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Valence-Bond Reading of a Correlated Wave Function. Bonding in Diborane Reappraised

Georges Trinquier,* Jean-Paul Malrieu, and Immaculada Garcia-Cuesta

Contribution from the Laboratoire de Physique Quantique, CNRS, URA No. 505, Université Paul-Sabatier, 31062 Toulouse Cedex, France. *Received February 7, 1991*

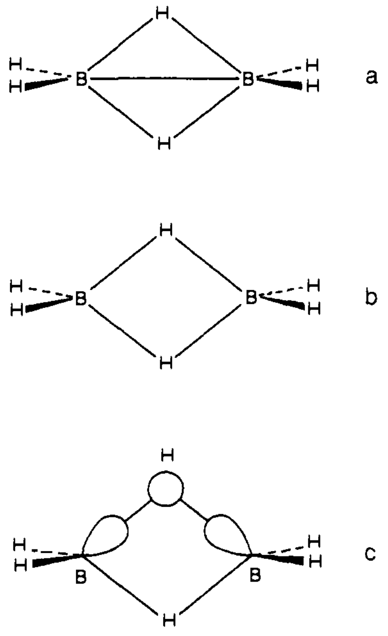
Abstract: A general procedure for analyzing correlated wave functions is explicited and applied to the double bridge of diborane. The procedure consists of four steps. First, a complete-active-space multiconfigurational SCF (CASSCF) calculation provides optimized valence molecular orbitals and treats the electronic correlation internal to the space associated with the given chemical group. Then, these orbitals are localized into a minimal set of molecularly adapted atomic orbitals called *nearly atomic molecular orbitals* (NAMOs). Next, these orbitals are used to build a basis set of orthogonal valence-bond (OVB) determinants on which the CASSCF wave function is reexpressed, weighting the various distributions of the active electrons in these local cells. The information is lastly reduced by further processing the OVB expansion to figure out the electron populations and their fluctuations within one NAMO or a subset of NAMOs. To measure the extent of interaction between given orbitals, an index is proposed that is related to the *covalent organization residual* two-electron *probability* (CORP). The whole method is proved to avoid the shortcomings of basis set dependence. For B_2H_6, the NAMOs are hydrogen-centered orbitals and B–H directed boron hybrids. The OVB expansion exhibits a clear hierarchy of situations, reflecting a compromise between the separation of the two bridges (91% probability for up/down 2e/2e partitioning) and the tendency to maintain the neutrality of the atoms. All indexes indicate that the B–H interactions definitely prevail over the B–B ones, although the latter are not negligible. This is further confirmed by a direct estimate of charge-transfer interactions in the OVB-CI matrix. In a way, each three-center two-electron bridge in diborane is roughly halfway between an allyl-like cation and a cyclopropenyl-like cation.

I. Introduction

Among the problems related to the interactions between atoms within a molecular arrangement, one which has received much attention is that of the through-space/through-bond interactions, especially in four-membered ring systems.[1-8] A common measure of the extent of direct binding between two atoms is the classical Mulliken overlap population. Mulliken analysis happens to be a simple and convenient index in many studies, but it is known to suffer some criticisms, especially when large basis sets are used. Several attempts have been made to get rid of the drawbacks, either by improving space partitioning[9-15] or by using other criteria such as those based on the properties of the gradient vector field.[16]

The two electron-deficient bridges in diborane, B_2H_6, and in its heavier analogues are a typical illustration of the dilemma of through-space/through-bond binding choice.[17] According to some descriptions,[18] supported by the reasonably short BB bond (1.76 Å),[19] there is significant direct B–B interaction, so that one can write a bar between these two atoms, **1a**. In other analyses,[17] including some classical Mulliken ones, such direct interaction is negligible so that the construction holds together only through the B–H–B bridges, **1b**.

The double bridge of diborane has been extensively explored through molecular orbital descriptions.[20-25] The classical orbital picture consists of six canonical molecular orbitals (MOs) spread out over the two bridges, with two occupied levels. A more local equivalent description in terms of a couple of three-center two-electron bonds may be obtained by localizing the two occupied MOs.[26-29] Such localized bonds are defined in two quasi-exclusive



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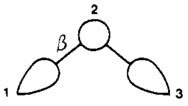
regions and may be considered as almost independent. Each of them involves a 1s atomic orbital (AO) on the hydrogen surrounded by two hybrid atomic orbitals located on the two boron atoms, **1c**. In this picture, the BB through-space interaction may be considered as negligible.

The good localizability of the SCF wave function is not sufficient to discard significant through-space interaction since localizability is compatible with two pictures of the bridge: an allylic cationlike system, **2**, with two electrons in three orbitals, linked by 1–2 and 2–3 bindings, and a cyclopropenyl cation (or H_3^+)-like aromatic system, **3**, involving almost equivalent 1–2 or 2–3(β) and 1–3(β') interactions.[17,30] Moreover, the definition of localized doubly occupied three-center orbitals is based on the use of a single determinantal wave function. The distribution of the four electrons in the bridges is certainly significantly correlated, and the inclusion of electronic correlation—at least within the valence shell—seems highly desirable in order to check the validity of the above-mentioned picture. This can be done by considering the best valence wave function, namely, the multiconfigurational valence complete-active-space self-consistent-field (CASSCF) wave function. Such a wave function variationally defines an optimal valence space, no longer taken from the free atoms but adapted to the molecular field in a self-consistent manner. It further includes all the correlation effects within the valence shell since all excited determinants (of correct symmetry) built from the valence MOs are introduced in the multiconfigurational expansion. This wave function accurately accounts for fragment dissociation processes and tends to become a new standard zero-order description in ab initio molecular calculations.[31] In the study of the electron-deficient bridge bond, attention may be focused on the bridges only. The extracyclic XH bonds are well localizable, and one may neglect their charge fluctuation, therefore assuming their electrons and bond orbitals to be inactive in the CASSCF process relevant to the ring. In other words, it is sufficient to perform a regional study, concentrated on the group or chemical function we are interested in. This restriction leads, in the present case, to an active space of six active MOs, localized on the bridges and occupied by four active electrons.



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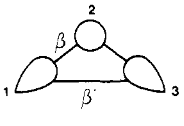

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The present work proposes to transform that wave function according to a suggestion of Ruedenberg et al.,[32] by applying a localization of the valence space provided by the active MOs of the CASSCF procedure. This space has the same size and qualitative features as a *minimal* basis set, but it is molecularly adapted and derived from the *extended* basis sets required for any reliable SCF or CI description. The localizing unitary transform of the active MOs proposed by Boys[33] leaves the active space and the CASSCF wave function invariant but provides a set of atomiclike equivalent MOs, which may be seen as orthogonal atomic orbitals spanning the optimal valence space. We will name these orbitals *nearly atomic molecular orbitals* (NAMOs). They may be used to build determinants that are similar to the usual valence-bond (VB) determinants. Each of them corresponds to a certain spread of *m* active electrons into *n* active orbitals (in the present case, 4 electrons in 6 orbitals). These VB-like determinants define an orthogonal basis that spans the same space as the symmetry-adapted determinants in the CASSCF wave function. Rewriting this wave function as a linear combination of the VB-like determinants makes its reading possible through an orthogonal valence-bond (OVB) transcription. This valence CASSCF wave function therefore builds a bridge between the VB and the MO-CI approaches. Such a strategy has already been embodied in previous studies.[34,35] We will define it here in a more general and systematic way and gauge all its potentialities.

