Frank WEINHOLD and Clark R. LANDIS
University of Wisconsin, Theoretical Chemistry Institute and Department of Chemistry (USA)

NATURAL BOND ORBITALS
AND EXTENSIONS OF LOCALIZED BONDING CONCEPTS

ABSTRACT: We provide a brief overview of "natural" localized bonding concepts, as implemented in the current natural bond orbital program (NBO 5.0), and describe recent extensions of these concepts to transition metal bonding. [*Chem. Educ. Res. Pract. Eur.*: 2001, *2*, 91-104]

WHAT ARE "NATURAL" LOCALIZED ORBITALS?

The concept of "natural'" orbitals was first introduced by Löwdin[1] to describe the unique set of orthonormal 1-electron functions $\theta_i(\vec{r})$ that are *intrinsic* to the *N*-electron wavefunction $\psi(1, 2, ..., N)$. Mathematically, the θ_i's can be considered as *eigen*orbitals of ψ (or, more precisely, of ψ's first-order reduced density operator), and they are therefore "best possible" (most rapidly convergent, in the mean-squared sense) for describing the electron density $\rho(\vec{r})$ of ψ. Compared to many other choices of orbitals that might be imagined or invented [e.g., the standard atomic orbital (AO) basis functions of electronic structure packages such as Gaussian 98[2]], the natural orbitals are singled out by ψ itself as "natural" for its own description.

One might suppose that natural orbitals would also be "best possible" for teaching chemistry students about ψ in qualitative orbital language. This would be so, *except* for the fact that natural orbitals (like the canonical molecular orbitals of Hartree-Fock theory) are necessarily *symmetry adapted*. Suppose, for example, that the quantum mechanical system of interest corresponds to two H atoms, one on earth and the other on the moon,

$$\psi_2 = \psi(H_{earth,} H_{moon}) \qquad (1a)$$

On physical grounds we might expect that the orbital description of ψ_2 is nearly identical to that for the corresponding localized wavefunctions

$$\psi_{1e} = \psi(H_{earth,}), \psi_{1m} = \psi(H_{moon,}) \qquad (1b)$$

However, due to the fact that ψ_2 must incorporate the superposition symmetry[3] between H_{earth}, H_{moon} (even if these atoms have no interactions of physical significance), the natural orbitals of ψ_2 will be found to differ *qualitatively* from those of ψ_{1e} or ψ_{1m}. This has the

unfortunate consequence of making the orbitals look "more delocalized" (and less transferable) than is physically meaningful, obscuring many simplicities of chemical bonding. (Similar spurious mixings occur when the atoms are merely separated by a few links of an alkane chain.) Thus, the natural orbitals as originally defined include bogus "delocalization effects" that have no physical significance,[4] limiting the usefulness of these orbitals for pedagogical purposes.

To remove spurious effects associated with symmetry adaptation, one can formulate[5] a *localized* criterion for orbitals that have the analogous maximum-occupancy (natural) character in localized 1-center and 2-center regions of the molecule. Because the maximum occupancy of an orbital is inherently limited to a pair of electrons[6] by the Pauli exclusion principle, local 1- and 2-center orbitals with occupancies sufficiently close to 2.000 can serve equally well as "true" natural orbitals for describing ψ . As anticipated by G. N. Lewis,[7] localized orbitals of near-double occupancy can be found in the 1- and 2-center regions suggested by the elementary Lewis structure diagram. Such *natural bond orbitals* (NBOs) provide the most accurate possible "natural Lewis structure" picture of ψ, because all orbital details (polarization coefficients, atomic hybrid compositions, etc.) are mathematically chosen to include the *highest possible* percentage of the electron density. This percentage (denoted %-ρ_L) gives an intrinsic measure of the accuracy of the natural Lewis structure picture, and is often found to be >99% for common organic molecules, dramatic testimony to the profound accuracy of Lewis's concept.

