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Going local: Exploring intricate bonding patterns with localized quasi-atomic orbitals

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Going local: Exploring intricate bonding patterns with localized quasi-atomic orbitals

by

Juan José Duchimaza Heredia

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2018

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DEDICATION

Dedicated to my family.

Gracias por sus sacrificios. Les quiero mucho.
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ABSTRACT

As chemists move to correct the approximations necessary to solve a quantum chemical problem, it remains an important task to extract all the information available from the theoretical treatment of a chemical system to keep methods grounded in chemical and physical principles. To this extent, it is important to build a bridge between theoretical methods and experimental observations. Such a bridge is developed by transformations of molecular orbitals into quasi-atomic orbitals (QUAOs) that align more with the concept of localized chemical bonds.

The QUAOs are the rigorous ab initio counterparts to the conceptual bond forming atomic hybrid orbitals of qualitative chemical reasoning. An automated analysis is developed to identify a QUAO as a bonding orbital, lone pair orbital, radical orbital, vacant orbital or orbital with intermediate character. The program determines the bonding characteristics of all QUAOs in a molecule on the basis of their occupations, bond orders, kinetic bond orders, hybridizations and local symmetries. These data are collected in a record and provide the information for a comprehensive understanding of the synergism that generates the bonding structure that holds the molecule together. Applications to a series of molecules exhibit the complete bonding structures that are embedded in their ab initio wave functions.

The origin of bonding in the rare gas containing molecules HXeCCH, HXeCCXeH, and HXeOXeH is explored using the QUAO analysis. The analysis suggests significant covalent bonding for Xe-Y (Y = C, O) as well as Xe-H, both bonds using the same pσ-type orbital on Xe. These covalent interactions are established by substantial charge shifts from Xe to Y as well as to H. Accordingly, a covalent three-
center four-electron bond links the atoms H-Xe-Y. Based on the analysis, electrostatic interactions do not play a significant role in the Xe-Y or Xe-H bonding.

A comprehensive analysis of the bonding structure of the disilyl zirconocene amide cation \( \{ \text{Cp}_2\text{Zr}[\text{N(SiHMMe}_2}_2] \}^+ \) is conducted by application of the QUAO analysis. An emphasis is placed on describing a previously characterized three-center two-electron interaction between zirconium, hydrogen, and silicon that presents structural and spectroscopic features similar to that of agostic bonds. By expressions of the first order density matrix in terms of the QUAOs, bonds orders, kinetic bond orders, and the extent of transfer of charge become available to determine the electronic nature of the Zr-H-Si bond. The QUAOs demonstrate the importance of vicinal interactions in the stabilization of the molecule. In addition, the evolution of the QUAOs during reactions with Lewis bases reveals the role of the Zr-H-Si interaction in facilitating the reaction.
CHAPTER 1. GENERAL INTRODUCTION

Overview

For centuries, scientists have developed theories, models, and methods to explain natural phenomena. Drawing from observations gathered by numerous scientists and philosophers over millennia, the concept that all physical matter is composed of atoms and electrons subsequently led to the study of how these particles interact. Observations in the mid-19th and early 20th centuries that could not be described using classical physics led to the development of quantum chemistry. The concept that electrons occupy orbitals is central to chemistry, and it arises from approximations to describe the behavior of electrons subject to quantum mechanics in a molecular system.

As chemists move to correct the approximations necessary to solve a quantum chemical problem, it remains an important task to extract all the information available from the theoretical treatment of a chemical system to keep methods grounded in chemical and physical principles. To this extent, it is important to build a bridge between theoretical methods and experimental observations. The present dissertation is concerned with developing such a bridge by transformations of molecular orbitals into orbitals that align more with the concept of localized chemical bonds.

Dissertation Organization

Chapter 1 provides a general overview of quantum chemistry and describes the relevant details of the methods used in subsequent chapters. Chapter 2 presents a criteria-based method to determine the chemical role that an orbital plays within a molecule.
Chapter 3 uses an intrinsically localized atomic orbital analysis to describe the bonding of xenon-containing molecules. Chapter 4 is an analysis of the bonding in a transition metal molecule that exhibits non-classical M-H-Si bonding. Together, Chapter 3 and Chapter 4 provide new insights into bonding motifs of rare gases and transition metals. Chapter 5 provides general conclusions drawn from the work presented in the previous chapters.

**Theoretical Background**

The evolution of the energy of a non-relativistic system subject to quantum mechanics may be determined by the time-dependent Schrödinger equation,

\[ i \hbar \frac{\partial}{\partial t} \Psi(r,t) = \hat{H}\Psi(r,t), \]

where \( \Psi(r,t) \) is the wave function that describes the position \( r \) at time \( t \) of all electrons and nuclei in the system and \( \hat{H} \) is the Hamiltonian operator that corresponds to the total energy of the system. Using atomic units, the Hamiltonian has the form,

\[ \hat{H} = \hat{T} + \hat{V} = -\sum_i \frac{1}{2m_i} \nabla_i^2 + V(r_1, r_2, \ldots, r_N, t), \]

where \( m_i \) is the mass of particle \( i \), \( \nabla_i^2 \) is the Laplacian with respect to the coordinates of particle \( i \), and \( V(r_1, r_2, \ldots, r_N, t) \) is the potential energy function acting on all \( N \) particles in the system.

For time-independent problems in which the potential does not vary with time, i.e. \( V(r_1, r_2, \ldots, r_N, t) = V(r_1, r_2, \ldots, r_N) \), the wave function must reflect that the probability of finding a particle at position \( r \) is independent of time. Thus, the wave function is written as a product \( \Psi(r,t) = \psi(r) \psi(t) \). With some mathematical manipulation, the time-independent Schrödinger equation is derived as\(^1\,^2\)
\[ \hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \]  

where \( E \) is the energy of the system.

The Hamiltonian for a chemical system with \( N \) electrons and \( M \) nuclei has the general form

\[ \hat{H} = -\sum_{i} \frac{1}{2} \nabla_{i}^{2} - \sum_{A} \frac{1}{2m_{A}} \nabla_{A}^{2} - \sum_{i} \sum_{A} \frac{Z_{A}}{r_{iA}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} + \sum_{A} \sum_{B>A} \frac{Z_{A}Z_{B}}{r_{AB}}, \]

where \( m_{A} \) is the mass of nucleus \( A \), \( Z_{A} \) is the atomic number of nucleus \( A \), \( r_{iA} \) is the distance between electron \( i \) and nucleus \( A \), \( r_{ij} \) is the distance between electrons \( i \) and \( j \), and \( r_{AB} \) is the distance between nuclei \( A \) and \( B \). The first two terms in the Hamiltonian in eq. (4) are the kinetic energy operators for the electrons and nuclei, respectively. The third term represents the Coulomb attraction between electrons and nuclei, while the last two terms represent the repulsion between electrons and between nuclei, respectively.

Nuclei move much more slowly than electrons. It is therefore reasonable to consider the electrons to move in a field of fixed nuclei. This assumption is the basis of the Born Oppenheimer approximation.\(^3\) Under the Born Oppenheimer approximation, the kinetic energy of the nuclei can be neglected and the repulsion between the nuclei is constant, and Eq. (4) can be simplified to the electronic Hamiltonian,

\[ \hat{H}_{\text{elec}} = -\sum_{i} \frac{1}{2} \nabla_{i}^{2} - \sum_{i} \sum_{A} \frac{Z_{A}}{r_{iA}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}}. \]

The solution to the corresponding Schrödinger equation involving the electronic Hamiltonian,

\[ \hat{H}_{\text{elec}}\psi_{\text{elec}} = E_{\text{elec}}\psi_{\text{elec}}, \]

is the electronic wave function \( \psi_{\text{elec}} = \psi \) with corresponding electronic energy \( E_{\text{elec}} \).
For systems with more than one electron, an exact analytic solution to the electronic Schrödinger equation cannot be determined because the electron-electron repulsion term is inseparable. For multi-electron systems it is therefore necessary to apply a method to approximate the contribution of the electron-electron repulsion term to the energy of the system.

The central starting point for most methods to account for electron-electron repulsion is the Hartree-Fock approximation. Rather than calculating the explicit electron-electron interaction, the Hartree-Fock method uses a mean field approximation, in which the electron-electron repulsion is treated in an average way. In this way, eq. 5 can be resolved into a sum of one-electron Fock operators of the form

\[ \hat{f}(i) = \hat{h}(i) + v_{\text{HF}}(i), \] (7)

where

\[ \hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A^M Z_A r_{iA} \] (8)

is the one-electron core Hamiltonian that describes the kinetic energy and the potential energy of a single electron \(i\), and \(v_{\text{HF}}(i)\) is the potential experienced by electron \(i\) in the field of the remaining electrons. The potential \(v_{\text{HF}}(i)\) is defined as

\[ v_{\text{HF}}(i) = \sum_a^N \left[ \hat{J}_a(i) - \hat{K}_a(i) \right]. \] (9)

In eq. (9), the index \(i\) indicates an electron, whereas the summation index \(a\) is used to indicate a spin orbital \(\chi_a\). The Coulomb operator in eq. (9), given by \(\hat{J}_a(i)\), sums over all spin orbitals where \(b \neq a\) to obtain the total average potential acting on electron \(i\) in orbital \(\chi_a\). The operator \(\hat{K}_a(i)\) is called the exchange operator and it arises due to the
requirement that the wave function must be antisymmetric with respect to the interchange of the space and spin coordinates of any two electrons.

Applying the Fock operator to one-electron spin orbitals yields the eigenvalue problem

$$\hat{f}(i)\chi_a(i) = \varepsilon_a \chi_a(i)$$

where the spin orbital $\chi_a(i)$ is an eigenfunction of the Fock operator, and the eigenvalue $\varepsilon_a$ is corresponding energy of the orbital. In general, the spin orbitals have the form

$$\chi_i(x) = \begin{cases} 
\psi_j(r)\alpha(\omega) \\
\psi_j(r)\beta(\omega) 
\end{cases},$$

where the function $\psi_j(r)$ depends only on spatial coordinates and the functions $\alpha$ and $\beta$ correspond to a spin up or spin down, respectively. Since the Coulomb and exchange operators in $\psi_{HF}(i)$ have a functional dependence on the remaining orbitals, eq. (10) must be solved iteratively. The set of equations for all electrons in the system of the form shown in equation 10 is known as the Hartree-Fock equations.

The goal of Hartree-Fock is to find a wave function expressed in terms of the spin orbitals $\chi_a(i)$ that are solutions to eq. (10). Because the Fock operator is a one-electron operator, the solution to the Hartree-Fock problem may be written as a product of one-electron orbitals, i.e.

$$\Psi_{HF}(1,2,\ldots,N) = \chi_1(1)\chi_2(2)\ldots\chi_N(N),$$

where $N$ is the number of electrons, and the numbers in parenthesis represent the coordinates of the corresponding electron. The wave function in eq. (12) fails to satisfy the antisymmetry principle, which states that a many-electron wave function must be
antisymmetric with respect to the interchange of any two electrons. To satisfy the antisymmetry principle, it necessary to consider a determinant of one-electron orbitals,

\[
\Psi_{HF}(1,2,\ldots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1(1) & \chi_2(1) & \ldots & \chi_N(1) \\
\chi_1(2) & \chi_2(2) & \ldots & \chi_N(2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1(N) & \chi_2(N) & \ldots & \chi_N(N)
\end{vmatrix},
\]

(13)

The expression of the wave function in eq. (13) is known as a Slater determinant. A standard shorthand notation for the Slater determinant where the normalization constant and the coordinates are understood is

\[
\Psi_{HF}(1,2,\ldots,N) = \left| \chi_1 \chi_2 \ldots \chi_N \right|
\]

(14)

Since the correct form of the wave function is unknown, the first step in applying the Hartree-Fock method to a system is to take an initial guess at the orbitals. Throughout the Hartree-Fock method, the variational principle is invoked to minimize the energy with respect to the spin orbitals to obtain an approximation of the true energy of the system with the constraint that the orbitals remain orthonormal. That is, at every step, a spin orbital will be altered by an arbitrary amount, i.e. \( \chi_a \rightarrow \chi_a + \delta \chi_a \), so as to minimize the energy of a system.

Because \( \nu^{HF}(i) \) depends on all orbitals, a single iteration of solving eq. (10) for all orbitals will change the Fock operator and require the process to be repeated. Thus, the process of finding the solutions to the Hartree-Fock equations must be done an iteratively until the orbitals and orbital energies \( e_a \) become consistent within a certain threshold. For this reason, Hartree-Fock is also known as the self-consistent field (SCF) method.

A systematic way of obtaining an initial guess at the spin orbitals is to express the spatial part \( \psi_j(r) \) of the spin orbital as a linear expansion of \( K \) known basis functions \( \phi(r) \),
\[ \psi_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_{\mu} \]  

(15)

where \( C_{\mu i} \) is the expansion coefficient of the basis function \( \phi_{\mu}(r) \). Typically, the basis functions are chosen to be atomic orbitals and the functions \( \psi_i \) are molecular orbitals that are formed by a linear combination of atomic orbitals (LCAO). Finding the molecular orbitals \( \psi \) therefore reduces to a problem of determining the expansion coefficients \( C_{\mu i} \).

For a closed shell system, substituting the expansion in eq. (15) in place of the spin orbitals in eq. (10) using the index \( \nu \), multiplying by \( \phi_{\mu}(r) \) on the left, and integrating yields the Hartree-Fock-Roothaan equations\(^5\), expressed in matrix form as

\[ FC = SC\varepsilon , \]  

(16)

where elements of the matrices \( F \) and \( S \) are given by

\[ F_{\mu \nu} = \int dr_{1} \phi_{\mu}^{*}(1) f(1) \phi_{\nu}(1) \]  

\[ S_{\mu \nu} = \int dr_{1} \phi_{\mu}^{*}(1) \phi_{\nu}(1) \]  

(17)

and \( C \) and \( \varepsilon \) are the matrices of the LCAO coefficients and orbital energies, respectively. Using this approach, because the basis functions \( \phi(r) \) are already known, one must take an initial guess at the density matrix \( P \), which is derived from the definition of the charge density as \( |\psi_a(r)|^2 \) and is related to the coefficients \( C_{\mu \nu} \) by the equation

\[ P_{\mu \nu} = 2 \sum_{a}^{N/2} C_{\mu a}^{*} C_{a \nu} . \]  

(18)

If the basis functions \( \phi(r) \) are orthogonal, the matrix \( C \) in eq. (16) is solved for by diagonalizing the Fock matrix \( F \).

By averaging the electron-electron interaction, the Hartree-Fock method neglects the dynamic electron correlation energy, defined as the difference between the exact non-
relativistic energy and the Hartree-Fock energy. One approach to recovering the
correlation energy adds a perturbation $V_{\text{Pert}}$ associated with a parameter $\lambda$ to the Hartree-
Fock Hamiltonian $\hat{H}_{\text{HF}}$. The eigenfunctions and eigenvalues of the new perturbed
Hamiltonian can be expanded in a Taylor series in powers of $\lambda$.

$$
E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \ldots
$$

$$
\psi_i = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \ldots
$$

The goal of this Rayleigh-Schrödinger perturbation approach, known as Møller-Plesset
type (MP), when applied directly to the molecular orbitals, is to systematically
incorporate higher order corrections to improve the energy and wave function. The first
correction to the Hartree-Fock energy comes from the second order perturbation,

$$
E_0^{(2)} = \sum_n \frac{|\langle \psi_0^{(0)} | V | \psi_n^{(0)} \rangle|^2}{E_0^{(0)} - E_n^{(0)}}.
$$

An alternate improvement on the Hartree-Fock method, known as the multi-
configurational self-consistent field (MCSCF) method, is possible by accounting for
different configurations of electrons in the system. The MCSCF wave function is given by

$$
|\Psi_{\text{MCSCF}}\rangle = \sum c_i |\psi_i\rangle.
$$

Solving for the wave function then requires optimizing the expansion coefficients $c_i$ as
well as for the orbitals contained in $|\psi_i\rangle$. Choosing the configurations to include in a
MCSCF calculation is non-trivial and requires chemical intuition. One important
approach is the complete active space SCF (CASSCF) method, which uses orbitals that
are relevant for the process of interest in a systematic manner by performing a full CI in a chosen active space.

The molecular orbitals obtained through the Hartree-Fock method are also called the *canonical molecular orbitals*. The single-determinant multi-electron wave function in eq. (14) is invariant with respect to unitary transformations among the molecular orbitals. The canonical molecular orbitals are therefore one of many possible sets of orbitals to describe a molecular system. In general, the canonical molecular orbitals are delocalized over an entire molecule and are eigenfunctions of the symmetry operators of the molecular point group. A unitary transformation of the canonical molecular orbitals is often desirable for an analysis that is more intuitive with the chemist’s notion of a bond. The transformed orbitals are commonly referred to as *localized molecular orbitals*. One popular localization algorithm introduced by Edmiston and Ruedenberg\(^8\) considers the maximization sum of the orbital self-repulsion energy. The goal of the Edmiston-Ruedenberg localization algorithm is to find orbitals \( \lambda \) given by the unitary transformation,

\[
\lambda_v(r) = \sum_n \psi_n(r) T_{nv},
\]

such that the sum

\[
\sum_v [\lambda_v^2|\lambda_v^2] ,
\]

with

\[
[f|g] = \int dV_1 \int dV_2 r_{12}^{-1} f(1) g(2)
\]

is maximized.
Localized orbitals are a useful tool for intrinsically elucidating bonding patterns. More recently, West et al. introduced a coherent scheme to obtain from the molecular orbitals a set of atomic orbitals that are deformed by the environment of the molecule.\textsuperscript{9,10}

For this scheme, one requires the wave function expressed in terms of the canonical orbitals obtained by a HF or MCSCF calculation and a set of atomic orbitals for each atom in the system. The atomic orbitals used in this localization method are the \textit{accurate atomic minimal basis set} (AAMBS)\textsuperscript{11,12}, which have been pre-determined from high-level calculations on isolated atoms and are stored to avoid the need to re-calculate them. The orbitals obtained by this method, known as \textit{quasi-atomic orbitals} (QUAOs), are obtained by projections of the canonical orbitals onto the AAMBS. In this discussion, the QUAOs are given by $|\alpha_a\rangle$ to indicate the $a^{\text{th}}$ QUAOs on atom A.

The general scheme of the method is as follows:

1. The canonical orbitals separated into the core, valence, and virtual (or unoccupied) orbitals.

2. The QUAOs that span the space of the canonical core orbitals are determined.

3. A set of virtual valence orbitals (VVOs) is determined from the virtual orbitals. The VVOs are the set of orbitals that most closely correspond to the concept of the lowest unoccupied molecular orbitals.

4. A set of precursor QUAOs $|\alpha A\rangle$ that span the combined space of the valence orbitals and the VVOs are determined.

5. On each atom, the precursor QUAOs are transformed so as to make bonding interactions more manifest. This transformation yields \textit{oriented} QUAOs, or just QUAOs.
(6) By using linear combinations of the QUAOs, a set of orbitals that are localized over bonds instead of atoms is obtained.

In step (4), the charge density is expressed in terms of the QUAOs and gives rise to a matrix $p$ with elements $p_{A\alpha,B\beta}$. The matrix $p$ is known as the population-bond-order matrix because the diagonal elements $p_{A\alpha,A\alpha}$ correspond to the population of orbital $A\alpha$ and the off-diagonal elements $p_{A\alpha,B\beta}$ correspond to bond orders between orbitals $A\alpha$ and $B\beta$. These orbitals are combined in step (5) to form the QUAOs $|A\alpha\rangle$ so that the off-diagonal blocks of the transformed density matrix $p$ from the density expansion

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

(25)

have as few quantitatively significant elements as possible. This transformation results in few large off-diagonal elements and many small off-diagonal elements. In practice, this corresponds to an orbital having few significant bond orders to other orbitals. The resulting QUAOs are observed to point in definite spatial directions and are also known as oriented QUAOs.

An approximation of the energy of a bond is furnished by considering kinetic energy integrals between two QUAOs. This energy, called the kinetic bond order (KBO),\textsuperscript{10} is given by

$$\text{KBO}=0.1 \times p_{A\alpha,B\beta} \langle A\alpha \rvert -\nabla^2 \rangle \frac{1}{2} \langle B\beta \rvert .$$

(26)

In step (6), a new set of orbitals $\lambda$ is obtained separately for the core and for the valence canonical orbitals with the goal that the new orbitals $\lambda$, known as the split-
localized orbitals, cover as few QUAOs as possible. By using the QUAOs, the split-localized orbitals take into account information from the density matrix.

References

CHAPTER 2. IDENTIFICATION AND CHARACTERIZATION OF
MOLECULAR BONDING STRUCTURES BY AB INITIO QUASI-ATOMIC
ORBITAL ANALYSES

A paper published in *The Journal of Physical Chemistry A*

Aaron C. West, Juan J. Duchimaza-Heredia, Mark S. Gordon, Klaus Ruedenberg

Abstract

The quasi-atomic analysis of *ab initio* electronic wave functions in full valence spaces, which was developed in preceding papers, yields oriented quasi-atomic orbitals in terms of which the *ab initio* molecular wave function and energy can be expressed. These oriented quasi-atomic orbitals are the rigorous *ab initio* counterparts to the conceptual bond forming atomic hybrid orbitals of qualitative chemical reasoning. In the present work, the quasi-atomic orbitals are identified as bonding orbitals, lone pair orbitals, radical orbitals, vacant orbitals and orbitals with intermediate character. A program determines the bonding characteristics of all quasi-atomic orbitals in a molecule on the basis of their occupations, bond orders, kinetic bond orders, hybridizations and local symmetries. These data are collected in a record and provide the information for a comprehensive understanding of the synergism that generates the bonding structure that holds the molecule together. Applications to a series of molecules exhibit the complete bonding structures that are embedded in their *ab initio* wave functions. For the strong bonds in a molecule, the quasi-atomic orbitals provide quantitative *ab initio* amplifications of the Lewis dot symbols. Beyond characterizing strong bonds, the quasi-atomic analysis also yields an understanding of the weak interactions, such as vicinal,
hyperconjugative and radical stabilizations, which can make substantial contributions to the molecular bonding structure.

1. Introduction

Accurate molecular electronic wave functions have complex structures. As a consequence, complex analyses are also required in order to distill, from quantitative \textit{ab initio} results, valid conceptual interpretations that can provide an \textit{ab initio} foundation for qualitative chemical reasoning, in contrast to unconstrained rationalizations by \textit{ad hoc} model assumptions.\textsuperscript{1} A relevant advance toward this goal was the recognition that, even for accurate correlated wave functions, the bond-creating changes are dominated by a limited number of configurations in the conceptual full valence space. The term \textit{full valence space} has two implications. First, the dominant configurations were found\textsuperscript{2,3,4} to be superpositions of determinants generated by a set of molecular orbitals whose number is no greater than the sum of the minimal basis set dimensions of all atoms. Second, it was found\textsuperscript{5,6,7,8,9,10} that the optimized molecular orbitals of such wave functions span a space that is also spanned by certain molecular orbitals that are extremely similar to atomic orbitals of the free atoms. These orbitals can be perceived as free-atom minimal basis set orbitals that have been somewhat deformed by the chemical environment in the molecule in order to be able to generate the molecular wave function. By virtue of the importance of full valence spaces, “non-dynamically correlated” calculations in these orbital spaces and their subspaces (FORS\textsuperscript{4,11} and CASSCF\textsuperscript{12,13} calculations) have proven to be extremely fruitful.
The aforementioned insights suggest a divide-and-conquer approach toward bonding interpretations, viz., first to develop an interpretation of the full valence space part of molecular electronic wave functions and their energies and, then, to complement this analysis by an interpretation of the dynamically correlated part. The present analysis focuses on full valence space wave functions. In the preceding papers of this series,\textsuperscript{8,14,15} a method was devised to extract from such a wave function a minimal basis set of \textit{quasi-atomic orbitals}, called QUAOs, with the following attributes:

(i) The molecular orbitals from which the original wave function is constructed can be exactly expressed in terms of the QUAOs.

(ii) The QUAOs have maximal overlap integrals with respective minimal basis set orbitals of the free atoms, given the constraint implicit in (i). (Most often overlaps larger than 0.9 can be achieved.)

(ii) The criteria and procedures for the QUAO formation are entirely independent of the “working atomic orbital basis”.\textsuperscript{16}

By virtue of these properties, a wave function in a full valence space, its density matrices, and its energy can be exactly expanded in terms of the determinants generated by the QUAOs. It has been shown\textsuperscript{17} that these expansions have an intrinsic atomic organization, \textit{i.e.}, the expansions can be additively resolved in terms of atomic subunits, which represent “\textit{quasi-atoms}” embedded in the wave functions, and bond-creating interactions between these quasi-atoms.

The quasi-atomic resolution of the molecular wave function described in ref 17 exhibits the different interactions that generate various bonding patterns in detail. However, substantial information regarding bonding structures of molecules can already
be obtained from closely examining the attributes of the valence shell QUAOs. Identifying and recording this information is the focus of the present investigation. To this end, specific relevant properties of valence QUAOs are quantitatively determined. Some of this information can be inferred by examining orbital contours, and previous studies have shown how such plots can exhibit bonding patterns as well as reactive changes of these patterns.\textsuperscript{14,18,19} However, the information conveyed by the visual images is limited, and the complete visual scanning through all orbital plots in a large molecule is impractical. The present algorithmic method determines various attributes of QUAOs and collects the relevant quantitative information for all QUAOs in a molecule. These characteristic data are readily sorted to yield the bonding implications for the entire molecule.

In section 2 the method and its theoretical basis are discussed. Section 3 illustrates the information that is produced by the analysis for various molecules with a range of bonding interactions.

It had been recognized early on\textsuperscript{6} that the expression of full valence space wave functions in terms of quasi-atomic orbitals creates valence-bond type representations of these wave functions. The present analysis of the QUAO properties shows that the QUAOs provide \textit{ab initio} quantifications and extensions of the Lewis dot structure model.\textsuperscript{20}

Over the years, a variety of other methods have been formulated for identifying orbitals with atomic-like character in molecules. Many of these approaches have been discussed in the previous papers of the present series.\textsuperscript{14,15} Therefore, only a few are commented upon here.
In the natural bond order (NBO) analysis of Weinhold, Landis and co-workers,\textsuperscript{21,22,23,24,25,26,27} the natural atomic orbitals (NAOs) are obtained as the leading orbitals in the diagonalization of the sub-block of the first order density matrix that is spanned by the atomic orbital basis of any given atom. One difference to the present approach is that, even for Hartree–Fock wave functions, the number of NAOs exceeds the number of minimal basis set orbitals (the additional orbitals are called “Rydberg orbitals). A comparison between NAO populations and QUAO populations, as well as other atomic populations has been given in ref 18.

In the approach of Mayer,\textsuperscript{28,29,30,31,32} nonorthogonal atomic-like molecular orbitals are formed that are equivalent to McWeeny’s “natural hybrid orbitals”.\textsuperscript{33} The natural hybrid orbitals are determined for each atom by maximizing the square of the norm of the projections of the molecular orbitals onto the atom-centered basis functions.\textsuperscript{34} For each atom, the resulting orbitals diagonalize Mulliken’s net density. Mayer also applies his overall approach to criteria other than Mulliken’s net density. Mayer’s method is basis set dependent and encounters numerical problems using basis sets with diffuse functions.\textsuperscript{30,31,35} Relationships between the different approaches are discussed in ref 30.

The natural orbitals for chemical valence (NOCV) are derived from the deformation density decomposition, developed by Ziegler and Rauk\textsuperscript{36,37,38} for Hartree–Fock and DFT wave functions. The deformation density matrix is the difference between the density matrix of the molecular wave function and the sum of the density matrices of the intuitively “prepared” atoms that contain the expected “distortions” by the molecular surroundings. The part of this density matrix that generates electron sharing (called the “orbital part”) is then resolved in terms of orbital contributions by a certain
diagonalization procedure that was developed by Mitoraj and Michalak. These orbitals are the NOCVs. The results are contingent on the preparation of the atoms.

In contrast to approaches based on orbital overlaps or first-order spatial density matrix diagonalization, the absolutely localized molecular orbitals (ALMOs) of Head-Gordon et al. are determined by a constrained energy minimization procedure. The ALMOs were originally developed to improve the efficiency of Hartree–Fock calculations on weakly interacting molecular fragments. Here, the ALMOs of a given fragment are expanded only in terms of the atomic orbitals of the atoms in that fragment. The ALMOs are then obtained by minimization of the energy of the total system with respect to these constrained ALMOs. Since the ALMOs of different fragments are mutually nonorthogonal, generalized self-consistent-field equations are required, which were formulated based on earlier developments that go back to Stoll et al. The resulting inter-fragment interaction energies are free of basis set superposition errors. Recently, Head-Gordon and coworkers have used ALMOs in an energy decomposition analysis of a single covalent bond.

In the General Valence Bond (GVB) method, which was originally formulated by Goddard, a single product of as many molecular space orbitals as there are electrons, multiplied by the most general superposition of spin functions of appropriate spin symmetry, is antisymmetrized. The space orbitals belonging to the same molecular symmetry are allowed to be nonorthogonal. The spin-coupled valence bond wave functions (SCVB), developed and implemented by Gerrat, Cooper and Thorsteinsson, are equivalent to the GVB functions. For this type of wave
function, the optimization with respect to orbitals and spin function mixing generates molecular orbitals that tend to be localized toward atoms.

The construction of the QUAOs of the present study is based on the combination of two criteria. The QUAOs must be as close as possible to the orbitals of the free atoms, and they must span the same orbital space as the molecular orbitals of the actual molecular wave function. These are essential prerequisites for the intrinsic energy decomposition analysis in ref 17. No other atomic-like orbitals are designed to satisfy both criteria.

While the visual images of various types of atom localized orbitals can be similar, the energetic consequences of the differences can nonetheless be substantial. Referring to this fact, Mulliken observed a long time ago that “a little bit can go a long way”.

2. Theory and method of quasi-atomic orbital analyses

2.1. Background and premises

The construction of the QUAOs for a given molecular wave function has been described in detail in the previous papers of this series.\textsuperscript{14,15,17} In the present context, the following aspects are relevant.

The QUAOs are formed in two steps. The first step is accomplished by using the Accurate Atomic Minimal Basis Set (AAMBS) orbitals that were determined through highly accurate free-atom self-consistent-field calculations.\textsuperscript{54,55} These orbitals are available in stored arrays for all atoms up to xenon. Using the AAMBS orbitals as templates, precursor QUAOs are generated for each atom by use of singular value decompositions. The precursor QUAOs of different atoms are then mutually
orthogonalized by an orthogonalization procedure that preserves maximal similarity to the AAMBS orbitals. Since the AAMBS orbitals have s-, p-, d-character on the respective atoms, the precursor QUAOs mimic the s-, p-, d-character of the AAMBS templates as much as possible within the constraints of the molecular environment. As a result, these orbitals have quasi-atomic but not ‘hybrid’ character. (In references 14 and 15 the precursor QUAOs were called canonical QUAOs.)

The ‘hybridization’, i.e., the mixing of s-, p-, and d-type orbitals for optimal adaptation to the chemical environment, is accomplished in the second step. On each atom, the QUAOs are formed as linear combinations of the precursor QUAOs. Since the resulting orbitals typically have shapes pointing into certain spatial directions, the QUAOs are also called ‘oriented’ QUAOs when it is desirable to emphasize the distinction from the precursor QUAOs.

The determination of the oriented QUAOs is based on the bonding implications that are inherent in the matrix elements $p_{Aa,Bb}$ of the spatial first order density representation

$$
\rho(1,2) = \sum_{Aa} \sum_{Bb} \left| Aa(1) \right> p_{Aa,Bb} \left< Bb(2) \right|
$$

in terms of any type of orthogonal quasi-atomic orbitals $|Aa\rangle$, $|Bb\rangle$, where the ket $|Aa\rangle$ denotes the QUAO ‘a’ on atom ‘A’. To be specific, the diagonal elements $p_{Aa,Aa}$ are the orbital occupations. The off-diagonal elements $p_{Aa,Bb}$ between orbitals on different atoms are known as bond orders because they are indicative of covalent interactions. Accordingly, the representation matrix $p$ is commonly called the population-bond-order matrix.
By virtue of the bonding implications inherent in the population-bond-order matrix, the oriented QUAOs are determined by the following bond order criterion. In each interatomic block of the first order density matrix, very few matrix elements shall have large magnitudes while the magnitudes of all other interatomic matrix elements shall be small. The algorithm that determines the oriented QUAOs maximizes this compaction of the interatomic interactions into as few orbitals as possible.\textsuperscript{14,58,59} The compaction results in a few bond orders with large magnitudes (between 0.6 and 1 with many larger than 0.9) and many bond orders less than 0.2 (many being smaller than 0.1). The implication is that \textit{the main bonding interactions occur only between a very few specific interacting oriented QUAOs from different atoms}. Thus, the oriented QUAOs, \textit{i.e.}, the QUAOs, correspond to the concept of hybrid atomic orbitals between which bonds form according to qualitative chemical reasoning. The transformation from the precursor to the oriented QUAOs applies only to the valence QUAOs.