In section II, this wave function will be analyzed so as to establish the electronic order prevailing in the double-bridge region. The analysis first concerns the hierarchy of the OVB coefficients, which clearly reveals the combined effect of two rules, namely, a tendency to keep one $\alpha\beta$ electron pair per bridge and a tendency to maintain the neutrality of the atoms. In section III, we will establish that the two-bridge separation is by far the best 2/2 partition of the electrons. Reduced information regarding the electronic population will next be considered by looking at the one-particle density matrix, i.e., atomic charges and bond orders. When expressed in terms of NAMOs, these indexes become meaningful (section III) and free of the usual basis set dependence (section VI). However they are of no help in giving an insight into the existence of a binding interaction between atoms. In order to obtain such information, we will consider in section IV the elements of the two-electron density matrix, which are related to the probability of finding two electrons in a subset of NAMOs, and we will propose a covalent-bonding index. In the OVB approach, the existence of strong one-electron transfers between two NAMOs may be easily traced by looking directly at the OVB-CI matrix; this also provides a measure of through-bond and through-space interactions (section V). Lastly, the Conclusion will address the advantages of the proposed procedure to rationally exploit the *n*-electronic wave function. In a forthcoming paper, the same tools that are applied here to a scrutiny of B_2H_6 will be applied to a series of isoelectronic electron-deficient bridges.[36]

II. Orthogonal Valence-Bond Reading of the Correlated Wave Function

The ab initio calculations reported here use valence basis sets of standard double-ζ + polarization quality. For the sake of consistency with the subsequent study on analogues of diborane containing heavy atoms, the calculations are reduced to valence electrons by using effective core potentials. Computational details are given in the Appendix. The valence complete active space, restricted to the double-bridge region, necessarily concerns the classical set of six valence orbitals (a_g, b_{1u}, b_{2g}, b_{3u}, a_g, b_{1u}) and four electrons. The CASSCF procedure perfectly localizes the active orbitals in the bridge region, i.e., on bonds where the electronic correlation is larger than in the strong extracyclic XH bonds. The localization will appear clearly from the shape of the equivalent orbitals obtained in the next step.

A. Nearly Atomic Molecular Orbitals (NAMOs). Such orbitals are obtained by applying Boys' unitary transformation[32] to the six active MOs. This transformation minimizes the fluctuation of the position of the electrons around their centroids. Let us call

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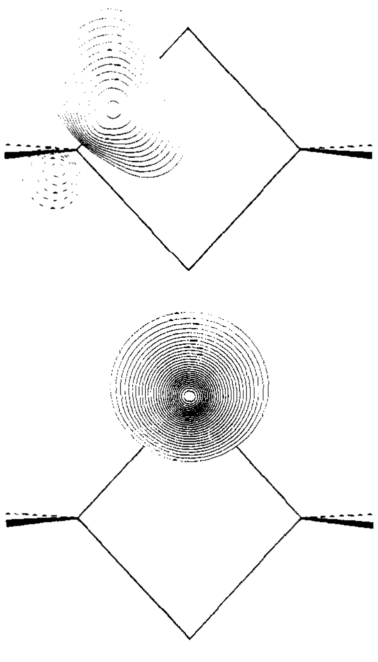


Figure 1. Contour lines for the two types of NAMOs in the bridge region of diborane: top, boron-centered BH-oriented hybrid; bottom, hydrogen-centered orbital. The lines start from $|\Psi| = 0.35$ (outer lines) and increase inward by regular steps of $\Delta|\Psi| = 0.05$.

$\{\varphi_i\}$ the six active orbitals. They are changed into six local orbitals $\{\chi_j\}$ such that

$$\{\chi_j\} = U\{\varphi_i\}$$

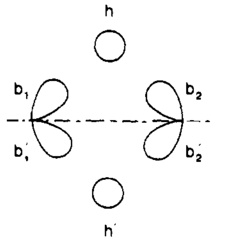
with U being a unitary transform that keeps the subspace unvariant and keeps the orthonormalization, i.e., rotates the basis set of the valence space, and such that

$$\sum_{j=1,6} \langle\chi_j|(\vec{r} - \vec{r}_{0j})^2|\chi_j\rangle = \text{minimum}$$

with $\vec{r}_{0j}$ being the centroid associated with the χ_j MO:

$$\vec{r}_{0j} = \langle\chi_j|\vec{r}|\chi_j\rangle$$

The more localized the orbitals, the smaller the fluctuation of the distance of their electrons to their centroids. This criterion is usually used after an SCF calculation to obtain equivalent occupied orbitals localized on bonds and lone pairs. Here, the process is applied to the whole active space of the MCSCF orbitals and is expected to lead to the NAMOs, which are even more localized since the whole valence space is transformed. Six NAMOs are obtained. Four of them, labeled b_1, b'_1, b_2, and b'_2, are hybrid orbitals centered on the boron atoms and directed toward the hydrogen atoms, and two of them, labeled h and h′, are 1s-type orbitals centered on the hydrogen atoms, **4**. Their amplitudes are plotted in Figure 1. Despite their orthogonality, which introduces nodal surfaces and small tails, the atomic character is well kept.



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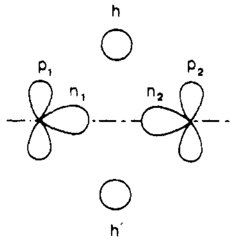

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This picture in terms of hybrids directed toward the hydrogen atoms is imposed by Boys' criterion, in the same way as banana bonds are obtained in ethylene. One may wonder whether this criterion could artificially favor the traditional view in terms of three-orbital two-electron bridges. An equivalent basis for the valence active space may be obtained by keeping the two hydrogen-centered NAMOs unchanged and by combining the b and b′ hybrids into n- and p-type NAMOs, **5**, defined as

$$n_1 = \frac{1}{\sqrt{2}}(b_1 + b'_1) \qquad p_1 = \frac{1}{\sqrt{2}}(b_1 - b'_1)$$

Table I. OVB Expansion of the CASSCF Wave Function in Diborane[a]

	configurations				% contributions[f]		
						random distribution	
	N[b]	S[c]	UD[d]	B–H–B–H[e]	CASSCF	weighted	pure
Φ_1	12	2	n	0 0 0 0	7.87	3.41	2.67
Φ_2	12	2	n	− 0 + 0	6.49	3.41	2.67
Φ_3	24	4	n	− + 0 0	4.92	2.04	2.67
Φ_4	8	4	n	0 − + 0	3.61	1.90	0.89
Φ_5	6	1	n	− + − +	3.27	1.22	2.67
Φ_6	4	2	n	0 + 0 −	2.65	1.14	0.89
Φ_7	1	1	n	+ − + −	1.62	1.59	0.44
Φ_8	8	4	n	0 + − 0	1.60	0.68	0.89
Φ_9	8	4	n	2− + + 0	1.06	0.68	0.89
Φ_{10}	8	4	n	2− + 0 +	0.84	0.41	0.89
Φ_{11}	12	2	i	0 0 0 0	0.81	3.41	2.67
Φ_{12}	4	4	n	− − + +	0.73	0.57	0.44
Φ_{13}	8	4	i	0 0 + −	0.44	1.90	0.89
Φ_{14}	24	4	i	0 + − 0	0.37	2.04	2.67
Φ_{15}	2	2	n	− + − +	0.34	0.20	0.44
Φ_{16}	8	4	i	− 0 + 0	0.32	1.14	0.89
Φ_{17}	8	4	i	0 + 0 −	0.21	1.14	0.89
Φ_{18}	8	4	i	− + + −	0.20	1.14	0.89
Φ_{19}	8	4	i	− + 0 0	0.16	0.68	0.89
Φ_{20}	2	2	n	3− + + +	0.14	0.20	0.44
Φ_{21}	8	4	i	2− + + 0	0.13	0.68	0.89
Φ_{22}	4	2	ii	0 + 0 −	0.01	1.14	0.89
Φ_{23}	8	4	i	2− + 0 +	0.01	0.41	0.89
Φ_{24}	8	4	i	0 + − 0	0.01	0.68	0.89
Φ_{25}	4	4	ii	− + + −	0.01	0.57	0.44
Φ_{26}	8	4	i	− + − +	0.00	0.41	0.89
Φ_{27}	2	2	ii	− + − +	0.00	0.20	0.44
Φ_{28}	8	4	ii	− + 0 0	0.00	0.68	0.89

[a] The configurations are explicited in Chart I. [b] Total number of determinants. [c] Space degeneracy. [d] Up/down partitioning: n, neutral; i, ionic; ii, di-ionic. [e] Atom ionicity. [f] Each contribution must be weighted by its space degeneracy for obtaining a total sum of 100%.