The NBOs are one of a sequence of natural localized orbital sets that include natural atomic (NAO), hybrid (NHO), and (semi-)localized molecular orbital (NLMO) sets, intermediate between basis AOs and canonical molecular orbitals (MOs)

$$AOs \rightarrow NAOs \rightarrow NHOs \rightarrow NBOs \rightarrow NLMOs \rightarrow MOs \qquad (2)$$
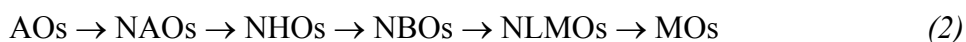
All these natural localized sets are complete and orthonormal, able to *exactly* describe any property of ψ. Compared to standard AOs, e.g., the NAOs give a much more condensed description of ψ, with only a small number (i.e., corresponding to the formal "minimal basis") having appreciable occupancy. Thus, a "minimal" description in terms of core and valence-shell NAOs is often found adequate for chemical purposes, providing a compact representation of ψ that is intimately related to standard valence concepts. The mutual orthogonality[8] of natural localized orbitals may seem to be a conceptual liability, inasmuch as the concept of "orbital overlap" seems to be lost. However, each orthogonal NAO (or NHO, NBO, etc.) can be uniquely associated with a corresponding "pre-orthogonal" PNAO (or PNHO, PNBO, etc.) which remains orthogonal to PNAOs on the same atom but has nonvanishing overlap integrals with those on other atoms. In accordance with the Mulliken approximation,[9] the corresponding Hamiltonian interaction elements are found to be closely proportional to these overlap integrals. That is, if $\hat{F}$ denotes the effective orbital Hamiltonian (Fock or Kohn-Sham operator), the interaction strength $<h_A | \hat{F} | h_B>$ of bonding NHOs h_A, h_B can be approximated in terms of overlapping PNHOs $\tilde{h}_A$, $\tilde{h}_B$ as

$$<h_A | \hat{F} | h_B> \cong k <\tilde{h}_A | \tilde{h}_B> \qquad (3)$$

where k is a proportionality constant of order unity. Thus, PNHO overlap diagrams remain highly effective for teaching students the "principle of maximum overlap," but without encouraging the frequent misconception that geometrical orbital overlaps (rather than matrix elements of the system Hamiltonian) are somehow the origin of chemical bonding.

In accordance with the simple bond orbital picture[10] each bonding NBO σ_{AB} can be written in terms of two directed valence hybrids (NHOs) h_A, h_B on atoms A and B, with corresponding polarization coefficients c_A, c_B,

$$\sigma_{AB} = c_A h_A + c_B h_B \tag{4a}$$

that vary smoothly from covalent ($c_A = c_B$) to ionic ($c_A \gg c_B$) limit. Each valence bonding NBO (4a) must in turn be paired with a corresponding valence *anti*bonding NBO

$$\sigma_{AB}^* = c_B h_A - c_A h_B \tag{4b}$$

to complete the span of the valence space. The "Lewis"-type (donor) NBOs (4a) are thereby complemented by the "non-Lewis"-type (acceptor) NBOs (4b) that are formally empty in an idealized Lewis structure picture. Weak occupancies of the valence antibonds (4b) signal irreducible departures from an idealized localized Lewis structure picture, i.e., true "delocalization effects." The energetic stabilization due to such $\sigma \to \sigma^*$ donor acceptor interactions can be estimated by 2nd-order perturbation theory, viz., for the $\sigma_i \to \sigma_j^*$ interaction,

$$\Delta E_{i \to j^*}^{(2)} = -2 \frac{\left\langle \sigma_i \left| \hat{F} \right| \sigma_j^* \right\rangle^2}{\varepsilon_{j^*} - \varepsilon_i} \tag{5}$$

where $\hat{F}$ is the effective orbital Hamiltonian (Fock or Kohn-Sham operator) and $\varepsilon_i = \langle \sigma_i | \hat{F} | \sigma_i \rangle$, $\varepsilon_{j^*} = \langle \sigma_j^* | \hat{F} | \sigma_j^* \rangle$ are the respective orbital energies of donor and acceptor NBOs. Consideration of valence antibonds (4b) therefore leads to far-reaching extension of elementary Lewis structure concepts to encompass leading delocalization corrections in simple NBO perturbative estimates such as Eq. (5).