The bonding implications of the bond orders are due to the fact that, in the full intrinsic energy decomposition analysis,\textsuperscript{17} the essential energy contributions that generate covalent bonding through electron sharing are the interference energies

\[
p_{Aa,Bb} \left\{ \langle Aa| - \frac{1}{2} \mathcal{V} |Bb \rangle + \langle Aa| \mathcal{V} |Bb \rangle \right\}
\]  

(1a)

where \( \mathcal{V} \) is a collection of one- and two-electron potential energy operators. For the comparison of different bonds, in particular when different interatomic distances are involved, the bond orders \( p_{Aa,Bb} \) have obvious limitations because the energy factor of the interference energy is omitted. Even the bond order \textit{signs} are in general not indicative of bonding or antibonding because the phases of the individual orbitals cannot always be aligned so as to accomplish this. This arbitrariness is eliminated in the interference
energy expression, which is manifestly invariant with respect to orbital phase changes. Since, in the large majority of cases, the interference energy is negative (i.e. bonding) due to its kinetic part, it has been found expedient to consider the kinetic part of the interference energy as an approximate energetic measure for bonding comparisons. To this end, the kinetic bond orders (KBOs) were defined by \(^{60}\)

\[
\text{KBO} = 0.1 \, p_{Aa,Bb} \, \langle Aa| - \frac{1}{2}V^2 |Bb \rangle
\]  

(1b)

The scale factor 0.1 is added in order that the KBO values of carbon-carbon single bonds are reasonably close to the magnitude of the empirically inferred C-C bond energy.\(^{61}\)

The expression (1a) for the interference energy is a consequence of the expansion of the molecular wave function in terms of determinants generated by orthogonal QUAOs. The pros and cons of orthogonal versus non-orthogonal quasi-atomic orbitals in the context of an energy decomposition analysis are discussed in Reference 17.

The present analysis generates quantitative properties of the QUAOs that are useful in exhibiting their roles in a molecular bonding context. In order to calculate these properties, the following information is needed: the expansions of the QUAOs in terms of the working atomic orbital basis, the elements of the first order density matrix in terms of the QUAOs, and the corresponding kinetic bond orders.

2.2. Characterization of QUAOs on the basis of populations and bond orders

By virtue of the antisymmetry of the wave functions and the orthogonality of the QUAOs, certain relationships hold between the orbital occupations and the bond orders. For instance, it is well known that, for any orbital with a population of 2, the bond orders between this orbital and all other orbitals vanish. This result is consequence of the
Theorem that, for antisymmetric wave functions, all eigenvalues of the first order density matrix lie between 0 and 2. More generally, Ivanic, Atchity and Ruedenberg\textsuperscript{62,63,64} have proven the following limits for orthogonal orbitals. Let $p_{11} = p_1$ and $p_{22} = p_2$ denote the occupations of any two orbitals, and let $p_{12} = p_{21} = p$ be the bond order between these orbitals in the first order density matrix. Let $p_{\text{Ave}} = (p_1 + p_2)/2$ denote the average occupation. Then the absolute value of the bond order $p$ is limited by two inequalities that can be written as:

\begin{align*}
p^2 &\leq p_1 p_2 = p_1 (2 - p_1) - 2 (1 - p_{\text{Ave}}) p_1, \quad \text{if } 0 \leq p_{\text{Ave}} \leq 1 \quad (2) \\
p^2 &\leq (2 - p_1) (2 - p_2) = p_1 (2 - p_1) - 2 (p_{\text{Ave}} - 1) (2 - p_1), \quad \text{if } 1 \leq p_{\text{Ave}} \leq 2 \quad (3)
\end{align*}

A graphic presentation of the implications for $p$ is given in reference 62.

Consider now the case that $p_1$ is given and $p_2$ can be anywhere between 0 and 2. By virtue of Eqs. (2) and (3), the largest value that $p^2$ can take occurs in both cases when $p_{\text{Ave}} = 1$. This maximal value is

\[ p_{\text{max}}^2 = p_1 (2 - p_1) \quad \text{for } p_1 + p_2 = 2 \quad (4) \]

It follows that the absolute value of the bond order $p$ for a given value of the occupancy $p_1$ is limited by the inequality

\[ p^2 + (p_1 - 1)^2 \leq 1 \quad (5) \]

In other words, $|p|$ is limited to the area on or below the red half circle on Figure 1. If $|p|$ lies on that circle, then $p_2$ has the value $(2 - p_1)$. The largest possible value of $|p|$ is 1.

Figure 1 provides a frame for discussing conceptual distinctions between QUAOs with regard to bonding: The occupation pertains to the participation of the QUAO in the
electron distribution; the bond order pertains to the participation of the QUAO in electron sharing. It should be noted that Figure 1 contains only information regarding the magnitudes of bond orders. Since any particular calculation can yield accidental phases that control the signs of bond orders, the bond order signs from a particular calculation do not directly indicate bonding or antibonding. This sign ambiguity is eliminated in the kinetic bond orders. For strongly bonded QUAOs, the kinetic bond order is always negative. Hence, large values of $|p|$ indeed imply strong bonds.

Four points $(p_1, |p|)$ on Figure 1 have clear meanings:
- Labeled by HB, the point (1,1) represents a singly occupied QUAO with the maximal bond order of 1, i.e., a QUAO involved in a strong homopolar bond.
- Labeled by LP, the point (2, 0) represents a non-bonded doubly occupied QUAO, i.e., a lone pair orbital.
- Labeled by RD, the point (1, 0) represents a non-bonded singly occupied QUAO, i.e., a radical orbital.
- Labeled by V, the point (0,0) represents a non-bonded vacant orbital.

While QUAOs with these attributes occur, the occupations and bond orders often do not have these exact values. On the basis of our limited observations (about 60 molecules), the following nine categories of population/bond order combinations are presently distinguished and indicated as areas in Figure 1. These distinctions are the basis for the labels, as described in Section 2.4, that are assigned to each orbital as a shorthand profile.

- A pair of interatomic QUAOs with a bond order value $|p| \geq 0.4$ is considered to be linked by a firm bond. For QUAOs definitively bonded to one other atom, the values of $|p|$ tend to be $\geq 0.9$; for QUAOs bonded to several atoms (as in conjugated
systems or multicenter bonds), the $|p|$ values tend to be lower. Accordingly, the area of the *firm* bonds in Figure 1 is divided into two parts labeled *strong firm* (i.e. $|p| \geq 0.6$ in Figure 1) and *moderate firm* (i.e. $0.6 > |p| \geq 0.4$ in Figure 1). All QUAOs that have $|p| < 0.4$ are weakly bonding or nonbonding.

- The weakly or non-bonded QUAOs with occupations in the range $0.8 \leq p_1 \leq 1.2$, in the area indicated by $rd$, are considered radical type orbitals.

- The weakly or non-bonded QUAOs with occupations $\geq 1.8$, in the area indicated by $(\ell)$, are considered lone pair type orbitals.

- The weakly bonded or non-bonded QUAOs with occupations $|p| \leq 0.2$, in the area labeled $nv$, are considered near vacant.

- The QUAOs with occupations between 1.8 and 1.9, in the area labeled $(\ell m)$, are considered lone pair orbitals that are involved in moderate firm bonding.

- Analogously, the orbitals with occupations between 0.1 and 0.2, in the area labeled $(nv m)$, are considered near-vacant that are involved in moderate firm bonds. A bond between QUAOs in the regions $(\ell m)$ and $(nv m)$ could form, for instance, when a lone pair of an electronegative atom donates some electronic charge to a vacant orbital of an electron acceptor atom, as in some hydrogen bonds.

- Two intermediate areas with weakly or non-bonded QUAOs remain, *viz.*, $(rd/\ell)$ with QUAOs intermediate between a lone pair and a radical, and $(rd/nv)$ with orbitals intermediate between being a radical and a vacant orbital.

The described category areas provide the basis for the labels, to be described in Section 2.4, that are assigned to the various orbitals as shorthand profile. It should be kept in mind, however, that the extent of these areas is approximate and that the boundaries
between them are somewhat fuzzy. In some cases, the kinetic bond orders may also have to be taken into account for an appropriate assessment. More extensive experience with more diverse chemical systems may suggest further classifications and additional intermediate categories.

2.3. Characterization of QUAOs on the basis of local symmetry

Two types of local symmetry are considered: (i) the composition of the QUAOs with respect to local s-type and p-type contributions on each atom, i.e., the hybridization, and (ii) the σ- and π-type character of the bonds.

(i) The hybridization of a QUAO is calculated by determining the hybridization fractions. The overlap integrals $\langle Aa | A^* \alpha \rangle$ are calculated between the QUAOs $|Aa\rangle$ and the valence AAMBS $|A^* \alpha \rangle$ all on the same atom A (see second paragraph of Section 2.1). Since the molecules considered in this study have only AAMBS with s- and p-character, the hybridization fractions of the oriented QUAO $|Aa\rangle$ are obtained as

$$s - \text{fraction} = S_s / S, \quad p - \text{fraction} = S_p / S$$

with

$$S_s = \langle Aa | A^* s \rangle^2, \quad S_p = \sum_{m=1}^{3} \langle Aa | A^* p_m \rangle^2, \quad S = S_s + S_p$$

where $|A^* s\rangle$ and $|A^* p\rangle$ are the s- and p-type AAMBS orbitals on atom A, and m sums over the p-components x,y,z. The QUAO is considered to be predominantly s-type or p-type based on the larger fraction in Eq. 6. The extension to d-type minimal basis set orbitals in heavier elements is evident. The hybridization fraction manifestly refers to the conceptual minimal basis hybridization. The expansions of the QUAOs in terms of
extended working atomic orbital bases contain, of course, polarizing admixtures from working atomic orbitals with higher spherical harmonics.

(ii) When a QUAO is involved in a bond that is firm in the sense of Section 2.2, its σ or π bonding character is determined as follows. Let the two partners of a firm bond be |Aa⟩ and |Bb⟩. The quadrupole moment tensor Q of the QUAO |Aa⟩ is calculated in the form

\[ Q_{ij} = \langle Aa| x_i x_j |Aa \rangle \] (8)

where the x_i are the spatial coordinates with reference to the nucleus A as the origin. This tensor Q is diagonalized. The eigenvector q_A that corresponds to the largest eigenvalue manifestly indicates the direction along which the orbital density |Aa⟩ accumulates. (The dipole moment would not be useful for this purpose because the dipole moment of a p-orbital vanishes.) If \( \mathbf{AB} \) denotes the vector pointing from nucleus A to nucleus B, then the normalized scalar product

\[ q_A = \frac{\mathbf{AB} \cdot q_A}{|\mathbf{AB}| |q_A|} \] (9)

yields the projection of the accumulation direction of the QUAO |Aa⟩ on the AB bond axis. The analogous projection q_B is calculated for the orbital |Bb⟩. The average

\[ q = \frac{|q_A| + |q_B|}{2} \] (10)

is typically slightly less than 1 for σ bonds and less than 0.01 for π-bonds. The bond is taken to be of σ type if q ≥ 0.8. It is taken to be of π type if q ≤ 0.2. For 0.2 < q < 0.8, it is considered to be σ/π intermediate.
2.4. Assignment of characteristics to QUAOs

Three tables are generated. The first table contains the hybridization fractions of all QUAOs, ordered by atom and, then, descending occupations within each atom. The second table contains all QUAOs and QUAO occupations in a list, which is ordered by descending occupation. The third table contains a list of all QUAO pairs between which the kinetic bond order is larger than 1.00 millihartree. For each QUAO pair in this table, the bond order and the kinetic bond order are listed. The QUAO pairs are ordered according to descending kinetic bond order magnitudes.

In the list of QUAO pairs, each QUAO is labeled according to the criteria discussed in Sections 2.2 and 2.3 by the following sequence of selections.

(i) Sort the bond orders by descending magnitude.

(ii) Form an initial list of firm bonds, i.e., interatomic QUAO pairs with |p| ≥ 0.4.

   a. If the QUAO population is ≥ 1.8, then assign a moderately bonded lone pair (ℓm) orbital.

   b. If the QUAO population is < 0.2, then assign a moderately bonded near vacant (nvm) orbital.

   c. If assignments a and b in step (ii) do not occur, then the bond is considered a firm bond and is assigned σ, π, or σ/π as described in Section 2.3.

(iii) Form an initial list for weak bonds, i.e., all remaining interatomic QUAO pairs not in the list of step (ii).

   a. If the QUAO population is ≥ 1.8, then assign a lone pair (ℓ) orbital.

   b. If 0.8 ≤ QUAO population is ≤ 1.2, then assign a radical (rd) orbital.
c. If assignments a and b of step (iii) do not occur and QUAO population $\geq 1.0$, then assign an intermediate radical lone pair ($\text{rd}/\ell$) orbital.

d. If assignments a, b, and c of step (iii) do not occur and $0.2 \leq \text{QUAO population} \leq 0.8$, then assign an intermediate near vacant ($\text{rd}/\text{nv}$) orbital.

e. If QUAO population $< 0.2$, then assign a near vacant (nv) orbital.

(iv) Combine the results from steps (ii) and (iii). Sort these assigned QUAO pairs by KBO magnitude to form the third table.

From the information in this third table, an acronymic label is then generated that conveys the QUAO bond characteristics. Each label consists of atomic symbols and characterizing symbols. The first atomic symbol identifies the atom on which the QUAO is located, i.e., the ‘home’ atom.

If the QUAO is involved in a firm bond, then that QUAO has a partner QUAO, and the home atom symbol is followed by the partner atom symbol. If the QUAO has firm bonds to several atoms, then the symbols of all partner atoms follow the symbol of the home atom. Lower case font is used for the symbols of all partner atoms. In molecules with identical atoms, subscripts distinguish different atoms. The atomic symbols are followed by the characterizing symbols $\sigma$, $\pi$, or $\sigma/\pi$.

If a QUAO is weakly bonded, then the symbol of the home atom is directly followed by one of the characterizing symbols ($\ell$), ($\text{rd}$), ($\text{rd}/\ell$), ($\text{rd}/\text{nv}$), or (nv), as appropriate, indicating lone pair, radical or intermediate character. For the lone pairs, the dominant hybridization fraction (i.e. either $s$ or $p$) precedes the ($\ell$) symbol. In the other cases, the $s$ or $p$ character can be found from the first table.
Note that any QUAO not involved in firm bonds can have weak bonds. For instance, \((p\ell)-lone\) pair QUAOs with occupations around 1.8 typically have weak hyperconjugative bonds to vicinal atoms, and weak bonds between radical QUAOs occur on dissociation paths. The QUAO labels do not include the partners of such weak bonds. However, these weak bonds can be found by examining the table of QUAO pairs.

3. Quasi-atomic orbital analyses of some basic molecules

The generation of oriented QUAOs from wave functions within full valence spaces and the characterization procedure described in the preceding sections are implemented as a set of modules in the GAMESS suite of molecular programs.\(^65,66\) The subsequent examples illustrate how, from a given wave function, these modules automatically generate all oriented QUAOs in a molecule, determine for each QUAO the bonding characteristics discussed in the preceding sections, and assign the QUAO labels that express these characteristics. This compilation of information conveys the molecular bonding pattern that is embedded in the \textit{ab initio} wave function.

Six molecules with a range of bonding interactions are considered: acetylene (C\(_2\)H\(_2\)), the methyl radical (CH\(_3\)), naphthalene (C\(_{10}\)H\(_8\)), formaldehyde (H\(_2\)CO), the carbonate ion (CO\(_3\))\(^2-\), nitrogen dioxide (NO\(_2\)), and diborane (B\(_2\)H\(_6\)).

Closed shell Hartree–Fock (HF) wave functions were used for C\(_2\)H\(_2\), H\(_2\)CO, CO\(_3\))\(^2-\), C\(_{10}\)H\(_8\), and B\(_2\)H\(_6\). Restricted open shell HF wave functions were used for CH\(_3\) and NO\(_2\). All calculations were performed with the Dunning augmented triple zeta (aug-cc-pVTZ) basis sets.\(^67\) The geometries were optimized within appropriate symmetries, \textit{viz.}, D\(_{4h}\) for C\(_2\)H\(_2\) and C\(_{10}\)H\(_8\), D\(_{3h}\) for CH\(_3\) and CO\(_3\))\(^2-\), C\(_{2v}\) for H\(_2\)CO and NO\(_2\), and D\(_{2h}\) for B\(_2\)H\(_6\).
Nuclear Hessian calculations verified that the optimized geometries are in fact minima. At these geometries, the QUAOs were determined.

The orbital contour surfaces displayed in the subsequent figures correspond to absolute orbital values of 0.1 \((e/\text{bohr}^3)^{1/2}\). Red and blue contours respectively imply positive and negative values. In order to show more information about the localization of the QUAOs, the Supporting Information contains several selected molecules with orbital contour surfaces displayed at smaller absolute orbital values.

### 3.1. Acetylene

The Lewis structure of acetylene, which is shown on Figure 2, implies the existence of a \(\sigma\) bond and two \(\pi\) bonds between the carbon atoms and a \(\sigma\) bond between each carbon atom to its adjacent terminal hydrogen atom. This description implies that 4 of the 10 valence electrons are on each carbon atom and one on each hydrogen atom.

Figure 2 shows 8 of the 10 QUAOs and the labels that are obtained by the calculation, \(\textit{viz.}\),

A \(\text{Hc}\sigma\) QUAO on each hydrogen,

Two sigma QUAOs on each carbon, \(\text{Ch}\sigma\) pointing to the nearest hydrogen and \(\text{Cc}\sigma\) pointing to the other carbon,

One of the two \(\text{Cc}\pi\) QUAOs on each carbon.

The arrows in the figure indicate bonding between QUAOs.

From the bond orders and kinetic bond orders listed in Table 1a for the QUAO pairs, it is apparent that all five QUAO pairs are strongly bonded (\(p = 0.97\) for each CH bond, 0.99 for the \(\sigma\)-CC bond, 1.00 for each \(\pi\)-bond). The label algorithm identifies these
strong bonds as $\sigma$ and $\pi$ bonds. A very small vicinal interaction exists between the $C_1C_2\sigma$ bond QUAO and the $H_2C_2\sigma$ QUAO, as also indicated in Table 1a.

Table 1b lists the occupations and hybridization fractions of the QUAOs. The table shows that the occupations of the two QUAOs associated with each bond add up to 2, and that 0.21e is transferred from each hydrogen atom to the respective carbon atom.

The hybridization fractions for the hydrogen $Hc\sigma$ QUAO and for the carbon $\pi$–QUAOs are self-evident. The two $\sigma$-QUAOs on each carbon exhibit near “sp” hybridizations, viz.: The $C_1C_2\sigma$ QUAO has an equal amount of s- and p-character, whereas the $C_1h_1\sigma$ QUAO has somewhat more p-character. This polarization of the $C_1h_1\sigma$ orbital is related to the charge transfer from hydrogen to carbon that occurs in the CH-bond.

### 3.2. Methyl radical

The Lewis structure of the methyl radical displayed in Figure 3 implies three CH-$\sigma$ bonds and a lone electron on the carbon atom, which makes the molecule a radical.

The calculation yields 7 oriented QUAOs: One $Hc\sigma$ orbital on each hydrogen, three $Ch\sigma$ orbitals on carbon, and a $Crd$ orbital on carbon. Figure 3 displays the symmetry-unique QUAOs and their labels. The arrow between the QUAOs $Ch\sigma$ and $Hc\sigma$ implies the existence of a bond.

The bond order of 0.99 in Table 2a shows that the QUAOs $Ch\sigma$ and $Hc\sigma$ are strongly bonded. The kinetic bond order of -36.8 kcal/mol is similar to the corresponding value of -39.4 kcal/mol for the CH-bond in acetylene.
The QUAO occupations listed in Table 2b show that each Chσ–Hcσ bond is associated with a charge transfer of 0.16e from the Hcσ orbital to the partner Chσ orbital, which compares to a similar transfer of 0.21e from hydrogen to carbon in acetylene.

The hybridizations listed in Table 2b show the respective s- and p-fractions of 0.29 and 0.71 for the Chσ QUAO. These values are halfway between sp² and sp³ hybridization even though the molecule has trigonal planar symmetry.

According to Table 2b, the Crd QUAO on carbon has an occupation of 1.00 and a p-fraction of 1.00, indicating pure p-character. The Crd orbital has no bonding interaction with the Hcσ orbitals. According to the discussion in Section 2.2, these occupation and bond order values are characteristic of a radical. Therefore, this QUAO is labeled by “rd”.

### 3.3. Naphthalene

Figure 4 shows the skeleton structure of naphthalene with the principal Kekulé structure. From the three Kekulé structures, the following Pauling π-bond orders⁶⁸,⁶⁹ are deduced: 2/3 for each of the bonds 1-2, 3-4, 5-6, 7-8, and 1/3 for all other CC bonds.

For each carbon atom, the algorithm yields three σ-type and one π-type oriented QUAOs. The carbon and hydrogen QUAOs are displayed on Figure 4 with their labels. Arrows indicate bonding between QUAOs.

The symmetry-unique bond orders and kinetic bond orders are listed in Table 3a. All σ-bonds have bond orders of 0.97 or 0.98. The kinetic bond orders of the CC σ-bonds lie between -52.7 and -54.8 kcal/mol. These values are markedly lower than the value of -75.0 kcal/mol of the CC σ-bond in acetylene. The CH σ-bonds have kinetic bond orders
of -38.6 and -38.7 kcal/mol, which are not very different from the corresponding value of -36.8 kcal/mol in the methyl radical.

The delocalization of the $\pi$-electrons is established by every $\pi$-QUAO having firm bond orders with all of its nearest neighbor $\pi$-orbitals. The bond order and the kinetic bond order of the $\pi$-bond between $C_1$ and $C_2$ is markedly stronger than the values for the other three $\pi$-bonds, in qualitative agreement with the Pauling $\pi$-bond orders mentioned above. The kinetic bond order of -18.5 kcal/mol of the $C_1$–$C_2$ $\pi$-bond is not much lower than the value of -25 kcal/mol of the $\pi$-bond in acetylene.

Table 3b lists the symmetry-unique occupations and hybridization fractions. All $C_iC_j\sigma$ QUAOs, which establish the $\sigma$-bonds between the carbon atoms, have a population of 1e. The QUAOs $C_ih_i\sigma$ and $H_iC_i\sigma$, which establish the C–H bonds, together contain 2 electrons, but 0.14 electrons are shifted from the hydrogen QUAO to the carbon QUAO. All three $\sigma$-QUAOs on any one carbon atom have a hybridization of about 30% s and 70% p, approximately corresponding to an intuitive $sp^2$ hybridization. The $\pi$-QUAOs are pure p-type and have a population of 1e.

### 3.4. Formaldehyde

#### 3.4.1. Firm bonds

The Lewis structure of formaldehyde, which is shown at the top of Figure 5, implies two lone pairs on oxygen, a CO $\sigma$-bond, a CO $\pi$-bond, and two CH $\sigma$-bonds. Figure 5 also displays the 10 oriented QUAOs that span the full valence space, viz.: two lone pair QUAOs $O\ell$ and $Op\ell$ on oxygen, the $\pi$-bonding QUAOs $O\pi$ and $C\pi$, and the
σ-bonding orbitals Oxσ, Coσ, Ch1σ, H1cσ, Ch2σ, H2cσ. The four firm bonds between these QUAOs are indicated by solid arrows on Figure 5.

Table 4a lists the occupations and hybridization fractions. On the oxygen atom, the two QUAOs Osℓ and Ocs are nearly sp hybridized, but the bonding QUAO Ocs has a little more p-character than the lone pair QUAO Osℓ. On carbon, the three QUAOs Coσ, Ch1σ, and Ch2σ all have about 30% s-character and 70% p-character, which is close to sp2 hybridization.

The Osℓ lone pair QUAO holds 2 electrons. The QUAO pair {Ocs, Coσ}, which forms the CO σ-bond, holds two electrons. The QUAO pair {Ocs, Coπ}, which forms the CO π-bond, also holds two electrons. Both CO bonds are considerably polarized toward the oxygen atom, the π-bond somewhat more so than the σ-bond. The CH bonds are polarized toward the carbon atom. But the charge loss of the two hydrogen atoms (0.10e each) is less than the charge gain of the oxygen atom (0.42e) so that the carbon atom also has an electron deficit (0.22e).

Table 4b lists the bond orders and kinetic bond orders. The bond orders of the CO-σ bond, the CO-π bond and each CH bond, respectively 0.97, 0.95, 0.96, identify these bonds as strong. According to the KBOs, the CO-σ bond is considerably stronger than the CO-π bond (-67.5 kcal/mol vs. -29.8 kcal/mol). The KBO of the CH bond (-36.0 kcal/mol) is within about 3 kcal/mol of the corresponding values in acetylene, methyl and naphthalene.

The preceding quantifications all agree with the qualitative expectations that current chemical intuition associates with the Lewis structures. The oriented QUAOs can be considered as an ab initio quantification of the Lewis electron dot model.
3.4.2. Weak vicinal interactions, hyperconjugation

In addition to the firm bonds, four weak bonds are indicated by the dashed arrows in Figure 5, viz., between the oxygen p-lone pair QUAO $O\ell$ and the four $\sigma$-QUAOs that form the two CH bonds. Table 4b lists the bond orders $\pm 0.21$ and $\pm 0.24$ between the $O\ell$ QUAO and the QUAOs $C_1\sigma$, $H_1c\sigma$, $C_2\sigma$ and $H_2c\sigma$. The negative KBO values show that all these weak interactions are bonding. Similar vicinal interactions of the oxygen p-lone pair have been found in every examined molecule in which an adjacent atom has $\sigma$-bonds whose QUAOs can have symmetry-allowed bond orders with the $O\ell$ QUAO (in contrast to the bond orders of $O\ell$ with the QUAOs in the CO bond, which vanish for local symmetry reasons). This kind of stabilization is known as carbonyl hyperconjugation. A careful analysis of the formaldehyde prototype is thus of general interest.

It is apparent from the discussion in Section 2.2 that the generation of a non-zero bond order between a lone pair and any other orbital is contingent on some electronic charge being moved from the lone pair to the other orbital. The weak bonds in formaldehyde are indeed established by partial electron donation from the $O\ell$ QUAO to the four QUAOs that form the CH $\sigma$-bonds: The $O\ell$ QUAO has only 1.89 electrons, and the sum of the occupations of $Ch\sigma$ and $Hc\sigma$ in each CH bond is 2.06e. Thus, 0.055–0.06e have moved from the p-lone pair on oxygen into each of the CH bonds. This partial charge donation implies some electron sharing between these orbitals, thereby lowering the energy.

The electron sharing can be further elucidated. One can replace the orbitals $C_1\sigma$ and $H_1c\sigma$ by the local bonding orbital $\phi_1$ and the local antibonding orbital $\phi_1^*$ that are
obtained by diagonalizing the $2 \times 2$ density matrix block that is formed from the occupations and the bond order of $\text{C}_1\sigma$ and $\text{H}_1\sigma$. The occupations of $\phi_1$ and $\phi_1^*$ are then found to be 1.999 and 0.061 respectively. In this representation, the bond order between $\text{Op}_\ell$ and $\phi_1$ must be zero (according to the first sentence of Section 2.2) so that the interaction is entirely between $\text{Op}_\ell$ and $\phi_1^*$. Thus, the excess of 0.06e in the $\text{CH}_1$ bond goes into the local anti-bonding orbital. The same holds for the analogous bonding and antibonding orbitals, $\phi_2$ and $\phi_2^*$, in the $\text{CH}_2$ bond.

The foregoing formulation shows one reason for the weakness of these bonds, viz.: The energy lowering through electron sharing between $\text{Op}_\ell$ and the CH antibonding orbitals is partially offset by the energy increase required to occupy antibonding orbitals.

It may be noted that localization of the occupied Hartree–Fock orbitals yields orbitals that are similar to the $\text{Op}_\ell$ QUAO and to the CH bonding QUAO superpositions $\phi_1$ and $\phi_2$ of the preceding paragraph. These localized Hartree–Fock orbitals incorporate the electron sharing of $\text{Op}_\ell$ by having larger extensions than their counterparts $\text{Op}_\ell$, $\phi_1$ and $\phi_2$.

Another reason for the weakness of these bonds is that the energy integrals between interacting QUAOs decrease with the distance of the QUAOs. This dependence also accounts for the KBOs for the nearer $\text{C}_2\sigma$ QUAOs being larger (-4.8 kcal/mol) than the KBOs for the farther $\text{H}_2\sigma$ QUAOs (-3.1 kcal/mol). The sum of all weak KBOs, -15.8 kcal/mol, is about 40% of the KBO of one CH bond.

Last, the signs of the bond orders have the following origins. First, the signs of the bond orders of $\text{Op}_\ell$ with $\text{C}_1\sigma$ and $\text{H}_1\sigma$ are opposite to the respective signs for the corresponding bond orders with $\text{C}_2\sigma$ and $\text{H}_2\sigma$ because the two CH bonds are mutual
mirror images with respect to the symmetry plane that is normal to the molecular plane. However, the Opℓ QUAO is antisymmetric with respect to that plane. Second, the signs of the bond orders of Opℓ with the Chσ QUAOs are opposite to the bond order signs of Opℓ with the respective Hcσ QUAOs because the shared electron uses the antibonding orbitals, in which the QUAOs Chσ and Hcσ have opposite signs. Regardless of the signs of the bond orders, however, all the KBOs are negative, *i.e.* bonding, by virtue of the orbital phase invariance of the KBOs, which was discussed between Eq.(1.a) and Eq.(1.b) at the end of Section 2.1.

### 3.5. Carbonate ion

Resonance theory describes the electronic structure of the carbonate ion CO$_3^{2-}$ as the superposition of three Lewis dot structures, one of which is shown in Figure 6. Averaging the three structures yields two σ-type lone pairs on each oxygen and three CO-σ bonds (σ-type meaning here symmetric with respect to the molecular plane), which implies 3 σ—electrons on carbon and 5 σ—electrons on each oxygen. Thus, all bonding σ-molecular orbitals are filled. Since the π-molecular orbitals offer one bonding A$_2$" orbital and two nonbonding E" orbitals, the remaining six electrons occupy these three π-molecular orbitals.

The present analysis generates the corresponding 16 QUAOs. They are displayed in Figure 6. Solid arrows between QUAOs indicate firm bonds. Dashed arrows indicate weak bonds. Each oxygen atom has two lone pair QUAOs, an Ocσ bonding QUAO, and an Ocπ bonding QUAO; the carbon atom has three Coσ bonding QUAOs and one Co$_1$O$_2$O$_3$π QUAO that bonds to the Ocπ QUAOs of all three oxygen atoms.
Table 5a lists the QUAO occupations and hybridization fractions. As in formaldehyde, the oxygen lone pair orbitals are labeled Osℓ and Opℓ because the Osℓ QUAO has an s-fraction of 0.60 (and a p-fraction of 0.40) whereas the Opℓ QUAO is a pure p-orbital. The Osℓ QUAO and the Ocσ bonding QUAO are diagonally related. But the s:p ratio is ~3:2 in the Osℓ QUAO and ~2:3 in the Ocσ QUAO, much further from sp hybridization than in formaldehyde. The QUAOs Osℓ and Opℓ have respective occupations of 2 and 1.92. The loss of 0.08 electrons in the Opℓ orbital is similar to the loss of 0.11 electrons in the Opℓ orbital in formaldehyde. The s:p ratio of the three σ-bonding carbon QUAOs Cokσ is 32:68, very close to sp² hybridization. Each of the Cokσ QUAOs has only 0.81 electrons.

Table 5b lists the bond orders and kinetic bond orders for the bonded QUAO pairs. The three Coσ–Ocσ sigma bonds are firm (BO = 0.93). The KBO value of -66.0 kcal/mol is close to the corresponding KBO value in formaldehyde (-67.5 kcal/mol).

According to Table 5a, these bonds are quite polarized: Relative to a homopolar two-orbital two-electron bond, the O₁cσ orbital gains 0.27 electrons. However, the Co₁σ orbital loses only 0.19 electrons. Hence, the total CO₁ σ-bond contains 2.08 electrons.

This gain of 0.08e in the CO₁ σ-bond is analogous to the corresponding gain of 0.06e in the CH bonds of formaldehyde, and it has the same reason. It is related to the weak bonds that are indicated by the dashed arrows on Figure 6 between the QUAO pair {O₁cσ, C₁oσ} and the vicinal lone pair QUAOs O₂pℓ and O₃pℓ. According to Table 5b, the BO and the KBO values between Co₁σ and Oₖpℓ (k= 2, 3) are respectively ±0.21 and -5.4 kcal/mol. The BO and KBO values between O₁cσ and Oₖpℓ (k= 2, 3) are respectively ±0.16 and -2.8 kcal/mol. Thus, a total KBO interaction of -8.2 kcal/mol
exists between the CO$_1$ $\sigma$-bond and each of the vicinal lone pair QUAOs O$_2$p$^\ell$ and O$_3$p$^\ell$. Analogous weak interactions exist for the $\sigma$-bonds CO$_2$ and CO$_3$.

These weak bonds are established by electron donations from the O$p^\ell$ lone pairs to the respective vicinal CO $\sigma$-bonds. As noted above, each lone pair QUAO O$p^\ell$ loses 0.08e, and each CO $\sigma$-bond gains 0.08e. To be specific, each O$p^\ell$ QUAO donates 0.04e to each of its two vicinal CO $\sigma$-bonds, and each CO $\sigma$-bond receives 0.04e from each of its two vicinal O$p^\ell$ lone pairs. These electron migrations generate the electron sharing that creates the six weak bonds between the O$p^\ell$ lone pairs and the vicinal CO $\sigma$-bonds. Thus, the $\sigma$-bond system in carbonate consists of three firm bonds and six interlocking hyperconjugative bonds. Because of this interlocking, it is not possible to choose the orbital phases such that all weak BOs are positive. Regarding the signs of the BOs, similar reasoning applies as for formaldehyde.

