the quantities

$$(C_{Aa})^2 / \sum_A \sum_a (C_{Aa})^2, \text{ and } \sum_a (C_{Aa})^2 / \sum_A \sum_a (C_{Aa})^2, \quad (5.7)$$

respectively, provide measures of how much each quasi-atomic orbitals $|Aa\rangle$ and each atom A contributes to the orbital λ . Here the summation \sum_a goes over all quasi-atomic orbitals on atom A. The resolution of Eq. (5.6) can be used with canonical or oriented quasi-atomic orbitals.

C. Split-localized valence-internal orbital basis

1. Attributes of split-localized orbitals

The quasi-atomic orbitals represent the strongest orbital localization that is possible in the full space of the valence-internal orbitals. In fact, atom-localized orbitals also result from applying any of the conventional localization procedures to full valence-internal spaces obtained from MCSCF calculations, even though these standard algorithms contain no explicit references to atoms.

On the other hand, additional valuable insights can be gained from certain orbitals that are less localized. In particular, the independent separate localizations in the space of the occupied Hartree-Fock orbitals and in the space of the valence-virtual orbitals yield instructive information on bonding patterns. These localizations are the next step in the analysis and indicated as **6** in Figure 1.

The idea of localizing the *occupied* Hartree-Fock orbitals goes back to work by Hund³⁶ in 1931. Around 1950, the subject was further developed by Coulson,³⁷ Lennard-Jones,³⁸ Hall,³⁹ and Pople,⁴⁰ in particular in the presence of symmetry. In order to achieve localization in the absence of symmetry, several criteria were then formulated and in 1963 Edmiston and Ruedenberg⁴¹ devised a viable algorithm for maximizing any of these localization measures (see Sec. V C 2). The localization of the occupied HF orbitals proved to be an extremely useful and popular tool because it creates bonding and lone pair orbitals that provide pictures of overall bonding patterns congruent with chemical intuition while, at the same time, leaving the single-determinant form of the HF wave function intact.

The localization algorithms used for the occupied orbitals can also be applied to the set of valence-virtual orbitals. As an illustration, Figure 6 exhibits all *localized occupied* HF orbitals as well as all *localized valence-virtual orbitals* in quinone. Only the unique orbitals are shown since the remaining orbitals can be generated by applying the operations of the D_{2h} symmetry group. It is apparent that there is a bonding occupied orbital as well as a matching antibonding VVO for each carbon-hydrogen bond, for each carbon-carbon σ -bond and for each carbon-carbon π -bond. In addition, there are two occupied lone-pair orbitals on each oxygen atom. The union of the localized occupied HF orbitals and the localized HF-VVOs manifestly provide a basis for the valence-internal space. Following the suggestion of Bytautas, Ivanic, and Ruedenberg,⁴² it is called the *split-localized* basis.

Although the Hartree-Fock VVOs are all empty LUMOs, they are important because, as was discussed in Sec. V A 2(iv), the VVOs are very close approximations to the weakly occupied *correlating* MCSCF orbitals in the full valence space. Thus, there also exists a corresponding *split-localized orbital basis set in the full valence MCSCF space*. Bytautas, Ivanic, and Ruedenberg⁴² have shown that this split-localized MCSCF orbital basis generates a more rapid full CI convergence for the valence-internal CI wave functions than is obtained by the natural orbital expansion. That is, the split-localized MCSCF orbital basis provides the most effective configurational basis for the valence-internal correlation. The split-localized HF orbitals can therefore also be expected to

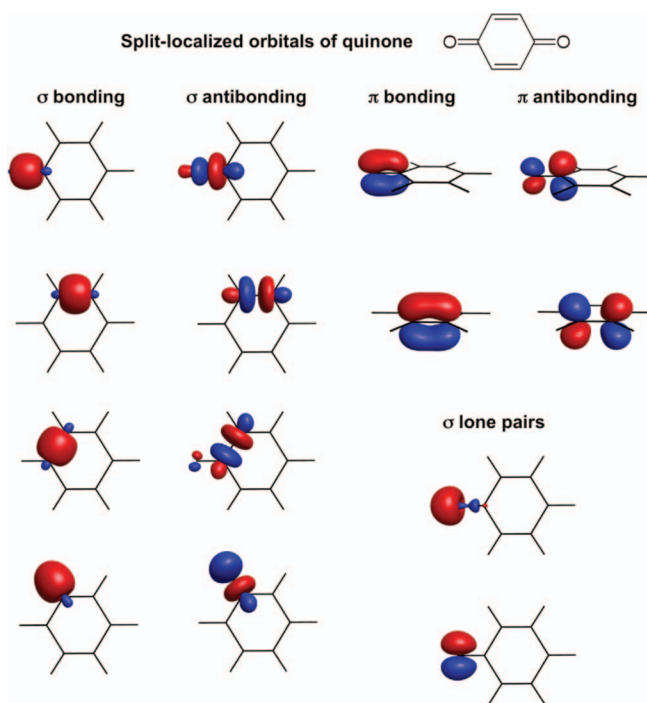


FIG. 6. Split-localized orbitals of quinone. The bonding orbitals and the lone pair orbitals are the localized occupied HF orbitals. The anti-bonding orbitals are the localized valence-virtual orbitals.

be effective in generating the non-dynamic valence-internal correlation expansion.