The possible existence of a direct BB bonding interaction should be examined in that basis set too, by scrutining the population in the n_1, n_2 set. However, most of the analysis that follows will use the b-hybrid basis set **4** since it proved to be the better partition according to several criteria.

B. OVB Decomposition and Hierarchy. The CASSCF wave function is now reexpressed in an OVB language. The four electrons may be spread out among the six NAMOs in $(C_6^2)^2 = 225$ different manners, generating 225 determinants. These can be gathered into 28 categories, corresponding to different types of nonequivalent space parts. They are depicted in Chart I and listed in Table I, according to their decreasing weight in the CASSCF function. The hierarchy of the OVB weights is easily understood if one recognizes the following trends.

(1) The tendancy of each bridge to keep two electrons. Actually the 10 largest weights concern structures that satisfy the 2/2 up/down partitioning of the electrons. The three other VB structures which satisfy that partition (Φ_{12}, Φ_{15}, Φ_{20}) have negligible weights because they strongly violate the second trend.

(2) The preference for atomic neutrality. The largest coefficient Φ_1 satisfies this neutrality, while the following ones are singly ionic. Notice that the largest component violating the 2/2 up/down partitioning, Φ_{11}, is again neutral with respect to the atoms.

(3) The preference for the electron spread on the atoms. This rule only concerns the ionic VB structures with B^- atoms. The two electrons on B^- occupy two different hybrids in Φ_2, Φ_3, and Φ_5. The first configuration with double occupancy of a hybrid, Φ_8, has a much smaller weight. The rules 2 and 3 have been well

Chart I. The Twenty-Eight Space Parts of the Orthogonal Valence-Bond Basis of Determinants

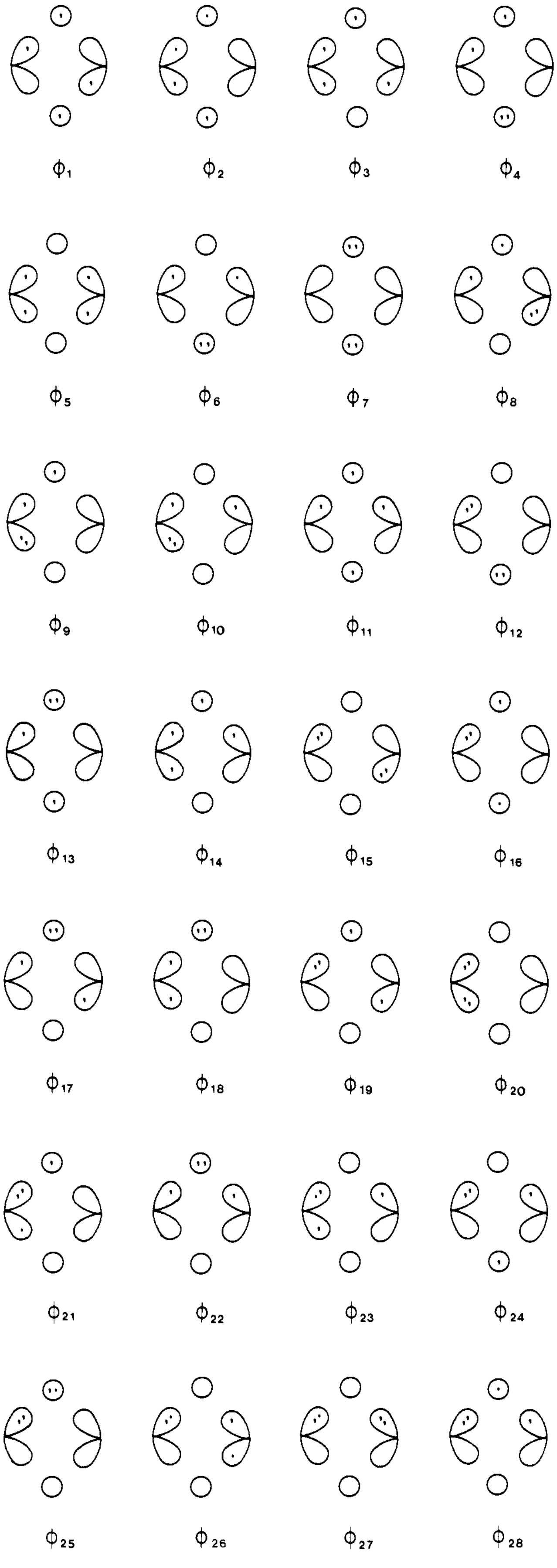

Table II. Calculated Probabilities of Having Two Electrons in Given Subsets of Orbitals[a]

orbital sets	CASSCF	random distribution	
		weighted	pure
$\{b_1, h, b_2\}$	90.9	44.7	44.0
$\{b_1, b'_1, h\}$	47.0	44.7	44.0
$\{n_1, n_2\}$	49.8	37.4	33.8
$\{b_1, h\}$	45.6	37.2	33.8
$\{b_1, b_2\}$	29.7	27.5	33.8
$\{b_1, b'_2\}$	27.0	27.5	33.8
$\{h, h'\}$	41.6	43.2	33.8
$\{b_1, h'\}$	35.0	37.2	33.8
$\{p_1, h\}$	34.9	32.9	33.8
$\{n_1, h\}$	41.6	41.1	33.8
$\{p_1, p_2\}$	16.4	16.7	33.8

[a] In percent. See **4** and **5** for orbital labeling.

established on other problems, and they apply here under the requirement of rule 1, i.e., the electron partitioning into two bridges.

Notice that the two bridges are not independent. If they were so, one would have the same weight for structures Φ_1 and Φ_2, Φ_8 and Φ_9, or Φ_{15} and Φ_{20}. The inequalities $\Phi_1 > \Phi_2$, $\Phi_8 > \Phi_9$, and $\Phi_{15} > \Phi_{20}$ reflect the correlation between the movement of the electrons in the two bridges: When they move leftward in the upper bridge, the others move rightward in the lower bridge in order to minimize the instantaneous electrostatic energy through a coupling of two dipoles of opposite directions.

C. **Comparison with Random Distributions.** The electronic ordering may be appreciated by comparing our calculated coefficients with the corresponding probabilities obtained by spreading out four electrons (2α and 2β, subject to the exclusion principle) over six boxes. These boxes may be of equal size, giving a pure random distribution, or may be of various sizes in order to reproduce the calculated atomic charges and giving a weighted random distribution. Details for the computation of these distributions are given in the Appendix. The random distributions are listed in Table I, right. Going from the random distributions to the CASSCF one, the wave function concentrates in a reduced number of determinants. The only six configurations Φ_1–Φ_6 thus contribute more than 71% to the function.[37] The random distributions will be useful to see the occurrence of unexpected large probabilities.