For the $\pi$-system, Tables 5a and 5b show that the Oc$\pi$ QUAOs on the three oxygen atoms are all bonded to the Co$_{102o3}$$\pi$ QUAO on the carbon atom. But the 6 $\pi$-electrons are not evenly distributed. The Oc$\pi$ QUAO on each oxygen contains 1.76 electrons so that only 0.73 electrons are left for the Co$_{102o3}$$\pi$ QUAO on carbon. The reason is that in the Hartree–Fock wave function only two electrons occupy a bonding $\pi$-orbital ($A_2^\pi$) with non-vanishing population at the carbon atom, whereas four electrons are in nonbonding $\pi$-orbitals ($E^\pi$) with no population at the carbon site. For the same reason, the three CO $\pi$-bonds are not strong: While the bond order is moderate (0.56), the KBOs are only -16.1 kcal/mol. Weak interactions (BO = 0.24, KBO = -3.4 kcal/mol) exist between the vicinal $\pi$-QUAOs.
A comparison of the total KBO contributions of the various bond types is instructive. The KBO sums are: -198 kcal/mol for the firm CO σ-bonds, -48.3 kcal/mol for the firm CO π-bonds, -49.2 kcal/mol for the hyperconjugation interactions, and -10.2 kcal/mol for the vicinal π-interactions.

The charge shifts in the σ- and π-systems result in the total valence electron populations of 6.95e for each oxygen atom and 3.15e for the carbon atom. The resonance model implies populations of 6.67e and 4e.

3.6. Nitrogen dioxide

Four possible Lewis dot structures are shown for nitrogen dioxide in Figure 7. The following analysis in terms of QUAOs leads to the conclusion that this resonance model cannot capture essential aspects of bonding in this molecule.

The 12 oriented QUAOs have standard shapes and are displayed in Figure 7. The solid arrows indicate firm bonds; the dashed arrows indicate weak bonds. The orbital occupations and hybridizations are listed in Table 6a. The bond orders and kinetic bond orders for QUAO pairs are listed in Table 6b.

Tables 6a and 6b show that the two strong primary NO σ-bonds, i.e. O1nσ–No1σ and O2nσ–No2σ, do not transfer charge between atoms. Significant charge transfers are involved in the additional bonding. For gaining insight in the additional bonding, it is useful to use a reference electron distribution without any interatomic charge transfers. Since Table 6a also shows that 13 electrons reside in the σ-orbital system (i.e. the QUAOs that are symmetric with respect to the molecular plane) and 4 electrons reside in the π-orbital system, the appropriate initial neutral reference charge distribution is
defined by the following occupations of the 8 QUAOs that are not involved in the two mentioned σ-bonds:

In the σ-system: Two doubly occupied lone pair QUAOs on each oxygen atom and a singly occupied nonbonding (radical) QUAO on the nitrogen atom.

In the π-system: A singly occupied π-QUAO on each oxygen atom and a doubly occupied π-QUAO on the nitrogen atom.

This reference electron distribution has the character of a “tri-radical”.

_Bonding in the π-electron system_

For the actual π-electron distribution, Table 6a shows 0.92 electrons on the nitrogen QUAO No1o2π, and 1.54 electrons on each of the oxygen QUAOs O1no2π and O2no1π. With respect to the reference occupations specified above, the actual occupations imply a charge transfer of 0.54e to each oxygen from nitrogen. Since the π-system is generated by a doubly occupied delocalized bonding HF-MO and a doubly occupied delocalized nonbonding HF-MO (which has no contribution on nitrogen), the implication is that the doubly occupied _atomic_ π-orbital of nitrogen in the reference distribution has morphed into the delocalized bonding π-HF _molecular_ orbital of the molecule by moving some charge to the oxygen π-QUAOs.

These charge transfers generate the electron sharing that creates firm π-bonds of the nitrogen QUAO No1o2π to the oxygen QUAOs O1no2π and O2no1π. Table 6b lists for these bonds the BO = 0.7 and the KBO = -21.5 kcal/mol, which are of a similar magnitude as the values for the π-bonds in acetylene and naphthalene.
Since, as shown in Table 6b, a BO = 0.46 > 0.4 exists between the \( \pi \)-QUAOs \( O_1n_2\pi \) and \( O_2n_1\pi \), the program generates two (lower case) partner atoms in the labels for these QUAOs. But, in view of the KBO of -7.4 kcal/mol, this \( \pi \)-bonding interaction between the vicinal oxygen atoms must be considered weak.

**Bonding in the \( \sigma \)-electron system**

As already noted, the QUAO pairs \( O_1n_\sigma–No_1\sigma \) and \( O_2n_\sigma–No_2\sigma \) form strong homopolar \( \sigma \)-bonds, each of which contains 2.04 electrons and is nearly unpolarized. The bond order is 0.97, and the kinetic bond order is -79.9 kcal/mol. (The values for the CO \( \sigma \)-bonds in formaldehyde and carbonate are -67.5 and -66.0 kcal/mol, respectively)

As in formaldehyde and the carbonate ion, each oxygen atom has an \( Os\ell \) lone pair QUAO with occupation 1.99e. The \( s/p \) hybridization ratio is \( \sim 7:3 \) in the \( Os\ell \) QUAO and correspondingly \( \sim 3:7 \) in the bonding \( On\sigma \) QUAO. These two orbitals are thus further from a \( s^1p^1 \)-hybridized pair than in \( H_2CO \) and \( CO_3^{2−} \).

As in formaldehyde and the carbonate ion, the third oxygen QUAO in the plane of the molecule is a pure \( p \)-QUAO perpendicular to the ON bond. However, its population is only 1.75e, whereas the corresponding values are 1.89e in formaldehyde and 1.92e in \( CO_3^{2−} \). The QUAO is therefore denoted as \( Od/rd \), implying a lone pair with considerable radical character, as discussed in Section 2.2.

The third nitrogen QUAO in the plane of the molecule has 81% \( p \)-character and an occupation of 1.43e. It is therefore denoted as \( Nrd/\ell \), i.e., a radical orbital with some lone pair character. Since each of the bonding QUAOs \( No_1\sigma \) and \( No_2\sigma \) has 61% \( p \)-character, the three orbitals \( \{Nrd/\ell, No_1\sigma, No_2\sigma\} \) represent a distorted \( sp^2 \) hybridized triple with the \( Nrd/\ell \) QUAO having more \( p \)-character than the two bonding QUAOs.
The bonding information in Table 6b shows that the oxygen orbital $O_1 l \, \text{rd}$ is involved in two weak bonding interactions, \textit{viz.}: (i) with the $Nrd/l \, \text{QUAO}$ and (ii) with the QUAOs $N_2\sigma, O_2\pi\sigma$, which form the $N$–$O_2 \sigma$-bond. The analogous converse interactions exist for $O_2 l \, \text{rd}$. These interactions are related to the charge shifts that are implicit in the orbital occupancies discussed in the preceding paragraphs. With respect to the reference occupations of 2 for the oxygen lone pairs $O_k l \, \text{rd}$, and of 1 for the nitrogen radical QUAO $Nrd/l$, the actual $\sigma$-QUAO occupations in the molecule result from each oxygen lone pair $O_k l \, \text{rd}$ losing 0.25e. Of these 0.25e, approximately 0.21e goes into the $Nrd/l$ QUAO and 0.04e goes into the $N_2\sigma$–$O_2\pi\sigma$ bond. Both electron migrations establish the respective sharing of electrons that generate the weak bonding energy lowerings in the $\sigma$-space.

The interaction of each $O_k l \, \text{rd}$ QUAO with the orbitals in the vicinal NO bond manifestly is of the same kind as the hyperconjugation interaction discussed for formaldehyde and also found in carbonate. On the other hand, the interactions between the nitrogen QUAO $Nrd/l$ and the two oxygen QUAOs $O_1 l \, \text{rd}$ and $O_2 l \, \text{rd}$ can be understood as an approximate five-electron three-center bond between these orbitals (the sum of the three QUAO occupations is 4.93). This three-center bond is weak because it has two electrons in a bonding HF-MO, two-electrons in a nonbonding HF-MO, and one electron in an antibonding HF-MO. According to Table 6b, the KBO total of the lone-pair-radical interactions, \textit{viz.} -10.2 kcal/mol is less than the sum of the kinetic bond orders of all hyperconjugation interactions, \textit{viz.} -14.6 kcal/mol.
Total bonding pattern and resonance structures

The two strong firm NO σ-bonds generate no charge transfer between the atoms. Charge transfer is part of the additional σ and π bonding patterns. The additional bonds can be understood by relating the actual occupations to the neutral-atom reference occupations discussed at the beginning of this section. The additional bonds are established by (i) a charge shift of 0.54e from the nitrogen atom to each oxygen atom in the π-system and (ii) a charge shift of 0.21e from each oxygen atom to the nitrogen atom in the σ-system. Because the two charge shifts move in opposite direction, both can be quite large without creating an unsupportable net shift. Each one can therefore generate the electron sharing that creates the described σ- and π-bonds. The total KBO sums of the strong firm σ-bonds, the π-bonds and the weak σ-bonds are, respectively, -159.8, -50.4 and -24.8 kcal/mol.

In view of the intricate electronic structure of this molecule, the bonding analysis has also been performed for the optimized multiconfiguration self-consistent-field wave function in the full valence space (i.e. FORS). The results are in qualitative agreement with the present Hartree–Fock results and support all conclusions, including the three-center five-electron bond.

The resulting net charge transferred from nitrogen to each oxygen is 0.33e. To accomplish this overall charge transfer by resonance structure mixing requires a weight of 1/3 for each ionic structure and a weight of 1/6 for each neutral structure. However, this resonance model does not embody essential aspects of the bonding pattern, viz.: (i) Since 13 electrons reside in the σ-system and four electrons in the π-system, one of the two dots on the nitrogen atom in the neutral resonance structures should in fact represent
a \( \sigma \)-electron and the other a \( \pi \)-electron. (ii) The distinct roles of the \( \sigma \)- and \( \pi \)-charge transfers, which create bonding by moving charges in opposite directions, cannot be adequately depicted by moving a single dot from the nitrogen atom to each oxygen atom.

3.7. Diborane

In diborane, \( \text{B}_2\text{H}_6 \), the two boron atoms are linked by two three-center two-electron bonds. Each bond contains a bridging hydrogen atom that is equally bonded to both boron atoms. In addition, each boron forms two regular two-center \( \sigma \)-bonds with two terminal hydrogens.

Figure 8 displays the oriented QUAOs and the labels that are generated by the program. One of the four symmetry-equivalent terminal BH bonds and one of the two symmetry-equivalent three-center BHB bonds are shown. The solid arrows indicate firm bonds. The dashed arrow indicates a weak bond. The orbital labels are deduced from the following bond orders and kinetic bond orders, which are listed in Table 7a.

The bond between the left boron atom and one of the left terminal hydrogen atoms is formed by the QUAO pair \( \text{B}_1\text{h}_1\sigma - \text{H}_1\text{b}_1\sigma \), which has the bond order \( \text{BO} = 0.99 \) and the KBO = -29.9 kcal/mol. These values imply a strong bond, though somewhat weaker than the CH bonds in acetylene, naphthalene and methyl, which have KBOs between -36 and -39 kcal/mol.

The three-center bridge bond shown in Figure 8 is formed by the QUAOs \( \text{B}_1\text{h}_0\text{b}_2\sigma , \text{H}_0\text{b}_1\text{b}_2\sigma \) and \( \text{B}_2\text{h}_0\text{b}_1\sigma \). The values \( \text{BO} = 0.69 \) and \( \text{KBO} = -14.3 \) kcal/mol for the QUAO pair \( \text{B}_1\text{h}_0\text{b}_2\sigma - \text{H}_0\text{b}_1\text{b}_2\sigma \) (and similarly for the QUAO pair \( \text{H}_0\text{b}_1\text{b}_2\sigma - \text{B}_2\text{h}_0\text{b}_1\sigma \)) indicate that each of the two legs of the three-center bridge is a firm bond,
although markedly weaker than the BH end bond: The bridge BH KBO -14.3 kcal/mol is less than half of the KBO of the BH terminal bond (-29.9 kcal/mol). The lower values of the bridging bond order and kinetic bond order are consistent with the corresponding lower values for delocalized \( \pi \)-bonds in naphthalene, carbonate, and nitrogen dioxide.

In addition to the two firm BH bonds of the BHB bridge, which are indicated by solid arrows, Figure 8 also shows a dashed arrow indicating a weak direct bond between the boron QUAOs \( \text{B}_1^\text{h}_0\text{b}_2\sigma \) and \( \text{B}_2^\text{h}_0\text{b}_1\sigma \), for which Table 7a lists a KBO of -4 kcal/mol. By virtue of the KBO value, this bond is in fact a weak bond between \textit{vicinal} QUAOs, and its KBO is of a similar order of magnitude as the KBOs of the vicinal bonds of the oxygen \( \text{O}_\text{f} \) orbital encountered in formaldehyde, carbonate and nitrogen dioxide. However, in contrast to those cases, the weak B-B bond has a BO value (0.56) that is larger than 0.4. Therefore, the QUAO labels \( \text{B}_1^\text{h}_0\text{b}_2\sigma \) and \( \text{B}_2^\text{h}_0\text{b}_1\sigma \) generated by the program include, for each of these QUAOs, the weak bond as well as the firm bond.

Identical BO and KBO values characterize the second bonding bridge (not shown in Figure 8), which is formed by the QUAOs \( \text{B}_1^\text{h}_0^\prime\text{b}_2\sigma \), \( \text{H}_0^\prime\text{b}_1\text{b}_2\sigma \) and \( \text{B}_2^\text{h}_0\text{b}_1\sigma \). These QUAOs are the mirror images of the QUAOs \( \text{B}_1^\text{h}_0\text{b}_2\sigma \), \( \text{H}_0\text{b}_1\text{b}_2\sigma \) and \( \text{B}_2^\text{h}_0\text{b}_1\sigma \) with respect to the plane in which the terminal hydrogen atoms and the boron atoms lie. Table 7a also shows that a small “Pauli repulsion” exists between the two central hydrogen QUAOs \( \text{H}_0\text{b}_1\text{b}_2\sigma \) and \( \text{H}_0^\prime\text{b}_1\text{b}_2\sigma \).

The QUAO occupations listed in Table 7b show that the two electrons in the BH terminal bond are equally shared by the two QUAOs \( \text{H}_1\text{b}_1\sigma \) and \( \text{B}_1^\text{h}_1\sigma \), generating an unpolarized bond without interatomic charge transfer.
The occupations listed for the three bridge-bond QUAOs $B_1h_0b_2\sigma$, $H_0b_1b_2\sigma$ and $B_2h_0b_1\sigma$, viz., 0.56e, 0.87e, 0.56e, imply the following inferences. Since two electrons on each boron atom are used for the BH terminal bonds, only 0.5e remain available for each of the two bridge QUAOs on a boron atom (thus, e.g., $B_1h_0b_2\sigma$). This low occupation is boosted by receiving 0.065e from the hydrogen QUAO $H_0b_1b_2\sigma$. The electron donation from the hydrogen QUAO to the boron QUAO decreases the B–H bond polarization and thereby enhances the electron sharing that generates the bridge bonds. The electron donations from the central hydrogen to both boron atoms decrease the population of the hydrogen by 0.13e.

The four bonds that emanate from each boron atom give a tetrahedral-like appearance. However, the angle between the terminal BH bonds is 122°, and the angle between the two bridge BH bonds from one boron atom is 95°. One would therefore expect that the QUAO $B_1h_0b_2\sigma$ for the bridge bond has markedly more p-character than the QUAO $B_1h_1\sigma$ of the terminal BH bond. Indeed, the hybridization ratios listed in Table 7b are $s/p = 26/74 \approx 1/2.8$ for the terminal QUAO $B_1h_1\sigma$ and $s/p = 13/87 \approx 1/6.7$ for the bridge QUAO $B_1h_0b_2\sigma$.

4. Summary

The previous papers of this series\textsuperscript{14,15,17,18,19} have shown that molecular \textit{ab initio} wave functions and energies can be rigorously expressed in terms of intrinsic quasi-atomic orbitals, which have the attributes of atomic minimal basis set orbitals that are hybridized and deformed through the optimization of the molecular wave function. In the present study, the quasi-atomic orbitals are classified according to the roles they play in
the context of the molecular bonding pattern. The characterizations are based on the values of the populations and bond orders (i.e. the first order density matrix elements), on the kinetic bond orders, on the orbital hybridizations, and on local molecular symmetries. The relevant attributes for all quasi-atomic orbitals and all quasi-atomic orbital pairs in a molecule are collected in tables.

On the basis of a relation that is derived between the ranges of orbital occupations and bond orders, the quasi-atomic orbitals are classified as follows:

Non-bonded orbitals
- Lone pair orbitals with no bonding interactions
- Radical (i.e. singly occupied) orbitals with no bonding interactions

Firmly bonded orbitals
- Bonding orbitals involved in two-center bonding
- Bonding orbitals involved in bonding with several other atoms

Weakly bonded orbitals
- Near lone pair type orbitals
- Near radical-type orbitals
- Near vacant orbitals
- Orbitals with intermediate character.

Each quasi-atomic orbital in a molecule is labelled by an acronym that conveys its location and bonding characteristics.

These collected data provide comprehensive information regarding the charge transfer and electron sharing between atoms that can be integrated to yield an
understanding of the synergism that generates the bonding structure that holds a molecule together.

The method has been implemented as part of the quasi-atomic analysis in the GAMESS program suite.\textsuperscript{65} Using this code, the bonding structure that is embedded in the \textit{ab initio} wave functions is extracted and analyzed for several molecules formed from the atoms H, B, C, N and O. For the strong major bonds, the program yields \textit{ab initio} quantifications of qualitative expectations inferred from intuitive reasoning. In addition, the program generates quantitative information for the weak interactions in a molecule, such as vicinal interactions, hyperconjugation, and radical interactions, for which intuitive expectations are vague and uncertain. In molecules where the weak bonds are more numerous than the strong bonds, a not uncommon situation, the total impact of the weak bonds can be substantial.

The analysis in terms of quasi-atomic orbitals also establishes a relationship between \textit{ab initio} quantum chemistry and the Lewis dot structure scheme. In many cases, the Lewis dots can be considered as representing occupied quasi-atomic orbitals. In these cases, the quasi-atomic occupations and interactions furnish quantitative \textit{ab initio} amplifications of the dot structures. Moreover, in the frequent cases of multicenter bonding, the quasi-atomic information provides a clearer description of the actual bonding situation than the artificial reduction to two-center interactions by the resonance structure symbolism. In addition, the results of the quasi-atomic analyses for the weak bonding interactions, which are frequently relevant, go beyond the capabilities of the dot structure scheme.
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References

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16 The working orbital basis is the orbital basis in which all electronic quantities are actually evaluated, such as, e.g., Dunning’s correlation corrected atomic bases cc-pVNZ. The working orbital basis can also consist of plane waves, as shown in Reference 10.


27 Natural Bond Orders 6.0 Website: http://nbo6.chem.wisc.edu/


34 Mayer, I., Bond orders and energy components: extracting chemical information from molecular wave functions (CRC Press, Boca Raton, 2017), p. 52-54.


37 Ziegler, T.; Rauk, A. “A theoretical study of the ethylene-metal bond in complexes between copper(1+), silver(1+), gold(1+), platinum(0) or platinum(2+) and ethylene, based on the Hartree-Fock-Slater transition-state method.” Inorg. Chem. 1979, 18, 1558-1565.


Ivanic, J.; Ruedenberg, K. “Intrinsic local constituents of molecular electronic wave functions II. Electronic structure analyses in terms of intrinsic oriented quasi-atomic molecular orbitals for the molecules FOOH, H₃BH₂BH₂, H₂CO and the isomerization HNO→NOH.” *Theor. Chem. Acc.* **2008**, *120*, 295-305.

See Section 3.3 of reference 15.

See Section 8 in reference 58. In that reference, the theorem was derived for just two orbitals. The formulation given in the present text follows by applying the bracketing theorem of References 63 and 64 to the diagonalization of the first order density matrix.


Table 1. Bonding characteristics of QUAOs in acetylene

a. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of symmetry-unique QUAO interactions

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1c_2\pi$</td>
<td>1.00</td>
<td>-25.0</td>
</tr>
<tr>
<td>$C_2c_1\pi$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_1c_2\sigma$</td>
<td>0.99</td>
<td>-75.0</td>
</tr>
<tr>
<td>$C_2c_1\sigma$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_1h_1\sigma$</td>
<td>0.97</td>
<td>-39.4</td>
</tr>
<tr>
<td>$H_1c_1\sigma$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_1c_2\sigma$</td>
<td>0.12</td>
<td>-3.1</td>
</tr>
<tr>
<td>$H_2c_2\sigma$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Only QUAO pairs for which the BO magnitude is $\geq 0.1$ and the KBO is $\leq -1.0$ kcal/mol are listed.

b. Occupations and hybridization fractions

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupation</th>
<th>s-fraction</th>
<th>p-fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1c_2\pi$</td>
<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$C_1c_2\pi$</td>
<td>1.00</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$C_1c_2\sigma$</td>
<td>1.00</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>$C_1h_1\sigma$</td>
<td>1.21</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>C Total</td>
<td>4.21</td>
<td>1.05</td>
<td>3.16</td>
</tr>
<tr>
<td>$H_1c_1\sigma$</td>
<td>0.79</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 2. Bonding characteristics of QUAOs in the methyl radical

a. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of symmetry-unique QUAO interactions.

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_1 \sigma )</td>
<td>0.99</td>
<td>-36.8</td>
</tr>
<tr>
<td>( \text{Ch}_1 \sigma )</td>
<td>\text{Crd}</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{Ch}_1 \sigma )</td>
<td>1.16</td>
<td>0.29</td>
</tr>
<tr>
<td>( \text{C Total} )</td>
<td>4.48</td>
<td>1.01</td>
</tr>
<tr>
<td>( \text{H}_1 \sigma )</td>
<td>0.84</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\(^a\) Only QUAO pairs for which the BO magnitude is \( \geq 0.1 \) and the KBO is \( \leq -1.0 \) kcal/mol are listed.
Table 3. Bonding characteristics of QUAOs in naphthalene

a. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of symmetry-unique QUAO interactions.\(^a\)

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_1)c(_2)σ</td>
<td>0.98</td>
<td>-54.8</td>
</tr>
<tr>
<td>C(_1)c(_8)σ</td>
<td>0.98</td>
<td>-52.7</td>
</tr>
<tr>
<td>C(_2)c(_9)σ</td>
<td>0.98</td>
<td>-53.8</td>
</tr>
<tr>
<td>C(_9)c(_10)σ</td>
<td>0.97</td>
<td>-54.5</td>
</tr>
<tr>
<td>C(_3)h(_2)σ</td>
<td>0.97</td>
<td>-38.7</td>
</tr>
<tr>
<td>C(_1)h(_1)σ</td>
<td>0.97</td>
<td>-38.6</td>
</tr>
<tr>
<td>C(_1)c(_2)π</td>
<td>0.78</td>
<td>-18.5</td>
</tr>
<tr>
<td>C(_9)c(_10)c(_2)π</td>
<td>0.59</td>
<td>-13.2</td>
</tr>
<tr>
<td>C(_1)c(_2)c(_8)π</td>
<td>0.53</td>
<td>-11.0</td>
</tr>
<tr>
<td>C(_2)c(_1)c(_9)π</td>
<td>0.51</td>
<td>-10.8</td>
</tr>
</tbody>
</table>

\(^a\)Only QUAO pairs for which the BO magnitude is \(\geq 0.1\) and the KBO is \(\leq -2.0\) kcal/mol are listed.

b. Occupations and hybridization fractions of symmetry-unique QUAOs

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupation</th>
<th>(s)-fraction</th>
<th>(p)-fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_1)c(_2)c(_8)π</td>
<td>1.004</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C(_2)c(_1)c(_9)π</td>
<td>1.004</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C(_9)c(_10)c(_2)c(_3)π</td>
<td>0.984</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C(_1)c(_2)σ</td>
<td>1.00</td>
<td>0.31</td>
<td>0.69</td>
</tr>
<tr>
<td>C(_1)c(_8)σ</td>
<td>1.00</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>C(_1)h(_1)σ</td>
<td>1.14</td>
<td>0.27</td>
<td>0.73</td>
</tr>
<tr>
<td>C(_2)c(_1)σ</td>
<td>1.00</td>
<td>0.32</td>
<td>0.68</td>
</tr>
<tr>
<td>C(_2)c(_9)σ</td>
<td>1.00</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>C(_2)h(_2)σ</td>
<td>1.14</td>
<td>0.27</td>
<td>0.73</td>
</tr>
<tr>
<td>C(_9)c(_2)σ</td>
<td>1.00</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>C(_9)c(_10)σ</td>
<td>1.00</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>H(_2)c(_2)σ</td>
<td>0.86</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>H(_1)c(_1)σ</td>
<td>0.86</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Table 4. Bonding characteristics of QUAOs in formaldehyde

a. Occupations and hybridization fractions of symmetry-unique QUAOs.

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupation</th>
<th>s-fraction</th>
<th>p-fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>O sℓ</td>
<td>1.99</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>O pℓ</td>
<td>1.89</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ocσ</td>
<td>1.24</td>
<td>0.44</td>
<td>0.56</td>
</tr>
<tr>
<td>Ocπ</td>
<td>1.30</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>O Total</td>
<td>6.42</td>
<td>1.60</td>
<td>4.82</td>
</tr>
<tr>
<td>Cσ</td>
<td>0.70</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Cσ</td>
<td>0.76</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>Chσ</td>
<td>1.16</td>
<td>0.30</td>
<td>0.70</td>
</tr>
<tr>
<td>C Total</td>
<td>3.78</td>
<td>0.92</td>
<td>2.86</td>
</tr>
<tr>
<td>H1cσ</td>
<td>0.90</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

b. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of the QUAO interactions.\(^a\)

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocσ</td>
<td>Cσσ</td>
<td>0.97</td>
</tr>
<tr>
<td>Ocσ</td>
<td>Cσπ</td>
<td>0.95</td>
</tr>
<tr>
<td>Ch1σ</td>
<td>H1cσ</td>
<td>0.96</td>
</tr>
<tr>
<td>Ch2σ</td>
<td>H2cσ</td>
<td>0.96</td>
</tr>
<tr>
<td>O pℓ</td>
<td>Ch1σ</td>
<td>0.21</td>
</tr>
<tr>
<td>O pℓ</td>
<td>H1cσ</td>
<td>-0.24</td>
</tr>
<tr>
<td>O pℓ</td>
<td>Ch2σ</td>
<td>-0.21</td>
</tr>
<tr>
<td>O pℓ</td>
<td>H2cσ</td>
<td>0.24</td>
</tr>
</tbody>
</table>

\(^a\)Only QUAO pairs for which the BO magnitude is \(\geq 0.1\) and the KBO is \(\leq -1.0\) kcal/mol are listed.
Table 5. Bonding characteristics of QUAOs in the carbonate ion

a. Occupations and hybridization fractions of symmetry-unique QUAOs.

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupation</th>
<th>s-fraction</th>
<th>p-fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_1$σ</td>
<td>0.81</td>
<td>0.32</td>
<td>0.68</td>
</tr>
<tr>
<td>Co$_1$o$_2$o$_3$π</td>
<td>0.73</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>C Total</td>
<td>3.16</td>
<td>0.78</td>
<td>2.38</td>
</tr>
<tr>
<td>O$_1$σ</td>
<td>1.27</td>
<td>0.38</td>
<td>0.62</td>
</tr>
<tr>
<td>O$_1$π</td>
<td>1.76</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>O$_1$ pℓ</td>
<td>1.92</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>O$_1$ sℓ</td>
<td>2.00</td>
<td>0.60</td>
<td>0.40</td>
</tr>
<tr>
<td>O Total</td>
<td>6.95</td>
<td>1.68</td>
<td>5.27</td>
</tr>
</tbody>
</table>

b. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of symmetry-unique QUAO interactions. $^a$

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_1$cσ</td>
<td>Co$_1$σ</td>
<td>0.93</td>
</tr>
<tr>
<td>O$_1$cπ</td>
<td>Co$_1$o$_2$o$_3$π</td>
<td>0.56</td>
</tr>
<tr>
<td>O$_1$cπ</td>
<td>O$_2$cπ</td>
<td>-0.24</td>
</tr>
<tr>
<td>O$_1$ pℓ</td>
<td>Co$_2$σ</td>
<td>-0.21</td>
</tr>
<tr>
<td>O$_1$ pℓ</td>
<td>Co$_3$σ</td>
<td>0.21</td>
</tr>
<tr>
<td>O$_1$ pℓ</td>
<td>O$_2$cσ</td>
<td>0.16</td>
</tr>
<tr>
<td>O$_1$ pℓ</td>
<td>O$_3$cσ</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

$^a$Only QUAO pairs for which the BO magnitude is $\geq 0.1$ and the KBO is $\leq -1.0$ kcal/mol are listed.
Table 6. Bonding characteristics of QUAOs in nitrogen dioxide

a. Occupations and hybridizations of symmetry-unique QUAOs.

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupation</th>
<th>s-fraction</th>
<th>p-fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>N rd/ℓ</td>
<td>1.43</td>
<td>0.19</td>
<td>0.81</td>
</tr>
<tr>
<td>N No₁σ</td>
<td>0.99</td>
<td>0.39</td>
<td>0.61</td>
</tr>
<tr>
<td>N No₁o₂π</td>
<td>0.92</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>N Total</td>
<td>4.33</td>
<td>1.04</td>
<td>3.29</td>
</tr>
<tr>
<td>O₁ ℓ/rd</td>
<td>1.75</td>
<td>0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>O₁ sℓ</td>
<td>1.99</td>
<td>0.67</td>
<td>0.33</td>
</tr>
<tr>
<td>O₁o₁σ</td>
<td>1.05</td>
<td>0.28</td>
<td>0.72</td>
</tr>
<tr>
<td>O₁o₂π</td>
<td>1.54</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>O Total</td>
<td>6.33</td>
<td>1.64</td>
<td>4.69</td>
</tr>
</tbody>
</table>

b. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of symmetry-unique QUAO interactions.ᵃ

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₁nσ</td>
<td>No₁σ</td>
<td>0.97</td>
</tr>
<tr>
<td>O₁o₂π</td>
<td>No₁o₂π</td>
<td>0.70</td>
</tr>
<tr>
<td>O₂no₁σ</td>
<td>O₁o₂π</td>
<td>0.46</td>
</tr>
<tr>
<td>O₁ ℓ/rd</td>
<td>N rd/ℓ</td>
<td>0.36</td>
</tr>
<tr>
<td>O₁ ℓ/rd</td>
<td>No₂σ</td>
<td>0.19</td>
</tr>
<tr>
<td>O₁ ℓ/rd</td>
<td>O₂nσ</td>
<td>0.13</td>
</tr>
</tbody>
</table>

ᵃOnly QUAO pairs for which the BO magnitude is ≥ 0.1 and the KBO is ≤ -1.0 kcal/mol are listed.
Table 7. Bonding characteristics of QUAOs in diborane

a. Bond orders (BOs) and kinetic bond orders (KBOs, in kcal/mol) of symmetry-unique QUAO interactions.\(^a\)

<table>
<thead>
<tr>
<th>Interacting QUAOs</th>
<th>BO</th>
<th>KBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_1)b(_1)σ</td>
<td>0.99</td>
<td>-29.9</td>
</tr>
<tr>
<td>H(_0)b(_1)b(_2)σ</td>
<td>0.69</td>
<td>-14.3</td>
</tr>
<tr>
<td>B(_1)h(_0)b(_2)σ</td>
<td>0.56</td>
<td>-4.0</td>
</tr>
<tr>
<td>H(_0)b(_1)b(_2)σ</td>
<td>-0.12</td>
<td>+0.6</td>
</tr>
</tbody>
</table>

\(^a\)Only QUAO pairs for which the BO magnitude is \(\geq 0.1\) and the KBO is \(\leq -2.0\) kcal/mol are listed, except for the last entry.