Consequently, the split-localized HF orbitals are particularly useful in furnishing an excellent starting point for formulating and calculating correlated wave functions that take into account *only* correlations in specific *local* regions of a larger molecule, e.g., for describing bond breaking or local spectroscopic properties, while treating other parts of the system at a lower level. This property is the basis of Fukui's frontier orbital analysis for chemical reactions.⁴

Quantitative information regarding the location of the various split-localized orbitals in a molecule can be generated, without inspection of contour maps (which are only qualitative in any case), by the procedure described in Sec. V B 4. The *atomic* contributions to the split-localized orbitals in quinone are given in Table VI, which lists all contributions of 0.01 and larger. The values (i) show that each of the split-localized orbitals is essentially confined to two atoms and (ii) exhibit the polarizations of the various bonds. Also apparent is the slight bonding between the oxygen p-lone pair and the $C_1C_2\sigma$ bond as well as the weak conjugation between the π -bonds.

2. Determination of split-localized orbitals

The objective of the split-localized orbitals is to reflect as closely as possible the bonding information that is contained in the *first-order* density matrix and, hence, exhibited in the population-bond-order matrix between quasi-atomic orbitals, as discussed in Sec. V B. To this end, the following criterion is posited for the determination of split-localized orbitals:

TABLE VI. Quasi-atomic contributions to the symmetry-unique split-localized orbitals of quinone, as measured by the second equation of Eq. (5.6). Contributions less than 0.01 are not shown.^a

| Spl-Loc | O atom | C ₁ atom | C ₂ atom | C ₃ atom | H atom |
|------------------------------------|--------|---------------------|---------------------|---------------------|--------|
| (O ₁ σℓ) | 1.00 | | | | |
| (O ₁ pℓ) | 0.95 | 0.02 | 0.01 | | |
| (C ₁ O ₁ σ) | 0.61 | 0.39 | | | |
| (C ₁ O ₁ σ)* | 0.39 | 0.61 | | | |
| (C ₁ O ₁ π) | 0.65 | 0.33 | | | |
| (C ₁ O ₁ π)* | 0.32 | 0.62 | 0.02 | 0.01 | |
| (C ₁ C ₂ σ) | | 0.49 | 0.50 | | |
| (C ₁ C ₂ σ)* | 0.02 | 0.49 | 0.48 | | |
| (C ₂ C ₃ σ) | | | 0.50 | 0.50 | |
| (C ₂ C ₃ σ)* | | | 0.50 | 0.50 | |
| (C ₂ C ₃ π) | | 0.02 | 0.47 | 0.47 | |
| (C ₂ C ₃ π)* | | | 0.49 | 0.49 | |
| (C ₂ Hσ) | | | 0.58 | | 0.41 |
| (C ₂ Hσ)* | | | 0.41 | | 0.58 |

^aCapital letters indicate atoms. As illustrated in Figure 2, atom C₁ is the neighbor of atom O₁. Atom C₂ is the neighbor of atoms C₁ and C₃. The first column lists the split-localized orbitals. Each split-localized orbital is labeled by the atoms on which it is predominantly located and by its symmetry σ or π. Asterisks indicate the localized antibonding VVOs. Absence of asterisks indicates the localized occupied bonding and lone pair MOs. The calculation of the contributions is described in the text.

Each localized occupied molecular orbital as well as each localized valence-virtual orbital shall cover as few of the oriented quasi-atomic orbitals as possible (subject to maintaining orbital orthogonality).

As explained in Subsection A 2 of the Appendix, this criterion is achieved by maximizing the sum $\sum_n \sum_a \sum_n (D_{Aa,n})^4$, where $D_{Aa,n}$ denotes the projection of the localized orbital ψ_n on the oriented quasi-atomic orbital $|Aa\rangle$. The algorithm to accomplish the maximization is described in Subsection A 2 of the Appendix. It is very fast. The idea for this algorithm was derived from our previous method for the chemical orientation of quasi-atomic orbitals¹⁹ (see Sec. V B 3). In fact, the algorithm is also related to the localization method of Pipek and Mezey.⁴³ The localized orbitals displayed in Figure 6 were obtained in this manner.