III. Search for the Best 2+2 Partition of the Electrons

For doing so, let us consider some possible partitionings of our six NAMOs into two subsets, each one bearing two electrons—and only two—and see how large are the corresponding probabilities. This is done in Table II, top. First of all, to confirm the classical view of the doubly bridged chemical system as made of two bonds, one for each bridge, one expects a high probability to find two electrons in the subset $\{b_1, h, b_2\}$. For symmetry reasons, the mean population in this subset is necessarily 2, but this does not determine the probability for two electrons in the subset. Such probability is calculated to be actually very high at 91%, while the probability to find 1 or 3 electrons in each bridge is only 4.5% and that to find 0 or 4 electrons is smaller than 0.5%. If the electrons were randomly distributed, the corresponding probabilities would be 44%, 24%, and 4%, respectively.

Next, let us look at the probability to find two electrons in each H_2B–H fragment, i.e., in the subset $\{b_1, b'_1, h\}$. This probability

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[37] In other words, moving from the pure random distribution to the weighted random one and to the CASSCF one, there is more and more information. This can be figured out by calculating the entropies S associated with the distribution of probabilities within the complete sets of 225 spin-orbital determinants

$$S = -\sum_i p_i \ln p_i$$

For the pure random case, this value is straightforward: $S = \ln 225 = 5.42$. For the weighted random distribution, S is calculated at 5.32. For the CASSCF one, this value reduces to 4.58.

Table III. First-Order Density Matrix Elements

	CASSCF wave function in the basis of NAMOs		SCF wave function in the basis of AOs[a]	
electronic populations	q_h	0.86	q_H	1.10
	q_b	0.57		
bond orders	P_{b_1h}	0.65	P_{BH}	0.20
	$P_{b_1b_2}$	0.56	P_{BB}	0.08
	$P_{b_1b'_2}$	0.15		
	$P_{b_1h'}$	−0.03		
	$P_{hh'}$	−0.29	P_{HH}	−0.07

[a] This is the classical Mulliken analysis.

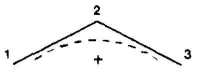
(47%) turns out to be very close to the pure random (44%) and weighted random (45%) expectations. The fragments do not persist in the bridge. A last partition will divide our space into a $\{n_1, n_2\}$ subset making a σ bond, and the complementary subset $\{p_1, p_2, h, h'\}$ linking the two remaining electrons in a more complex way. The probability to find two—and only two—electrons in the $\{n_1, n_2\}$ subset (50%) is significantly larger than that associated to pure random (34%) or weighted random (37%) situations. However, it remains much lower than that obtained for the $\{b_1, h, b_2\}$, $\{b'_1, h', b'_2\}$ partitioning (91%). Thus, the relevance of the traditional view of two bridges bearing two electrons each is confirmed at this level. This further justifies to focus the discussion on the partitioning into B–H oriented hybrids, **4**, rather than that into B–B oriented hybrids, **5**, although all our analyses have been carried out in the two OVB basis.

IV. Bonding Character between Two Orbitals

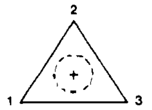
A. Charges and Bond Orders. The first-order density matrix may be expressed in various basis sets. One usually uses the atomic orbitals basis set in order to get an insight on the local features of the wave function. This procedure furnishes atomic charges and bond orders, through some rather arbitrary sharing of overlap populations. It keeps reasonable meaning when minimal basis sets are used but may become rather unreliable when large basis sets are involved. Since our NAMOs provide some kind of orthogonal molecularly adapted minimal basis set, one may express the first-order density matrix in terms of NAMOs. Their orthogonality avoids the sharing of overlap population, and one should fall on the simplest analysis as in the elementary Hückel frame.

Such charges and bond orders are listed in Table III, together with the SCF Mulliken indexes. The net charge on hydrogen is positive (+0.14), despite the electronegativity difference,[38] and sounds reasonable for an electron-deficient system. This is in contrast with the Mulliken charge (−0.10). The off-diagonal elements are both large for the directional b–h NAMO pairs (0.65) and for the two b–b hybrids of the same bridge (0.56). The h–h′ off-diagonal element is large and negative (−0.29). These values are somewhat larger then the Mulliken's bond indexes. At this stage, and if relying on the first-order density matrix, we would conclude that the B–H and B–B interactions are similar.

B. Selected Bielectronic Probabilities. As mentioned in the Introduction, there are two limiting cases for a three-center two-electron problem, namely, the allyl cation situation, **6**, and the cyclopropenyl cation situation, **7**. In the former case, where there is no 1–3 interaction, the simplest resonating valence-bond wave function would not consider any covalent bond between 1 and 3 and therefore would exclude configurations like **8**. Such exclusion from our OVB expansion for diborane would discart the determinants Φ_3, Φ_5, Φ_6, and Φ_{10}. In this case, the probability to find two electrons in a given bridge set $\{b_1, h, b_2\}$ falls from 91% to 59%, indicating that situation **8** occurs frequently in our molecule.



6



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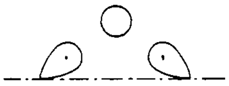


8

Turning back to a Hückel picture, for **6** and **7**, the corresponding wave functions write as

$$\psi_{\text{all}} = \left|\left\{\tfrac{1}{2}(b_1 + b_2) + h/\sqrt{2}\right\}\overline{\left\{\tfrac{1}{2}(b_1 + b_2) + h/\sqrt{2}\right\}}\right|$$

$$\psi_{\text{cycl}} = \tfrac{1}{3}\left|(b_1 + b_2 + h)\overline{(b_1 + b_2 + h)}\right|$$

The classical bond indexes defined as

$$P_{ij} = \sum_{m=\text{occ}} C_{im}C_{jm}$$

would give, for the allyl case

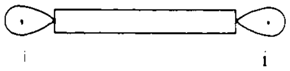
$$P_{b_1h} = \frac{1}{\sqrt{2}} = 0.71 \qquad P_{b_1b_2} = \tfrac{1}{2} = 0.50$$

This rather small difference between b_1–h and b_1–b_2, despite the lack of bond between the external atoms, is a clear illustration of the impossibility to rely on such indexes to assess the existence of a bond.

In an uncorrelated description, the situation **8** would occur with a probability of $^1/_8$(13%) in the allyl cation and a probability of $^2/_9$(22%) in the cyclopropenyl cation. From our OVB expansion in B_2H_6, the probability to find the configuration **8** in a given bridge is found to be 17%. This is halfway between the two limiting cases, and suggests some significant binding interaction between the two boron hybrids.

From the OVB expansion, it is easy to calculate the probability to find two—and only two—electrons in any couple i, j of NAMOs. The calculation is explicited in the Appendix, and the values are given in Table II. When comparing them to the corresponding pure random or weighted random probabilities, the strongest deviation concerns the $\{b_1, h\}$ NAMO pair. The $\{b_1, b_2\}$ occurrence is nearly equal to the weighted random probability. For $\{h, h'\}$, the probability to find two electrons is high, but this essentially reflects the effect of the charges since it is almost identical with the weighted random probability. Using the differences (CASSCF-weighted random), these two-electron probabilities would lead to the following reasonable hierarchy of i–j interactions: b_1–h, 8.4%; b_1–b_2, 2.2%; b_1–b'_2, −0.5%; h–h′, −1.7%; b_1–h′, −2.1%. The same analysis may be performed in terms of the equivalent NAMOs $\{n, p, h\}$. As can be seen in Table II, the probability to find two electrons in the subset $\{n_1, n_2\}$ of the two B–B directed NAMOs is high and, again, significantly larger (by 12%) than the corresponding weighted random probability. This result would support the existence of a rather strong B–B interaction. Notice however that there is only one such interaction instead of the four B–H interactions, so that the latter will prevail in fixing the electronic wave function.