As a result of each $\sigma_i \to \sigma_j^*$ perturbation, the starting NBO acquires a weak antibonding "tail" in the final (doubly occupied) NLMO Ω_i. More generally, each semi-localized NLMO Ω_i can be expressed as a linear combination of the parent Lewis-type NBO σ_i (with coefficient $c_{ii} \cong 1$) and residual weak contributions ($c_{ji} \cong 0$) from non-Lewis (NL) NBOs σ_j^*

$$\Omega_i = c_{ii}\sigma_i + \sum_{j}^{NL} c_{ji}\sigma_j^* \tag{6}$$

that reflect the irreducible physical effect of $\sigma_i \to \sigma_j^*$ delocalizations. Despite the compact, recognizable forms of NLMOs and their close connection to chemical structure concepts, it is important to recognize that a Slater determinant of doubly occupied NLMOs is *equivalent* to the usual MO wavefunction. Hence, the simplicity of NBO-based expansions such as (6) is achieved with *no* loss of accuracy in the description of ψ.

OVERVIEW OF THE NATURAL BOND ORBITAL PROGRAM

A modern electronic structure system (ESS) such as Gaussian 98, Jaguar,[11] NWChem,[12] Q-Chem,[13] PQS,[14] or GAMESS[15] makes it increasingly easy for the chemistry student or teacher to obtain an accurate ψ. Similarly, the NBO analysis of ψ is performed by a computer program, currently NBO 5.0, that attaches to these and other ESS hosts.[17]

Compared to earlier "generations" of the program (NBO 3.0 and 4.0), NBO 5.0 contains extensive new capabilities related to magnetic properties and transition metal bonding (as discussed below), as well as numerous extensions and improvements of established NBO analysis tools. Some of these advanced options are mentioned below and in Sec. 3, but we primarily focus on generic input and output features that are common to all recent NBO versions.

Input to the NBO program is in the form of keywords within the $NBO...$END *keylist*, usually following the host ESS input file, viz.,

```
$NBO keyword1 keyword2 ... $END
```

These keywords (about 95 in the current version) can direct output for analyses of specialized properties, e.g.,

```
NJC (natural chemical coupling[18])
NCS  (natural chemical shielding[19])
```

NBO-based wavefunction or energy decompositions, e.g.,

```
NRT (natural resonance theory[20])
NEDA (natural energy decomposition analysis[21])
```

printing and display options, e.g.,

```
PLOT (graphical orbital display)
```

operator matrices in localized bases, including

```
F (Fock), K (kinetic), V (1-e potential), DI (dipole), DM (density), S (overlap)
```

as well as other options. For example, the keylist

```
$NBO STERIC FNBO PLOT FILE=C2H4 $END
```

would perform natural steric analysis,[22] print the matrix of the Fock operator $\hat{F}$ in the NBO basis, and print disk files for the ORBPLOT or NBOView orbital viewers under the filename "C2H4" for this job.

Output from the NBO program may consist of (i) printed tables in the .LOG file, (ii) disk files for input to other programs (e.g., graphical utilities), and/or (iii) modifications of the host ESS checkpoint file that can affect performance of subsequent jobs. An example of the latter is storage of the NBOs from a starting single-determinant self-consistent-field (SCF) treatment into the checkpoint file for use in post-SCF correlation corrections (e.g., of complete active space CAS/NBO type[23]). Most important is the default .LOG file output, whose major sections we briefly summarize below:

Natural population analysis

This section displays a list of all NAOs and their "type," population, and energy (if one-electron HF/DFT Hamiltonian is available). The orbital populations are then summed to

give the table of atomic *natural charges* and the effective *natural electron configuration* on each atom.