The new localization method differs from previous ones in that, by virtue of using the oriented quasi-atomic orbitals, bonding information from the density matrix is taken into account. Previous localization methods did not do so. Lennard-Jones and Pople⁴⁰ had proposed the criterion of maximizing the sum of the self-energies of the localized orbitals. Edmiston and Ruedenberg⁴¹ had suggested the criterion of maximizing expressions obtained by replacing, in the self-energy, the term $(1/r_{12})$ by the term $(-r_{12})^2$ or by the term (δ_{12}) . The $(r_{12})^2$ criterion had been simplified and further developed by Boys,⁴⁴ who had shown that it is equivalent to maximizing the sum of the squares of the distances between the centroids of the orbitals. The (δ_{12}) criterion had been implemented by von Niessen.⁴⁵ A criterion based on Mulliken populations with respect to the atomic orbital basis (i.e., the BAOs of Sec. III B 1) had been formulated by Pipek and Mezey.⁴³ The quantitative implementation of all of these criteria had been made possible by the algorithm of Edmiston and Ruedenberg.^{41,43,46} (For the

$(1/r_{12})$ criterion, it had been made efficient by Raffanetti⁴⁷). More recently, an alternative algorithm for these criteria has been proposed by Subotnik, Shao, Liang, and Head Gordon.⁴⁸ For a criterion proposed earlier by Foster and Boys,⁴⁹ viz. the maximization of the *product* of the squares of the distances between the orbital centroids, no viable algorithm has so far been found. A localization method for external orbitals without reference to atomic centers has recently been proposed by Jørgenson and co-workers.⁵⁰

These older localization methods were employed in all previous work on localization in the occupied and in the VVO space. While this route, which is indicated by (6') in Figure 1, leads to similar shapes for most orbitals, there are notable differences. For instance, use of the $(1/r_{12})$ or the $(r_{12})^2$ criterion yields “rabbit-ear” type lone-pair orbitals on the oxygen atoms in quinone instead of the σ- and p-type lone pairs shown in Figure 6. Since the p-lone pair is weakly bonded to the ring, whereas the σ-lone pair is not, the orbitals obtained by the new localization method seem chemically more informative in this molecule.

VI. VALENCE-EXTERNAL SPACE

The final step in the orbital analysis is concerned with the external orbitals, which are needed for the recovery of dynamic electron correlation. In the past, two types of external orbitals have been found to be useful for that purpose: natural external orbitals and quasi-atomic external orbitals. Natural external orbitals generate a rapid CI convergence and are effective in smaller molecules. They are less practical in larger molecules since they typically extend over the entire system and, therefore, do not take advantage of the short-range character of electron correlation. In that respect, quasi-atomic external orbitals, as suggested by Pulay⁵¹ and developed by Werner and co-workers,⁵² have proven to be useful. The determination of such orbitals in the context of the present scheme is indicated by 7 in the outline of Figure 1. The resulting orbitals are analogous to the set of “hard virtual orbitals” that Subotnik, Dutoi, and Head-Gordon²⁶ obtained by another route.

A. Atomic localization

The delocalized *canonical* valence-external orbitals were simultaneously determined with the valence-virtual orbitals as described in Sec. V A 1 (Step 3 of Figure 1). From the canonical external orbitals, a *quasi-atomic* basis is now determined in the valence-external orbital space (Step 7 of Figure 1). The objective is achieved by the following SVD.

The basal atomic orbitals (BAOs), which are defined in Sec. III B 1, are orthogonalized on a given single atom A. Then, one forms the overlap matrix

$\langle VEn | Aa^\perp \rangle$, where $|VEn\rangle$ runs over *all valence-external orbitals in the molecule* and $|Aa^\perp\rangle$ runs over *all orthogonal BAOs on atom A*.

For this rectangular overlap matrix, the SVD is performed. Since the total number of valence-external orbitals is larger than the number of BAOs on any one atom, the number of non-zero singular values is equal to the number of BAOs on the atom A. One chooses the N_{VEA} singular vectors in the external space that correspond to the largest singular values, where N_{VEA} is the number of external orbitals on atom A, viz.:

$$N_{\text{VEA}} = (\text{total \# of BAOs on A}) - (\text{\# of core orbitals on A}) \\ - (\text{\# of valence-internal orbitals on A}).$$

If the *molecular* symmetry group allows for degenerate representations, this criterion must be amended by the additional condition that *all or none* of a set of orbitals with exactly the same singular value must be selected so that the external orbitals span a representation of the molecular symmetry group. In order to accomplish this, one or several *non-degenerate* singular vectors near the bottom of the list (i.e., corresponding to small singular values) may have to be excluded even though these excluded non-degenerate singular values are larger than the included degenerate singular value(s).

B. Ordering of quasi-atomic external orbital basis

In the external orbital space of a given atom A, which is obtained as described in Sec. VI A, it is desirable to determine an orbital basis that yields effectively converging contributions to the correlation energy. This objective is most likely achieved by generating external orbitals of decreasing absolute overlap with the occupied valence-internal orbital space, since strong correlation interactions generally result from correlating orbitals that have large absolute overlaps with the correlated orbitals.