C. CORP: A Bielectronic Bond Index. In order to have a covalent bond between two orbitals i and j, the probability $P_{ij}^{(2)}$ to find two electrons, and only two, in that subset must be as large as possible. But this is not sufficient. Let us consider for instance



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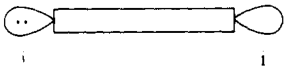

10

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[38] The electronegativities for B and H are 2.0 and 2.1, respectively, in Pauling's scale and 2.0 and 2.2, respectively, in Allred and Rochow's scale.

a diradical where the orbitals i and j, located far apart, are always occupied by one and only one electron, **9**. The wave function associated to these electrons is

$$\psi = \frac{1}{\sqrt{2}}|i\bar{j} + j\bar{i}| \tag{1}$$

and the probability $P_{ij}^{(2)}$ is 1 although there is obviously no bond at all between i and j. In this case, the probabilities to find one electron in i or in j are equal to 1:

$$P_i^{(1)} = P_j^{(1)} = 1$$

so that $P_{ij}^{(2)}$ is the simple product

$$P_{ij}^{(2)} = P_i^{(1)}P_j^{(1)} \tag{2}$$

Oppositely, if one considers a system with a lone pair located in orbital i and a remote empty orbital j, as in **10**, the wave function associated to this set is

$$\psi = |i\bar{i}| \tag{3}$$

and again the probability $P_{ij}^{(2)}$ is 1 although there is no bond between i and j. In that case, we have

$$P_i^{(2)} = P_j^{(0)} = 1$$

so that $P_{ij}^{(2)}$ is the simple product

$$P_{ij}^{(2)} = P_i^{(2)}P_j^{(0)} \tag{4}$$

A covalent bond, in its naive chemical meaning, requires to have both important diradicalar *and* ionic instantaneous distributions, i.e., an important charge fluctuation within the bond. In order to measure the existence and extent of a *covalent* bond between two orbitals, we propose to use the remainder obtained when the products such as in (2) and (4) are substracted from $P_{ij}^{(2)}$. This index, which we shall call CORP, standing for *covalent organization residual probability for two electrons*, is thus defined as

$$\text{CORP} = P_{ij}^{(2)} - \{P_i^{(1)}P_j^{(1)} + P_i^{(2)}P_j^{(0)} + P_i^{(0)}P_j^{(2)}\} \tag{5}$$

This quantity is the probability to find two electrons in the set $\{i, j\}$ diminished by the *independent* probabilities corresponding to purely neutral or purely ionic situations. Note that the global probability $P_{ij}^{(2)}$ is the sum of the probabilities to find neutral $P_{ij}^{(1,1)}$ and ionic $P_{ij}^{(2,0)}$ and $P_{ij}^{(0,2)}$ situations in the $\{i, j\}$ subset:

$$P_{ij}^{(2)} = P_{ij}^{(1,1)} + P_{ij}^{(2,0)} + P_{ij}^{(0,2)}$$

CORP is in general different from zero since usually

$$P_{ij}^{(1,1)} \neq P_i^{(1)}P_j^{(1)} \qquad P_{ij}^{(0,2)} \neq P_i^{(0)}P_j^{(2)}$$

This bielectronic index measures the occurrence of two electrons in a given set, which is not statistical but comes from the binding interaction. It is a dimensionless real number smaller than 1, which as the other probabilities, will be expressed in percent. The concept may be extended to a set of any number n of orbitals, and in its most general expression, the index is defined as

$$\text{CORP} = P^{(2)} - \{\sum_{i \neq j} P_i^{(1)}P_j^{(1)} \prod_{k \neq i \neq j} P_k^{(0)} + \sum_i P_i^{(2)} \prod_{j \neq i} P_j^{(0)}\}$$

Turning to two-orbital sets, let us see how it works in typical situations.

For a pure diradical system, from expression 1 of the wave function, the following elements of (5) are obtained:

$$P_i^{(1)} = P_j^{(1)} = 2\left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$P_i^{(0)} = P_j^{(0)} = P_i^{(2)} = P_j^{(2)} = 0$$

$$P_{ij}^{(2)} = 2\left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

so that

$$\text{CORP} = 1 - \{1 + 0 + 0\} = 0$$

Similarly, for a pure ionic bond, expression 3 leads to

$$P_i^{(0)} = P_j^{(0)} = P_i^{(2)} = P_j^{(2)} = 0$$

$$P_i^{(2)} = P_j^{(0)} = 1 \qquad P_{ij}^{(2)} = 1$$

so that again

$$\text{CORP} = 1 - \{0 + 1 + 0\} = 0$$

The index therefore cancels for the situations **9** and **10** involving a pair of noninteracting orbitals. Let us now consider a more general homopolar simple bond. Its *uncorrelated* wave function writes as

$$\psi = \tfrac{1}{2}|(i + j)(\overline{i + j})|$$

$$\psi = \tfrac{1}{2}|(i\bar{j} + j\bar{i}) + (i\bar{i} + j\bar{j})|$$

which results in

$$P_i^{(1)} = P_j^{(1)} = 2(\tfrac{1}{2})^2 = \tfrac{1}{2}$$

$$P_i^{(0)} = P_j^{(0)} = P_i^{(2)} = P_j^{(2)} = (\tfrac{1}{2})^2 = \tfrac{1}{4}$$

$$P_{ij}^{(2)} = 4(\tfrac{1}{2})^2 = 1$$

The bielectronic bond index is therefore

$$\text{CORP} = 1 - \{\tfrac{1}{2} \times \tfrac{1}{2} + 2 \times \tfrac{1}{4} \times \tfrac{1}{4}\} = \tfrac{5}{8} = 63\%$$

The *correlated* wave function writes as

$$\psi = \tfrac{1}{2}|\lambda(i\bar{j} + j\bar{i}) + \mu(i\bar{i} + j\bar{j})|$$

with $\lambda > \mu$ and $\lambda^2 + \mu^2 = 2$. This results in

$$\text{CORP} = 1 - \left\{\frac{\lambda^4}{4} + \frac{\mu^4}{8}\right\} = \tfrac{1}{2}\{1 + \lambda^2 - \tfrac{3}{4}\lambda^4\}$$

The index is maximum for $\lambda = \mu = 1$ and decreases to zero when $\lambda \to \sqrt{2}$ and $\mu \to 0$, as expected since the correlation increases the diradical character of the bond. Since it vanishes for purely diradical or purely ionic wave functions, the index may be seen as reflecting the electronic delocalization of a pair of electrons between the NAMOs i and j. At this step, a vocabulary remark is needed. In the VB terminology, the term covalent sometimes stands for neutral or diradical, by opposition to ionic. In traditional VB approach, however, owing to the nonorthogonality of the orbitals, the covalent forms incorporate part of the electronic fluctuation—therefore of the ionic forms. In GVB calculations, for instance, such fluctuation is properly taken into account by variationally optimizing the atomic orbitals, which are given tails on the neighboring atoms. In the present strategy, the use of probabilities prevents, of course, the use of nonorthogonal orbitals.