\(^b\) The H\(_0\)b\(_1\)b\(_2\)σ QUAO is equivalent by symmetry to the H\(_0\)b\(_1\)b\(_2\)σ QUAO.

b. Occupations and hybridizations of symmetry-unique QUAOs

<table>
<thead>
<tr>
<th>Label</th>
<th>Occupation</th>
<th>s-fraction</th>
<th>p-fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(_1)h(_1)σ</td>
<td>1.00</td>
<td>0.26</td>
<td>0.74</td>
</tr>
<tr>
<td>B(_1)h(_0)b(_2)σ</td>
<td>0.56</td>
<td>0.13</td>
<td>0.87</td>
</tr>
<tr>
<td>B(_1) Total</td>
<td>3.13</td>
<td>0.67</td>
<td>2.46</td>
</tr>
<tr>
<td>H(_0)b(_1)b(_2)σ</td>
<td>0.87</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>H(_1)b(_1)σ</td>
<td>1.00</td>
<td>1.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
**Figure 1.** The various bond orders and bond types possible for a QUAO with a given occupation. $V =$ vacant orbital, $RD =$ nonbonded radical orbital, $LP =$ nonbonded lone pair orbital, $HB =$ Most strongly bonded orbital in a homopolar bond. The meanings of the various fields are discussed in Section 2.2. Occupation-bond order combinations above the red circle do not exist. The dashed lines imply that these boundaries between bond categories are approximate.
Figure 2. Oriented QUAOs in acetylene. The orbital label is given beneath each orbital. Only one set of $\pi$ orbitals is shown. An arrow between two orbitals indicates a firm bond between the orbitals.
Figure 3. Oriented QUAOs in the methyl radical. The orbital label is given beneath each orbital. Only the orbitals that are unique by symmetry are shown. The arrow indicates a firm bond between the two orbitals.
Figure 4. Oriented QUAOs in naphthalene. The numbers 1 to 8 apply to the respective carbon and hydrogen orbitals. The orbital label is given beneath each orbital. Several symmetry-related orbitals are not shown. An arrow between two orbitals indicates a firm bond between the orbitals.
Figure 5. Oriented QUAOs in formaldehyde. The orbital label is given beneath each orbital. A solid arrow between two orbitals indicates a firm bond between the orbitals. A dashed arrow between two orbitals indicates a weak bond between the orbitals.
Figure 6. Oriented QUAOs in carbonate. The orbital label is given beneath each orbital. A solid arrow between two orbitals indicates a firm bond between the orbitals. A dashed arrow between two orbitals indicates a weak bond between the orbitals. (The two dashed arrows for the weakly bonded pairs \{O_2p\ell, O_3c\sigma\} and \{O_3p\ell, O_2c\sigma\} are not shown.)
Oriented QUAOs in nitrogen dioxide

Figure 7. Oriented QUAOs in nitrogen dioxide. The orbital label is given beneath each orbital. A solid arrow between two orbitals indicates a firm bond. A dashed arrow between two orbitals indicates a weak bond. The \( \pi \)-bonding orbitals are shown as seen from the \( C_2 \) axis of the molecule to show the two \( \pi \) lobes.
Figure 8. Oriented QUAOs in diborane. The orbital label is given beneath each orbital. A solid arrow between two orbitals indicates a firm bond between the orbitals. A dot-dashed arrow between two orbitals indicates a weak bond between the orbitals in terms of the kinetic bond order (see text). Only one of the four equivalent terminal bonds and one of the two three-center bridge bonds are shown.
CHAPTER 3. QUASI-ATOMIC BONDING ANALYSIS OF Xe-CONTAINING COMPOUNDS

A paper published in The Journal of Physical Chemistry A

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Abstract

The origin of bonding in the rare gas containing molecules HXeCCH, HXeCCXeH, and HXeOXeH is explored using a quasi-atomic orbital (QUAO) analysis. The QUAOs provide qualitative and quantitative data about bonding through transformations of the density matrix. Bond orders, kinetic bond orders, and the extent of transfer of charge are analyzed. Localized molecular orbitals formed from the QUAOs provide additional insights about the relative polarity of bonds formed by xenon. The analysis suggests significant covalent bonding for Xe-Y (Y = C, O) as well as Xe-H, both bonds using the same pσ-type orbital on Xe. These covalent interactions are established by substantial charge shifts from Xe to Y as well as to H. Accordingly, a covalent three-center four-electron bond links the atoms H-Xe-Y. Based on the analysis, electrostatic interactions do not play a significant role in the Xe-Y or Xe-H bonding.

1. Introduction

Rare gas atoms are extremely stable and nearly chemically inert in their ground states. Pauling hypothesized in 1933 that Kr and Xe should be able to form compounds like KrF₆, XeF₆, and H₂XeO₄. It was not until 1962, however, that Bartlett reported the first successful synthesis of a xenon compound. In the years following, the reactivity of
rare gases was explored extensively. It was found that the heavier gases, namely xenon and krypton, were the most reactive of the rare gases. In 2000, the first successful synthesis of a neutral argon compound was reported, heightening the interest in the nature of bonding of rare gases.

A particular family of rare gas compounds with the general formula HRgY (Rg = Kr or Xe, Y = electrophile) has been prepared and identified by Pettersson et al. since 1995. The stability of these molecules is usually attributed to an ionic (H-Rg)+Y- interaction, in which the (H-Rg)+ fragment is covalently bound while the interaction between (H-Rg)+ and Y- is due to Coulombic attraction. Compounds that result from the insertion of rare gas atoms into hydrocarbons raise the need for further studies to understand the reactivity of rare gases. Theoretical predictions of compounds including HXeCCH, HXeCCXeH, and polymers HXe(CCXe)nH with arbitrarily large n, illustrate the possibility of forming polymers of rare gas compounds, while investigations of analogous XRgCCX and XRgCCRgX (X = F or Cl) species predict stable compounds of Kr and Ar. Further, rare gas compounds of atmospheric species, such as HXeOH and HXeOXeH, prompt the investigation of environmental effects of rare gas chemistry. Theoretical investigations of the bonding in HRgY molecules, where Y=C or O, with the electron localization function and with the natural bond order analysis (NBO) support the interpretation that Xe-C and Xe-O bonds are electrostatic in nature due to the Coulombic attraction of a positively charged HRg fragment and a negatively charged Y fragment. A Rundle-Pimentel three-center four-electron (3c/4e) bonding model has been suggested and explored for rare gas molecules containing xenon and fluorine and for xenon and radon hydrides. The structures of numerous rare gas compounds
have been described as resonance hybrids of several possible structures.\textsuperscript{23,24} Most recently, Weinhold and co-workers have attributed the bonding in halogen rare gas hydrides to a hybrid of three cooperating resonance structures: (HRg)\textsuperscript{+}Y\textsuperscript{−}, H(RgY)\textsuperscript{+}, and the long-bonding interaction H\textsuperscript{^}Y, in which H and Y form a bond despite being separated by Xe.\textsuperscript{25}

Several rare gas molecules have been observed to exist as metastable molecules. The potential energies for the formation of the molecules analyzed in the present study have been previously reported and compared to several dissociation limits. Using second order perturbation theory (MP2), HXeCCH was predicted to be 4.5 eV above the energy of separated xenon and acetylene, but it is more stable than the separated H+Xe+C\textsubscript{2}H fragments by 1.46 eV.\textsuperscript{10} HXeCCXeH is 9.3 eV above the energy of 2Xe+HCCH and is more stable than H+Xe+C\textsubscript{2}XeH by 2.7 eV.\textsuperscript{10} The energy of HXeOXeH was calculated to be 8.3 eV higher than the energy of 2Xe+H\textsubscript{2}O and 1.38 eV lower than the energy of H+Xe+OXeH.\textsuperscript{15} Interestingly, for HXeCCH (HXeOXeH), the energy of the rare gas molecule is 2.18 eV (0.57 eV) below the H-Xe-C (H-Xe-O) bending barrier for the decomposition of the respective rare gas molecule, leading to the metastability of these molecules.\textsuperscript{10,15}

Recently, West et al. introduced an intrinsic quasi-atomic orbital (QUAO) localization scheme for the Hartree-Fock (HF) method\textsuperscript{26} and for strongly correlated (complete active space self-consistent field = CASSCF) wave functions in valence spaces.\textsuperscript{27} The scheme is based on expressing the molecular wave function in terms of orbitals that resemble atomic orbitals in the environment of the molecule. These localized quasi-atomic orbitals yield quantitative data about the nature of interactions between
atoms in terms of bond orders and energies. Applications of the analysis to study the nature of the bonding in urea\textsuperscript{28} and the dissociation of dioxetane\textsuperscript{29} illustrate the capability of the method for understanding the bonding in molecules on a fundamental level.

The present study applies the quasi-atomic localized orbital analysis to understand the nature of chemical bonding in selected rare gas molecules. Section 2 summarizes the relevant parts of the theory of the quasi-atomic orbital localization scheme. The bonding in three rare gas molecules, HXeCCH, HXeCCXeH, and HXeOXeH is analyzed in Section 3.

2. Method: the quasi-atomic analysis

2.1. Quasi-atomic orbitals

The intrinsic quasi-atomic orbital analysis, which is available in the electronic structure program GAMESS\textsuperscript{,30,31} is presented in detail in references 26 and 27 and is only summarized here. Through a series of transformations of molecular orbitals (MOs) from Hartree-Fock (HF) or multiconfigurational wave functions in valence spaces, orthogonal quasi-atomic orbitals (QUAOs) are obtained. The QUAOs are localized orbitals that have the characteristics of deformed orbitals of the respective free atoms. The first-order density matrix is expressed in terms of the QUAOs, giving rise to a population-bond-order matrix \( p \),\textsuperscript{32,33}

\[ \rho(1,2) = \sum_{Aa} \sum_{Bb} |Aa(1)\rangle p_{Aa,Bb} \langle Bb(2)|, \]  

\( (1) \)

where \( |Aa\rangle \) is the \( a^b \) QUAO on atom A. The diagonal elements of the matrix \( p \) represent the electron populations of the QUAOs and can have a maximum value of two. The off-diagonal elements represent “bond orders” between the QUAOs and can have a
maximum absolute value of one.\textsuperscript{34} In addition to being localized on atoms, the QUAOs |Aa\rangle are also ‘chemically adapted’ by a procedure\textsuperscript{34} that minimizes the total number of off-diagonal elements that have quantitatively significant magnitudes in the expansion of Eq.(1). As a result, the population-bond-order matrix in terms of |Aa\rangle contains very few bond order magnitudes that are large (greater than 0.6) while most bond order magnitudes are small (below 0.2). The implication is that each chemically adapted QUAO interacts with just a small number of orbitals on other atoms. These QUAOs turn out to be oriented in definite spatial directions and are therefore also called oriented QUAOs. (The terms QUAO and oriented QUAO will be used interchangeably.) They represent an \textit{ab initio} analogue to the concept of hybrid orbitals, which goes back to the earliest days of quantum chemistry. Because bonding interactions do not involve core orbitals, oriented QUAOs are determined only for the valence space.

\textbf{2.2 Kinetic bond orders}

In diatomic molecules, one usually expects positive values of the off-diagonal p matrix elements to correspond to covalent bonding interactions and negative values to correspond to anti-bonding interactions between oriented QUAOs. In polyatomic molecules, this is not necessarily so. Another shortcoming of the bond orders is that they contain no energetic information. Both shortcomings are remedied by the \textit{kinetic bond orders (KBOs)} that were introduced by West et al. (see Section 3.3 of ref 27). The KBOs are obtained as the product of bond orders and the kinetic energy integrals between the corresponding interacting QUAOs, scaled by the factor 0.1. Because covalent bonding is driven by changes in the kinetic energy,\textsuperscript{35} the KBOs furnish an indication of the covalent
character of a bond. In accordance with the general analysis of covalent bonding, it is found that, for bonding interactions between QUAOs, the KBOs are always negative, regardless of the local phases of the QUAOs and the signs of the corresponding bond orders.

2.3. Virtual valence orbitals and accurate atomic minimal basis set orbitals

For the determination of the QUAOs, auxiliary accurate atomic minimal basis set orbitals (AAMBS) are required for each atom, which serve as templates. The total number of AAMBS is equal to the dimension of the full orbital valence space of the molecule. They have been calculated as highly accurate self-consistent field (SCF) orbitals of all free atoms up to Xe and stored. Non-relativistic as well as relativistic AAMBS are available.

If the number of MOs from which the wave function is constructed, i.e., the occupied MOs, is less than the total number of minimal basis set orbitals that span the full valence space, e.g., for HF wave functions, then the determination of the QUAOs also requires a set of virtual valence orbitals (VVOs), which are determined according to the following criteria: (i) The number of VVOs + the number of occupied MOs is equal to the total number of AAMBS orbitals; (ii) The VVOs are linear combinations of all virtual orbitals; (iii) The expansion coefficients of the VVOs are determined by maximizing the overlap between the space spanned by all AAMBS orbitals and the space spanned by the (VVOs + occupied MOs). Thus, the VVOs supply the minimal basis set complement in the virtual space that is needed to provide the full set of (occupied + virtual) molecular
minimal basis set orbitals from which the QUAOs on each atom are then constructed by maximal overlap with the AAMBS space of that atom.

2.4. Split-localized molecular orbitals

As noted in Section 2.1, each oriented QUAO interacts only with a small number of QUAOs on other, typically close atoms. As a result, the interacting QUAOs from different atoms form disjointed interactive QUAO groups, each of which is characterized by a set of certain orthogonal localized MOs. In the case of HF wave functions, these localized orbitals are determined separately in the occupied orbital space and in the VVO space, and are therefore called split-localized orbitals.\textsuperscript{26, 38} The localization procedure is designed to achieve that, within each of these two orbital spaces, the split-localized orbitals involve as few of the oriented QUAOs as possible.\textsuperscript{26} Typically, the split-localized orbitals in the occupied space correspond to bonding or nonbonding lone pair orbitals, while the split-localized orbitals in the VVO space are anti-bonding orbitals. The contribution of the QUAO $|Aa\rangle$ to the split-localized orbital $\psi$ is given by the square of the coefficient $C_{Aa}$ in the expansion

$$\psi = \sum_A \sum_a |Aa\rangle C_{Aa}.$$  \hfill (2)

2.5. Wave functions

The present analysis is based on the HF-SCF wave functions of the rare gas molecules HXeCCH, HXeCCXeH, and HXeOXeH, calculated with the relativistic Sapporo split-valence triple-$\zeta$ basis set with diffuse functions (Sapporo-DK-TZP-
The infinite order two-component (IOTC) relativistic method was used to account for scalar relativistic effects.\textsuperscript{39,40,41,42,43}

The present calculations were performed at the optimized geometries that were previously obtained by the Gerber group\textsuperscript{44} for these three molecules. HXeCCH and HXeOXeH were optimized at the CCSD(T) level of theory and HXeCCXeH was optimized using the B3LYP functional.\textsuperscript{10,15,44} All geometries were optimized by the previous authors with the 6-311G(2d,2p) basis set using the 18-electron core potential developed by LaJohn for xenon. The analysis of HF wave functions constructed at the geometries obtained at CCSD(T) level of theory is not expected to largely change the results discussed in section 3.

All orbital contours shown in the figures were drawn with the MacMolPlt graphics program.\textsuperscript{45} The contour values correspond to $0.1 \text{ (electron/bohr}^3\text{)}^{1/2}$.

3. Results and Discussion

3.1 Geometry

The equilibrium geometries of HXeCCH, HXeCCXeH, and HXeOXeH are shown in Figures 1a, 1b, and 1c, respectively, and the corresponding internal coordinates are listed in Table 1.

Comparison of the geometries of HXeCCH and HXeCCXeH gives some initial insight into the effect that inserting a second Xe atom has on the bonding interpretation of the molecule. Insertion of the second Xe atom lengthens the H-Xe bond by 0.026Å and shortens the Xe-C bond by 0.027Å, implying that the Xe-C bond is strengthened while the H-Xe bond is weakened. This phenomenon has been noticed previously in substituted silatranes and was referred to in that context as “sacrificial bonding”.\textsuperscript{46} The C-C bond is
very slightly shortened, suggesting that the second Xe atom has almost no effect on the C-C bond. The insertion of Xe into acetylene does not affect the linear geometry of the molecule. In contrast, insertion of two Xe atoms into the water molecule opens up the Xe-O-Xe angle (128.2°) in HXeOXeH considerably from the Xe-O-H angle in HXeOH (108.7°). The H-Xe bond in HXeOXeH is similar in length to the H-Xe bonds in HXeCCH and HXeCCXeH.

3.2 Oriented QUAOs, populations, and bond orders

The oriented QUAOs are labeled as follows. The atomic symbol of the atom on which a QUAO is centered is listed first in capital letters. If a QUAO interacts with another orbital on a different atom with a bond order magnitude greater than 0.4, the atomic symbol for that partner (complement) atom follows in lower case. An orbital may have more than one complementary atom. Numerical subscripts for the atomic symbols differentiate between atoms of the same element in the molecule. A QUAO is characterized as σ-bonding, π-bonding, or lone pair according to a set of criteria. The symbols σ, π, sℓ, and pℓ indicate that the orbital is a σ-bonding orbital, a π-bonding orbital, an s-type lone pair orbital, or a p-type lone pair orbital, respectively. Thus, the label H1xe1σ represents an orbital on hydrogen H1 that forms a σ bond to xenon Xe1. This notation will be used for QUAOs throughout the discussion in this section.

When discussing a bond, the notation consists of capital letters for the atomic symbols of all participating atoms, followed by the symbol σ to represent a σ bond and π to represent a π bond. Thus, the notation HXeσ represents a σ bond between hydrogen and xenon. When differentiating between orbitals or bonds of similar symmetry, as is the
case with $\pi$ bonds in the following discussion, numerical subscripts will be used. Thus, $\text{CC}_{\pi_1}$ and $\text{CC}_{\pi_2}$ are two different $\pi$ bonds between two carbon atoms. When discussing orbitals or bonds of similar symmetry collectively, the numerical subscripts are omitted.

The oriented QUAOs obtained for HXeCCH, HXeCCXeH, and HXeOXeH are shown in Figures 2, 3, and 4, respectively. The orbital labels and orbital occupations are provided under the respective orbital. Bond orders are shown in bold between the two orbitals participating in the bond, and kinetic bond orders (in kcal/mol) are shown in parentheses under the respective bond orders in the figures. Only interactions with bond order magnitudes greater than 0.50 and KBOs less than -1.0 kcal/mol are shown (all other bond orders are 0.10 or smaller).

### 3.2.1 HXeCCH

The oriented QUAOs on HXeCCH, shown in Figure 2, represent the triple bond between the carbon atoms, the CH$\sigma$ bond, and the interaction between hydrogen, xenon, and carbon. The significant bonding interactions are summarized in Table 2. The interactions involving oriented QUAOs on xenon, listed at the top of Table 2, are of particular interest. Xenon uses one orbital, labeled $\text{Xe}_1h_1c_1\sigma$, to form a $\sigma$ bond to both a hydrogen atom and a carbon atom. $\text{Xe}_1h_1c_1\sigma$ has a bond order with the $H_1\text{xe}_1c_1\sigma$ orbital of 0.82 and a bond order of 0.54 with the $\text{C}_1\text{xe}_1h_1\sigma$ orbital. The kinetic bond order (KBO) of the $\text{Xe}_1h_1c_1\sigma-H_1\text{xe}_1c_1\sigma$ interaction (-30.7 kcal/mol) is correspondingly more negative than the KBO of the $\text{Xe}_1h_1c_1\sigma-C_1\text{xe}_1h_1\sigma$ interaction (-23.5 kcal/mol), indicating that the $\text{XeH}\sigma$ bond has more covalent character than the $\text{CXe}\sigma$ bond. The $H_1\text{xe}_1c_1\sigma$ orbital has a non-negligible bond order to the $\text{C}_1\text{xe}_1h_1\sigma$ orbital of -0.53 (KBO = -4.1 kcal/mol). The
negative sign of the KBO indicates that the geminal $\text{H}_1\text{Xe}_1\sigma\text{C}_1\text{Xe}_1\text{h}_1\sigma$ interaction corresponds to a weak conjugation between the two orbitals. This interaction is consistent with the $\delta$ $\text{H}^\text{Y}$ long-bond in HRgY molecules studied by Weinhold and co-workers, in which the terminal atoms are predicted to share electrons in spite of being separated by the central Rg atom. In general, the energy integrals between two orbitals decay faster than the corresponding BOs as the distance between the QUAOs increases. This accounts for the relatively low KBO of the $\text{H}_1\text{Xe}_1\sigma\text{C}_1\text{Xe}_1\text{h}_1\sigma$ interaction compared to the BO of that interaction.

The interactions between the orbitals that form the CC bonds are summarized in the middle of Table 2. The bond orders for the $\text{C}_1\text{C}_2\sigma\text{C}_2\text{C}_1\sigma$ and both $\text{C}_1\text{C}_2\pi\text{C}_2\text{C}_1\pi$ interactions are 0.99 and 1.00, correspondingly. As one would expect, the KBO of the $\text{C}_1\text{C}_2\sigma\text{C}_2\text{C}_1\sigma$ interaction (-71.0 kcal/mol) is larger in magnitude than the KBO of an individual $\text{C}_1\text{C}_2\pi\text{C}_2\text{C}_1\pi$ interaction (-25.9 kcal/mol).

The bottom section in Table 2 shows the $\text{H}_2\text{C}_2\sigma\text{C}_2\text{H}_2\sigma$ interaction. The bond order of this interaction (0.97) is consistent with the magnitude of a C-H single bond. The KBO of the $\text{H}_2\text{C}_2\sigma\text{C}_2\text{H}_2\sigma$ interaction is -39.7 kcal/mol.

The lone pair orbitals in xenon are shown in Figure 2 and are labeled $\text{Xe}_1s\ell_1$, $\text{Xe}_1p\ell_1$, and $\text{Xe}_1p\ell_2$. The lone pair orbitals do not have a strong bonding interaction with any other orbital, so they are not shown in Table 2.

The occupations of all oriented QUAOs in HXeCCH and the population and charge of each atom are summarized in Table 3. The rows correspond to the oriented QUAOs in each atom. The columns correspond to the different sets of bonding interactions. The last row of the table gives the total number of electrons involved in each
bonding set. The first and second columns of the table, respectively, list the atoms and the oriented QUAOs on the respective atom. The rightmost two columns give the population and charge of the corresponding atom.

The third column of Table 3 contains the occupation of the lone pairs in xenon. The Xe_1s orbital has an occupation of 2.00e and both Xe_1p_ℓ orbitals have an occupation of 1.99e, indicating that the lone pair orbitals are not associated with a significant transfer of charge. The total occupation of the lone pair orbitals accounts for 5.98 of the valence electrons in xenon.

The bonding interactions of xenon are presented in the fourth column of Table 3. The Xe_1h_1c_1σ orbital is expected to have an occupation of 2 in the free atom to complete the valence octet in xenon, while the H_1xe_1c_1σ and C_1xe_1h_1σ orbitals are each expected to have an occupation of 1 in the free atom. The occupation of Xe_1h_1c_1σ is 1.16e, indicating that there is a transfer of charge from the Xe_1h_1c_1σ orbital of 0.84e. This transfer of charge is divided into a transfer of 0.19e to the H_1xe_1c_1σ orbital and a transfer of 0.64e to C_1xe_1h_1σ. There is a total of 3.99 electrons involved in the HXeCσ interaction. The occupation of the orbitals involved in the HXeCσ interaction, along with the bond order and KBOs for this interaction discussed above and shown in Table 2, imply that the HXeCσ bond may be described as a three-center four-electron bond.

Column five in Table 3 contains the occupations of the orbitals involved in the CCσ and CCπ bonds in HXeCCH. It is apparent that there is a comparatively small transfer of charge (~0.03e) from each of the C_1c_2σ, C_1c_2π_1, and C_1c_2π_2 orbitals into the complementary C_2c_1σ, C_2c_1π_1, and C_2c_1π_2 orbitals. The CCσ and CCπ bonds in acetylene display no such transfer of charge. The small transfer of charge from the carbon vicinal
to xenon to the carbon bonded to hydrogen is due to the symmetry of acetylene being broken by the presence of a xenon atom. The column corresponding to the remaining interaction (CHσ) indicates that there is a transfer of charge of 0.19e from the H2C2σ orbital to the C2h2σ orbital.

The Atom Population column lists the sum of the populations of all valence oriented QUAOs within each atom to give the total atom valence population. The difference between the total atom valence population and the neutral valence population (1 for H, 4 for C, and 8 for Xe) is taken to be the charge of the atom in HXeCCH; these charges are listed in the rightmost column in Table 3. The charge on Xe based on the QUAO population is +0.86, while the charge on the H-atom bound to Xe is -0.19. The charge on the carbon atom bound to xenon (-0.55) is much more negative than the charge on the carbon atom bound to hydrogen (-0.31), reflecting the relative electronegativities of Xe and H. The charge on the H-atom bonded to C is +0.19, fairly typical of C-H bonds in hydrocarbons.

The charges of the atoms in HXeCCH calculated by the QUAO analysis compares to the charges obtained by Lundell and co-workers based on CCSD(T) natural bond order (NBO) calculations10 as follows. The NBO charges on the carbon and hydrogen atoms bonded to each other, -0.31 and +0.20, respectively, are in good agreement with the charges obtained in the present analysis. The NBO charge on xenon is 0.09 less positive than the charge calculated by the QUAO population analysis. The NBO charges on the hydrogen and carbon atoms bound to xenon are correspondingly less negative than the QUAO charges. The NBO charge on the hydrogen bonded to xenon is -0.17, similar to the QUAO charge of -0.19. The NBO charge on the carbon bonded to xenon is -0.49.
Thus, the QUAO analysis assigns a larger separation of charge between xenon and carbon than does the NBO calculation. However, the BOs and KBOs between the orbitals involved in the HXeC interaction imply that, despite the separation of charge, there is a non-negligible covalent interaction between Xe and C.

3.2.2 HXeCCXeH

Figure 3 shows the oriented QUAOs in HXeCCXeH. Only the symmetrically unique interactions are included in the figure. Thus, the orbitals shown in Figure 3 represent one of the two HXeCσ bonds, the CCσ and CCπ bonds, and the Xe lone pairs on one xenon.

The bond orders and KBOs of the significant bonding interactions in HXeCCXeH are shown in Table 4. The HXeCσ bonding interactions are listed at the top of the table, and the CC bonding interactions are listed at the bottom of the table. Similarly to HXeCCH, the bond order between hydrogen and xenon (0.79) is greater than the bond order between carbon and xenon (0.58) and the XeH interaction is associated with a more negative KBO, suggesting that the H1\text{Xe}1c1σ-Xe1h1c1σ covalent interaction (-29.5 kcal/mol) is stronger than the Xe1h1c1σ-C1xe1h1σ interaction (-25.7 kcal/mol). Compared to HXeCCH, the magnitudes of the BO and the KBO of the H1\text{Xe}1c1σ-Xe1h1c1σ interaction are smaller, while the magnitudes of the BO and the KBO of the Xe1h1c1σ-C1xe1h1σ are larger. The H1\text{Xe}1c1σ-C1xe1h1σ interaction is present in HXeCCXeH and has a BO of -0.55 and a KBO of -4.4 kcal/mol.

Each of the CCσ and CCπ interactions in HXeCCXeH has a bond order of 0.99. The C1c2σ-C2c1σ interaction has a KBO of -69.4 kcal/mol and is more negative than the
C_1C_2\pi-C_2C_1\pi KBO of -27.0 kcal/mol, as one would expect. The lone pairs on xenon do not display any significant bonding interactions, so they are not included in Table 4.

The occupations of all oriented QUAOs and the total populations and charges of all atoms in HXeCCXeH are listed in Table 5. The occupations of the lone pair orbitals in both xenon atoms, listed in the third column, are all around 2.00e. The fourth and sixth columns contain the populations for the QUAOs involved in the H_1Xe_1C_1\sigma and H_2Xe_2C_2\sigma interactions. The populations of the Xe_1h_1C_1\sigma and Xe_2h_2C_2\sigma orbitals are both 1.17e due to transfer of charge into the corresponding H_1xe_1C_1\sigma and H_2xe_2C_2\sigma orbitals of 0.24e each and to the complementary C_1xe_1h_1\sigma and C_2xe_2h_2\sigma orbitals of 0.59e each. Therefore, the presence of the second xenon atom results in more charge being transferred to H. The sum of the occupations of the interacting orbitals is 4.00e, in agreement with the analogous observations for HXeCCH, suggesting that insertion of xenon into acetylene leads to a three-center four-electron bond between hydrogen, xenon, and carbon.

The CC column in Table 5 shows the occupations of the orbitals in C_1 and C_2 that form the CC\sigma bond and CC\pi bonds. Each orbital that participates in the carbon-carbon bond has an occupation of 1.01e, indicating that there is no transfer of charge between the carbon atoms. The excess of 0.01e in the QUAOs that form the carbon-carbon bonds is due to very weak interactions (BO < 0.1, KBO \geq -1.1 kcal/mol) with the lone pairs on xenon.

Both xenon atoms in HXeCCXeH have positive charges (+0.85) that are balanced by negative carbon atom (-0.60) and hydrogen atom (-0.24) charges. Compared to the hydrogen atom bound to xenon in HXeCCH, the hydrogen atom in HXeCCXeH has a
more negative charge. The difference in the charge on hydrogen is directly due to the extra transfer of 0.05e from xenon in HXeCCXeH. The charge on xenon in HXeCCXeH is comparable to that in HXeCCH. The similar Xe charges in HXeCCH and HXeCCXeH imply that the higher transfer of charge to H in HXeCCXeH is accompanied by a corresponding lower transfer of charge to C. Carbon in HXeCCXeH, however, has a more negative charge due to the insertion of a second Xe atom. Further, comparison of Tables 2 and 4 shows that, based on the kinetic bond orders, the XeCσ bond is stronger in HXeCCXeH than in HXeCCH, while the HXeσ bond is weaker in HXeCCXeH than in HXeCCH. The presence of the second xenon atom thus leads to an increase in negative charge on the hydrogen and carbon atoms and a consequent strengthening of the XeC bond, in agreement with the geometry arguments discussed in Section 2.1.3.

3.2.3 HXeOXeH

The xenon atoms in HXeOXeH each use one orbital to form a bond to oxygen and to hydrogen, as the oriented QUAOs in Figure 4 and the bond orders and KBOs in Table 6 demonstrate. Only the symmetrically unique interactions are included in Figure 4 and Table 6.

Oxygen uses two different orbitals (O₁xe₁h₁σ and O₁xe₂h₂σ) to form the bonds to each xenon atom. As summarized in Figure 4 and Table 6, the Xe₁h₁O₁σ-O₁xe₁h₁σ interaction is associated with a bond order of 0.52 and a KBO of -22.1 kcal/mol. Similar to HXeCCH and HXeCCXeH, the H₁xe₁O₁σ-Xe₁h₁O₁σ interaction in HXeOXeH is associated with a higher bond order (0.83) and a more negative kinetic bond order (-29.2 kcal/mol) than the orbitals forming the XeOσ bond. There is also a non-negligible
$H_1\sigma_{\text{Xe}1}\text{O}_1\sigma_{\text{H}1}$ interaction with bond order -0.49 and KBO -6.0 kcal/mol. The remaining three QUAOs on xenon ($\text{Xe}_1s\ell$, $\text{Xe}_1p\ell_1$, and $\text{Xe}_1p\ell_2$) and two QUAOs on oxygen ($\text{O}_1s\ell$ and $\text{O}_1p\ell$), shown in Figure 4, are lone pair orbitals that are not associated with bonding interactions.

The occupations of the oriented QUAOs and charges on the atoms in HXeOXeH are presented in Table 7. The leftmost two columns list the atoms and oriented QUAOs in the molecule. The third and fourth columns list the occupations of the lone pair orbitals. All lone pair orbitals have an occupation of 2.00e and account for 6 electrons in each xenon atom and 4 electrons in oxygen. The fifth and sixth columns list the occupations of the orbitals that contribute to the equivalent $H_1\text{Xe}_1\text{O}_1\sigma$ and $H_2\text{Xe}_2\text{O}_1\sigma$ interactions. The occupations of the $\text{Xe}_1h_{101}\sigma$ and $\text{Xe}_2h_{201}\sigma$ orbitals (1.13e each) indicate a transfer of charge of 0.87e from the orbital on each xenon that is split into the complementary orbitals on hydrogen and oxygen. The $H_1\sigma_{\text{Xe}1}\text{O}_1\sigma$ and $H_2\sigma_{\text{Xe}2}\text{O}_1\sigma$ QUAOs have an occupation of 1.20e each due to a transfer of charge of 0.20e from xenon. The $\text{O}_1\sigma_{\text{Xe}1}\text{H}_1\sigma$ and $\text{O}_1\sigma_{\text{Xe}2}\text{H}_2\sigma$ QUAOs have an occupation of 1.67e each, indicating a transfer of charge of 0.67e from xenon into oxygen. Interestingly, the transfer of charge from xenon to its complementary atoms in HXeOXeH is comparable to the transfer of charge from xenon to its complementary atoms in HXeCCH.

The last column in Table 7 lists the charges on the atoms in HXeOXeH. H, Xe and O are calculated to have charges of -0.20, +0.87 and -1.34, respectively. The NBO charges calculated by Khriachtchew and co-workers at the CCSD level of theory\textsuperscript{15} for H, Xe, and O, are -0.180, +0.896, and -1.431, respectively. The two sets of charges on the three atoms are similar to each other. The QUAO population analysis assigns a lower
flow of charge out of Xe and a smaller charge separation between Xe and O by about 0.1 than does the NBO method.