In the present analysis, such an orbital basis is obtained by using the exchange integral criterion, which was used in 1972 by Das and Wahl⁵³ for initiating MCSCF calculations and by Whitten⁵⁴ for CI calculations. To this end, the valence-internal orbitals $|A^*\alpha\rangle$ of the highly accurate atomic minimal basis set (AAMBS) of atom A (see Sec. III B 2) are projected on the BAO basis of atom A and renormalized. Then the following population weighted sum of exchange integral matrices is formed:

$$\Xi_{jk}^A = \sum_{\alpha} p_{A\alpha, A\alpha} [v_j^A(A\alpha^+) | v_k^A(A\alpha^+)]. \quad (6.1)$$

Here, $[f|g]$ denotes the electron repulsion integral as defined by Eq. (3.5), and

- v_j^A and v_k^A denote the external quasi-atomic orbitals on atom A determined as described in Sec. VI A;
- $(A\alpha^+)$ are the normalized projections of the valence-internal AAMBS orbitals $|A^*\alpha\rangle$ of atom A [see Eq. (3.3)] onto the BAO basis of atom A;
- $|A\alpha\rangle$ are the canonical quasi-atomic internal orbitals on atom A *before* orientation, deduced as discussed in Sec. V B 1 from the valence-internal AAMBS orbitals $|A\alpha^+\rangle$.

- $p_{A\alpha, A\alpha}$ are the populations that are defined for these canonical quasi-atomic valence-internal orbitals $|A\alpha\rangle$ by Eq. (5.2) in Sec. V B 2;
- \sum_{α} runs over all canonical quasi-atomic valence-internal orbitals $|A\alpha\rangle$ on atom A.

The matrix Ξ^A is diagonalized. The linear combinations, say ϕ_n^A , of the external orbitals v_j^A that diagonalize Ξ^A are then ordered according to decreasing magnitudes of the eigenvalues ξ_n^A , which are equal to the values of $\sum_{\alpha} p_{A\alpha, A\alpha} [\phi_n^A(A\alpha^+) | \phi_n^A(A\alpha^+)]$ and always positive.

This ordering is performed for each atom. There may exist alternative, possibly more effective, ordering schemes.

C. Weighted inter-atomic orthogonalization

The ordered external orbitals, which are determined by the preceding procedure, are orthogonal within each quasi-atomic set but not between the sets of different atoms. Here, orthogonalization by $S^{-1/2}$ would seem somewhat unsatisfactory in as much as this type of orthogonalization treats all orbitals on an equal footing and is therefore expected to degrade the compactness of the tight orbitals without significantly improving the compactness of the diffuse orbitals. This argument was advanced by Subotnik, Dutoi and Head-Gordon²⁶ in connection with their hard virtual orbitals.

In the present scheme, this problem is addressed by using the *weighted* modification of the $S^{-1/2}$ orthogonalization derived by Carlson and Keller,⁵⁵ who proved the following theorem. If the f_n form a set of non-orthogonal orbitals and the g_n are the orthogonal orbitals that minimize the weighted average of mean square deviations,

$$\sum_n w_n \int dv (g_n - f_n)^2, \quad (6.2)$$

where the w_n are arbitrary weights, then this orthogonal orbital set ψ_n is given by the transformation,

$$g_m = \sum_n f_n T_{nm}, \quad T = W (W S W)^{-1/2}, \\ W_{nm} = w_n \delta_{nm}, \quad S_{nm} = \langle f_n | f_m \rangle. \quad (6.3)$$

In the present case, the f_n are the non-orthogonal external orbitals ϕ_n^A of Sec. VI B, and the g_n are the orthogonal external orbitals ψ_n^A .

The choice of the weights in Eq. (6.3) is based on the eigenvalues of the exchange diagonalization that determined the ordering of the quasi-atomic external orbitals in Sec. VI B. Orbitals ϕ_n^A with larger exchange eigenvalues ξ_n^A are to be assigned larger weights w_n^A , so that, according to Eq. (6.2), the corresponding orthogonal orbitals ψ_n^A will deviate less from the non-orthogonal orbital ϕ_n^A than will be the case for orbitals ϕ_n^A with small eigenvalues ξ_n^A . This objective is accomplished by choosing the weights to be the following functions of the exchange eigenvalues ξ_n^A :

$$w_n^A = w (x_n^A) \quad x_n^A = \xi_n^A / \xi_{\text{max}}^A. \quad (6.4)$$

where ξ_{max}^A is the largest eigenvalue on atom A and the weighting function is