Natural bond orbital analysis

This section displays the NBOs in terms of their constituent hybrids, polarization coefficients, occupancies, and NAO composition. Each NBO is labeled as being of core (CR), bond (BD), valence lone pair (LP), or extra-valence Rydberg (RY) type, with affixed asterisk (*) for non-Lewis orbitals. Thus, the label "LP(1) N 2" identifies a valence lone pair on nitrogen 2 (n_{N2}), and "BD*(1) C 1-H 4" identifies a valence C1-H4 antibond (σ^*_{C1H4}). Parenthesized label numbers such as BD(1), BD(2), BD(3) distinguish multiple bonds between the same atoms, and similar LP or RY* labels distinguish multiple lone pair or Rydberg orbitals at each center.

NHO directionality and "bond bending" analysis

This section displays the angular deviations between the bonding hybrids and the direct line-of-sight between nuclei, showing where significant bond bending is present.

2nd-order perturbation theory analysis

This section tabulates, for all possible donor-acceptor pairs, the values of the donor-acceptor stabilization energy as estimated by Eq. (5). The table also includes the corresponding Fock matrix elements in the numerator and denominator of this equation. Where appropriate, interactions are separated into intra- and inter-molecular types for different "molecular units," i.e., contiguously bonded atomic networks (usually equivalent to "molecules" or "ions"). This section of the output is normally the first to be examined by the experienced NBO user in searching for significant delocalization effects.

NBO summary

This section summarizes the NBOs, occupancies, energies, and principal delocalizing interactions grouped by molecular units. The table also includes net charge and valence/Rydberg occupancy statistics for each unit.

Further details of NBO output tables and their interpretation are provided on the NBO website[24] and in the NBO 5.0 program manual, which is mandatory for intelligent use of the program.

EXTENSION OF LOCALIZED BONDING CONCEPTS TO TRANSITION METALS

G.N. Lewis's octet rule and shared electron pair concepts[7] underlie the most broadly accepted models of localized bonding in common main group elements. However, it is important that a quantitative wavefunction analysis should not only conform to our prejudices in these cases, but also suggest useful *extensions* of localized concepts to less well understood species. In the present section we sketch empirical and NBO-based computational evidence for a far-reaching extension of Lewis-like diagrams and bonding concepts to transition metal compounds.

As a practical empirical criterion for what transition metal compounds might be considered "common," Table 1 exhibits the formulas and number of unpaired electrons (e_u) for the Group 3-12 binary oxides, chlorides, and alkyl compounds that are available *most cheaply and in largest quantities* from a standard chemical supply catalog.[25] From this table a

TABLE 1. "*Most common*[a]" ML_n *compounds* (L = *chloride, oxide, alkyl*) *and number of unpaired electrons*[b] (e_u) *for Group 3-12 transition metals* M. *Asterisks mark the few apparent exceptions to Eq. (7).*