The sum of the occupations of the orbitals that contribute to the HXeOσ interactions show that each HXeO interaction involves 4 electrons. Based on the occupations of the orbitals and the magnitude of the KBOs in Table 6, the HXeO interaction should be described as a weak three-center four-electron bond. Further, based on the atomic charges, the XeO interaction is slightly less polar than posited by Khriachtchev et al.15

3.3 Split-localized orbitals

The bonding patterns in the molecules HXeCCH, HXeCCXeH, and HXeOXeH are exhibited by the split-localized orbitals (SPLOs)26, which are displayed in Figures 5, 6, and 7, respectively. Only SPLOs that are unique by symmetry are shown. The orbital labels are indicated under the orbital plots. All atomic symbols are written with capital letters. Bonding orbitals are labeled σ or π, anti-bonding orbitals are labeled σ* or π*, and nonbonding orbitals are labeled sℓ and pℓ for s-type or p-type lone pair orbitals, respectively. Tables 8, 9, and 10 list the contribution of each QUAO to each SPLO in HXeCCH, HXeCCXeH, and HXeOXeH, respectively. The values listed are the squares of the expansion coefficients in Eq.(2). Only contributions greater than 0.02 are shown. All occupied SPLOs are doubly occupied. The SPLOs that are the anti-bonding complements to the occupied bonding SPLOs are unoccupied.

The SPLOs of HXeCCH in Figure 5 illustrate the bonding and corresponding anti-bonding orbitals for the CC and CH interactions. Table 8 shows that the two carbon atoms contribute almost equally to the C1C2σ and C1C2π bonds. The C2H2σ bonding
SPLO has a slightly larger contribution from the carbon atom, consistent with the relative electronegativities of the atoms.

The remaining SPLOs in HXeCCH involve the xenon atoms, and they are the focus of this study. Xenon has three lone pair SPLOs, labeled Xe\textsubscript{1}s\ell, Xe\textsubscript{1}p\ell\textsubscript{1}, and Xe\textsubscript{1}p\ell\textsubscript{2}. Only the Xe atom has a significant contribution to the lone pair orbitals, confirming that they are nonbonding. The remaining SPLOs are two bonding orbitals, HXe\sigma and HXeC\sigma, and one corresponding anti-bonding orbital, labeled H\textsubscript{1}Xe\textsubscript{1}C\textsubscript{1}\sigma\ast. The H\textsubscript{1}Xe\textsubscript{1}\sigma orbital has a contribution of 0.51 from hydrogen and 0.49 from xenon, indicating that this bond is largely non-polar. The H\textsubscript{1}Xe\textsubscript{1}C\textsubscript{1}\sigma orbital has a contribution of 0.08 from hydrogen, 0.09 from xenon and 0.82 from carbon, illustrating the interaction between the three atoms and the polarity of the bond toward carbon. The anti-bonding SPLO H\textsubscript{1}Xe\textsubscript{1}C\textsubscript{1}\sigma\ast has contributions from all three atoms, \textit{viz.}, 0.40 (H), 0.42 (Xe), and 0.17 (C).

The SPLOs of HXeCCXeH, shown in Figure 6 and tabulated in Table 9, reveal a similar bonding motif. The C\textsubscript{1}C\textsubscript{2}\sigma orbital, both C\textsubscript{1}C\textsubscript{2}\pi orbitals, and the corresponding anti-bonding orbitals have equal contributions from the two carbon atoms. The Xe lone pair SPLO orbitals only have contributions from the corresponding Xe atom of 1.00, indicating that all lone pair orbitals are fully localized on xenon.

The SPLOs corresponding to the HXe and HXeC interactions show that the second Xe atom increases the covalent nature of the XeC bond, in agreement with the oriented QUAO analysis in Section 3.2.2. The H\textsubscript{1}Xe\textsubscript{1}\sigma orbital has a contribution of 0.54 from the H atom and 0.46 from the Xe atom. Compared to the H\textsubscript{1}Xe\textsubscript{1}\sigma orbital in HXeCCH, the H\textsubscript{1}Xe\textsubscript{1}\sigma orbital in HXeCCXeH has a larger contribution from hydrogen and lower contribution from xenon. The H\textsubscript{1}Xe\textsubscript{1}C\textsubscript{1}\sigma SPLO has a contribution of 0.08 from
H, 0.12 from Xe, and 0.79 from C. Compared to the H₁Xe₁C₁σ orbital in HXeCCH, the presence of the second xenon atom shifts some contribution in this orbital from the C atom to the Xe atom, while the contribution from the H atom remains the same. Accordingly, the H₁Xe₁C₁σ* orbital in HXeCCXeH has contributions of 0.38 (H), 0.42 (Xe), and 0.20 (C), demonstrating that the presence of the second xenon atom slightly shifts contributions in the H₁Xe₁C₁σ* orbital from the H atom to the C atom.

The SPLOs of HXeOXeH, shown in Figure 7, include σ bonding orbitals that correspond to the HXeσ bond and XeOσ bond, an anti-bonding HXeOσ* orbital, and nonbonding lone pair orbitals on Xe and O. The contribution from each atom to each SPLO is listed in Table 10. The O atom has two lone pairs, O₁sℓ and O₁pℓ. The O₁sℓ and O₁pℓ orbitals have contributions of 0.99 and 1.00 from O, respectively. Each Xe atom has three distinct lone pairs, identified as Xe₁sℓ, Xe₁pℓ₁, and Xe₁pℓ₂. These three lone pairs all have contributions close to 1.00 from the xenon atom.

The quasi-atomic contributions to the H₁Xe₁σ SPLO show that H and Xe contribute almost equally to the bond, indicating a non-polar bond. The H₁Xe₁O₁σ SPLO on the other hand, has a large contribution of 0.83 from O, indicating, not surprisingly, that the HXeOσ bond is more polar than the HXeCσ bond. The H₁Xe₁O₁σ SPLO has a very small contribution of 0.03 from H. The anti-bonding H₁Xe₁O₁σ* SPLO orbital has a contribution of 0.41 from H, 0.38 from Xe, and 0.20 from O.
3.4 **The bonding of the xenon atom**

3.4.1 **Conclusions from the quasi-atomic analysis**

The preceding quantitative analyses of the QUAO populations, bond orders, kinetic bond orders and split-localized orbital ranges reveal unambiguous bonding patterns that are similar in the molecules HXeCCH, HXeCCXeH and HXeOXeH.

The CC bonds and the CH bond are standard σ and π pair bonds. The lone pairs on the xenon and the oxygen atoms also correspond to standard expectations.

In all three molecules, the xenon atom is linked with its two neighbor atoms by the following three-orbital four-electron bond. The pσ-type QUAO on xenon is covalently bonded to the hydrogen QUAO on one side as well as to the σ hybrid QUAO of the atom (carbon or oxygen) on the other side. These covalent bondings are generated by electrons that are shared between the pσ QUAO on xenon and the QUAOs on hydrogen as well as on carbon or oxygen. These electron sharings come about because the two electrons, which occupy the xenon pσ orbital in the free xenon atom, partially move into the half-filled orbitals on the two other atoms, *i.e.*, by partial electron migration in both directions. The differences between the molecules as regards the extent of the electron migrations are in accord with the atomic electronegativities.

One might wonder whether the ionic attractions between the net atomic charges that are generated by these substantial electron donations might be an additional cause for the electron migrations. However, these ionic attractions, in combination with the electron affinities of hydrogen, carbon, and oxygen, are too weak to overcome the ionization energy of xenon and pry electron charge loose from xenon. The estimates of these interactions are exhibited in Table 11 and were calculated as follows.
Consider the neutral atoms, between which no electrons are shared, placed at the positions they have in the molecule. Partial electron migration between these atoms generates charged atoms and interatomic orbital interferences. The resulting total energy change is estimated as the sum of the following contributions:

\[ \Delta E = \Delta(AF) + \Delta(IE) + \Delta(IA) + \Delta(IR) + \DeltaE\text{(interference)}, \]

where,

\[ \Delta(AF) = \sum_i q_i AF_i = \text{sum over all atoms that have acquired a negative charge } q_i \] (see last column of Tables 3, 5, 7). \( AF_i \) is the electron affinity of atom \( i \).

\[ \Delta(IE) = \sum_j q_j IP_j = \text{sum over all atoms that have acquired a positive charge } q_j \] (see last column of Tables 3, 5, 7). \( IP_j \) is the ionization energy of atom \( j \).

\[ \Delta(IA) = \sum_{mn} q_mq_n/R_{mn} = \text{ionic attractions between the atom pairs for which the product } q_mq_n \text{ is negative.} \]

\[ \Delta(IR) = \sum_{rs} q_rq_s/R_{rs} = \text{ionic repulsions between the atom pairs for which the product } q_rq_s \text{ is positive.} \]

\[ \DeltaE\text{(interference)} = \text{energy lowering as a result of interatomic orbital interference} \]

\[ = \text{covalent interactions resulting from electron sharing.} \]

The sum of the first four terms is an estimate of the change in energy due to “non-covalent” interactions. For \( \Delta(IA) \) and \( \Delta(IR) \), the CH group in HXeCCH is not included since it is not part of the three-center bond. In the other two molecules, all atoms are included.

The values in Table 11 (negative for attractive interactions, positive for repulsive interactions) imply that these “non-covalent” interactions in fact disfavor the actual charge transfers that are listed in Tables 3, 5, and 7. Thus, these charge transfers occur
entirely because they create electron sharing and, thereby, covalent bonding by lowering the kinetic energy, as evidenced by the kinetic bond order values listed in Tables 2, 4 and 6. (As noted in Section 2.2, the corresponding covalent bonding contributions are the KBOs times 10.) It is therefore difficult to see how electrostatic attractions can play a significant role in establishing these three-center four-electron bonds.

3.4.2 Relation to resonance interpretations

Coulson suggested in 1964 that the bonding of rare gas atom containing molecules can be understood in several possible ways. A number of interpretations of such molecules have been given in the papers discussed in the second paragraph of the Introduction. Recent computational studies of rare gas hydrogen halide molecules HRgY (Y=halide) using the electron localization function and the NBO-based natural resonance theory describe the bonding in these molecules as hybrids of several resonance structures.

In the opinion of the present authors, the straightforward quantitative analysis summarized in the preceding section 3.4.1 gets to the heart of the matter, while descriptions of multicenter bonding in terms of two-center resonance structures invite problematic complications. Nonetheless, an attempt is made in the following paragraphs to deduce implications for a possible resonance interpretation from the results of the quasi-atomic analysis. In this context, it is important to recognize that the use of ionic resonance structures does not, per se, imply the existence of electrostatic bond contributions.

Molecules that have a single resonance structure have all bond orders close to an integer value. In molecules with several resonance structures, bonds that may be
represented differently through resonance, e.g., delocalized bonds, have a bond order that is significantly non-integer. For single bonds, the integer value is close to unity, while the non-integer values are typically greater than 0.40 but significantly lower than 1.00.

The CC σ bonds in HXeCCH and HXeCCXeH and the CH bond in HXeCCH all have bond orders >0.97, indicating that these bonds have a single resonance contributor. The bonds to Xe, however, have bond orders below 0.90 that are associated with significant KBOs, so that the rationalization of these interactions would require multiple possible resonance structures; for example, a σ bond may be drawn between H-Xe, Xe-Y, or H-Y. Due to the transfer of electrons from Xe to both H and Y, it is expected that a H-Xe or Xe-Y fragment could have an excess or deficit of electrons. Thus, the possible major contributing resonance structures are (H-Xe)^+Y^-, H^+(Xe-Y), and H^Y. H^Y is a non-ionic resonance structure proposed by Coulson, in which the atoms H and Y form a covalent bond despite being separated by xenon. The symbol ± indicates that a fragment is ionic, without specifying a charge of a fragment. The signs of the charges on the ionic fragments of each resonance structure may be inferred from the charges in Tables 3, 5, and 7. The magnitude of the charge on a fragment in the hybrid structure should be lower than the charge in a single resonance structure. For the (H-Xe) fragment, the positive charge on xenon has a larger magnitude than the negative charge on hydrogen in all three rare gas molecules studied, giving the (H-Xe) fragment a net positive charge. The Y fragment necessarily has a net negative charge. Thus, the first ionic resonance structure has the form (H-Xe)^+Y^-. In the second resonance structure, in which Xe and Y are covalently bound, the (Xe-Y) fragment has a net positive charge and
H has a net negative charge in all three molecules. The second ionic resonance structure therefore has the form $H^-(Xe-Y)^+$. 

The magnitudes of the bond orders and kinetic bond orders can help determine the relative weights of the resonance structures. The H-Xe bond order (~0.80 in the three cases) is higher than the Xe-Y and H-Y (range of 0.49-0.58) bond orders, indicating that the $(H-Xe)^+Y^-$ structure is more important than the $H^-(Xe-Y)^+$ and $H^Y$ structures for the three molecules. In all three molecules, the values of the KBOs indicate that the H-Xe interaction has stronger covalent character than the Xe-Y and H-Y interactions, further demonstrating that the actual structures of the molecules studied resemble the $(H-Xe)^+Y^-$ structure most closely. The dominance of the structure $(H-Xe)^+Y^-$ is further demonstrated by the split-localized orbitals discussed in Section 3.3.

The comparable Xe-Y and H-Y bond orders indicate that the $H^-(Xe-Y)^+$ and $H^Y$ structures have similar contributions to the resonance hybrid structure of HXeY. However, the Xe-Y and H-Y KBOs indicate that the actual structure of HXeY attributes more covalent character to the Xe-Y bond than to the H-Y bond, implying that the $H^-(Xe-Y)^+$ structure has a larger influence on the structure of HXeY than the $H^Y$ resonance structure. The smaller H-Y than Xe-Y KBO is due to the longer distance between the QUAOs that participate in the H-Y interaction, despite the similar BOs of the Xe-Y and H-Y interactions.
4. Conclusions

The analysis in terms of quasi-atomic orbitals and split-localized orbitals has been applied to the Hartree-Fock wave functions of the molecules HXeCCH, HXeCCXeH and HXeOXeH in order to elucidate the bonding of the rare gas atom.

It is shown that the $p_\sigma$ orbital of Xe simultaneously forms bonds with orbitals on H and Y ($Y = \text{C or O}$). The remaining orbitals in Xe remain lone pairs and have no interactions with other atoms. The bond orders and kinetic bond orders of the orbitals that generate the H-Xe-Y interactions indicate that significant covalent bonding exists not only between Xe and H, but also between Xe and Y. In addition, there is some geminal bonding between H and Y. The presence of a second Xe atom in HXeCCXeH strengthens the XeC bond compared to HXeCCH, while the HXe bond is slightly weakened. The atomic charges calculated from the orbital populations indicate that the covalent HXe and XeY interactions are both created by electron sharing that is generated through charge transfers (“donations”) from the $p_\sigma$ orbital on Xe to the orbitals on both H and Y. The combination of these features constitutes the essentials of three-center four-electron bonds of the kind that was qualitatively proposed for rare gas atoms more than half a century ago by Rundle and Pimentel.\textsuperscript{17,18,19,20}

The split-localized orbitals are a bonding HXe$\sigma$ orbital, a bonding HXeY$\sigma$ orbital, and an anti-bonding HXeY$\sigma^*$ orbital. The atomic contributions indicate that the HXeY$\sigma$ bond is polarized toward Y while the HXe$\sigma$ bond has similar contributions from H and Xe. The polarity of the HXeY$\sigma$ orbital decreases by insertion of the second Xe atom while the HXe$\sigma$ orbital is polarized toward hydrogen, in agreement with the results of the oriented QUAO analysis.
From the aforementioned quantitative results, a possible bonding description in terms of a superposition of the resonance structures (H-Xe)⁺\(Y^−\), H⁻(Xe-Y)⁺ and H⁺Y is inferred. The relative bond orders and KBOs for the H-Xe, Xe-Y, and H-Y interactions imply that, although the structure (H-Xe)⁺\(Y^−\) is the major contributor, the structures H⁻(Xe-Y)⁺ and H⁺Y are non-negligible. The need for contributions from all three structures challenges the single-resonance ionic description proposed in early studies. The use of ionic resonance structures does not imply the existence of electrostatic bond contributions, as demonstrated in Section 3.4.1.

Future investigations of these molecules will consider multiconfigurational treatments of the HXeY bonding and application of a recently developed quasi-atomic energy decomposition analysis.

Acknowledgements. This work was supported by a National Science Foundation grant (CHE-1147446) to KR and MSG, and an AGEP supplement to that grant. The authors are grateful to Professor Benny Gerber and his group for supplying the coordinates of the rare gas molecules that were studied in this work. Insightful discussions with Dr. Aaron West are gratefully acknowledged.

References


Table 1. Optimized geometry coordinates of HXeCCH calculated with CCSD(T), HXeCCXeH calculated with B3LYP, and HXeOXeH calculated with CCSD(T).\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>HXεCCH</th>
<th>HXεCCXεH</th>
<th>HXεOXεH</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r(\text{H-Xe}) )</td>
<td>1.766</td>
<td>1.792</td>
<td>1.779</td>
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<tr>
<td>( r(\text{Xe-Y}) \textsuperscript{b} )</td>
<td>2.351</td>
<td>2.324</td>
<td>2.186</td>
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<tr>
<td>( r(\text{C-C}) )</td>
<td>1.224</td>
<td>1.221</td>
<td></td>
</tr>
<tr>
<td>( r(\text{C-H}) )</td>
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<td></td>
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<tr>
<td>( \angle (\text{H-Xe-Y}) \textsuperscript{b} )</td>
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<td>180.0</td>
<td>176.7</td>
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<tr>
<td>( \angle (\text{Xe-Y-Xe}) \textsuperscript{b} )</td>
<td></td>
<td>180.0</td>
<td>128.2</td>
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</table>

\textsuperscript{a} The bond distances are given in angstroms and angles are given in degrees. \textsuperscript{b} \( Y = C \) for HXεCCH and HXεCCXεH, and O for HXεOXεH.
Table 2. Bond orders (BO) and kinetic bond orders (KBO) between oriented valence quasi-atomic orbitals (QUAOs) of HXeCCH.

<table>
<thead>
<tr>
<th>Interacting oriented QUAOs</th>
<th>BO</th>
<th>KBO (kcal/mol)</th>
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</thead>
<tbody>
<tr>
<td>HXeC interaction</td>
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<tr>
<td>Xe₁h₁c₁σ – H₁xe₁c₁σ</td>
<td>0.82</td>
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<td>C₁xe₁h₁σ – Xe₁h₁c₁σ</td>
<td>0.54</td>
<td>-23.5</td>
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<tr>
<td>C₁xe₁h₁σ – H₁xe₁c₁σ</td>
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<td>-4.1</td>
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<tr>
<td>CC bonds</td>
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<td></td>
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<tr>
<td>C₁c₂σ – C₂c₁σ</td>
<td>0.99</td>
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<tr>
<td>C₁c₂π₁ – C₂c₁π₁</td>
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<tr>
<td>C₁c₂π₂ – C₂c₁π₂</td>
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<td>-25.9</td>
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<tr>
<td>CH bond</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂c₂σ – C₂h₂σ</td>
<td>0.97</td>
<td>-39.7</td>
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</table>
Table 3. Occupations of oriented valence quasi-atomic orbitals (QUAOs) by atom and net atomic charge of atoms in HXeCCH.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Oriented QUAO</th>
<th>Lone Pairs</th>
<th>HXeCσ</th>
<th>CC^a</th>
<th>CHσ</th>
<th>Atom Population^b</th>
<th>Charge^c</th>
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<tr>
<td>H_1</td>
<td>H_1Xe_1c_1σ</td>
<td>1.19</td>
<td>1.19</td>
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<td>C_1c_2π_2</td>
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<tr>
<td></td>
<td>C_1c_2σ</td>
<td>0.97</td>
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<tr>
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<td>C_2c_1σ</td>
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<td>C_2c_1π_2</td>
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<td></td>
<td>C_2h_2σ</td>
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<tr>
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<td>0.81</td>
<td>+0.19</td>
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</tbody>
</table>

^a The CC column accounts for the CCσ and both CCπ bonds. ^b Atom population is taken as the sum of the occupations of all QUAOs in that atom. ^c Charge is taken as the difference between the atom population of the atom in the molecule and the neutral valence population of a single atom (1 for H, 4 for C, and 8 for Xe).
Table 4. Bond orders (BO) and kinetic bond orders (KBO) between oriented valence QUAOs of HXeCCXeH.

<table>
<thead>
<tr>
<th>Interacting oriented QUAOs</th>
<th>BO</th>
<th>KBO (kcal/mol)</th>
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<tbody>
<tr>
<td>HXeC interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe\textsubscript{1}c\textsubscript{1}\sigma – H\textsubscript{1}xe\textsubscript{1}c\textsubscript{1}\sigma</td>
<td>0.79</td>
<td>-29.5</td>
</tr>
<tr>
<td>C\textsubscript{1}xe\textsubscript{1}\sigma – Xe\textsubscript{1}h\textsubscript{1}c\textsubscript{1}\sigma</td>
<td>0.58</td>
<td>-25.7</td>
</tr>
<tr>
<td>C\textsubscript{1}xe\textsubscript{1}\sigma – H\textsubscript{1}xe\textsubscript{1}c\textsubscript{1}\sigma</td>
<td>-0.55</td>
<td>-4.4</td>
</tr>
<tr>
<td>CC bonds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}c\textsubscript{2}\sigma – C\textsubscript{2}c\textsubscript{1}\sigma</td>
<td>0.99</td>
<td>-69.4</td>
</tr>
<tr>
<td>C\textsubscript{1}c\textsubscript{2}\pi – C\textsubscript{2}c\textsubscript{1}\pi</td>
<td>0.99</td>
<td>-27.0</td>
</tr>
<tr>
<td>C\textsubscript{1}c\textsubscript{2}\pi – C\textsubscript{2}c\textsubscript{1}\pi</td>
<td>0.99</td>
<td>-27.0</td>
</tr>
</tbody>
</table>
Table 5. Occupations of oriented valence QUAOs by atom and net atomic charge of atoms in HXeCCXeH.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Oriented QUAO</th>
<th>Lone Pairs</th>
<th>H1Xe1C1σ</th>
<th>CC</th>
<th>H2Xe2C2σ</th>
<th>Atom Population</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>H1Xe1C1σ</td>
<td>1.24</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
<td>-0.24</td>
</tr>
<tr>
<td>Xe1</td>
<td>Xe1sℓ</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xe1pt1</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xe1pt2</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xe1h1C1σ</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>C1xe1h1σ</td>
<td>1.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C1c2π1</td>
<td>1.01</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>C1c2π2</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>C1c2σ</td>
<td>1.01</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>C2c1σ</td>
<td>1.01</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>C2c1π1</td>
<td>1.01</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>C2c1π2</td>
<td>1.01</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>C2xe2c2σ</td>
<td>1.59</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Xe2</td>
<td>Xe2sℓ</td>
<td>2.00</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Xe2pt1</td>
<td>1.99</td>
<td></td>
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<tr>
<td></td>
<td>Xe2pt2</td>
<td>1.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xe2h2c2σ</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>H2Xe2c2σ</td>
<td>1.24</td>
<td>1.24</td>
<td></td>
<td></td>
<td></td>
<td>-0.24</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>11.96</td>
<td>4.00</td>
<td>6.06</td>
<td>4.00</td>
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<td></td>
</tr>
</tbody>
</table>
Table 6. Bond orders (BO) and kinetic bond orders (KBO) between oriented valence QUAOs of HXeOXeH.

<table>
<thead>
<tr>
<th>Interacting oriented QUAOs</th>
<th>BO</th>
<th>KBO (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HXeO interaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe₁h₁o₁σ – H₁xe₁o₁σ</td>
<td>0.83</td>
<td>-29.2</td>
</tr>
<tr>
<td>O₁xe₁h₁σ – Xe₁h₁o₁σ</td>
<td>0.52</td>
<td>-22.1</td>
</tr>
<tr>
<td>H₁xe₁h₁σ – O₁xe₁o₁σ</td>
<td>-0.49</td>
<td>-6.0</td>
</tr>
</tbody>
</table>
Table 7. Occupations of oriented valence QUAOs by atom and net atomic charge of atoms in HXeOXeH.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Oriented QUAO</th>
<th>Xe Lone Pairs</th>
<th>O Lone Pairs</th>
<th>$H_1Xe_1O_1\sigma$</th>
<th>$H_2Xe_2O_1\sigma$</th>
<th>Atom Population</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1$</td>
<td>$H_1Xe_1O_1\sigma$</td>
<td>1.20</td>
<td>1.20</td>
<td>-0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe$_1$</td>
<td>$Xe_1s\ell$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Xe_1p\ell_1$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Xe_1p\ell_2$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Xe_1h_1O_1\sigma$</td>
<td>1.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_1$</td>
<td>$O_1s\ell$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_1p\ell$</td>
<td>2.00</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$O_1xe_1h_1\sigma$</td>
<td>1.67</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$O_1xe_2h_2\sigma$</td>
<td>1.67</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Xe$_2$</td>
<td>$Xe_2s\ell$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$Xe_2p\ell_1$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Xe_2p\ell_2$</td>
<td>2.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Xe_2h_2O_1\sigma$</td>
<td>1.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2$</td>
<td>$H_2Xe_2O_1\sigma$</td>
<td>1.20</td>
<td>1.20</td>
<td>-0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>12.00</td>
<td>4.00</td>
<td>4.00</td>
<td>4.00</td>
<td></td>
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</tr>
</tbody>
</table>
Table 8. Quasi-atomic contributions to the split-localized orbitals of HXeCCH.

<table>
<thead>
<tr>
<th></th>
<th>H₁ atom</th>
<th>Xe₁ atom</th>
<th>C₁ atom</th>
<th>C₂ atom</th>
<th>H₂ atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁Xe₁σ</td>
<td>0.51</td>
<td>0.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁Xe₁C₁σ</td>
<td>0.08</td>
<td>0.09</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₁Xe₁C₁σ*</td>
<td>0.40</td>
<td>0.42</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe₁sσ</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe₁pℓ₁</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe₁pℓ₂</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁C₂σ</td>
<td>0.48</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁C₂σ*</td>
<td>0.51</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁C₂π₁</td>
<td>0.48</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁C₂π₁*</td>
<td>0.52</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁C₂π₂</td>
<td>0.48</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁C₂π₂*</td>
<td>0.52</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂σ</td>
<td>0.60</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂σ*</td>
<td>0.40</td>
<td>0.59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Table 9.** Quasi-atomic contributions to the split-localized orbitals of HXeCCXeH.

<table>
<thead>
<tr>
<th></th>
<th>H\textsubscript{1} atom</th>
<th>Xe\textsubscript{1} atom</th>
<th>C\textsubscript{1} atom</th>
<th>C\textsubscript{2} atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{1}Xe\textsubscript{1}\sigma</td>
<td>0.54</td>
<td>0.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{1}Xe\textsubscript{1}C\textsubscript{1}\sigma</td>
<td>0.08</td>
<td>0.12</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{1}Xe\textsubscript{1}C\textsubscript{1}\sigma\ast</td>
<td>0.38</td>
<td>0.42</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Xe\textsubscript{1}s\ell</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe\textsubscript{1}p\ell\textsubscript{1}</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe\textsubscript{1}p\ell\textsubscript{2}</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}\sigma</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}\sigma\ast</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}\pi\textsubscript{1}</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}\pi\textsubscript{1}\ast</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}\pi\textsubscript{2}</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}C\textsubscript{2}\pi\textsubscript{2}\ast</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td></td>
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</tbody>
</table>
Table 10. Quasi-atomic contributions to the split-localized orbitals of HXeOXeH.

<table>
<thead>
<tr>
<th></th>
<th>H(_1) atom</th>
<th>Xe(_1) atom</th>
<th>O(_1) atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_1)Xe(_1)(\sigma)</td>
<td>0.52</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>H(_1)Xe(_1)O(_1)(\sigma)</td>
<td>0.03</td>
<td>0.13</td>
<td>0.83</td>
</tr>
<tr>
<td>H(_1)Xe(_1)O(_1)(\sigma^*)</td>
<td>0.41</td>
<td>0.38</td>
<td>0.20</td>
</tr>
<tr>
<td>Xe(_1)s(\ell)</td>
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<td></td>
<td>0.97</td>
</tr>
<tr>
<td>Xe(_1)p(\ell)(_1)</td>
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<td></td>
<td>1.00</td>
</tr>
<tr>
<td>Xe(_1)p(\ell)(_2)</td>
<td></td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>O(_1)s(\ell)</td>
<td></td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>O(_1)p(\ell)</td>
<td></td>
<td></td>
<td>1.00</td>
</tr>
</tbody>
</table>
Table 11. Estimates of electrostatic contributions to the HXeY bonds. (in kcal/mol)

<table>
<thead>
<tr>
<th>Non-covalent interactions (Y=C, O)</th>
<th>HXeCCH</th>
<th>HXeCCXeH</th>
<th>HXeOXeH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum of population weighted H atom electron affinities&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>-3</td>
<td>-8</td>
<td>-7</td>
</tr>
<tr>
<td>Sum of population weighted Y atom electron affinities&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>-16</td>
<td>-35</td>
<td>-45</td>
</tr>
<tr>
<td>Sum of population weighted Xe atom ionization potentials&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>+241</td>
<td>+476</td>
<td>+487</td>
</tr>
<tr>
<td>Sum of all interatomic ionic attractions&lt;sup&gt;b,c,d&lt;/sup&gt;</td>
<td>-98</td>
<td>-335</td>
<td>-440</td>
</tr>
<tr>
<td>Sum of all interatomic ionic repulsions&lt;sup&gt;b,c,e&lt;/sup&gt;</td>
<td>+8</td>
<td>+182</td>
<td>+111</td>
</tr>
<tr>
<td>Total estimated non-covalent interactions&lt;sup&gt;f&lt;/sup&gt;</td>
<td>+132</td>
<td>+280</td>
<td>+106</td>
</tr>
<tr>
<td>Adjusted totals&lt;sup&gt;g&lt;/sup&gt;</td>
<td>+132</td>
<td>+140</td>
<td>+53</td>
</tr>
</tbody>
</table>

<sup>a</sup> The electron affinities of H, C, and O (-17.4, -29.14, -33.7 kcal/mol, respectively) and the ionization potential of Xe (+279.74 kcal/mol) are taken from Ref 48. These values are multiplied by the respective fractional atomic charges listed in the last column of Tables 3, 5 and 7.

<sup>b</sup> For HXeCCXeH and HXeOXeH, the listed values represent sums over all atoms of the same kind in the molecule. For HXeCCH, the values represent only the three atoms in the HXeC three-center bond.

<sup>c</sup> The ionic interactions between two atoms 1 and 2 is estimated by the formula $E_{12} = 332.06 \times (Q_1Q_2/R_{12})$ kcal/mol, where $Q_1$ and $Q_2$ are the respective atomic charges (in electron fractions) listed in the last columns of Tables 3, 5, and 7, and $R_{12}$ is the interatomic distance (in Angstroms) listed in Table 1. The factor 332.06 yields the energy in kcal/mol.

<sup>d</sup> Listed are the sums $\sum_{i<j} E_{ij}$, where each term is negative.

<sup>e</sup> Listed are the sums $\sum_{i\neq j} E_{ij}$, where each term is positive.

<sup>f</sup> Listed is the sum of the first five entries in the column.

<sup>g</sup> Listed is the sum of the first five entries in the column, where the appropriate values of HXeCCXeH and HXeOXeH have been halved to create values for comparison with HXeCCH.
Figure 1. Literature structures\textsuperscript{10,15,44} of (a) HXeCCH, (b) HXeCCXeH, and (c) HXeOXeH. Hydrogen is shown in white, xenon is shown in teal, carbon is shown in black, and oxygen is shown in red.
**Figure 2.** Oriented QUAOs of the HXeCCH RHF wave function (Sapporo-DK-TZP-2012+diffuse basis set) at the optimized geometry. The orbital labels are shown below each orbital. The orbital occupations are shown next to the orbital label. The bond order between orbitals is shown in bold between the bonding orbitals. KBOs (kcal/mol) are shown in parentheses beneath the corresponding bond order.
Oriented QUAOs of HXeCCXeH

HXeC interaction

-0.55
(-4.4)

0.79
(-29.5)

0.58
(-25.7)

H_x,e_x,c_1\sigma, 1.24
Xe_e,h_1,c_1\sigma, 1.17
C_1,x_e,h_1,\sigma, 1.59

Xe lone pairs

Xe_1s\ell, 2.00
Xe_1p\ell_1, 1.99
Xe_1p\ell_2, 1.99

CC bonding

C_1,c_2\sigma, 1.01
C_2,c_1\sigma, 1.01

0.99
(-69.4)

0.99
(-27.0)

0.99
(-27.0)

0.99

C_1,c_2\pi_1, 1.01
C_2,c_1\pi_1, 1.01
C_1,c_2\pi_2, 1.01
C_2,c_1\pi_2, 1.01

Figure 3. Oriented QUAOs of the HXeCCXeH RHF wave function using the Sapporo-DK-TZP-2012+diffuse basis set. The orbital occupation is shown below each orbital. The bond order between orbitals is shown in bold between the bonding orbitals. KBOs (kcal/mol) are shown in parentheses beneath the corresponding bond order.
**Figure 4.** Oriented HXeOXeH RHF QUAOs using the Sapporo-DK-TZP-2012+diffuse basis set at the CCSD(T)/6-311++G(2d,2p)/LJ-18 geometry. The orbital occupation is shown below each orbital. The bond order between orbitals is shown in bold between the bonding orbitals. KBOs (kcal/mol) are shown in parentheses beneath the corresponding bond order.
Figure 5. HXeCCH RHF split localized orbitals (using the Sapporo-DK-TZP-2012+diffuse basis set) at the equilibrium geometry. Only orbitals that are unique by symmetry are shown. The orbital symbols are shown below the corresponding orbital.
Figure 6. HXeCCXeH RHF split localized orbitals (using the Sapporo-DK-TZP-2012+diffuse basis set) at the equilibrium geometry. Only orbitals that are unique by symmetry are shown. The orbital symbols are shown below the corresponding orbital.
**Split Localized Orbitals of HXeOXeH**

- **σ bonding**
  - $H_2Xe_2\sigma$
  - $H_2Xe_2O_1\sigma$
  - $H_2Xe_2O_4\sigma^*$

- **Xe lone pairs**
  - $Xe_1s\ell$
  - $Xe_1p\ell_1$
  - $Xe_1p\ell_2$

- **O lone pairs**
  - $O_1s\ell$
  - $O_1p\ell$

**Figure 7.** HXeOXeH RHF split localized orbitals (using the Sapporo-DK-TZP-2012+diffuse basis set) at the equilibrium geometry. Only orbitals that are unique by symmetry are shown. The orbital symbols are shown below the corresponding orbital.
CHAPTER 4. A QUASI-ATOMIC ANALYSIS OF THREE-CENTER TWO-ELECTRON Zr-H-Si INTERACTIONS

Juan J. Duchimaza Heredia, Aaron D. Sadow, Mark S. Gordon

Abstract

A comprehensive analysis of the bonding structure of the disilyl zirconocene amide cation \( \text{Cp}_2\text{Zr[N(SiHMe_2)_2]}_2^+ \) is conducted by application of an intrinsic orbital localization method that yields quasi-atomic orbitals (QUAOs). An emphasis is placed on describing a previously characterized three-center two-electron interaction between zirconium, hydrogen, and silicon that presents structural and spectroscopic features similar to that of agostic bonds. By expressions of the first order density matrix in terms of the QUAOs, bonds orders (BOs), kinetic bond orders (KBOs), and the extent of transfer of charge become available to determine the electronic nature of the Zr-H-Si bond. The QUAOs demonstrate the importance of vicinal interactions in the stabilization of the molecule. In addition, the evolution of the QUAOs during reactions with Lewis bases reveals the role of the Zr-H-Si interaction in facilitating the reaction.