$$w(x) = 1 + 99(a+1)/(a+x^{-p}). \quad (6.5)$$

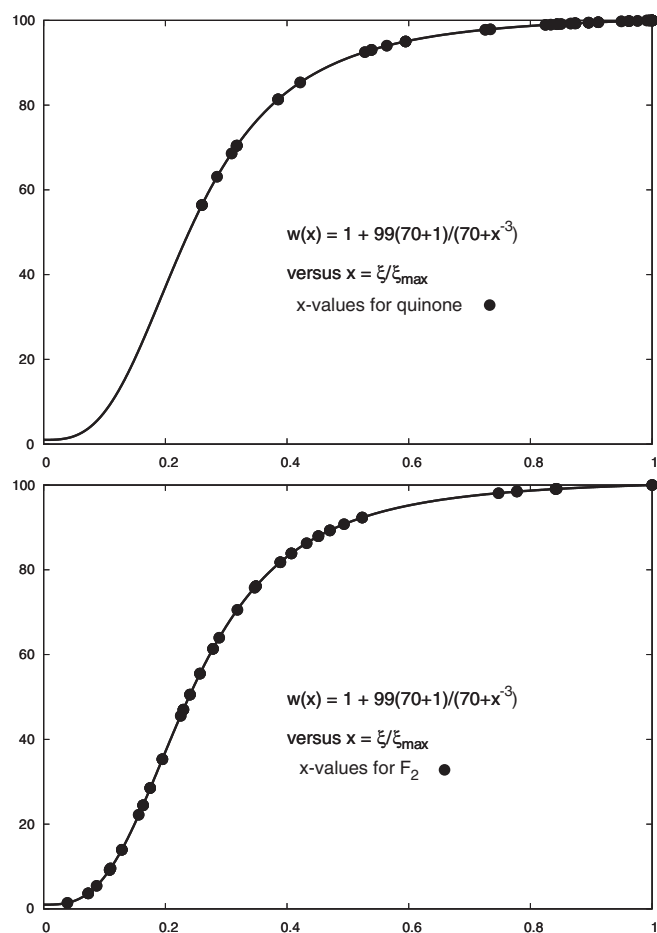


FIG. 7. Weights for the orthogonalization of external orbitals as functions of relative orbital size, measured by ratios of exchange integral eigenvalues. Upper panel: Quinone (cc-pVDZ basis). Lower panel: F_2 (cc-pVQZ basis).

Manifestly, w runs from 1 to 100 if the respective ξ_n^A run from 0 to ξ_{\max}^A . After examining several cases, it seemed reasonable to choose the parameters a and p such that $w(0.5) \approx 0.9$, $w(0.25) \approx 0.5$, and $w(0.1) \approx 0.1$, which is accomplished by the parameter values $a = 70$, $p = 3$. Whether these choices are the best remains to be seen.

Figure 7 shows how the function (6.5) determines weights for the x_n values in quinone (upper panel) and in the F_2 molecule (lower panel). The quinone data come from a calculation with a double-zeta basis, for which all external orbitals remain relatively compact, as shown by the ratios ξ_n/ξ_{\max} , which are the x -coordinates of the data points. The F_2 data were obtained with a quadruple-zeta basis, where the ratios $x_n = \xi_n/\xi_{\max}$ along the x -axis exhibit a large compactness-diffuseness range of the external orbitals, thereby yielding a wider spread in the weights w along the y -axis.

Figure 8 displays quasi-atomic external orbitals on the four symmetry-unique atoms of the quinone molecule for the cc-pVDZ basis. On the H atom, all four external orbitals are shown; on the other atoms the first six are shown. Also listed are the x_n values for each orbital.

For molecular calculations that are based on very large sets of working BAOs, it is often necessary to delete some eigenfunctions of the BAO overlap matrix with very small

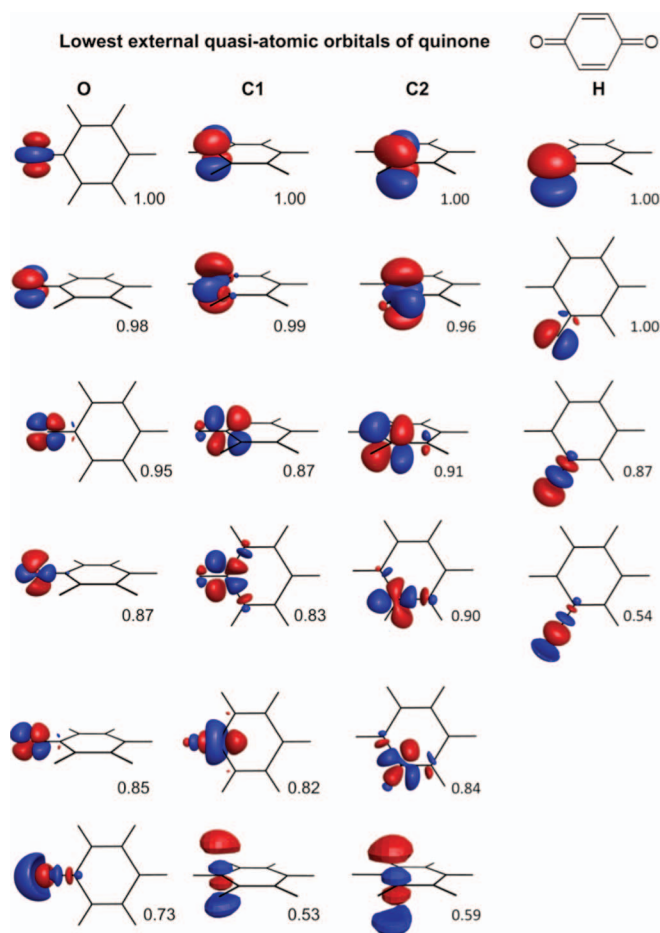


FIG. 8. Lowest quasi-atomic external orbitals of quinone. Each column contains the orbitals for the atom indicated at the top, shown in the order of decreasing x_n values [see Eq. (6.4)], which are listed next to each orbital.

eigenvalues in order to avoid near linear dependencies. A corresponding reduction is then also required for the external QUAO basis. Exploratory experience suggests that the number of *localized* external QUAOs that have to be deleted to this end may be slightly larger than the number that has to be deleted from a *delocalized* MO basis. This problem will be addressed in a separate paper.