Let us now apply this index to our NAMOs of diborane. This is done in Table IV. The CORP index is found to be much larger for $\{b_1, h\}$ than for $\{b_1, b_2\}$ (11% vs 3%). The other CORP probabilities seem to be rather marginal. This index suggests some nonnegligible interaction between the boron hybrids of the same bridge. Going to the equivalent {n, p, h} representation, one actually finds a large bielectronic bond index (16%) between the two σ-type NAMOs of the boron atoms directed along the B–B bond. Comparing the values of the indexes for the CASSCF wave function with those for the weighted random distributions supports these trends. The index is increased by 5% for b_1–h and only 0.4% for b_1–b_2 (see Table IV). Note that the CORP index for h–h′ is *decreased* by as much as 6%, which would indicate that this index of 1.4% is not originated in H–H binding interactions.

V. Direct Research of Electron-Transfer Integrals

A. Reading the OVB-CI Matrix. One advantage of the use of a CASSCF wave function and of its transcription into a localized NAMO basis is the possible determination of the in-

Table IV. Calculated Bielectronic CORP Indexes[a]

orbital pairs	CASSCF	random distribution weighted	random distribution pure
$\{b_1, h\}$	10.8	5.2	4.1
$\{b_1, b_2\}$	2.9	2.5	4.1
$\{b_1, b'_2\}$	0.2	2.5	4.1
$\{b_1, h'\}$	0.3	5.2	4.1
$\{h, h'\}$	1.4	7.3	4.1
$\{n_1, n_2\}$	16.0	5.5	4.1
$\{p_1, p_2\}$	−0.6	0.3	4.1
$\{n_1, h\}$	4.4	6.7	4.1
$\{p_1, h\}$	4.5	3.7	4.1

[a] In percent. See relation 5 for the definition of the index and **4** and **5** for orbital labeling.

Table V. Mean Values for the Off-Diagonal Elements F_{ij} of the OVB-CI Matrix (au)

intrabridge		interbridge	
b_1–h	−0.29	b_1–b'_1	−0.09
b_1–b_2	−0.17	b_1–b'_2	−0.17
		b_1–h′	+0.01
		h–h′	+0.05

tensities of the interactions between the NAMOs. One may for instance calculate the off-diagonal elements of the Fock operator associated with the leading configuration Φ_0 of the symmetry-adapted multiconfigurational expansion

$$\Phi_0 = |a_{1g}^2 b_{2u}^2|$$

in the basis of the NAMOs:

$$F_{ij} = \langle i|F|j\rangle$$

$$F_{ij} = \langle i|h + 2J_{1g} - K_{1g} + 2J_{2u} - K_{2u}|j\rangle$$

where h is the monoelectronic part of the Hamiltonian. One may also calculate the interaction between two OVB determinants Φ_I and Φ_J, which only differ by one orbital, i.e., such that

$$\Phi_I = a_i^+ a_j \Phi_J$$

with a_i^+ and a_j being the creation and anihilation operators, respectively. This relation simply means that Φ_I is obtained from Φ_J by replacing j, occupied in Φ_J, by i, which was empty in Φ_J. Then the hopping integral ($j \rightarrow i$) may be evaluated as

$$\langle a_i^+ a_j \Phi_J|H|\Phi_J\rangle = F_{ij} + \delta_J^{ij}$$

We have checked that δ_J^{ij} is small with respect to F_{ij} (by about 1 order of magnitude) so that one gets directly from the OVB-CI matrix an estimate of the amplitude of the hopping integrals. As a measure of the invariance of these integrals, one may notice that, starting from the leading configuration Φ_1, the b → h charge transfer leads to Φ_4 with a matrix element of −0.30 au while the h → b charge transfer leading to Φ_8 has a matrix element of −0.28 au. Similarly, the h → b′ charge transfers corresponding to $\Phi_1 \rightarrow \Phi_{14}$ or $\Phi_1 \rightarrow \Phi_{19}$ have amplitudes around +0.01 au differing by less than 0.002 au. One may therefore consider that the amplitudes of the electron-transfer integrals between two NAMOs are weakly dependent of the instantaneous electronic environment.

Examination of the elements of the OVB-CI matrix calculated for B_2H_6 provides an evaluation of the respective intensities of the B–H, B–B, and H–H interactions. The amplitudes corresponding to the b–h, b–b, b–b′ and h–h′ interactions are listed in Table V, which shows that (1) the b–h interaction is the largest one; (2) the b–b interaction within the same bridge is rather important (about half of the preceding one); (3) the interbridge integral b–b′ is as large as the intrabridge one b–b; (4) the integrals corresponding to the interbridge interactions b–h′ and h–h′ are positive and small. Turning to the {n, p, h} basis set, the transfer integral $\langle n_1|F|n_2\rangle$ between the two NAMOs directed along the B–B axis would be very large since it is the sum

$$\langle n_1|F|n_2\rangle = \langle b_1|F|b_2\rangle + \langle b_1|F|b'_2\rangle \simeq -0.34 \text{ au}$$

This would plead again for a significant transannular interaction between the boron atoms.

B. Back to a Hückel Picture. It is tempting to build a purely monoelectronic matrix spanned by the NAMOs, by using as off-diagonal elements the mean F_{ij} elements of Table V. The only lacking information, the diagonal energy difference between the b and h NAMOs, may be extracted from the energies of the singly ionic configurations Φ_4 and Φ_8. The corresponding energy difference is 0.045 au in favor of h, in agreement with the electronegativities.

This Fock-like or Hückel-like matrix defined in the basis of the NAMOs has been diagonalized, providing two occupied MOs a_g and b_{1u}. From them, a density matrix is recalculated in the NAMO basis, which in turn provides orbital populations and bond orders. These happen to be very close to the exact CASSCF values, as exemplified for three typical parameters:

	one-electron	CASSCF
q_h	0.87	0.86
P_{b_1h}	0.66	0.65
$P_{b_1b_2}$	0.57	0.56

This emphasizes the consistency in our analysis of the physics of the electronic interactions in the bridge. The relative influence of the various through-space interactions may be further explored by putting to zero some of the off-diagonal elements of this Hückel-type matrix. The suppression of all interactions between the two bridges only results in a weak perturbation of the electronic populations ($q_h = 0.85$, $P_{b_1h} = 0.70$, $P_{b_1b_2} = 0.57$). On the other hand, the cancellation of the interactions between the boron hybrids of the same bridge results in a significant increase of the electronic population on hydrogen ($q_h = 1.03$), while little affecting P_{b_1h} (0.66) and expectedly reducing $P_{b_1b_2}$ (0.48). This numerical experiment illustrates how the electronic populations are sensitive to the through-space interactions within a bridge. Although some interbridge interactions have the same amplitudes, they have a lesser influence on the electronic population.

VI. Stability toward Basis Sets

The above analysis rests on the definition of some sort of molecularly adapted minimal basis set, provided by the CASSCF calculation and redefined in terms of nearly atomic orbitals. This description is only effective if it proves to be stable under basis set changes. It is well experienced that the CASSCF energy and wave function are weakly sensitive to basis set extension beyond, say, the double-ζ-plus-polarization level. The stability of the NAMOs and of the OVB decomposition has to be measured in the same way. To check it, our DZP basis set has been extended by adding supplementary s and p orbitals on the bridging hydrogen atoms, which become triple-ζ double-polarization (see Appendix for the exponents). We have deliberately chosen an unbalanced basis set, since unbalance dramatizes the instability of Mulliken population analysis. Notice that if a molecule was treated in an almost complete basis set centered on a given atom, which is in principle correct, the overlap populations would vanish.

The results are summarized in Table VI. The Mulliken analysis on the SCF wave functions exhibits dramatic changes in both diagonal and off-diagonal elements. The net charge on the bridging hydrogen changes its sign when going from basis set 1 to basis set 2 (−0.10 and +0.10, respectively). The overlap population between B and H is divided by 2, while that between the two boron atoms is multiplied by 2, now being the leading one and suggesting larger bonding character along B–B rather than along B–H.