Group	M	chloride	(e_u)	oxide	(e_u)	alkyl	(e_u)
3	Sc	$ScCl_3$	(0)	Sc_2O_3	(0)	---	
	Y	YCl_3	(0)	Y_2O_3	(0)	---	
	La	$LaCl_3$	(0)	La_2O_3	(0)	---	
4	Ti	$TiCl_4$	(0)	TiO_2	(0)	$Ti(benzyl)_4$	(0)
	Zr	$ZrCl_4$	(0)	ZrO_2	(0)	$ZrMe_4$	(0)
	Hf	$HfCl_4$	(0)	HfO_2	(0)	$HfMe_4$	(0)
5	V	VCl_4	(1)	V_2O_5	(0)	$V(CH_2TMS)_4$	(1)
	Nb	$NbCl_5$	(0)	Nb_2O_5	(0)	$NbMe_5$	(0)
	Ta	$TaCl_5$	(0)	Ta_2O_5	(0)	$TaMe_5$	(0)
6	Cr	$CrCl_3$	(3)	CrO_3	(0)	$Cr(cyclohexyl)_4$	(2)
	Mo	$MoCl_5$	(1)	MoO_3	(0)	$Mo(cyclohexyl)_4$	(2)
	W	WCl_5	(1)	WO_3	(0)	WMe_6	(0)
7	Mn	$MnCl_2$	(5)*	MnO	(5)*	$Mn[C(TMS)_3]_2$	(5)*
	Tc	$TcCl_4$	(1-2)*	Tc_2O_7	(?)	---	
	Re	$ReCl_5$	(~2)*	Re_2O_7	(0)	$ReMe_6$	(1)*
8	Fe	$FeCl_3$	(5)*	Fe_2O_3	(5)*	$Fe(norbornyl)_4$	(0)
	Ru	$RuCl_3$	(0)	RuO_2	(0)	$Ru(mesityl)_4$	(0)
	Os	$OsCl_3$	(?)	OsO_2	(0)[c]	$Os(mesityl)_4$	(0)
9	Co	$CoCl_2$	(4)*	Co_3O_4	(~4)*	$Co(norbornyl)_4$	(1)
	Rh	$RhCl_3$	(0)	Rh_2O_3	(0)	$Rh(mesityl)_3$	(0)
	Ir	$IrCl_3$	(0)	Ir_2O_3	(0)	$Ir(mesityl)_3$	(0)
10	Ni	$NiCl_2$	(2)*	NiO	(4)*	---	
	Pd	$PdCl_2$	(0)	PdO	(?)	---	
	Pt	$PtCl_2$	(0)	PtO	(?)	---	
11	Cu	CuCl	(0)	Cu_2O	(0)	$[Cu(CH_2TMS)]_4$	(0)
	Ag	AgCl	(0)	Ag_2O	(0)	---	
	Au	AuCl	(0)[d]	Au_2O_3	(?)	---	
12	Zn	$ZnCl_2$	(0)	ZnO	(0)	---	
	Cd	$CdCl_2$	(0)	CdO	(0)	---	
	Hg	$HgCl_2$	(0)	HgO	(0)	$HgMe_2$	(0)

[a] According to criterion of lowest cost or availability in largest quantities (Ref. 25).
[b] Inferred from magnetic susceptibility measurements.
[c] OsO_4 (0) is comparable.
[d] $AuCl_3$ (0) is comparable.

remarkable regularity becomes apparent. If G_M denotes the group number, n the stoichiometric ML_n formula ratio, and V_L the valency of the ligand, the relationship

$$\left| G_M - 6 \right| + n\, V_L + e_u = 6 \qquad (7)$$

can be seen to be satisfied for an overwhelming majority of common ML_n species.

We now assume, following Lewis, that each "bond" linkage to a monovalent ligand is associated with a shared electron pair, so that the total number (e_{bp}) of valence bond-pair electrons is $e_{bp} = 2nV_L$. We also recognize that the maximum possible number (e_{1p}) of nonbonded lone-pair electrons is $e_{1p} = 2(G_M - 6)$ for any group $G_M \geq 6$. Thus, for mid to late d-block elements, Eq. (7) becomes

$$\tfrac{1}{2}\,(e_{1p} + e_{bp}) + e_u = 6 \qquad (6 \leq G_M \leq 11) \qquad (8)$$