VII. SUMMARY

A system of inter-related orbital transformations, in particular localizations, is created that generates a finite set of orbitals with the following attributes: (i) the molecular electronic wave function can be expressed in terms of these orbitals; (ii) the intrinsic atomic structure of the molecule is exhibited; (iii) the internal orbitals change very little as the working basis increases; and (iv) the bonding pattern is characterized. The orbital space is divided into an internal space, which has minimal-basis-set characteristics and contains the short-range chemical information, and an external space that is required for dynamic correlations. In both spaces quasi-atomic orbital bases are determined.

Bonding patterns are displayed by the density matrix between oriented quasi-atomic orbitals as well as by split-localized orbitals in the internal space. An illustrative

application to quinone yields bond orders that (i) confirm the primary σ - and π -bonds, (ii) show the absence of aromaticity, (iii) exhibit weak conjugations between neighboring π -bonds, (iv) reveal weak hyperconjugative bonding between oxygen lone-pairs between and vicinal CC-s-bonds.

New methods are developed for determining quasi-atomic orbitals as well as localizing occupied and virtual orbitals. The details of the analysis are formulated for Hartree-Fock wave functions. Formulations for correlated wave function and further applications will be given in subsequent papers. The analysis is available as a module in the GAMESS program suite.^{29,30}

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APPENDIX: ALGORITHMS FOR LOCALIZATIONS

1. Identifying the subspace of an orbital space that is closest to a different orbital space of lower dimension by means of the singular value decomposition of the overlap matrix

Let the orthonormal functions $f_j(x)$ span the function space F of dimension $\text{Dim}(F)$ and let the orthonormal functions $g_a(x)$ span the function space G of dimension $\text{Dim}(G)$. The overlap matrix between these two bases

$$S_{ja} = \langle f_j | g_a \rangle, \quad j = 1, \dots, \text{Dim}(F), \quad a = 1, \dots, \text{Dim}(G), \quad (\text{A1})$$

is not symmetric and, in general, rectangular.

Take first the case that the space F is larger than the space G, i.e., $\text{Dim}(F) > \text{Dim}(G)$. Consider a normalized function $\phi(x)$ in the space F

$$\phi(x) = \sum_j f_j(x) C_j, \quad j = 1, \dots, \text{Dim}(F). \quad (\text{A2})$$

The projection of ϕ onto the basis G is

$$\begin{aligned} \text{proj}(\phi) &= \sum_a g_a \langle g_a | \phi \rangle = \sum_a g_a \sum_j \langle g_a | f_j \rangle C_j \\ &= \sum_a g_a \sum_j C_j S_{ja}. \end{aligned} \quad (\text{A3})$$

To find that function ϕ in the space F that has the largest projection in the space G, one has to maximize the norm of

$\text{proj}(\phi)$, i.e.,

$$\begin{aligned} \langle \text{proj}(\phi) | \text{proj}(\phi) \rangle &= \sum_a \left(\sum_j C_j S_{ja} \right)^2 \\ &= \sum_j \sum_k C_j (\mathbf{S}\mathbf{S}^\dagger)_{jk} C_k, \end{aligned} \quad (\text{A4})$$

where \mathbf{S}^\dagger is the transpose of \mathbf{S} . The maximum of this expression is reached for the vector $\{C_1, C_2, \dots\}$ that is the eigenvector with the largest eigenvalue obtained by diagonalizing the matrix $\mathbf{S}\mathbf{S}^\dagger$, i.e., from

$$\sum_j \sum_k U_{jn} (\mathbf{S}\mathbf{S}^\dagger)_{jk} U_{km} = \lambda_n \delta_{nm}, \quad (\text{A5})$$

and this eigenvalue is the largest projection. (By virtue of Eq. (A4) all eigenvalues are non-negative.) The eigenvector with the second largest eigenvalue yields the coefficients for the function ϕ' in the space F that has the largest projection in that part of the space G that is orthogonal to the projection of ϕ , and so on. The matrix $(\mathbf{S}\mathbf{S}^\dagger)$ is of dimension $\text{Dim}(F) \times \text{Dim}(F)$. But since $\text{Dim}(G)$ is smaller than $\text{Dim}(F)$, only at most $\text{Dim}(G)$ of its eigenvectors have non-zero eigenvalues. The diagonalization manifestly selects that orthogonal basis in the larger space F for which the sum of the projections into the smaller space G is maximal. The sum of these projections is the sum of the eigenvalues λ_n .