1. Introduction

Bond formation and cleavage through \( \beta \)-elimination and 1,2-migratory insertion have been well-studied processes in organometallic chemistry. The characterization of agostic bonds, in which a carbon-hydrogen group forms a three-center two-electron (3c2e) bond with the transition metal center so that the metal is simultaneously bonded to carbon and hydrogen, is an important aspect of many organometallic reaction
mechanisms. For example, the role of agostic bonds in stable intermediates of β-elimination and 1,2-migratory insertion reactions has provided an interesting insight into the pathway of the conversion of a metal alkyl to a metal hydride/metal olefin.\(^1\) While the coordination of a bond to a metal center is not exclusive to carbon-hydrogen bonds, the relative inertness of the carbon-hydrogen bond and the unusual nature of 3c2e interactions involving C-H bonds led to the initial use of the term *agostic* to refer to C-H→M interactions.\(^1\)

Analogous three-center interactions between the metal center and B-H, Si-H, N-H, C-F, and C-Cl have been observed and described as agostic.\(^4\) Interactions involving Si-H are of particular interest in the present work. Interactions between the transition metal and a ligand containing a Si-H bond were observed prior to the first use of the term agostic.\(^5\) Si-H→M interactions, where M is a transition metal, are not uncommon, and literature from the past three decades have used the terms *nonclassical* and *agostic* to refer to these interactions.\(^6\) However, because the range of interactions that should be defined as *agostic* as intended by Brookhart and Green is limited to C-H→M 3c2e bonds,\(^2\) it is necessary to differentiate between *bona fide* agostic bonds and the analogous Si-H→M bonds. In an effort to refer to 3c2e Si-H→M bonds succinctly, the term *pyragostic* will be used throughout this paper to refer to such bonds.\(^7\)

Agostic and pyragostic interactions at similar positions with respect to the metal have several similar structural and spectroscopic features that may be observed by X-ray diffraction, NMR, and IR spectroscopy. For example, in the case of β-agostic and β-pyragostic bonds, common structural features include relatively short M-H distances (1.8-2.3Å for agostic interactions and 1.8-2.5Å for pyragostic interactions) and relatively
small M-H-C (90-140°) or M-H-Si (usually < 100°) angles.\textsuperscript{3,8} Structural determination often poses a challenge because hydrogen cannot be accurately located with X-ray diffraction. Spectroscopic evidence for agostic and pyragostic bonding includes atypically low $^1J_{\text{CH}}$ and $^1J_{\text{SiH}}$ values and low C-H and Si-H stretching frequencies due to a reduced bond order of the C-H or Si-H bond.\textsuperscript{8,9}

The nature of agostic and pyragostic interactions has been computationally studied using the Quantum Theory of Atoms in Molecules (QTAIM) procedure and the Natural Bond Orbital (NBO) method. QTAIM uses the electron density to determine atom locations, bond critical points, and bond paths that connect two atoms. However, only certain density functionals can accurately reproduce the electron density in the area of a β-agostic bond.\textsuperscript{10,11} Thus, a correct AIM analysis is only feasible in cases for which a proper functional is used. The NBO method has been widely used to study agostic and pyragostic interactions.\textsuperscript{12,13,14} However, applications of the NBO analysis to a large number of transition metal hydrides\textsuperscript{15} have yielded results that depend on the assignment of the transition metal $np$ orbitals as valence or “Rydberg” orbitals and on the type of resonance model used.

Studies of agostic and pyragostic bonds have provided numerous interpretations for the nature of the bond. In the case of α-agostic molecules, it has been suggested that agosticity is not due to bonding interactions between the metal and hydrogen, but rather that the agostic geometry is the result of rearrangement to alleviate short-range repulsion between the metal and electrons on carbon.\textsuperscript{16,17} In a study of $d^0$ metal alkyls, Scherer and McGrady have concluded that agostic stabilization is possible due to hyperconjugative delocalization of M-C bonding electrons.\textsuperscript{9} In other transition metal complexes, agostic
and pyragostic bonding is attributed to back-bonding by the metal into the antibonding \( \sigma^*_{\text{CH}} \) or \( \sigma^*_{\text{SiH}} \) orbital.\(^\text{18,19}\) Particularly for Si-H bonds, there has been an effort to differentiate between pyragostic interactions, \( \sigma \)-bonding, and what has been described as interligand hypervalent interactions.\(^\text{20,21,22}\)

One important property of interest is the strength of agostic and pyragostic interactions. Studies have estimated the strength of the interaction as the difference between the energy of an agostic structure and the energy of an optimized model with constraints imposed so that the agostic interaction is no longer present.\(^\text{23,24}\) Though this method approximates agostic interactions to provide a stabilization in the range of 1 to 20 kJ/mol,\(^\text{9,23,24}\) the electronic nature of the ligand in the system can be significantly changed, often even leading to weak C-C or Si-C bonds.\(^\text{25,26}\) This approach is thus more effective in observing trends rather than obtaining a quantitative analysis. In an attempt to determine the strength of an agostic bond without altering the geometry of the system, von Frantzius et al. used the generalized compliance matrix, which measures the strength of a bond as the displacement of a bond due to a force being applied on it.\(^\text{27}\) Using this method, an agostic bond has been measured to be in the range of a typical hydrogen bond (\( \leq 10.0 \text{ kcal/mol} \)).

A promising novel method to study intramolecular interactions is the analysis in terms of intrinsic quasi-atomic orbitals (QUAO) developed by Ruedenberg, Gordon and collaborators.\(^\text{28,29}\) The method extracts orbitals that have the quality of atomic orbitals that have been deformed by the intramolecular environment. Through the expression of the first order density matrix in terms of the QUAOs, quantitative data regarding bonding interactions are obtained in terms of bond orders and interaction energies.
Demonstrative applications of the method to study the bonding in urea\textsuperscript{30} and the dissociation of dioxetane\textsuperscript{31} have shown that the method provides chemically relevant information. A recent application of the method to study the bonding in rare gas molecules exhibits the power of the QUAOs to analyze uncommon interactions\textsuperscript{32}.

In the present study, the QUAO localization is used to obtain an in depth analysis of all bonding interactions in the disilyl zirconocene amide cation \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} where Cp denotes cyclopentadienyl. In a previous study by Sadow and co-workers,\textsuperscript{33} \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} was synthesized through the reaction of Cp\textsubscript{2}ZrH[N(SiHMe\textsubscript{2})\textsubscript{2}] and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} or [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] and it was confirmed through experiment and by computational methods that the cationic \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} has two β-pyragostic interactions. In that study, the vibrational and geometrical features of \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} were obtained with MP2 calculations, and Edmiston-Ruedenberg localization\textsuperscript{34} of the molecular orbitals provided some initial computational evidence of significant interactions between the metal and silyl groups. Further, \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} was experimentally shown to have interesting reactivity possibly driven by the β-pyragostic interaction.\textsuperscript{33} Reactions of \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} with Lewis bases resulted in the following observation: 4-dimethylaminopyridine (DMAP) proceeds through β-SiH attack, forming a new Si-N bond, while a reaction with OPEt\textsubscript{3} proceeds by coordination to Zr. These reactions are summarized in Scheme I.

Relevant details of the QUAO analysis are summarized in Section 2. The bonding interactions in \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} are discussed in Section 3. Insights about the role of the pyragostic interaction during reactions with Lewis bases are discussed in Section 4.
The quasi-atomic picture of the non-classical Zr-H-Si interaction leads to an interpretation of the bonding in highly coordinated transition metal complexes.

2. Method

2.1 Quasi-atomic orbitals

The QUAOs are localized orbitals constructed with the goal of obtaining orbitals that have the character of atomic orbitals that have been deformed by the environment of the molecule. The theoretical details for obtaining the QUAOs are described in reference 28. In this discussion, the following details are relevant.

The QUAOs are basis set independent atomic-like orbitals obtained from the molecular orbitals that generate the determinants that make up a molecular wave function. By maximizing the overlap of the molecular orbitals with a set of pre-determined accurate atomic minimal basis set (AAMBS) orbitals through singular value decompositions, precursor QUAOs are formed. These precursor QUAOs are then mutually orthogonalized between the different atoms by a procedure that maintains as much of the AAMBS character as possible.

In order to account for the chemical environment of the molecule, the precursor QUAOs on each atom are then mixed via linear combinations to obtain the QUAOs. This mixing is accomplished using the criterion that each QUAO has significant interactions with as few QUAOs on other atoms as possible. Because bonding interactions occur between valence orbitals, the valence QUAOs are distinct from the valence precursor QUAOs in that they are typically oriented in definite spatial directions. Thus, the QUAOs are referred to as “oriented QUAOs”. They are analogous to hybrid orbitals.
The bonding interactions are obtained from the matrix elements of the spatial first order density representation,

\[
\rho_{1,2} = \sum_{Aa} \sum_{Bb} \langle Aq(1) \rangle p_{Aa,Bb} \langle Bb(2) \rangle
\]

in terms of the QUAOs |Aa⟩ and |Bb⟩, which indicate orbitals ‘a’ and ‘b’ on atoms ‘A’ and ‘B’, respectively. The matrix \( p \) contains the interactions between the QUAOs. The diagonal elements \( p_{Aa,Aa} \) are the orbital occupations. The off-diagonal elements \( p_{Aa,Bb} \) where \( A \neq B \), are the bond orders (BOs) between orbitals on different atoms. Therefore, the \( p \) matrix is called the population-bond-order matrix.\(^{38}\) The diagonal elements of \( p \) can have a value between 0, indicating an unoccupied orbital, and 2, indicating a lone pair orbital. The off-diagonal elements of \( p \), the BOs, can have values between \(-1 \) and \(+1 \). Only few BOs have magnitudes greater than 0.6, which imply a “firm” bond, while many BO magnitudes are below 0.2. There exists a relationship between the bond orders and QUAO occupations. Generally, a QUAO with an occupation close to 2 has BOs that are close to zero, whereas two interacting QUAOs, each with an occupation close to 1, have a high BO. The relations between populations and bond orders are discussed in detail in reference 39.

While a significant BO usually indicates that two QUAOs form a bond, the BOs have shortcomings. First, the BOs are unitless and give no energetic measure of the strength of a bond. Second, since the phases of the QUAOs cannot be controlled during formation of the QUAOs, bonding QUAO pairs can have mismatching phases and be associated with negative BOs. The analysis of the QUAOs is therefore quantified by considering the energy integrals between interacting QUAOs. In particular, because covalent bonding is driven by changes in the kinetic energy,\(^{40}\) the kinetic part of the
interference energy is an effective estimation of bonding strengths. The kinetic part of the interference energy in terms of QUAOs is called the kinetic bond order (KBO)\textsuperscript{29} and is defined as

\[
\text{KBO} = 0.1 \times \rho_{a_{A}, b_{B}} \left\langle A_{a} \mid -1/2V^2 \mid B_{b} \right\rangle.
\]

The scaling factor 0.1 is an empirical adjustment to approximately match magnitudes of KBO values of a carbon-carbon single bond to the magnitude of the C-C bond energy.\textsuperscript{41} The relations between kinetic bond orders and bond strengths are elaborated in references 37 and 39.

### 2.2 Computational Details

The geometries of \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}])\textsuperscript{+}, 4-dimethylaminopyridine (DMAP), triethylphosphineoxide (OPE\textsubscript{3}), the product of the reaction between \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}])\textsuperscript{+} and DMAP, [Cp\textsubscript{2}Zr{N(SiHMe\textsubscript{2})(SiMe\textsubscript{2}DMAP)}H\textsuperscript{+}, and the product of the reaction between \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}])\textsuperscript{+} and OPE\textsubscript{3}, [Cp\textsubscript{2}Zr{N(SiHMe\textsubscript{2})\textsubscript{2}OPE\textsubscript{3}\textsuperscript{+}, were optimized at the Hartree–Fock level of theory. Because an all-electron basis set is needed, the Huzinaga 21 split valence basis set (MIDI) with three d and one f polarization functions on heavy atoms, referred to here as MIDI,\textsuperscript{42} was used for all calculations. The starting coordinates for \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}])\textsuperscript{+}} were obtained from a previous MP2 calculation with a model core potential triple-\(\zeta\) basis (MCP-TZP).\textsuperscript{33}

The intrinsic quasi-atomic localization by West, Schmidt, Gordon, and Ruedenberg\textsuperscript{28,29} was applied to all molecules. The full valence AAMBS for zirconium, which includes the 5p orbitals in the valence space, was used.\textsuperscript{36} Including the \(np\) orbitals
in the AAMBS for transition metals has been shown\textsuperscript{36} to enhance hybridization and allow bonding QUAOs to be more oriented toward complementary QUAOs, resulting in a better representation of bonding for transition metals. All of the results discussed in the following sections were obtained from calculations using GAMESS\textsuperscript{43}.

The QUOA\textsubscript{s} were drawn with the MacMolPlt graphics program\textsuperscript{44}. The contour surfaces of the orbitals shown in the figures in the following sections correspond to a value of 0.1 (electron/bohr\textsuperscript{3})\textsuperscript{1/2}.

3. Analysis of \{Cp\textsubscript{2}Zr[N(SiHMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+}

The localization procedure recovers 101 valence QUAOs, the total number of AAMBS orbitals required to describe the molecule. Nine valence QUAOs are localized on Zr, corresponding to the 4d5s5p full AAMBS valence space used. Each C and Si atom, and the N atom, have a total of four valence orbitals that correspond to the nsnp valence space, while each H atom has one valence orbital that corresponds to the 1s orbital.

Each QUAO is assigned a label that describes its chemical interactions and properties for easy reference. Each QUAO label has several components. The first component is the atomic symbol of the atom on which the orbital is centered. If the QUAO participates in bonding, the next component of the label is a list of atomic symbols of the atoms to which the QUAO forms a bond, in lower case. In cases where a distinction between atoms with the same atomic symbol is needed, an alphanumeric subscript is used. For a bonding QUAO, the final component of the label is the appropriate symbol that characterizes the bond in which the QUAO participates as a \(\sigma\)-
bond or π-bond. If a QUAO does not form a bond, the second and final component of the label identifies it as a lone pair orbital if its occupation is close to two electrons. For example, the label Nsi_1σ indicates a QUAO centered on nitrogen that forms a σ-bond to a silicon atom, whereas the label N_pℓ indicates a p-type lone pair QUAO on nitrogen.

The σ and π character of a bond between two QUAOs on main group elements (i.e., H, C, N, Si) is automatically determined by considering the bond orders between the atoms and the direction of the accumulation of charge in the QUAOs. Similar considerations, in addition to inferences based on qualitative features of the QUAOs, are used to determine the character of σ and π bonds that are formed by QUAOs on Zr.

An overview of the occupations of all symmetry unique QUAOs in the molecule is given in Table 1. The QUAOs are grouped according to the atoms to which they belong. Also listed are the resulting total population of each atom and the corresponding charge of the atom calculated as the nuclear charge minus atomic electron population. Table 1 reveals the distribution of the missing electronic charge of the cation. One deduces an electronic population increase with respect to the neutral moiety for each methyl fragment (0.29e⁻), for each pyragostic H atom (0.19e⁻), and for N (1.15e⁻), whereas an electronic population decrease with respect to the neutral moiety is found for each Cp fragment (0.08e⁻), for Zr (0.71e⁻), and for each Si (1.39e⁻). The moiety [N(SiHMe₂₂)] has a total electronic population deficit of 0.09e⁻ with respect to the neutral entity. Thus, approximately 30% of the cationic charge is divided between the two Cp fragments and the [N(SiHMe₂₂)] fragment, while 70% of the cationic charge is on Zr.
3.1 Geometry of \( \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2]_2]\}^+ \)

The RHF/MIDI optimized geometry of \( \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2]_2]\}^+ \) is shown in Figure 1. The Cp rings and methyl groups are shown as wireframes. Although no symmetry constraints were imposed, the geometry of the optimized structure has near \( \text{C}_{2v} \) symmetry.

Table 2 lists the relevant geometric features of \( \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2]_2]\}^+ \). For comparison, the coordinates calculated by MP2 calculations and as obtained through x-ray crystallography\(^{33} \) are also included in Table 2. The RHF/MIDI optimized Zr-H distances of 2.19 Å are longer than the experimental and MP2 bond lengths (2.06 Å in both cases) by \( \sim 0.1 \) Å. The precursor \( \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2]_2] \) molecule has one classical Zr-H \( \sigma \) bond and one non-classical Zr-H\(^{\cdots}\)Si pyragostic interaction. Thus, comparison to the lengths of the Zr-H interactions in \( \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2]_2] \) obtained by X-ray crystallography is informative.\(^{45} \) The classical Zr-H bond in \( \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2]_2] \) has a bond length of 1.90 Å, whereas the Zr-H distance in the non-classical Zr-H\(^{\cdots}\)Si interaction in \( \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2]_2] \) is 2.47 Å. The pyragostic Zr-H distances in \( \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2]_2]\}^+ \) in the RHF/MIDI optimized geometry fall between the classical Zr-H and pyragostic Zr-H bond lengths in \( \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2]_2] \).

The Zr-Si distance in \( \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2]_2]\}^+ \) calculated by RHF/MIDI (2.91 Å) is only \( \sim 0.04 \) Å longer than the experimental distance of 2.87 Å and the MP2 distance of 2.86 Å. The RHF/MIDI bond length (1.59 Å) is in good agreement with the MP2 Si-H bond length (1.57 Å). In comparison to the average Si–H bond length of 1.48Å,\(^{46} \) the calculated pyragostic Si–H bond is stretched. Thus, the geometric effects of the pyragostic interaction are reasonably well reproduced in the RHF/MIDI structure.
3.2 QUAOs on zirconium

Zirconium has nine valence QUAOs that are generated by the 4d5s5p full AAMBS valence space. Figure 2 shows the QUAOs on zirconium that are qualitatively unique along with their labels and occupations. The QUAOs labeled Zr\textsubscript{1a}, Zr\textsubscript{1b}, and Zr\textsubscript{1b} bond to the cyclopentadienyl ring denoted \textit{Cp\textsubscript{1}}. The subscripts ‘a’ and ‘b’ indicate that these orbitals interact with \textit{Cp\textsubscript{1}} differently. The QUAOs Zr\textsubscript{1b} and Zr\textsubscript{1b} are equivalent by symmetry. Not shown in Figure 2 are the QUAOs Zr\textsubscript{2a}, Zr\textsubscript{2b}, and Zr\textsubscript{2b} that bond with \textit{Cp\textsubscript{2}} in a similar manner to the QUAOs that bond to \textit{Cp\textsubscript{1}}.

The orbitals labeled Zr\textsubscript{nσ} and Zr\textsubscript{hσ} form, respectively, a σ bond with nitrogen and a σ bond with a pyragostic hydrogen. An equivalent Zr\textsubscript{hσ} QUAO oriented toward the second pyragostic hydrogen is omitted from Figure 2. The bonding of Zr will be explored in the following sections.

The s-, p-, and d-characters of the Zr QUAOs, determined by the overlap of the QUAOs with the AAMBS orbital of a given symmetry,\textsuperscript{39} are shown in Table 3. All QUAOs are hybridized and show some degree of s-, p-, and d-character. Notably, the QUAOs show much more p-character than s-character, which is in marked contrast to the free Zr atom where the 5p orbitals are empty and the 5s orbital is fully used.

Note that (Figure 2) all nine QUAOs on Zr are occupied. As seen from Table 1, all Zr QUAOs have significant occupations, the lowest (0.29) being that of the QUAO Zr\textsubscript{hσ}. This is in contrast to the diatomic transition metal molecules studied by Schoendorff et al.,\textsuperscript{36} for which certain QUAOs obtained using the full valence AAMBS remain largely unoccupied (occupation < 0.10). The fact that all QUAOs on Zr are occupied is due to the number of ligands in the \{\textit{Cp\textsubscript{2}}Zr[N(SiMe\textsubscript{2})\textsubscript{2}]\}\textsuperscript{+} complex, which
requires all Zr orbitals to establish bonds. The sum of the occupations of the orbitals on Zr is 3.29 e\textsuperscript{-}, indicating that 0.71 e\textsuperscript{-} have migrated from the neutral Zr to the atoms to which Zr is bonded.

### 3.3 Bonding in cyclopentadienyl

The BOs and KBOs of the CH and CC σ bonds in cyclopentadienyl are comparable to those found in other organic systems.\textsuperscript{39} However, the π bonding is important to consider in detail, as Zr bonds to Cp via the π QUAOs on carbon.

\textit{σ bonds in the cyclopentadienyl fragments.} The unique σ bonding interactions in one cyclopentadienyl are displayed in Figure 3. Based on valence populations of atoms, one would expect the QUAO on hydrogen and each QUAO on carbon to have an occupation of one for the isolated atom. The occupations of the QUAOs that form the CH σ bonds in cyclopentadienyl indicate a transfer of 0.17 e\textsuperscript{-} from hydrogen to the bonding QUAO on carbon that reflects the relative electronegativity of the atoms. All CH σ bonds have a bond order of 0.97 and a KBO ranging from -38.8 to -38.3 kcal/mol. Table 4 shows that the occupations of the QUAOs, bond orders, and KBOs of the CH σ bonds are comparable to the corresponding values of the CH σ bonds in other organic molecules. The QUAOs that form the CC σ bonds all have an occupation of 0.99, indicating an absence of transfer of charge between the carbon atoms. The bond orders between the QUAOs that form the CC σ bonds are 0.97 and the KBOs lie between -47.7 and -47.9 kcal/mol. According to Table 4, the σ bonds of the cyclopentadienyl rings show little deviation from the σ bonds in other cyclic organic compounds.
π bonding in the cyclopentadienyl fragments. The CCπ bonds in one cyclopentadienyl are shown in Figure 4. Not shown in the figure is the orbital C_2c_1c_2Zrπ that is centered on C_2 and is symmetrically equivalent to C_2c_1c_3Zrπ with equivalent occupation as C_2c_1c_3Zrπ and correspondingly equivalent BO and bonding KBOs. All CCπ bonds have a bond order of 0.56 and are associated with a KBO of -8.9 or -9.1 kcal/mol. Since each CCπ QUAO has ~equal bond orders with its neighboring CCπ QUAOs, the π bonding is delocalized over multiple QUAOs. The occupations of the π orbitals on carbon are close to one, indicating there is no net transfer of charge between carbon atoms upon formation of the π bonds.

Atom populations and orbital hybridization. Assuming a neutral ligand, the valence population of cyclopentadienyl prior to electron migration is expected to be 25e⁻. Summing the occupations of the Cp QUAOs on \{Cp_2Zr[N(SiHMe_2)_2]\}⁺, the valence population of each cyclopentadienyl is 24.92 e⁻. According to the data in Table 1, the loss of 0.08 e⁻ occurs in the σ-system. The charge is likely transferred to the Zr atom. The Chσ orbitals have 30% s character and 70% p character, while the Ccσ orbitals have 27% s character and 73% p character. The carbon π orbitals are almost pure p-orbitals, with 1% s character. The slight hybridization to s character is presumably due to the coordinating bonds between the π-QUAOs on Cp and the zirconium.

3.4 Coordination between Zr and Cp

The QUAO analysis gives an interesting insight about the coordination between Zr and cyclopentadienyl. The Extended Hückel Molecular Orbital (EHMO) model of bent-sandwich compounds suggests that 3 bonds exist between Cp and the metal center
On the other hand, because the metal-carbon distances are similar for all carbon atoms in the ligand, the bonding is also described as “η⁵” to indicate that all five atoms coordinate to the metal center. The QUAO analysis reveals a balance between these concepts.

The QUAOs that form the CCπ bonds have non-negligible bond orders to certain QUAOs on Zr. In particular, the orbitals identified as Zrcp₁₆ and Zrcp₁₇ discussed in Section 3.2 are shown in Figure 4 along with the corresponding bond orders and KBOs to the π bonding QUAOs on the carbon atoms. The QUAO Zrcp₁₆ has a bond order of 0.48 and a KBO of -7.4 kcal/mol with the QUAO C₁c₂c₃zrπ on C₁. The QUAO Zrcp₁₇ has an interaction with C₃c₂c₃zrπ that has a similar BO of 0.50 and KBO of -7.6 kcal/mol. The Zrcp₁₇ QUAO is also bonded to the QUAO C₂c₁c₃zrπ with a BO of 0.41 and a KBO of -4.4 kcal/mol. Additional interactions between Zr and the Cp ring exists due to the QUAO Zrcp₁₈, which is symmetrically equivalent to the QUAO Zrcp₁₇ and forms bonds with the Cp QUAOs C₂c₂c₃zrπ and C₂c₁c₃zrπ. Correspondingly, the Zrcp₁₈–C₂c₂c₃zrπ bond has a BO of 0.50 and a KBO of -7.7 kcal/mol and the Zrcp₁₈–C₂c₁c₃zrπ bond has a BO of 0.40 and a KBO of -4.3 kcal/mol. According to the KBO values, the three stronger of all five coordinating bonds are comparable in strength to the CC π-bonds in Cp. The two weaker coordinating bonds, viz. the Zrcp₁₇–C₂c₁c₃zrπ and Zrcp₁₇–C₂c₁c₃zrπ bonds, are about half as strong, presumably due to a lower overlap between the respective bonding orbitals.

Thus, the Zr atom interacts with all five C atoms in cyclopentadienyl through three coordinating zirconium QUAOs with a total BO of 2.3 and a total KBO of -31.4 kcal/mol, not much less than the KBO of a typical CH σ-bond. The total population of the three QUAOs on Zr that are involved in the bonding to Cp is 1.13 e⁻. Thus, while the
number of QUAOs Zr uses to bond to Cp is consistent with the EHMO model description, the Zr atom interacts with the π QUAOs on all five carbon atoms in Cp in agreement with the η⁵ description of bonding.

Analogous bonding interactions exist between the other Cp fragment and the symmetry equivalent Zr QUAOs.

3.5 Bonding of the disilazido ligand

Zirconium primarily binds to the disilazido ligand through the nitrogen atom. It is therefore instructive to consider the bonding interactions of the nitrogen atom to the atoms within the disilazido ligand and to the metal center. The valence QUAOs on nitrogen are shown in Figure 5, along with the bonding QUAOs on Si and Zr. Not shown in Figure 5 is the QUAO Nsi₂σ that forms a bond with the Si₂nσ QUAO that is centered on the second Si atom and is symmetrically equivalent to the Nsi₁σ QUAO. The lone pair QUAO labeled Npℓ is perpendicular to the plane in which N, Zr, Si₁ and Si₂ lie. Also shown in Figure 5 are the QUAOs Siₘₑσ and Cₘₑₛισ that establish the bond between Si and the carbon atom Cₘₑ on one of the methyl groups.

The σ bond between Zr and N has a bond order of 0.73 and a KBO of -20.9 kcal/mol. It is associated with 1.94 electrons. A charge of 0.48 has been transferred from Zr to the Nzσ QUAO. The Nsiσ–Sinσ interaction is a σ bond with a bond order of 0.83 and a KBO of -31.1 kcal/mol. The occupations of the QUAOs that form the N-Si bonds sum to 2 and embody a transfer of charge of 0.48 e⁻ from the Sinσ QUAO to the bonding Nsiσ QUAO. The Si atom is bonded to the Cₘₑ atom of the methyl group through the interaction between Siₘₑσ and Cₘₑₛισ. The Si–Cₘₑ bond has a BO of 0.91 and a KBO of
-29.4 kcal/mol. This bond involves a total of 2.055 e\textsuperscript{-} with a transfer of about 0.3 e\textsuperscript{-} from Si to C\textsubscript{me}.

The BOs of the \( \sigma \) bonds formed by nitrogen are noticeably lower than the maximum possible BO of 1.00. (By comparison the NO \( \sigma \)-bond in NO\textsubscript{2} has BO = 0.97 and KBO = -80 kcal/mol).\textsuperscript{39} The nitrogen lone pair QUAO N \( p\ell \) has an occupation of 1.71 that is considerably less than the expected population of 2.00. These defects in occupations and bond orders of the QUAOs on N and the excess occupation in the Si–C\textsubscript{me} bonds are related to weak vicinal interactions in the disilazido ligand.

The weak vicinal interactions in the disilazido ligand and zirconium atom are summarized in Table 5. Vicinal interactions formed by N occur primarily through the N \( p\ell \) and Nzr\( \sigma \) QUAOs. The N \( p\ell \) QUAO has an interaction with each of the Sic\textsubscript{me}\( \sigma \) orbitals that form the four Si-Me bonds in the disilazido ligand. The N\( p\ell \)-Sic\textsubscript{me}\( \sigma \) interaction has a low BO (0.23) and correspondingly low KBO (-3.5 kcal/mol). This interaction implies charge donation from the N\( p\ell \) QUAO to the Sic\textsubscript{me}\( \sigma \) QUAO. As noted above, each Sic\textsubscript{me}\( \sigma \)-C\textsubscript{me}\( \sigma \) interaction is associated with an excess of 0.055 e\textsuperscript{-}. The excess in the four Sic\textsubscript{me}\( \sigma \) bonds accounts for 0.22 e\textsuperscript{-} of the deficit of 0.29 e\textsuperscript{-} for the lone pair N\( p\ell \). The excess of 0.055 e\textsuperscript{-} in the Sic\textsubscript{me}\( \sigma \) bond is not caused by electronic rearrangement within the C\textsubscript{me} atom. This can be seen from Table 6, which lists the BOs, KBOs, and QUAO occupations for the bonds formed by a C\textsubscript{me} atom in the SiHMe\textsubscript{2} moiety. All C\textsubscript{me} atoms have equivalent interactions. According to the values in Table 4, the interactions of the C\textsubscript{me} atom in the CH\textsubscript{3} group are similar to those found in CH\textsubscript{3} radicals.\textsuperscript{39} In particular, the three CH bonds are equivalent and show a transfer of 0.14 e\textsuperscript{-} from each hydrogen to the
respective $C_{\text{me}}h\sigma$ orbital on carbon. The remaining charge lost by N $p\ell$ ($\sim 0.07e^-$) is due to vicinal interactions with $\text{Zrcp}_{1a}$ and $\text{Zrcp}_{2a}$ (BO = 0.25 and KBO = -2.7 kcal/mol).

There also exists a small N$zr\sigma$--Si$_1h\sigma$ interaction with a BO of 0.24 and KBO of -2.8 kcal/mol. This interaction draws some charge from the N$zr\sigma$ QUAO toward the Si$_1h\sigma$ QUAO, leading the Zr--N $\sigma$ bond to be associated with 1.94 electrons, a small deficit from a 2-electron bond. The additional charge in Si$H\sigma$ may be a factor for establishing the three-center pyragostic interaction.