In contrast, the CASSCF + OVB procedure displays more stability. The CASSCF energy gain from basis set 1 to basis set 2 is very small (0.1 kcal/mol). The isodensity maps of the NAMOs are hardly discernable. The elements of the first-order density matrix are fairly constant. The net charge on the bridging hydrogen only changes from +0.14 to +0.16, while the bond orders

Table VI. Stabilities toward Basis Sets[a]

	basis set 1	basis set 2
	AOs-SCF Mulliken Analysis	
q_H	1.10	0.90
P_{BH}	0.20	0.12
P_{BB}	0.08	0.19
P_{HH}	−0.07	−0.12
	NAMOs-CASSCF Analysis	
q_h	0.86	0.84
P_{bh}	0.65	0.65
P_{bb}	0.56	0.56
$P_{hh'}$	−0.29	−0.29
CORP(b, h)[b]	10.8	10.4
CORP(b, b)	2.9	3.3
CORP(h, h')	1.4	1.4

[a] The basis set 1 is the DZP basis set used throughout the work; the basis set 2 is TZDP on the bridging hydrogens and DZP on the remaining atoms. [b] CORP indexes in percent.

keep unchanged. The OVB decomposition is almost identical, as exemplified hereafter on the weights of the four leading configurations:

	basis set 1	basis set 2
Φ_1	7.87	7.79
Φ_2	6.49	6.42
Φ_3	4.92	5.07
Φ_4	3.61	3.39

The stability of the valence-bond decomposition can be estimated from a measure of the formal overlap between the coefficients C_{i1} and C_{i2} of Φ_i in the expansions calculated with basis sets 1 and 2, respectively:

$$S = \sum_i C_{i1} C_{i2}$$

This value happens to be very close to 1 ($S = 0.9998$). The above-proposed CORP indexes, which measure the covalent bond character between two NAMOs, also happen to be stable. While the Mulliken overlap population hierarchy is affected by the basis set change, the CORP index produces unchanged estimates for the through-bond and through-space interactions.

VII. Conclusion

The analysis in terms of NAMOs provides a stable and efficient picture of the electronic population and avoids the defect of Mulliken population analyses. Other attempts have been formulated to avoid these shortcomings. For instance, the population can be expressed in terms of free-atom SCF atomic orbitals, which keep an invariant intrinsic character.[9-12] The results so-obtained are indeed quite stable and more meaningful than the usual ones. Our procedure avoids the requirement for such extra information. The NAMOs are orthogonal; this has both advantages and defects. The defects are in the tails, which distort the pure atomic character and may pollute the atomic charges. The advantages lie in the simplicity of the partitioning. The sum of the charges is the number of electrons, and there is no need to partition the overlap populations.

Although almost basis set independent, the bond orders expressed in the basis of NAMOs do not appear as significant measures of the existence of bonds in such problematic constructions. We believe elements of the second-order density matrix or related two-particle quantities give a beter insight into the local electronic population and its fluctuation since a covalent bond implies electronic delocalization and ionic/neutral mixing (at least in an orthogonal basis). The CORP index is certainly an interesting tool to study hypercoordinated systems such as metallic clusters and other controversial architectures where local two-electron pairing is not straightforward.

The present methodology defines a somewhat paradoxical trajectory since it starts from a rather elaborate wave function using nonminimal basis sets and including nondynamic correlation effects[39] and then moves back to some kind of minimal basis set description. It even makes it possible to propose a simple Hückel-type matrix (without overlap) quantitatively schematizing the interactions in a given system, by using the diagonal and off-diagonal energies of the CAS-CI matrix, as shown in section V. A CNDO-type Hamiltonian might be built as well, at an intermediate level of complexity. The main advantage of these backward procedures is pictorial. They suggest that simple pictures are available from the elaborate calculations and that physical trends may be traced simply and accurately, provided that rigorous reduction of information is considered to be as important to the modern scientist as the actual production of rigorous information.

The present work leads to a balanced picture of the double bridge in B_2H_6. It confirms the description in terms of a partition of the four electrons into two pairs. The interaction between the two bridges is not negligible, as exemplified by the correlation of the electronic up/down distributions, but it remains rather weak. This view is in line with the existence of singly bridged structures as in B_2H_5,[40] $B_2H_7^-$,[41] and various other systems,[35,42] or oppositely with the existence of triply bridged frames.[22,43] Regarding the relative BH versus BB interactions (a particular version of the through-bond versus through-space dilemma, especially important in small rings), all our evaluations are consistent. Both the analysis of the wave function in terms of rationnally conceived indexes, such as the probability of finding two electrons in a subset of NAMOs or its fraction of covalent origin (CORP), and the relative amplitudes of the hopping integrals in the OVB-CI matrix, yield the same conclusion: The directional B–H interactions prevail as the leading interactions in the double bridge, but direct through-space B–B interactions also exist, of smaller but nonnegligible amplitude. This is not in contradiction with the "inwardly bent" BH bonds related to the inwardly curved bond paths, obtained in the study of the Laplacian of the charge density.[16] In some sense, referring to the two limiting models of the two-electron three-center problem, i.e., the allyl cation and the cyclopropenyl cation or H_3^+ cluster, one may say that diborane is halfway between the two extremes. However, the through-bond/through-space proportion has no reason to be constant in isoelectronic doubly bridged structures. The occurrence of a dominant X–X bond between the two heavy atoms remains, in principle, possible for some of them. In a following paper, the above analysis is applied to a broad series of electron-deficient bridges, disclosing systematic trends and illustrating the interpretative power of the methodology.

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Appendix

1. CASSCF Calculations. The SCF step is performed with the PSHONDO program,[44] which introduces nonempirical effective core potentials[45] in the HONDO program.[46] Double-ζ plus polarization (DZP) basis sets are used. The exponent for the d function on boron is taken at 0.60, the exponent for the p function on hydrogen is taken at 0.80. The geometry taken for B_2H_6 is that obtained from SCF optimization, within D_{2h} symmetry, using

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(39) Dynamical correlation effects might be included as well by dressing the CAS-CI matrix, as done in ref 34c.

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the gradient version of the program. Such geometry corresponds to B–H_b = 1.327 Å, B–H_t = 1.195 Å, B–**B** = 1.791 Å, H_b**B**H_b = 95.1°, H_tBH_t = 122.3°, which is close to the gas-phase structure of diborane (B–H_b = 1.320 Å, B–H_t = 1.201 Å, B–B = 1.763 Å, H_bBH_b = 96.2°, H_tBH_t = 121.0°).[47] In section VI, a comparative study of the CASSCF + OVB procedure is performed with a basis set that is enriched on H_b. Only on these two atoms, a diffuse s function is added with exponent 0.03, while the p function is splitted into two parts, with exponents 1.12 and 0.20. This basis set is therefore triple-ζ s and double-ζ p on H_b. The geometry considered in that part is not reoptimized and is therefore the DZP one, which permits a better comparison.