In the converse case, that the space F is smaller than the space G, i.e., $\text{Dim}(F) < \text{Dim}(G)$, consider a normalized function $\gamma(x)$ in the space G

$$\gamma(x) = \sum_a g_a(x) k_a, \quad a = 1, \dots, \text{Dim}(G). \quad (\text{A6})$$

According to analogous reasoning, the function γ in the space G for which the norm of the projection into the space F is largest is obtained by the vector $\{k_1, k_2, \dots\}$ that is the eigenvector with the largest eigenvalue of the matrix $\mathbf{S}^\dagger\mathbf{S}$, i.e., resulting from the diagonalization.

$$\sum_a \sum_b V_{ac} (\mathbf{S}^\dagger\mathbf{S})_{ab} V_{bd} = \lambda_c \delta_{cd}, \quad (\text{A7})$$

The eigenvector with the second largest eigenvalue yields the coefficients for the function γ' in the space G that has the largest projection in that part of the space F that is orthogonal to the projection of γ , and so on. The matrix $(\mathbf{S}\mathbf{S}^\dagger)$, which is of dimension $\text{Dim}(G) \times \text{Dim}(G)$, has at most only $\text{Dim}(F) < \text{Dim}(G)$ non-zero eigenvectors. The diagonalization now selects that orthogonal basis in the larger space G for which the sum of the projections into the smaller space F is maximal.

The singular value decomposition⁵⁶ (SVD) of the overlap matrix \mathbf{S} yields two orthogonal matrices \mathbf{U} and \mathbf{V} that transform the matrix \mathbf{S} into a diagonal matrix $\mathbf{\Lambda}$, i.e.,

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{V} = \mathbf{\Lambda} = \{\Lambda_\nu \delta_{\nu\mu}\}, \quad (\text{A8})$$

where the singular values Λ_ν can be chosen positive by using appropriate phases for U and V. From Eq. (A8) follow the two diagonalizations:

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{S}^\dagger \mathbf{U} = \mathbf{\Lambda}^2 \text{ and } \mathbf{V}^\dagger \mathbf{S}^\dagger \mathbf{S} \mathbf{V} = \mathbf{\Lambda}^2. \quad (\text{A9})$$

The SVD yields therefore the solutions to *both* projection maximizations discussed above, regardless of the dimensions

of the spaces F and G. Moreover, the SVD equation (A8) is equivalent to the equation

$$\langle \phi_v | \gamma_\mu \rangle = \Lambda_v \delta_{v\mu}, \quad (\text{A10})$$

where ϕ_v and γ_μ are the orthogonal “singular bases,”

$$\phi_v(x) = \sum_j f_j(x) U_{jv} \text{ and } \gamma_\mu(x) = \sum_a g_a(x) V_{a\mu}, \quad (\text{A11})$$

in the spaces F and G, respectively. Thus, in all cases, the projection of a singular function of one space into the other space is parallel to a singular function in the other space, the singular value being the value of the projection.

The singular value decomposition achieves therefore the *optimal alignment* of the orthonormal bases in the two spaces, as measured by mutual projections. This feature of the SVD is specific to its application to overlap matrices. It is furthermore apparent that the reasoning in Eqs. (A3) and (A4), and (A7) regarding maximizing the projections is contingent on the premise that projections are identical with overlap integrals, which is only valid for orthogonal bases. The maximization properties of the projections follow therefore from the mini-max properties of the diagonalizations in Eq. (A9) *only if both, the basis in F as well as the basis in G, are chosen to be orthonormal*. Equivalently, the same procedure can of course be formulated for non-orthogonal bases by using the projection operators for such bases, which involve the inverse metric overlap matrices. The resulting orbital spaces will be the same.

The use of the SVD to identify, in a large (e.g., molecular) orbital space, a subspace that is “closest” to a different (e.g., atomic) orbital space of a smaller dimension was introduced in Ref. 21. Previously, the SVD had been used in different quantum chemical contexts. Amos and Hall⁵⁷ had analyzed the relation between the α and β molecular orbitals in a single-determinant unrestricted Hartree-Fock wave function by means of the singular value decomposition. They coined the term *corresponding orbitals* for the orbitals that result from the SVD. King, Stanton, Kim, Wyatt, and Parr⁵⁸ showed that corresponding orbitals offer computational advantages and interpretative insights when dealing with Slater determinants of identical dimensions, but constructed with molecular orbitals from mutually non-orthogonal orbital spaces.

2. Localization with respect to quasi-atomic orbitals

The premise is that, in the *valence-internal* space, (i) the canonical or oriented *quasi-atomic* basis χ_α has been determined, and (ii) there exists a *subspace* of interest in the valence-internal space, which is spanned by an orbital basis ϕ_v , for instance the space of the VVOs or the space of the occupied HF-MOs. The number of orbitals ϕ_v is thus less than the number of QUAOs.

The objective is to find, in the subspace spanned by the ϕ_v , a new orthogonal basis ψ_n in which *each basis orbital covers as few QUAOs χ_α as possible*.