3.6 Localization of the Pyragostic (Si-H$\rightarrow$M) Interaction

The three-center pyragostic bond between the QUAOs Si$h\sigma$, H$_{zir}r\sigma$ and Z$_{rh}h\sigma$ on silicon, hydrogen and zirconium in $\{\text{Cp}_2\text{Zr}[\text{N(SiHMMe}_2]_2]\}^+$ is depicted in Figure 6. The arrows indicate the interactions between the QUAOs. Figure 6 includes the labels and occupations of the QUAOs, as well as the BOs and KBOs of the interactions that make up the pyragostic bond. The procedure to identify QUAO bonding characteristics\textsuperscript{39} produces the label H$_{zir}r\sigma$ for the QUAO on hydrogen, implying that the accumulations of charges of the QUAOs H$_{zir}r\sigma$ and Z$_{rh}h\sigma$ are oriented in the direction of the Zr-H axis. The Z$_{rh}h\sigma$-H$_{zir}r\sigma$ interaction has a BO of 0.55 and KBO of -15.1 kcal/mol. The H$_{zir}r\sigma$-Si$h\sigma$ interaction has a BO of 0.76 and KBO of -15.0 kcal/mol. The Z$_{rh}h\sigma$-H$_{zir}r\sigma$ and Si$h\sigma$-H$_{zir}r\sigma$ bonds are comparable in strength. A weaker interaction between Z$_{rh}h\sigma$ and Si$h\sigma$ QUAO is present with a BO of 0.37 and a KBO of -3.3 kcal/mol. The BO and KBO of the Z$_{rh}h\sigma$-Si$h\sigma$ interaction are comparable to the BO and KBO of the vicinal interactions formed by N discussed in the previous section. The sum of the occupations
of the three QUAOs is 2.10 electrons, a small excess of the common two electrons for a 3c2e bond.

The SiHσ-Hsizrσ bond is associated with a transfer of electrons from Si to H that reflects the relative electronegativities of the atoms. The occupation of the Hsizrσ QUAO (1.19 e⁻) shows that hydrogen gains 0.19 e⁻ from Si. The occupation of the SiHσ QUAO in the isolated atom is 1 e⁻. Considering the gain of 0.03 e⁻ due to the vicinal interactions to the Nzrσ QUAO, SiHσ should have 1.03 e⁻. The actual occupation of the SiHσ QUAO in the system (0.62 e⁻) implies a loss of 0.41 e⁻. Of the charge lost by SiHσ, 0.19 e⁻ are transferred to H and remain part of the Si–H bond, while the remaining 0.22 e⁻ are transferred elsewhere. This charge of 0.22e⁻ from the SiHσ-Hsizrσ bond is likely donated to the Zrhσ QUAO, resulting in a pyragostic interaction.

3.7 Summary of the bonding structure of {Cp₂Zr[N(SiHMe₂)₂]}⁺

The essential elements of the complex bonding pattern elaborated in detail in the previous sections can be brought together as follows.

The cyclopentadienyl fragments have electronic structures that are consistent with that of other cycloalkenes. The (rounded) KBOs of -38, -48 and -9 kcal/mol of the CHσ, the CCσ and the CCπ bonds in Cp, respectively, provide convenient gauges for an assessment of the relative strengths of the various bonds in the molecule.

Zirconium bonds through nine oriented QUAOs that are formed in the full space of all nine 5s5p4d valence orbitals. Thus, Zr is coordinatively saturated. *Three of the Zr QUAOs (with a total population of 1.13 e⁻) bond to all five π orbitals in one Cp*. The sum of all KBOs between the three Zr QUAOs and the five Cp QUAOs is -31 kcal/mol.
Another three QUAOs on Zr bond to the five π-orbitals of the second Cp with an equivalent total KBO. A seventh QUAO on zirconium forms a σ-bond to a nitrogen QUAO associated with 1.94 electrons (0.46 e⁻ on Zr and 1.48 e⁻ on N) and a KBO of -21 kcal/mol. The remaining two QUAOs on Zr are involved in the pyragostic interactions via the hydrogen atoms, as discussed below.

At the other end of the molecule, each CH bond in the methyl groups has a KBO of -36 kcal/mol. The electronic structures of all methyl groups are comparable to those of similar bonds in other organic molecules. The fourth QUAO on each methyl carbon forms a σ-bond to a silicon QUAO that contains 2.06 e⁻ (1.32 e⁻ on C and 0.74 e⁻ on Si) and has a KBO of -29 kcal/mol. In turn, a third silicon QUAO is linked to a respective nitrogen QUAO by a σ-bond containing 2.00 e⁻ (0.52 e⁻ on Si and 1.48 e⁻ on C) with a KBO of -31 kcal/mol. The fourth Si QUAO is involved in the pyragostic interaction. In addition to the aforementioned bonds to Zr and the two Si atoms, nitrogen has a lone pair orbital with an occupation of 1.71 e⁻.

As noted in the preceding paragraphs, each pyragostic hydrogen is bonded to a QUAO on Zr as well as to a QUAO on Si. Each of the pyragostic bonds has a total population of 2.10 e⁻ (0.29 e⁻ on Zr, 0.62 e⁻ on Si, and 1.19 e⁻ on H). The interactions of H to Zr and to Si are about equally strong as implied by the approximate KBO of -15 kcal/mol for each. Additionally, Zr and Si have an interaction with KBO of -3.3 kcal/mol.

_Hence, the pyragostic bond in this molecule is a three-center two-electron bond that uses Zr hybrid orbitals with substantial 5p admixture._ The total KBO of each pyragostic interaction is -33.4 kcal/mol.
All aforementioned bonds, including the 3c2e interaction, are not much weaker than a typical CH \( \sigma \)-bond.

In addition, a number of weak vicinal interactions that contribute to the stability of the molecule, each of them with a KBO of about -3 kcal/mol, are present. Two of these interactions are the interactions between the respective Zr and Si QUAOs that participate in each pyragostic bond. Further, the lone pair on nitrogen has several vicinal interactions as is apparent from its low occupation of 1.71 e\(^{-}\), which implies bond generating charge donations. Four of these are interactions with the \( \text{Si}_{\text{me}}\sigma \) QUAOs that link the Si atoms to the respective CH\(_3\) groups. Another two interactions of the N lone pair are with zirconium QUAOs that bond Zr to the two Cp rings. Finally, there are vicinal interactions between the Nzr\( \sigma \) QUAO and the silicon QUAOs in each of the two pyragostic SiH bonds. In aggregate, the vicinal interactions contribute about -30 kcal/mol to the total KBO stabilization, a substantial contribution.

Taking the bonds to Cp and the vicinal interactions in consideration, the distribution of the total cationic charge deficit of 1 e\(^{-}\) can be interpreted as follows. The dehydrogenation of the precursor Cp\(_2\)ZrH[N(SiHMe\(_2\))\(_2\)] removes one total electron from Zr, giving zirconium a +1 charge. There is a 0.08 e\(^{-}\) deficit with respect to the neutral moiety on each Cp. This charge is transferred to zirconium from each Cp. There is a deficit of 0.09 e\(^{-}\) with respect to the neutral moiety on the [N(SiHMe\(_2\))\(_2\)] complex that is also transferred to zirconium. The latter transfer can be ascribed to the donation from the lone pair orbital on nitrogen to the Zr\(\text{cp} \) orbitals (above estimated at 0.07 e\(^{-}\)). Thus, zirconium receives a total of about 0.25 e\(^{-}\) from its three ligands. The charge distributed
to Zr therefore agrees, within rounding errors, with the charge of +0.70 listed for Zr in Table 1.

4. Reaction with Lewis Bases

The reactions that yield \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2\}\text{SiMe}_2\text{DMAP}]\text{H}^+\) and \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2\}\text{OEt}_3]^+\), summarized in Scheme I, were determined in the present work to be barrierless through a series of constrained optimizations using the MIDI basis set with one set of d and one set of f polarization functions, referred to as MIDI(d,f) in the present work. For the reaction between \({\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\}_2]}^+\) and DMAP, the bond length between one of the silicon atoms participating in the pyragostic bond and pyridinic nitrogen in DMAP was chosen as the reaction coordinate, while the rest of the system was allowed to optimize. The bond distance was stretched from that of the optimized geometry of \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2\}\text{SiMe}_2\text{DMAP}]\text{H}^+\) to a distance where the bond was completely dissociated. Similarly, the energy reaction coordinate of the reaction between \({\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\}_2]}^+\) and \text{OEt}_3 to give \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2\}\text{OEt}_3]^+\) was obtained with the same basis set using the Zr-O distance as the reaction coordinate, while the rest of the system was allowed to optimize. Using the constrained geometries, the energy at the MP2 level with a model core potential triple-\(\zeta\) basis energies was calculated. In both cases, the energy of the system was verified to decrease monotonically along the reaction path to the final products.
4.1 Reaction with DMAP

4.1.1 Analysis of $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}\{\text{SiMe}_2\text{DMAP}\}\}\text{H}]^+$

A fully analytic Hessian calculation on the RHF/MIDI(d,f) optimized geometry of $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}\{\text{SiMe}_2\text{DMAP}\}\}\text{H}]^+$ yields one very small imaginary frequency of 10.69 cm$^{-1}$ that corresponds to a rotation of the Cp rings. Several attempts to remove the imaginary frequency were not successful. However, it is concluded that the imaginary mode indicates that there is essentially free rotation of the Cp rings and that therefore the optimized geometry essentially corresponds to a potential energy minimum.

The geometry of $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}\{\text{SiMe}_2\text{DMAP}\}\}\text{H}]^+$ is shown in Figure 7. In agreement with experiment, $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}\{\text{SiMe}_2\text{DMAP}\}\}\text{H}]^+$ features a new zirconium-hydrogen bond and a silicon-hydrogen bond. For clarity in this section, atoms will be labeled as follows. The atoms that form the bond between $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}\}]^+$ and DMAP are Si$_1$ and N$_D$. The nitrogen that originally formed the disilazido ligand is N. The hydrogen atom that forms the zirconium-hydrogen bond is H$_1$, and the atoms that form the silicon-hydrogen bond are Si$_2$ and H$_2$.

The Si$_1$–N$_D$ bond length is 1.88 Å, compared to the bond length of 1.65 Å between Si$_1$ and N. The Si$_1$–N–Si$_2$ angle ($136.60^\circ$) becomes more acute than in the reactant due to the loss of one pyragostic interaction. The Zr–H$_1$ bond length is 1.86 Å, about 0.33 Å shorter than the Zr–H$_1$ distance in $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}]}^+$, whereas the β-H$_2$–Zr distance in the product (2.55 Å) is longer than the Zr–H$_2$ distance in the reactant.

The QUAO localization of $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}\{\text{SiMe}_2\text{DMAP}\}\}\text{H}]^+$ provides useful information about the interactions present. Figure 8 shows select important QUAOs, namely those that correspond to the Si$_1$–N$_D$ bond, the zirconium-hydrogen
bond, and the silicon-hydrogen bond. All other QUAOs in the system are similar to the corresponding QUAOs in the reactants and they are not discussed in this section.

The bond between the cation and DMAP is formed by the $\text{Si}_1\text{N}_D\sigma$ and $\text{N}_D\text{Si}_1\sigma$ QUAOs and has a bond order of 0.72 ($\text{KBO} = -28.5 \text{ kcal/mol}$). While the BO of the new $\text{Si}_1\text{N}_D$ bond is slightly lower than that of the pyragostic $\text{Si}_1\text{H}_1$ bond in $\{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\text{)}_2]\}^+$, the KBO is nearly double in magnitude. The formation of the $\text{Si}_1\text{N}_D$ bond in $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\text{)(SiMe}_2\text{DMAP)}\}^+\text{H}]$ is accompanied by a migration of hydrogen $\text{H}_1$ to zirconium. The new Zr–H$_1$ bond has a large bond order of 0.95 ($\text{KBO} = -38.6 \text{ kcal/mol}$) and is associated with a total of 1.99 electrons. The zirconium-hydrogen bond thus exhibits the strongest $\sigma$ character of all the bonds formed by zirconium.

The remaining orbitals in Figure 8 depict the silicon-hydrogen bond. The QUAOs that form the silicon-hydrogen bond also have interactions with a QUAO on zirconium, indicating that the silicon-hydrogen bond can be considered to be part of a weakened pyragostic bond. The $\text{H}_2\text{Si}_2\sigma$-$\text{Si}_2\text{H}_2\sigma$ interaction has a bond order of 0.87 ($\text{KBO} = -20.2 \text{ kcal/mol}$) that is stronger than the same interaction in the reactant. In contrast, the interactions with the $\text{Zr}_2\sigma$ QUAO in $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\text{)(SiMe}_2\text{DMAP)}\}^+\text{H}]$ are weaker than in the reactant: the $\text{Zr}_2\sigma$-$\text{H}_2\text{Si}_2\sigma$ interaction has a bond order of 0.37 ($\text{KBO} = -7.8 \text{ kcal/mol}$) and the $\text{Zr}_2\sigma$-$\text{Si}_2\text{H}_2\sigma$ interaction has a bond order of 0.29 ($\text{KBO} = -3.4 \text{ kcal/mol}$). The bond orders and KBOs of these interactions fall within the range of the vicinal interactions for nitrogen discussed in section 3.5. The changes in BOs and KBOs for the Zr-H$_2$ and Zr-Si$_2$ interactions therefore indicate that the second pyragostic interaction resembles a weak vicinal interaction.
4.1.2 Reaction Path and QUAO representation of bond formation/dissociation

The reaction between \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2)_2]\}^+ and DMAP does not have an activation barrier. An RHF/MIDI(d,f) geometry optimization of the reactants at a Si$_1$-N$_D$ separation of 6.00 Å yields the product \[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2)(\text{SiMe}_2\text{DMAP})\}\text{H}]^+. The energy of the system from the separation of 6.00 Å to the products is plotted in Figure 9. At larger separations of the reactants, the energy is lower than the sum of the energy of the reactants. A Morokuma energy decomposition analysis at larger distances reveals that the energy lowering at large distances is due solely to electrostatic attraction. Overall, the energy of the product is 28.9 kcal/mol lower than the energy of the separated reactants.

The evolution of each pyragostic interaction into a Zr–H bond or a weak three-center interaction can be discerned by analyzing the QUAOs of the molecule at several points along the reaction path. The points on Figure 9 labeled Reacts, RP1, RP2, and Prod are used for the QUAO analysis. RP1 and RP2 correspond to Si$_1$-N$_D$ distances of 2.83Å and 1.98Å, respectively. RP1 is a point on the reaction path just before a steep energy decrease. RP2 is a point on the reaction path that is halfway between RP1 and the product. Figure 10 shows the evolution of the active oriented QUAOs in the reaction. The orbital labels and occupations for the QUAOs in the corresponding step of the reaction are included beneath each QUAO. The labels of the QUAOs indicate their chemical function; thus, the labels of certain QUAOs necessarily change throughout the reaction. Specifically, the QUAOs that form the new Si$_1$-N$_D$ bond change labels: the Si$_1$h$_1$σ QUAO in the reactants becomes Si$_1$n$_D$σ in the product, and the N$_D$ pℓ QUAO becomes N$_D$s$_1$σ in the product. In turn, the QUAO on the pyragostic hydrogen in the reactants, H$_1$s$_1$zrσ,
becomes the QUAO $H_1zr\sigma$ that exclusively bonds to zirconium and does not have a significant bond order to $Si_1$.

The remaining QUAOs in Figure 10 serve a similar chemical purpose at different points on the reaction path. As noted in section 4.1.1, the pyragostic interaction in the reactant that includes $H_2$ and $Si_2$ resembles a weak vicinal interaction in the products. Accordingly, the $Zrh_2\sigma$ QUAO becomes $Zr\,nv$ (near vacant) and $H_2si_2zr_2\sigma$ becomes $H_2si_2\sigma$. The need for QUAO label changes is more apparent when one considers changes in the bond orders and in the populations at each step of the reaction. For brevity, as indicated on the left side of Figure 10, the QUAOs centered on $H_1$, $Si_1$, and $Nd$ and the $Zr$ QUAO that becomes part of the weakened pyragostic interaction are referred to as $H_1\,w$, $Si_1\,x$, $Nd\,y$, and $Zr\,z$, respectively, for the remainder of this discussion.

The Cp QUAOs, the QUAOs on N and on the methyl groups in the disilazido ligand, and the remaining QUAOs on DMAP change very little throughout the reaction and they are omitted from Figure 10.

4.1.3 Analysis based on changes in QUAO populations

The QUAO $Zrh_1\sigma$ that forms the zirconium-hydrogen bond has the most significant change in population along the reaction path. Overall, $Zrh_1\sigma$ gains 0.56 electrons. The bonding QUAO $H_1\,w$, which changes from $H_1si_1zr\sigma$ to $H_1zr\sigma$ along the reaction path, loses 0.04 electrons. At RP1 and RP2, $Zrh_1\sigma$ gains a considerable amount of charge, whereas $H_1\,w$ maintains a constant population compared to the reactant.

To analyze the origin of the charge gained by $Zrh_1\sigma$, the sum of the QUAO populations of $Zrh_1\sigma$, $Si_1\,x$, and $Nd\,y$ is considered. This sum at the reactants, RP1, RP2,
and the products is 2.85, 2.81, 2.79, and 2.94, respectively. The sum of the populations changes very slightly from reactants (2.85) to RP1 (2.81) and from RP1 to RP2 (2.79), confirming that the change in population of the Zrh$_1$σ QUAO is due primarily to transfer of charge from Si$_1$ x and indirectly from N$_D$ y. Further, the total population of individual atoms or groups of atoms shown in Table 7 reveals that while DMAP loses a total of 0.07e at RP1, Si$_1$ and H$_1$ maintain a fairly constant population, suggesting that the charge lost by DMAP through N$_D$ is indirectly transferred to Zr. At RP2, DMAP loses an additional 0.26 e$^-$ while Zrh$_1$σ gains 0.26 electrons compared to RP1. Overall, Zr gains 0.05 e$^-$ at RP2 while Si$_1$ loses 0.05 e$^-$. The plausible flow of electrons is therefore a simultaneous transfer of electrons from DMAP to Si$_1$ x and from Si$_1$ x to the remainder of the Cp$_2$Zr{N(SiHM$_{2}$)$_2$} moiety, with the majority of electron population accumulating in the Zrh$_1$σ QUAO.

From RP2 to the product, DMAP loses 0.08 e$^-$/ to the remainder of the molecule. At the same time, Zrh$_1$σ gains 0.23 e$^-$/ through a transfer from H$_1$zr$σ$ to Zrh$_1$σ and through electron rearrangement within the Zr QUAOs.

The populations of Zr $z$, H$_2$si$_2$$σ$, and Si$_2$h$_2$$σ$ show a negligible change from the reactants to RP1. Changes in population from RP1 to the products indicate that charge from Zr $z$ is transferred to Si$_2$h$_2$$σ$ throughout the reaction. H$_2$si$_2$$σ$ maintains a population of 1.19 e$^-$/ throughout the reaction. The transfer of charge from Zr to Si$_2$ that weakens the second pyragostic interaction is largely driven by the need to redistribute charge gained from DMAP.

The rows that correspond to Cp and N in Table 7 are helpful to complete the picture of charge redistribution throughout the reaction. Each Cp ring steadily gains
charge throughout the reaction and ultimately has a population of 24.99 e⁻, which is essentially the same as the expected valence occupation of 25 electrons of an isolated Cp ring. N, by contrast, has similar occupations in reactants and in the product. However, at each reaction point the population changes as charge is redistributed. The nature of the bonds between Si and C throughout the reaction is constant.

**4.1.4 Analysis on the basis of bond orders and kinetic bond orders**

Table 8 lists the BOs and KBOs for the interacting QUAOs in Figure 10. A blank entry in Table 8 implies that the BO and KBO of an interaction are negligible or nonexistent.

*SiN bond formation.* At RP1, the interaction between Si₁₁σ and N pℓ has a bond order of 0.24 and a KBO of -4.2 kcal/mol, indicating that the interaction between the reactants is weak but not negligible. At RP2, the two QUAOs interact with a significant BO of 0.63 and KBO of -23.9 kcal/mol. At this point, the QUAO on Si simultaneously has a significant interaction with the H₁₁zrsi₁σ QUAO with a BO of 0.41 and KBO of -7.4 kcal/mol. As a consequence of the interactions at RP2, N pℓ is relabeled N₀₁σ and Si₁₁σ becomes Si₁₁n₀₁σ. At RP2, the KBO of the Si₁₁H₁σ bond is almost half compared to the reactant KBO. The Si₁₁H₁ bond is entirely dissociated in the product, while the Si₁₁N₀₁σ bond, formed by the interaction between the QUAOs Si₁₁n₀₁σ and N₀₁σ₁, has a higher BO of 0.71 and lower KBO of -25.6 kcal/mol than in RP2.

*ZrH bond formation.* The dissociation of the Si₁₁H₁σ bond is accompanied by a complete migration of H₁ to Zr. In the pyragostic interaction of the reactant, the ZrH₁ interaction has a BO of 0.55 and a KBO of -15.1 kcal/mol. As the reaction progresses, the
BO (and KBO) of the Zr\textsubscript{1} h\textsubscript{1}\sigma-H\textsubscript{1}zr\textsubscript{1}\sigma interaction increase considerably from 0.62 (-19.1 kcal/mol) at RP1 to 0.82 (-29.0 kcal/mol) at RP2. At RP2, Si\textsubscript{1} and Zr maintain a non-negligible interaction via the Si\textsubscript{1} h\textsubscript{1}n\textsubscript{D}\sigma and Zr\textsubscript{1}\sigma QUAOs with a bond order of 0.25, compared to 0.37 in the reactants, and a KBO that is only 0.1 kcal/mol lower than in the reactants. The weak interaction between Zr\textsubscript{1} h\textsubscript{1}\sigma and Si\textsubscript{1} h\textsubscript{1}n\textsubscript{D}\sigma at RP2 allows electrons to be donated to Zr\textsubscript{1}\sigma to form the zirconium-hydrogen bond in the product.

*Pyragostic bond weakening.* The Zr\textsubscript{2} h\textsubscript{2}\sigma-H\textsubscript{2}si\textsubscript{2}\sigma and Zr\textsubscript{2} h\textsubscript{2}\sigma-Si\textsubscript{2} h\textsubscript{2}\sigma interactions remain largely constant from the reactants to RP2. At the product, the ZrH\textsubscript{2} interaction has a lower BO than in the reactants of 0.37 and a KBO of -7.8 kcal/mol (almost half compared to the reactants). The ZrSi\textsubscript{2} interaction changes negligibly in the product. It is therefore possible that the weakening of the pyragostic interaction proceeds by donation of electrons from Zr to Si\textsubscript{2}. In the products, the highest BO of the Zr z QUAO (0.37) falls below the threshold of 0.40 to be considered firmly bonding,\textsuperscript{39} making Zr z a weakly-bonding nearly vacant QUAO.

The BO of the Si\textsubscript{2} h\textsubscript{2}\sigma and H\textsubscript{2}si\textsubscript{2}\sigma interaction steadily increases from 0.76 (KBO=-15.0 kcal/mol) in the reactants to 0.87 (KBO = -20.2 kcal/mol) in the product. Due to the non-negligible interactions between Zr n\nu and H\textsubscript{2}si\textsubscript{2}\sigma and Si\textsubscript{2} h\textsubscript{2}\sigma QUAOs, the final BO of the Si\textsubscript{2}H\textsubscript{2}\sigma bond is lower than the expected BO of 1.00 for a \sigma-bond.

### 4.2 Reaction with OPEt\textsubscript{3}

#### 4.2.1 Analysis of \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2}\text{OPEt}_3]^+\)

The product of the reaction between \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\}_2]\}^+ and triethylphosphine oxide (OPEt\textsubscript{3}) is \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2}\}\text{OPEt}_3]^+\). The optimized structure
of $[\text{Cp}_2\text{Zr}\{N(\text{SiHMe}_2)_2\}\text{OPEt}_3]^+$ is shown in Figure 11. A nuclear Hessian verified that the structure is a minimum on the potential energy surface.

OPEt$_3$ coordinates to Zr and breaks both pyragostic interactions in the process. The Zr–O bond length is 2.13Å and is comparable to the Zr–N bond length. Both Si–H bonds have a bond length of 1.51Å that is shorter than in the reactant. The Si–H bonds have a bond length that 0.03Å longer than the average Si–H bond.$^{46}$ The Si$_1$-N-Si$_2$ angle (118.5°) is dramatically more acute than in $[\text{Cp}_2\text{Zr}[N(\text{SiHMe}_2)_2]]^+$ and in $[\text{Cp}_2\text{Zr}[N(\text{SiHMe}_2)(\text{SiMe}_2\text{DMAP})]\text{H}]^+$. More notably, the H$_1$-Si$_1$-Si$_2$-H$_2$ dihedral angle is 55.1° due to a rotation the Si$_1$-N bond that moves H$_1$ away from Zr and allows OPEt$_3$ to approach Zr more closely.

The QUAOs on $[\text{Cp}_2\text{Zr}\{N(\text{SiHMe}_2)_2\}\text{OPEt}_3]^+$ that perform a different chemical function than in the reactants are shown in Figure 12. The QUAO occupations and the BOs and KBOs between each interaction are included in Figure 12.

The QUAOs on H$_1$, Si$_1$, H$_2$, and Si$_2$ that formed the pyragostic interactions in the reactants become strictly SiHσ bonding QUAOs in the product. The QUAO on each hydrogen has an occupation of 1.22 e$^-$ and SiHσ QUAO in each Si has an occupation of 0.80 e$^-$, giving each SiH bond a total of 2.02 electrons. Both SiH bonds have a BO of 0.93 and comparable KBOs (Si$_1$H$_1$ KBO = -23.3 kcal/mol; Si$_2$H$_2$ KBO = -23.9 kcal/mol). The low BO compared to the maximum of 1.00 and the excess of 0.02 electrons imply the existence of some weaker vicinal interactions, the strongest of which is between Si$_2$h$_2$σ and N$_{\text{Si}_1}\sigma$ and has a BO of 0.14 and a KBO of -1.2 kcal/mol.

The stabilization of the pyragostic interaction in $[\text{Cp}_2\text{Zr}[N(\text{SiHMe}_2)_2]]^+$ may be approximated by considering the KBOs of the Zr–H–Si interaction compared to the Si–H
interaction. Each pyragostic interaction in \{Cp_2Zr[N(SiHMe_2)_2]\}^+ has a KBO of -33.4 kcal/mol. By comparison, the SiH bonds in [Cp_2Zr{N(SiHMe_2)_2}OPEt_3]^+ have KBOs of -23.3 and -23.9 kcal/mol. The difference in energy between the two types of interactions suggests that the pyragostic interaction provides a stabilization of -10.1 to -9.5 kcal/mol.

The remaining orbitals in Figure 12 show a QUAO on Zr, labeled Zr $nv$, and the QUAOs Zr$\sigma$ and Oz$\sigma$ that form the Zr-O bond. The Zr-O bond has a BO of 0.69 with a KBO of -28.4 kcal/mol. The occupations of the QUAOs reasonably show that most of the 2.02 electrons in the bond are in the Oz$\sigma$ QUAO.

The QUAO Zr $nv$ has a very low occupation of 0.16 e$^-$ and does not participate in any significant interactions. The shape of the QUAO shows four large lobes that appear to be slightly polarized toward the SiN bonds. Indeed, this QUAO has weaker interactions with the Nsi$_1\sigma$ and Nsi$_2\sigma$ QUAOs, with BOs of 0.24 (KBO = -2.6 kcal/mol) and 0.15 (KBO = -2.0 kcal/mol), respectively.

4.2.2 Reaction path and QUAO representation of bond formation

No activation barrier was observed for the reaction between \{Cp_2Zr[N(SiHMe_2)_2]\}^+ and OPEt_3. The RHF/MIDI(d,f) energy of the system as the reaction progresses is shown in Figure 13. The energy of the product is 46.2 kcal/mol lower than the energy of the reactants. Similarly to the reaction with DMAP, the energy of the system at large separation of the reactants was lower than the sum of the energy of the reactants due to long-range interactions.

The QUAOs that eventually form the Zr-O bond and the QUAO on Zr that becomes $nv$ show a noticeable change in appearance throughout the reaction. These
QUAOs are shown in Figure 14 as determined at the points in the reaction labeled Reacts, RP1, RP2, and Prod in Figure 13. The Zr-O distances at RP1 and RP2 are 3.50 Å and 2.51 Å, respectively. Throughout the reaction, the Zroσ QUAO becomes tilted toward the QUAO on O. Similarly, the QUAO Ozrσ remains oriented toward Zr while the remainder of the OPEt₃ molecule is reoriented due to steric repulsion.

The QUAO Zrₓ, which changes from participating in the Zr-H₂-Si₂ pyragostic interaction to becoming a non-bonding near vacant QUAO, does not change qualitatively from the reactants to RP1 and is labeled Zrh₂σ. At RP2, the QUAO resembles a free-atom d orbital, as indicated by the four large lobes and d-character of 0.81. At this point in the reaction, the QUAO does not have any strong interactions with other QUAOs and a low occupation. It is thus labeled Zr nv at RP2 and in the product.

4.2.3 Analysis on the basis of bond orders

Table 9 summarizes the changes in bond orders and KBOs for interactions of interest.

The Zr w–H₁Si₁σ and Zr w–Si₁H₁σ interactions are already dissociated at RP1. Zr w and O y interact with a BO of 0.42 and a KBO of -15.8 kcal/mol, resulting in the respective QUAO labels Zroσ and Ozrσ. The Zroσ–Ozrσ interaction becomes stronger at RP2 and at the product. The Si₁H₁σ–H₁Si₁σ interaction maintains a constant BO and KBO of ~0.93 and -23.3 kcal/mol from RP1 to the product.

The interaction between Zr, H₂, and Si₂ is slightly weaker in RP1 than in the reactant. Nonetheless, by RP2, the BO and KBO between any QUAO on Zr and the QUAOs that form the Si₂H₂σ bond is negligible. Therefore, the QUAO on Zr becomes a
non-bonding QUAO at RP2 and in the product. The Si$_2$H$_2$σ bond accordingly becomes slightly stronger at RP1 than in the reactants. By RP2 and at the product, the Si$_2$H$_2$σ bond has a comparable BO and KBO to that of the Si$_1$H$_1$σ bond.

4.2.4 Analysis on the basis of changes in QUAO and atom population

The flow of electrons as the reaction progresses can be determined by analyzing the occupation of relevant QUAOs and total valence populations of atoms at different points along the reaction path. Table 10 lists the valence populations of various atoms and groups of atoms in the reactants, at RP1 and RP2, and in the product.

OPEt$_3$ continually donates electrons to the \{Cp$_2$Zr[N(SiHMe$_2$)$_2$]$_2$\}$^+$ moiety throughout the reaction. In the product, OPEt$_3$ has a total of 49.58 e$, which is 0.42 e$ lower than the reactant occupation. At RP1, the reacting QUAO on oxygen loses 0.10 e$ while the QUAO on Zr also loses 0.14 e$. The electrons lost by the QUAOs that form the ZrOσ bond are transferred to the Si$_1$ bond, as evidenced by Si$_1$h$_1$σ gaining 0.21 e$. At RP1, the sum of the occupations of Zroσ and Ozrσ is 2.03 e$, showing that the interaction is favorable for becoming a classical bond. As the reaction progresses, electrons from Ozrσ are transferred to Zroσ, but the sum of the occupations of the QUAOs remains constant.

Inspection of the valence populations of atoms in Table 10 shows that OPEt$_3$ loses 0.14 e$ at RP2 compared to RP1, 0.10 e$ of which are accounted for by the change in occupation of Ozrσ. In the same step, Zroσ gains 0.08 e$, but Zr only gains a net 0.01 e$ due to transfer of charge to Si$_2$h$_2$σ and H$_2$si$_2$σ: Zrh$_2$σ loses 0.12 e$ as it changes to Zr nv, while Si$_2$h$_2$σ gains 0.15 e$ and H$_2$si$_2$σ gains 0.04 e$.
From RP2 to the product, OPEt$_3$ loses an additional 0.15 e$^-$ that are transferred into the Zro$\sigma$ QUAO and to Cp to give each cyclopentadienyl a final valence population of 25.01 e$^-$. The Zr $nv$ QUAO also gains 0.03 e$^-$ in the product compared to RP2, although this electron gain is due to the vicinal interactions with Nsi$_1\sigma$ and Nsi$_2\sigma$.

5. Conclusions

The bonding in \{Cp$_2$Zr[N(SiHMe$_2$)$_2$]\}$^+$ was interpreted by extracting quasi-atomic orbitals (QUAOs) with a specific emphasis on the three-center two-electron Zr-H-Si interaction. The analysis showed that all QUAOs on zirconium are used for bonding. The application of the QUAO analysis to \{Cp$_2$Zr[N(SiHMe$_2$)$_2$]\}$^+$ shows the viability of the method to study highly coordinated transition metal compounds. In the case of the three-center interaction, one QUAO on Zr has significant interactions with both QUAOs that form the SiH bond. The three-center interaction a total energy of -33.4 kcal/mol. Compared to the energy of an SiH bond in a similar environment, the stabilization of a pyragostic interaction can be estimated to be between -10.1 and -9.5 kcal/mol.