The MCSCF step is performed with the program described in ref 48. The complete active space related to the double bridge involves six orbitals (a_g, b_{1u}, b_{2g}, b_{3u}, a_g, b_{1u}) and four electrons. This generates 33 singlet configurations. The MCSCF procedure brings a valence correlation energy of 29.8 kcal/mol. The main coefficients of the multiconfigurational wave function are as follows:

$$\psi = 0.99|a_g^2b_{1u}^2| - 0.12|a_gb_{1u}b_{2g}b_{3u}| - 0.08|a_gb_{1u}a_gb_{1u}| - 0.07|a_g^2b_{2g}^2| - 0.06|a_g^2b_{1u}a_g| - 0.05|b_{1u}^2a_g^2| - 0.05|a_gb_{1u}^2b_{3u}| - 0.04|a_g^2b_{1u}b_{1u}| + \ldots$$

2. Random Distributions. a. Pure Random. The problem reduces to a set of six equal boxes (the NAMOs), to be filled with four balls (the electrons). The four balls decompose into two white balls (spin α) and two red balls (spin β), and each box can contain only one ball or two balls of different colors (exclusion principle). The total number of possibilities for the distribution of these four balls into the six boxes is given by $C_6^2C_6^2$ = 225 (total number of determinants). Each elemental probability of Table I, referring to a given space part, is the simple ratio of the number of favorable cases over the number of possible cases. The determinants corresponding to four singly filled boxes (Φ_1, Φ_2, Φ_3, Φ_5, Φ_{11}, and Φ_{15}) have a probability of $C_4^2/225$ = 2.67%. The determinants corresponding to two doubly filled boxes (Φ_7, Φ_{12}, Φ_{15}, Φ_{20}, Φ_{25}, and Φ_{27}) have a probability of 1/225 = 0.44%. The remaining determinants, corresponding to one doubly filled box and two singly filled boxes have a probability of $C_2^1/225$ = 0.89%. Note that the number of favorable cases is nothing else than the spin degeneracy given by the ratio N/S in Table I.

b. Weighted Random. This corresponds to a set of six boxes of different sizes, four small ones (b NAMOs, of mean population 0.57) and two large ones (h NAMOs, of mean population 0.86). The preceding reasoning must be refined by assigning a probability to the occupation of each type of boxes. Let us call p_s and p_l the probabilities associated to the small boxes and large boxes, respectively. The elemental probabilities of Table I are now multiples of the different terms ${p_s}^4$, ${p_s}^3p_l$, ${p_s}^2{p_l}^2$, $p_s{p_l}^3$, and ${p_l}^4$. p_s and p_l can be fitted numerically, so as to reproduce the mean charges on each NAMO q_b and q_h. Each term ${p_s}^{4-n}{p_l}^n$ can also be straightly evaluated from its analytical expression in function of one orbital charge:

$${p_s}^{4-n}{p_l}^n = \frac{\alpha^n}{(\alpha^2 + 8\alpha + 6)^2}$$

$$\alpha = \frac{4(q_h - 1) + (10{q_h}^2 - 20q_h + 16)^{1/2}}{2 - q_h}$$

The general treatment of such problem is addressed in ref 49.

3. Probabilities within Given Subsets. The probability of finding a given number of electrons in a given subset of NAMOs is obtained by summing all the contributions ρ_i (given in Table **I**) of the configurations that satisfy such occupation in the given subset, with properly taking into account relevant space degeneracies. Some examples are explicited in the following.

$$P_h^{(0)} = 2\rho_3 + \rho_5 + \rho_6 + 2\rho_8 + 2\rho_9 + 4\rho_{10} + 2\rho_{12} + 2\rho_{14} + 2\rho_{15} + 2\rho_{17} + 2\rho_{18} + 2\rho_{19} + 2\rho_{20} + 2\rho_{21} + \rho_{22} + 4\rho_{23} + 2\rho_{24} + 2\rho_{25} + 4\rho_{26} + 2\rho_{27} + 2\rho_{28}$$

$$P_{h_1}^{(1)} = \rho_1 + \rho_2 + 3\rho_3 + \rho_4 + \rho_5 + \rho_6 + \rho_8 + \rho_9 + 2\rho_{10} + \rho_{11} + \rho_{13} + 3\rho_{14} + 2\rho_{17} + 2\rho_{18} + \rho_{19} + \rho_{21} + \rho_{22} + 2\rho_{23} + \rho_{24} + 2\rho_{26} + \rho_{28}$$

$$P_{b_1,h}^{(2)} = \rho_1 + \rho_2 + \rho_3 + 3\rho_4 + \rho_6 + \rho_7 + 2\rho_8 + 2\rho_9 + \rho_{10} + \rho_{11} + 3\rho_{12} + \rho_{13} + 2\rho_{14} + \rho_{15} + \rho_{17} + \rho_{18} + \rho_{20} + \rho_{23} + \rho_{24} + \rho_{25} + \rho_{26} + \rho_{27} + \rho_{28}$$

$$P_{b_1,h,b_2}^{(2)} = 2\rho_1 + 2\rho_2 + 4\rho_3 + 4\rho_4 + \rho_5 + 2\rho_6 + \rho_7 + 4\rho_8 + 4\rho_9 + 4\rho_{10} + 4\rho_{12} + 2\rho_{15} + 2\rho_{20}$$

For the pure random distribution, this procedure can be applied by using, of course, the coefficients given in the last column of Table I. In this case, however, such probabilities can be expressed straightforwardly, from simple counting considerations. The preceding examples can thus be written as

$$P_i^{(0)} = \frac{C_5^2C_5^2}{C_6^2C_6^2} = 44.4\%$$

$$P_i^{(1)} = \frac{2C_5^1C_5^2}{C_6^2C_6^2} = 44.4\%$$

$$P_{i,j}^{(2)} = \frac{2C_4^2 + C_2^1C_2^1C_4^2C_4^2}{C_6^2C_6^2} = 33.8\%$$

$$P_{i,j,k}^{(2)} = \frac{2C_3^2C_3^2 + C_3^1C_3^1C_3^1C_3^1}{C_6^2C_6^2} = 44.0\%$$

The orbital populations given by the first-order density matrix (q_b = 0.57, q_h = 0.86) can also be obtained from the probabilities associated to the various occupations of the given orbital:

$$q_i = \sum_{j=0}^{2} jP_i^{(j)}$$

For the analysis that uses the NAMOs respecting the fragment symmetry, **5**, the same kind of treatment is applied on an equivalent distribution of 30 space-part configurations. The population on each atom is of course unchanged, but the total population on each boron atom (1.14 e⁻) now decomposes into q_n = 0.72 and q_p = 0.42.

The OVB decomposition step is not compulsory to obtain the bielectronic probabilities. These may receive an operatorial definition using creation and annihilation operators. As an example, the probability of finding two electrons in a set $\{i, j\}$ is given by

$$P_{i,j}^{(2)} = \langle\Psi|P_{i,j}^{1,1} + P_{i,j}^{2,2} + P_{i,j}^{0,2}|\Psi\rangle$$

$$P_{i,j}^{1,1} = (a_i^+a_ia_{\bar{i}}a_{\bar{i}}^+ + a_{\bar{i}}^+a_{\bar{i}}a_ia_i^+)(a_j^+a_ja_{\bar{j}}a_{\bar{j}}^+ + a_{\bar{j}}^+a_{\bar{j}}a_ja_j^+)$$

$$P_{i,j}^{2,0} = (a_i^+a_{\bar{i}}^+a_{\bar{i}}a_i)(a_ja_{\bar{j}}a_{\bar{j}}^+a_j^+)$$

Such four-body operators have been used in ref 49. Of course, their mean values can be calculated on the Hartree–Fock wave function as well as on the CASSCF one or on more sophisticated ones incorporating the dynamical correlation effects. Note however that this formulation requires orthogonal monoelectronic functions. It would be difficult to define such quantitites with nonorthogonal (purely atomic or GVB) orbitals. The advantage of using orthogonal sets is the possibility of defining disjoint events and of thinking in terms of probabilities.

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