Let the expansion of ϕ_v in terms of the QUAOs be

$$\phi_v = \sum_\alpha \chi_\alpha C_{\alpha v} \quad C_{\alpha v} = \langle \chi_\alpha | \phi_v \rangle \quad (\text{A12})$$

and let the new basis be given by the orthogonal transformation

$$\psi_n = \sum_v \phi_v T_{vn}. \quad (\text{A13})$$

The expansion of the new basis in terms of the QUAOs is then

$$\psi_n = \sum_\alpha \chi_\alpha R_{\alpha n}, \quad \text{where} \quad R_{\alpha n} = \sum_v C_{\alpha v} T_{vn}. \quad (\text{A14})$$

It is relevant that the orthogonality of **T** entails the invariance $\sum_\alpha (R_{\alpha n})^2 = \sum_\alpha (C_{\alpha v})^2 = 1$ for all n and v . By virtue of this invariance, maximization of $\sum_\alpha (R_{\alpha n})^4$ with respect to the elements of **T** will generate a few large and many small coefficients $R_{\alpha n}$. Since such a “disproportionation” is desired for all new basis functions ψ_n , the criterion for determining **T** is chosen to be the maximization of

$$\begin{aligned} \sum_n \sum_\alpha (R_{\alpha n})^4 &= \sum_n \sum_\alpha \left(\sum_v C_{\alpha v} T_{vn} \right)^4 \\ &= \sum_\kappa \sum_\lambda \sum_\mu \sum_\nu P_{\kappa\lambda\mu\nu} J_{\kappa\lambda\mu\nu} \end{aligned} \quad (\text{A15})$$

where

$$\begin{aligned} P_{\kappa\lambda\mu\nu} &= \sum_\alpha C_{\alpha\kappa} C_{\alpha\lambda} C_{\alpha\mu} C_{\alpha\nu}, \\ J_{\kappa\lambda\mu\nu} &= \sum_n T_{\kappa n} T_{\lambda n} T_{\mu n} T_{\nu n}. \end{aligned} \quad (\text{A16})$$

These expressions are analogous to expressions encountered in the determination of oriented quasi-atomic orbitals. The maximization is therefore achieved by the algorithm developed in that context by Ivanic, Atchity, and Ruedenberg.¹⁹ The problem is solved by a sequence of 2×2 Jacobi rotations. If, for instance, the rotation,

$$\psi_1 = \phi_1 \cos \gamma + \phi_2 \sin \gamma, \quad \psi_2 = -\phi_1 \sin \gamma + \phi_2 \cos \gamma, \quad (\text{A17})$$

is considered, then Eqs. (A15) and (A16) simplify to

$$\begin{aligned} \sum_n \sum_\alpha (R_{\alpha n})^4 &= P_{1111} J_{1111} + P_{2222} J_{2222} \\ &\quad + 4P_{1112} J_{1112} + 4P_{2221} J_{2221} \\ &\quad + 6P_{1122} J_{1122}, \end{aligned} \quad (\text{A18})$$

where

$$\begin{aligned} P_{1111} &= \sum_\alpha (C_{\alpha 1})^4, \quad P_{2222} = \sum_\alpha (C_{\alpha 2})^4, \\ P_{1122} &= \sum_\alpha (C_{\alpha 1} C_{\alpha 2})^2, \end{aligned} \quad (\text{A19a})$$

$$P_{1112} = \sum_\alpha (C_{\alpha 1})^3 C_{\alpha 2}, \quad P_{2221} = \sum_\alpha (C_{\alpha 2})^3 C_{\alpha 1}, \quad (\text{A19b})$$

and

$$J_{1111} = J_{2222} = (3 + \cos 4\gamma) / 4, \quad (\text{A20a})$$

$$J_{1112} = -J_{2221} = (\sin 4\gamma) / 4, \quad J_{1122} = (1 - \cos 4\gamma) / 4. \quad (\text{A20b})$$

The expression (A18) can thus be simplified to

$$\sum_n \sum_\alpha (R_{\alpha n})^4 = P + P_c \cos 4\gamma + P_s \sin 4\gamma, \quad (\text{A21})$$

where

$$P = \frac{3}{4} (P_{1111} + P_{2222} + 2P_{1112}), \quad (\text{A22a})$$

$$P_c = \frac{1}{4} (P_{1111} + P_{2222} - 6P_{1112}), \quad P_s = P_{1112} - P_{2221}, \quad (\text{A22b})$$

so that finally

$$\sum_n \sum_\alpha (R_{\alpha n})^4 = P + Q \cos(4\gamma - \theta) \quad (\text{A23})$$

with

$$Q = [P_c^2 + P_s^2]^{1/2}, \quad \cos \theta = P_c/Q, \quad \sin \theta = P_s/Q. \quad (\text{A24})$$

As discussed in Ref. 19, the appropriate choice for the maximum is $\gamma_{\max} = \theta/4 + n\pi/2$, with n being the integer that yields γ_{\max} in the range $-\pi/4 < \gamma_{\max} < \pi/4$.

¹See, e.g., K. Ruedenberg and W. H. E. Schwarz, "Three millennia of atoms and molecules," *Pioneers of Quantum Chemistry*, ACS Symposium Series Vol. 1122, edited by E. T. Strom, A. K. Wilson (ACS, Washington DC, 2013).

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