The role of the pyragostic interaction was explored for reactions with DMAP and OPEt$_3$. In both cases, the reaction was observed to be barrierless in the gas phase, as long-range effects drive the reaction between the Lewis base and the cation. In agreement with experiment, the product of the reaction with DMAP is [Cp$_2$Zr{N(SiHMe$_2$)(SiMe$_2$DMAP)}H]$^+$ and features a new Si-N, a Zr-H bond, and a weakened pyragostic interaction. By contrast, the product of the reaction with OPEt$_3$, [Cp$_2$Zr{N(SiHMe$_2$)$_2$}OPEt$_3$]$^+$, shows that oxygen coordinates to Zr while the pyragostic interactions are dissociated. In the reaction with DMAP, it was found that electrons are
indirectly transferred from DMAP to Zr via the pyragostic interaction. Once enough electrons were transferred to the Zr-h$_1$σ QUAO to form a two-electron bond with H$_1$Zrσ, the pyragostic interaction was completely dissociated. In the reaction with OPEt$_3$, electrons are indirectly transferred from OPEt$_3$ to each SiH bond. At first, as O begins to interact with Zr-h$_1$σ, the electrons are transferred to Si-h$_1$σ, allowing the bond to become a full silicon hydride bond and rotate to allow OPEt$_3$ to approach Zr. As the reaction progresses, Zr-h$_2$σ loses some charge to the second pyragostic interaction to accommodate the charge gained from OPEt$_3$, ultimately dissociating the second pyragostic interaction. Remarkably, the bonds to the base in each product have a comparable KBO: the Si-N bond in [Cp$_2$Zr{N(SiHMe$_2$)(SiMe$_2$DMAP)}H]$^+$ has a KBO of -28.5 kcal/mol and the Zr-O bond in [Cp$_2$Zr{N(SiHMe$_2$)$_2$}OPEt$_3$]$^+$ has a KBO of -28.4 kcal/mol.

The QUAO analysis is also instructive to describe bonding to Cp in sandwich compounds. In the present study, it was shown that Zr uses three QUAOs to interact with all five carbon atoms in Cp. The bonds to Zr are formed by the π-bonding QUAOs in Cp, which align more directly to the QUAOs in Zr. Overall, the interaction between each QUAO on Zr that bonds to Cp and a π QUAO on Cp was observed to be energetically similar to the interaction between two π-bonding QUAOs on Cp.

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References


7. The term *pyragostic* is a portmanteau of pyrítio (πυρίτιο, the modern Greek word for silicon) and *agostic*, which itself is a term inspired by the Ancient Greek word for "to hold close to oneself."


Scheme I. Reactions of \{\text{Cp}_2\text{Zr}[\text{N(SiMe}_2\text{)}_2]\}\textsuperscript{+} with DMAP and OPEt\textsubscript{3}. 
Table 1. Occupations of oriented valence QUAOs by atom and net atomic charges of atoms in the \( \{ \text{Cp}_2 \text{Zr}[\text{N(SiHMe}_2]_2]\}^+ \) complex.

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<sup>a</sup> Atom population is the sum of the occupations of all QUAOs on that atom. <sup>b</sup> Charge is taken as the difference between the atom population of the atom in the molecule and the neutral valence population of a single atom (1 for H; 4 for C, Si, and Zr; and 5 for N).
Table 2. Bond lengths and angles for relevant interactions in \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\text{)}_2]\}^+ and in \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2\text{)}_2].^a

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<td>\angle \text{Si–N–Si}</td>
<td>163.67</td>
<td>171.78</td>
<td>171.78</td>
</tr>
<tr>
<td>\angle \text{Zr–H–Si}^d,f</td>
<td>99.65</td>
<td>103.12</td>
<td>103.11</td>
</tr>
</tbody>
</table>

\(^a\) MP2/MCP-TZP and X-ray coordinates for \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\text{)}_2]\}^+ are taken from ref. 33. X-ray coordinates for \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2\text{)}_2] are taken from ref. 44

\(^b\) Bond lengths are given in angstroms (Å). Bond angles are denoted by the symbol \angle and are given in degrees (°).

\(^c\) Length measured to the geometric center of the Cp ring.

\(^d\) (pyr) indicates that the coordinate is from a pyragostic interaction. The given coordinate is the same for both \text{Zr–Si}, both \text{Zr–H}, and both \text{Si–H} bond lengths and for both \text{Zr–H–Si} angles in \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\text{)}_2]\}^+.

\(^e\) (nonpyr) indicates that the \text{Zr–Si} distance is given for the non-pyragostic silicon.

\(^f\) (classical) indicates that the bond is given for a classical \(\sigma\) bond. These interactions are not present in \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\text{)}_2]\}^+.

\(^f\) The \text{Zr–H–Si} angle is given for the pyragostic interaction in \text{Cp}_2\text{ZrH}[\text{N(SiHMe}_2\text{)}_2].
Table 3. s-, p-, and d-character of QUAOs on zirconium.

<table>
<thead>
<tr>
<th>Orbital</th>
<th>s-Character</th>
<th>p-Character</th>
<th>d-Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zrnσ</td>
<td>0.04</td>
<td>0.12</td>
<td>0.84</td>
</tr>
<tr>
<td>Zrcpₐ</td>
<td>0.07</td>
<td>0.31</td>
<td>0.62</td>
</tr>
<tr>
<td>Zrcpₐ</td>
<td>0.07</td>
<td>0.24</td>
<td>0.69</td>
</tr>
<tr>
<td>Zrcpₐ</td>
<td>0.07</td>
<td>0.24</td>
<td>0.69</td>
</tr>
<tr>
<td>Zrhσ</td>
<td>0.11</td>
<td>0.27</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Table 4. Comparison of CC $\sigma$, CH $\sigma$, and CC $\pi$ bond characteristics of various organic molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>CC $\sigma$ bond BO</th>
<th>KBO$^a$</th>
<th>CH $\sigma$ bond BO</th>
<th>KBO$^a$</th>
<th>Ch-Tr$^b$</th>
<th>CC $\pi$ bond BO</th>
<th>KBO$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp fragment$^c$</td>
<td>0.97</td>
<td>-48</td>
<td>0.97</td>
<td>-38</td>
<td>0.17</td>
<td>0.56</td>
<td>-9</td>
</tr>
<tr>
<td>Naphthalene$^d$</td>
<td>0.98</td>
<td>-53</td>
<td>0.97</td>
<td>-39</td>
<td>0.16</td>
<td>0.51</td>
<td>-11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>to -55</td>
<td></td>
<td></td>
<td></td>
<td>to 0.78</td>
<td>to -19</td>
</tr>
<tr>
<td>Quinone$^e$</td>
<td>0.96</td>
<td></td>
<td>0.97</td>
<td></td>
<td>0.17</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>Methyl fragment$^c$</td>
<td>0.98</td>
<td>-36</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl radical$^d$</td>
<td>0.99</td>
<td>-37</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde$^d$</td>
<td>0.96</td>
<td>-36</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In kcal/mol.

$^b$ Charge transfer from H to C in electron units.

$^c$ In $\{\text{Cp}_2\text{Zr}[\text{N(SiMe}_2\text{)}_2]\}^+$.

$^d$ See reference 39.

$^e$ See reference 28. KBOs were not calculated at that time.
Table 5. Vicinal interactions of nitrogen. KBOs are in kcal/mol.

<table>
<thead>
<tr>
<th>BO</th>
<th>KBO</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>-3.5</td>
<td>N πℓ – Si1cme1σ</td>
</tr>
<tr>
<td>0.23</td>
<td>-3.5</td>
<td>N πℓ – Si2cme1σ</td>
</tr>
<tr>
<td>0.22</td>
<td>-3.5</td>
<td>N πℓ – Si1cme2σ</td>
</tr>
<tr>
<td>0.22</td>
<td>-3.5</td>
<td>N πℓ – Si2cme2σ</td>
</tr>
<tr>
<td>0.25</td>
<td>-2.7</td>
<td>N πℓ – Zrcep1a</td>
</tr>
<tr>
<td>0.25</td>
<td>-2.7</td>
<td>N πℓ – Zrcep2a</td>
</tr>
<tr>
<td>0.24</td>
<td>-2.8</td>
<td>Nzrσ – Si1hσ</td>
</tr>
<tr>
<td>0.24</td>
<td>-2.8</td>
<td>Nzrσ – Si2hσ</td>
</tr>
</tbody>
</table>
Table 6. Bonding interactions formed by QUAOs on carbon on the –SiHMe₂ moiety and occupations (Occ.) of the interacting QUAOs. KBOs are in kcal/mol.

<table>
<thead>
<tr>
<th>BO</th>
<th>KBO</th>
<th>Orbital 1</th>
<th>Orbital 2</th>
<th>Occ. 1</th>
<th>Occ. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.91</td>
<td>-29.4</td>
<td>C(meSiσ)</td>
<td>Si(cmeσ)</td>
<td>1.32</td>
<td>0.74</td>
</tr>
<tr>
<td>0.98</td>
<td>-37.0</td>
<td>C(meH₁σ)</td>
<td>H₁(cmeσ)</td>
<td>1.13</td>
<td>0.86</td>
</tr>
<tr>
<td>0.98</td>
<td>-35.9</td>
<td>C(meH₂σ)</td>
<td>H₂(cmeσ)</td>
<td>1.14</td>
<td>0.85</td>
</tr>
<tr>
<td>0.98</td>
<td>-35.7</td>
<td>C(meH₃σ)</td>
<td>H₃(cmeσ)</td>
<td>1.14</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Table 7. [Cp₂Zr{N(SiHMe₂)₂}]⁺ and DMAP⁴ valence populations along the reaction path

<table>
<thead>
<tr>
<th></th>
<th>React</th>
<th>RP1</th>
<th>RP2</th>
<th>Prod</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>3.29</td>
<td>3.39 (+0.10)</td>
<td>3.44 (+0.05)</td>
<td>3.49 (+0.05)</td>
</tr>
<tr>
<td>Cpᵃ</td>
<td>24.92</td>
<td>24.93 (+0.01)</td>
<td>24.98 (+0.05)</td>
<td>24.99 (+0.01)</td>
</tr>
<tr>
<td>N</td>
<td>6.14</td>
<td>6.08 (-0.06)</td>
<td>6.11 (+0.03)</td>
<td>6.13 (+0.02)</td>
</tr>
<tr>
<td>Si₁</td>
<td>2.61</td>
<td>2.62 (+0.01)</td>
<td>2.57 (-0.05)</td>
<td>2.53 (-0.04)</td>
</tr>
<tr>
<td>Me₁ᵇ</td>
<td>7.28</td>
<td>7.27 (-0.01)</td>
<td>7.30 (+0.03)</td>
<td>7.30</td>
</tr>
<tr>
<td>H₁</td>
<td>1.19</td>
<td>1.18 (-0.01)</td>
<td>1.18</td>
<td>1.14 (-0.04)</td>
</tr>
<tr>
<td>Si₂</td>
<td>2.61</td>
<td>2.66 (+0.05)</td>
<td>2.70 (+0.04)</td>
<td>2.73 (+0.03)</td>
</tr>
<tr>
<td>Me₂ᶜ</td>
<td>7.28</td>
<td>7.28</td>
<td>7.29 (+0.01)</td>
<td>7.31 (+0.02)</td>
</tr>
<tr>
<td>H₂</td>
<td>1.19</td>
<td>1.18 (-0.01)</td>
<td>1.19 (+0.01)</td>
<td>1.19</td>
</tr>
<tr>
<td>Nd</td>
<td>5.39</td>
<td>5.41 (+0.02)</td>
<td>5.37 (-0.04)</td>
<td>5.39 (+0.02)</td>
</tr>
<tr>
<td>DMAPᵈ</td>
<td>48.00</td>
<td>47.93 (-0.07)</td>
<td>47.67 (-0.26)</td>
<td>47.59 (-0.08)</td>
</tr>
</tbody>
</table>

ᵃ Changes in population relative to the previous step are given in parentheses.ᵇ The population of Cp is taken as sum of the occupation of all the QUAOs of five carbon and five hydrogen atoms. Populations of Cp₁ and Cp₂ are equivalent.ᶜ The population of Me is taken as the sum of occupation of all the QUAOs of one carbon and three carbon atoms that make up a methyl group. The two Me₁ groups have equivalent occupations and the two Me₂ groups have equivalent occupations.ᵈ The population of DMAP is given as the sum of the occupation of all the QUAOs of the atoms that make up DMAP, including Nd.
Table 8. Bond Orders and KBOs of interactions along the reaction path of \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2}\]^+ and DMAP\(^a\,^b\)

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Reactants BO (KBO)</th>
<th>RP1 BO (KBO)</th>
<th>RP2 BO (KBO)</th>
<th>Product BO (KBO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(_1) x – N(_D) (_y)(^c)</td>
<td>0.24 (-4.2)</td>
<td>0.63 (-23.9)</td>
<td>0.72 (-28.5)</td>
<td></td>
</tr>
<tr>
<td>Si(_1) x – H(_1) (_w)(^c)</td>
<td>0.76 (-15.0)</td>
<td>0.70 (-14.8)</td>
<td>0.41 (-7.4)</td>
<td></td>
</tr>
<tr>
<td>Zr(<em>1)(</em>\sigma) – H(_1) (_w)(^c)</td>
<td>0.55 (-15.1)</td>
<td>0.62 (-19.1)</td>
<td>0.82 (-29.0)</td>
<td>0.95 (-38.6)</td>
</tr>
<tr>
<td>Zr(<em>1)(</em>\sigma) – Si(_1) (_x)(^c)</td>
<td>0.37 (-3.3)</td>
<td>0.37 (-3.3)</td>
<td>0.25 (-3.2)</td>
<td></td>
</tr>
<tr>
<td>Zr (_z) – H(<em>2)(</em>\sigma) (_x)(^c)</td>
<td>0.55 (-15.1)</td>
<td>0.53 (-15.2)</td>
<td>0.47 (-12.4)</td>
<td>0.37 (-7.8)</td>
</tr>
<tr>
<td>Zr (_z) – Si(<em>2)(</em>\sigma) (_x)(^c)</td>
<td>0.37 (-3.3)</td>
<td>0.36 (-3.5)</td>
<td>0.34 (-3.6)</td>
<td>0.29 (-3.4)</td>
</tr>
<tr>
<td>Si(<em>2)(</em>\sigma) – H(<em>2)(</em>\sigma)</td>
<td>0.76 (-15.0)</td>
<td>0.78 (-16.7)</td>
<td>0.82 (-18.2)</td>
<td>0.87 (-20.2)</td>
</tr>
</tbody>
</table>

\(^a\) RP1 and RP2 correspond to a Si\(_1\)-N\(_D\) distance of 2.83 Å and 1.98Å, respectively. The product Si\(_1\)-N\(_D\) bond length is 1.88Å. \(^b\) A blank entry indicates that the interaction is negligible (KBO < -1.0 kcal/mol) or not present. \(^c\) H\(_1\)\(_w\) changes from H\(_1\)\(_\text{Si}_1\)\(_\sigma\) to H\(_1\)\(_\text{Zr}\)\(_\sigma\), Si\(_1\)\(_x\) changes from Si\(_1\)\(_h\)\(_1\)\(_\sigma\) to Si\(_1\)\(_n\)\(_D\)\(_\sigma\) to Si\(_1\)\(_n\)\(_D\)\(_\sigma\), N\(_D\)\(_y\) changes from N\(_D\)\(_p\ell\) to N\(_D\)\(_\text{Si}_1\)\(_\sigma\), and Zr \(_z\) changes from Zr\(_2\)\(_\sigma\) to a non-bonding Zr \(_n\)\(_v\) QUAO.
Table 9. Bond Orders and KBOs of interactions throughout the reaction path of
\([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2)_2}\}]^+\) and OPEt\(^{a,b}\)

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Reactants BO (KBO)</th>
<th>RP1 BO (KBO)</th>
<th>RP2 BO (KBO)</th>
<th>Product BO (KBO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr (w) – H(_1)Si(_1)(^c)</td>
<td>0.55 (-15.1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr (w) – Si(_1)H(_1)(^c)</td>
<td>0.37 (-3.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(_1)H(_1) – H(_1)Si(_1)</td>
<td>0.76 (-15.0)</td>
<td>0.94 (-23.3)</td>
<td>0.93 (-23.4)</td>
<td>0.93 (-23.3)</td>
</tr>
<tr>
<td>Zr (x) – H(_2)Si(_2)(^c)</td>
<td>0.55 (-15.1)</td>
<td>0.50 (-13.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr (x) – Si(_2)H(_2)(^c)</td>
<td>0.37 (-3.3)</td>
<td>0.35 (-4.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(_2)H(_2) – H(_2)Si(_2)</td>
<td>0.76 (-15.0)</td>
<td>0.80 (-16.8)</td>
<td>0.93 (-23.6)</td>
<td>0.93 (-23.9)</td>
</tr>
<tr>
<td>Zr (w) – O (y)(^c)</td>
<td>0.42 (-15.8)</td>
<td>0.60 (-27.6)</td>
<td>0.69 (-28.4)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) RP1 and RP2 correspond to a Zr-O distance of 3.50 Å and 2.51 Å, respectively. The
product has a Zr-O bond length of 2.13 Å. \(^b\) A blank entry indicates that the interaction is
negligible (KBO < -1.0 kcal/mol) or not present. \(^c\) Zr \(w\) changes from Zrh\(_1\)\(\sigma\) to Zr\(\sigma\), Zr \(x\)
changes from Zrh\(_2\)\(\sigma\) to Zr \(nv\), O \(y\) changes from O \(s\ell\) to Ozr\(\sigma\).
**Table 10.** Valence populations along the reaction path of $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2)_2\}]^+$ and OPEt$_3^a$

<table>
<thead>
<tr>
<th></th>
<th>React</th>
<th>RP1</th>
<th>RP2</th>
<th>Prod</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>3.29</td>
<td>3.14 (-0.15)</td>
<td>3.15 (+0.01)</td>
<td>3.18 (+0.03)</td>
</tr>
<tr>
<td>Cp$^a$</td>
<td>24.92</td>
<td>24.96 (+0.04)</td>
<td>24.96</td>
<td>25.01 (+0.05)</td>
</tr>
<tr>
<td>N</td>
<td>6.14</td>
<td>6.06 (-0.08)</td>
<td>6.02 (-0.04)</td>
<td>6.03 (+0.01)</td>
</tr>
<tr>
<td>Si$_1$</td>
<td>2.61</td>
<td>2.73 (+0.12)</td>
<td>2.79 (+0.06)</td>
<td>2.79</td>
</tr>
<tr>
<td>Me$_1^{b}$</td>
<td>7.28</td>
<td>7.31 (+0.03)</td>
<td>7.30 (-0.01)</td>
<td>7.31 (+0.01)</td>
</tr>
<tr>
<td>H$_1$</td>
<td>1.19</td>
<td>1.22 (+0.03)</td>
<td>1.21 (-0.01)</td>
<td>1.22 (+0.01)</td>
</tr>
<tr>
<td>Si$_2$</td>
<td>2.61</td>
<td>2.67 (+0.06)</td>
<td>2.79 (+0.12)</td>
<td>2.79</td>
</tr>
<tr>
<td>Me$_2^{c}$</td>
<td>7.28</td>
<td>7.28</td>
<td>7.29 (+0.02)</td>
<td>7.29</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1.19</td>
<td>1.18 (-0.01)</td>
<td>1.22 (+0.04)</td>
<td>1.22</td>
</tr>
<tr>
<td>O</td>
<td>7.04</td>
<td>7.03 (-0.01)</td>
<td>6.93 (-0.10)</td>
<td>6.85 (-0.08)</td>
</tr>
<tr>
<td>OPEt$_3^{d}$</td>
<td>50.00</td>
<td>49.87 (-0.13)</td>
<td>49.73 (-0.14)</td>
<td>49.58 (-0.15)</td>
</tr>
</tbody>
</table>

$^a$ Changes in population from the previous step are given in parenthesis.  $^b$ The population of Cp is taken as sum of the occupation of all the QUAOs of five carbon and hydrogen atoms. Populations of Cp$_1$ and Cp$_2$ are equivalent.  $^c$ The population of Me is taken as the sum of occupation of all the QUAOs of one carbon and three carbon atoms that make up a methyl group. There are two Me$_1$ groups that have equivalent occupations and two Me$_2$ groups that have equivalent occupations.  $^d$ The population of OPEt$_3$ is given as the sum of the occupation of all the QUAOs of the atoms that make up OPEt$_3$, including O.
**Figure 1.** RHF/MIDI optimized structure of \{\text{Cp}_2\text{Zr}[\text{N(SiHMe}_2\text{)}_2]\}^+. Zirconium is shown in turquoise, silicon in tan, and nitrogen in blue. The pyragostic hydrogen atoms are shown as white spheres.
Figure 2. Unique QUAOs on zirconium. The orbital label and occupation are shown beneath each orbital. The orbitals labeled Zrcp\textsubscript{1a}, Zrcp\textsubscript{1b}, and Zrcp\textsubscript{1b} form bonds to carbon atoms in the cyclopentadienyl ring Cp\textsubscript{1}. Equivalent QUAOs labeled Zrcp\textsubscript{2a}, Zrcp\textsubscript{2b}, and Zrcp\textsubscript{2b} that bond to the second cyclopentadienyl ring (Cp\textsubscript{2}) are equivalent by symmetry and they are omitted.
Figure 3. Oriented QUAOs that form the unique (a) CHσ and (b) CCσ bonds in cyclopentadienyl. The orbital labels and electron occupations are provided beneath the corresponding QUAOs. Double-headed arrows drawn between two QUAOs indicate a bonding interaction. The bond orders and KBOs (kcal/mol, in parentheses) of the interaction are shown next to the respective arrow. The numbering on the inset figure refers to the respective carbon and hydrogen atoms and serves to distinguish the atoms for labeling. Underlined numbers are used to show that two atoms are equivalent by symmetry.
Figure 4. Oriented QUAOs that form the unique CC$\pi$ bonds on cyclopentadienyl and the bonds between cyclopentadienyl and zirconium. The orbital labels and electron occupations are provided beneath the corresponding QUAO. Double-headed arrows drawn between two QUAOs indicate a bonding interaction. The bond orders and KBOs (kcal/mol, in parentheses) of the interaction are shown next to the corresponding arrow.
Figure 5. Oriented QUAOs centered on nitrogen, interacting orbitals on zirconium and silicon, and oriented QUAOs that form the silicon-methyl bond. The lone pair orbital is shown from a perpendicular axis relative to the rest of the orbitals. The orbital labels and electronic occupations are provided beneath the corresponding QUAO. The label $C_{me}$ indicates that the C is part of the methyl group. Double-headed arrows drawn between two QUAOs indicate a bonding interaction. The bond orders and KBOs (kcal/mol, in parentheses) of the interaction are shown next to the respective arrow.
Figure 6. Oriented QUAOs that form the three-center pyragostic interaction. The orbital labels and electron occupations are provided beneath the corresponding QUAOs. Double-headed arrows drawn between two QUAOs indicate a bonding interaction. The bond orders and KBOs (kcal/mol, in parentheses) of the interaction are shown next to the respective arrow.
Figure 7. RHF/MIDI(d,f) optimized structure of [Cp₂Zr{N(SiHMe₂)(SiMe₂DMAP)}H]⁺.

Zirconium is shown in turquoise, silicon is shown in tan, and nitrogen is shown in blue.

The hydrogen atoms that migrate during the reaction are shown as white spheres.
**Figure 8.** Oriented QUAOs in [Cp₂Zr{N(SiHMe₂)(SiMe₂DMAP)}H]^+. Only the reaction active QUAOs are shown. The corresponding QUAO label and occupation is shown beneath each QUAO. A solid arrow between QUAOs indicates a strong bonding interaction. A dashed arrow indicates a weak bonding interaction. The bond orders and KBOs (kcal/mol, in parentheses) of the interaction are shown next to the respective arrow.
Figure 9. RHF/MIDI(d,f) energy changes along the reaction path between

\{Cp_2Zr[N(SiMe_2)_2]\}^+ and DMAP. The points marked by solid dots and labeled Reacts,

RP1, RP2, and Prod indicate geometries that are explicitly analyzed.
Figure 10. QUAOs of the reaction between \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2)_2\}]^+\) and DMAP. The reactant QUAOs are from individual geometry optimizations. RP1 corresponds to a \(\text{Si}_1-\text{N}_D\) separation of 2.83Å. RP2 corresponds to a \(\text{Si}_1-\text{N}_D\) separation of 1.98Å. See Figure 9. The QUAO labels and occupations are given beneath the corresponding QUAO. See text for explanation of notation.
Figure 11. RHF/MIDI(d,f) optimized structure of $[\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2\text{OPEt}_3}\]^+$. Zirconium is shown in turquoise, silicon is shown in tan, nitrogen is shown in blue, oxygen is shown in red, and phosphorus is shown in orange. The hydrogen atoms that migrate during the reaction are shown as white spheres.
Figure 12. Oriented QUAOs on \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2}\text{OPEt}_3]^+\). Only the reaction active QUAOs are shown. The corresponding QUAO label and occupation is shown beneath each QUAO. A solid arrow between QUAOs indicates a strongly bonding interaction.
Figure 13. RHF/MIDI(d,f) energy changes along the reaction path between \({\text{Cp}_2\text{Zr}[\text{N(SiMe}_2\text{)}_2]}^+\) and OPEt$_3$. The points marked by solid dots and labeled Reacts, RP1, RP2, and Prod indicate geometries that are explicitly analyzed.
**Figure 14.** QUAOs of the reaction between \([\text{Cp}_2\text{Zr}\{\text{N(SiHMe}_2\}_2}\]^- and \(\text{OPE}_3\). The reactant QUAOs are from individual geometry optimizations. RP1 corresponds to a Zr-O separation of 3.50Å. RP2 corresponds to a Zr-O separation of 2.51Å. The QUAO label and occupation are given beneath the corresponding QUAO.
CHAPTER 5. GENERAL CONCLUSIONS

The transformation of canonical molecular orbitals into localized molecular orbitals is helpful to discern information about bonding patterns in a molecular system. The previous chapters centered on a comprehensive analysis of bonding interactions in terms of intrinsic quasi-atomic orbitals. By projections of the molecular orbitals onto the accurate atomic minimal basis set (AAMBS) for all atoms in the molecule, a set of quasi-atomic orbitals (QUAOs) is obtained. The QUAOs are “quasi-atomic” because they have the quality of atomic orbitals that are deformed by the chemical environment of the other atoms in the molecule. The expression of the first-order density matrix in terms of the QUAOs yields quantitative data in terms of orbital occupations and bond orders between the QUAOs. A quantification of the strength of a bond formed between two orbitals is possible by considering the product of bond orders and kinetic energy integrals. This product is called the kinetic bond order (KBO).

In Chapter 2, a systematic method to identify the chemical role of a QUAO in a molecule was introduced. By considering the intrinsic attributes of a QUAO, i.e., the QUAO occupation, the bond order (BO) and KBO to other QUAOs, and the direction in which its charge accumulates, a label for the QUAO is automatically generated that simplifies the process of understanding the bonding structure of a molecule. A QUAO label contains the atomic symbol for the atom on which the QUAO is centered, followed by the atomic symbol for all atoms to which the QUAO has bonding interactions, termed as “firm” bonds, if any. In cases where a QUAO forms a firm bond with multiple other QUAOs, such as in conjugated systems, it is considered to be part of a delocalized bond.
For bonding QUAOs, the list of atomic symbols is followed by a symbol characterizing the bond that the QUAO forms as a \( \sigma \)-bond or as a \( \pi \)-bond. For non-bonding QUAOs, the orbital occupation is used to characterize the QUAO as a lone pair, radical, or vacant orbital. Additionally, the overlaps of the QUAO with the AAMBS orbitals on the same atom are used to determine the degree of s- and p-character of the QUAO.

The procedure to determine the characteristics of a QUAO is exemplified on a set of molecules with a range of bonding interactions. For strong bonds, the labeling generated for the QUAOs is shown to agree with intuitive chemical reasoning. The labels of the QUAOs are shown to correctly identify that the QUAO is part of a delocalized bond, such as is the case in the conjugated \( \pi \) system in naphthalene. In cases of weaker interactions in a molecule, as in hyperconjugative and vicinal interactions, intuitive reasoning can be vague and uncertain. The program that identifies the chemical role of a QUAO exposes these cases of uncertainty and furnishes quantitative information about the bond to allow the chemist to determine the best characterization for a bond. This scheme allows for the investigation of large and complex molecules to help characterize ambiguous bonding scenarios.

The automatic identification of bonding interactions is used in Chapters 3 and 4 to characterize the bonding in rare gas molecules and in transition metal complexes, respectively.

In Chapter 3, rare gas molecules HXeCCH, HXeCCXeH, and HXeOXeH are analyzed. These molecules belong to a family of molecules with the general formula HRgY, where Rg is a rare gas (Kr or Xe) and Y is an electrophilic fragment. Prior investigations have provided different interpretations for the bonding in these molecules.
The bonding in these molecules has been characterized as an ionic interaction between a covalently bound \((HRg)^+\) fragment and a \(Y^-\) fragment. Alternatively, the bonding of rare gas molecules has been attributed to three-center bonding, resonance, and a long-bonding interaction between H and the Y fragment.

Application of the QUAO localization scheme to the xenon molecules HXeCCH, HXeCCXeH, and HXeOXeH reveals a consistent bonding picture. Xenon uses a \(p\sigma\) QUAO to simultaneously bond to H and to Y, where Y is either C or O, while the remaining three valence QUAOs on Xe are lone pairs. The BOs and KBOs for the HXe and XeY bonds indicate a high covalent character for both bonds. There is an additional bonding interaction between H and Y. While the BO for this interaction is high, the KBO shows a weaker interaction due to the distance between both QUAOs. Changes in the QUAO occupations compared to expected occupations of QUAOs on the isolated atoms show that the bonding interactions are due to charge transfers from the \(p\sigma\) QUAO on Xe to the bonding QUAOs on H and Y. These results favor the three-center four-electron bonding model.

Molecular orbitals are generated separately for the core and for the valence spaces with the constraint that each molecular orbital spans as few QUAOs as possible. These orbitals are known as split-localized orbitals (SPLOs), and they span the same space as the original canonical molecular orbitals. The SPLOs that span the \(p\sigma\) QUAO on xenon are orbitals that correspond to a HXe\(\sigma\) bonding orbital, a HXeY\(\sigma\) bonding orbital, and a HXeY\(\sigma^*\) anti-bonding orbital. These orbitals indicate that the HXeY\(\sigma\) bond is polarized toward Y, while the HXe\(\sigma\) orbital has almost equivalent contributions from H and Xe. It
is nevertheless important that the HXeYσ SPLO has a contribution from all three atoms, favoring a three-center bonding description.

In Chapter 4, the QUAO procedure was applied to analyze the highly coordinated transition metal complex \( \{ \text{Cp}_2\text{Zr}[\text{N(SiHMe}_2)_2]\}^+ \). The cation \( \{ \text{Cp}_2\text{Zr}[\text{N(SiHMe}_2)_2]\}^+ \) was previously characterized experimentally and it was observed to be stabilized by two three-center interactions between zirconium, a β-hydrogen, and silicon. In Chapter 4, this type of interaction is called *pyragostic* due to its structural similarities to agostic bonds. The analysis showed that the nine QUAOs on Zr that result from the 4d5s5p valence space of the Zr full valence AAMBS are used for bonding. Three QUAOs on Zr are used to bond to all five π orbitals on one Cp ring and another three QUAOs are used to bond to the five π QUAOs on the other Cp ring. The sum of KBOs between Zr and each Cp is not much lower than the KBO of a typical CH σ-bond. Another QUAO on Zr is used to bond to N. The BO of the bond between Zr and N is lower than the maximum bond order of 1.00 characteristic of σ bonds. The low BO can be attributed to weak vicinal interactions of the Nzrσ QUAO and Sihσ QUAOs. Finally, each of the two remaining QUAOs on Zr, labeled Zrh1σ and Zrh2σ, is used to bond to each of the β-hydrogen atoms. The Zrh1σ and Zrh2σ QUAOs have non-negligible interactions with the corresponding Si1h1σ and Si2h2σ QUAOs, verifying the existence of three-center Zr–H–Si interactions. The sum of the KBOs that constitute the three-center interaction is -33.4 kcal/mol.

The role of the Zr–H–Si interaction in reactions of \( \{ \text{Cp}_2\text{Zr}[\text{N(SiHMe}_2)_2]\}^+ \) with the Lewis bases DMAP and OPEt₃ was investigated. In agreement with prior experimental results, the product of the reaction with DMAP showed that DMAP coordinated to silicon, whereas the product of the reaction with OPEt₃ showed
coordination of OPEt$_3$ to Zr. No barrier was found for both reactions in the gas phase. In the reaction with DMAP, electrons are transferred to Zr indirectly through the SiH bond of the Si that eventually forms the new SiN bond. A new ZrH bond is formed, and electronic rearrangement in Zr results in the second pyragostic interaction being very weakened. In the reaction with OPEt$_3$, electrons are transferred from OPEt$_3$ to the QUAOs that form the SiH bond. Formation of the new ZrO bond results in both pyragostic interactions being broken. Comparison of the KBO of the pyragostic interaction in the reactant \{Cp$_2$Zr[N(SiHMe$_2$)$_2$]\}$_1$ to the KBO of the SiH bonds in the product of the reaction between {Cp$_2$Zr[N(SiHMe$_2$)$_2$]}$_1^+$ and OPEt$_3$ indicates that the pyragostic interactions provide a net stabilization between -10.1 and -9.5 kcal/mol.

As approaches to solve the Schrödinger equation for a multi-electron system become more sophisticated, it remains an important challenge to make findings accessible to a general audience. The present dissertation helps to create a bridge between rigorous theoretical treatment of a chemical problem and the chemical understanding of a general audience. While the ultimate goal of the resolution of the molecular wave function in terms of QUAOs is to develop a comprehensive energy decomposition scheme, the amount of information available by simply considering the KBOs shows that non-traditional bonding can already be better understood.