This is analogous to the corresponding Lewis-type formula for normal-valent elements

$$\tfrac{1}{2}\,(e_{1p} + e_{bp}) + e_u = 4 \qquad (14 \leq G_M \leq 18) \qquad (9)$$

which for closed-shell species ($e_u = 0$) becomes

$$e_{1p} + e_{bp} = 8 \qquad (14 \leq G_M \leq 18;\; e_u = 0) \qquad (10)$$

the famous "Rule of 8" (octet rule). Thus, for d-block elements the corresponding relationship is

$$e_{1p} + e_{bp} = 12 \qquad (6 \leq G_M \leq 11;\; e_u = 0) \qquad (11)$$

which may be termed the "Rule of 12" (dodectet rule) for stable closed-shell transition metal species. Just as the four valence orbitals ($s + 3p$) of the p-block underlie the usual Lewis octet rule (10), so may the six valence orbitals ($s + 5d$) of the d-bock be expected to underlie the corresponding dodectet rule (11) for transition metals.
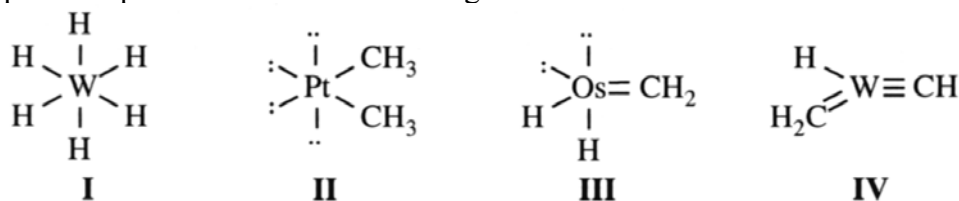
The distribution of six electron pairs around a dodectet-conforming transition metal atom M can be represented with a hexagonally-shaped "dot diagram"
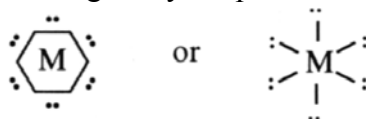
analogous to the usual square dot-diagram for an octet-conforming main-group element X
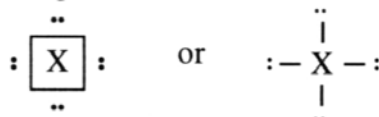
Some simple examples of dodectet conforming Lewis-like formulas include **I-IV**

illustrating the extended capacity for multiple metal-metal bonding with main-group ligands. One can also consider a still more unusual possibility such as **V**

$$H\text{-}W \equiv W\text{-}H$$

V

illustrating the extended capacity for multiple metal-metal bonding.

Like its octet counterpart (13), the dodectet diagram (12) depicts the valence electron configuration and bond connectivity, but not (necessarily) the 3-dimensional geometry about the transition metal. In the spirit of the Pauling-Slater[26] theory of main-group hybridization, the actual molecular geometry of transition metal compounds is expected to correspond approximately to the separation angles α of idealized sd^μ bonding hybrids ($\mu = n-1$) that form the sigma skeleton. Equivalent sd^μ hybrids can be shown[27] to allow *two* possible separation angles, the acute angle (α_{acute}) or obtuse angle (α_{obtuse}) satisfying

$$\alpha_{acute} = \cos^{-1}\left(+\left[\frac{\mu-2}{3\mu}\right]^{1/2}\right) \qquad (14a)$$

$$\alpha_{obtuse} = \cos^{-1}\left(-\left[\frac{\mu-2}{3\mu}\right]^{1/2}\right) \qquad (14b)$$

Numerical values of these idealized "natural" bond angles are shown in Table 2 for various μ [corresponding to percentage d-character $= \mu(\mu+1)$]. Note that acute hybrid angles down to $\sim 55^o$ are perfectly possible for transition metal sd-hybridization, whereas hybrid angles $< 90^o$ are forbidden in main-group sp-hybridization.[28]

TABLE 2. *Natural bond angles* (α_{acute}, α_{obtuse}, degrees) *and percentage d-character of equivalent sd^μ hybrids; cf. Eqs. (14a b).*

hybrid	μ	α_{acute}	α_{obtuse}	%-d
sd^2	2	90.00	90.00	66.67
sd^3	3	70.53	109.47	75.00
sd^4	4	65.91	114.09	80.00
sd^5	5	63.43	116.57	83.33
sd^{10}	10	58.91	121.09	90.91
d	∞	54.74	125.26	100.00
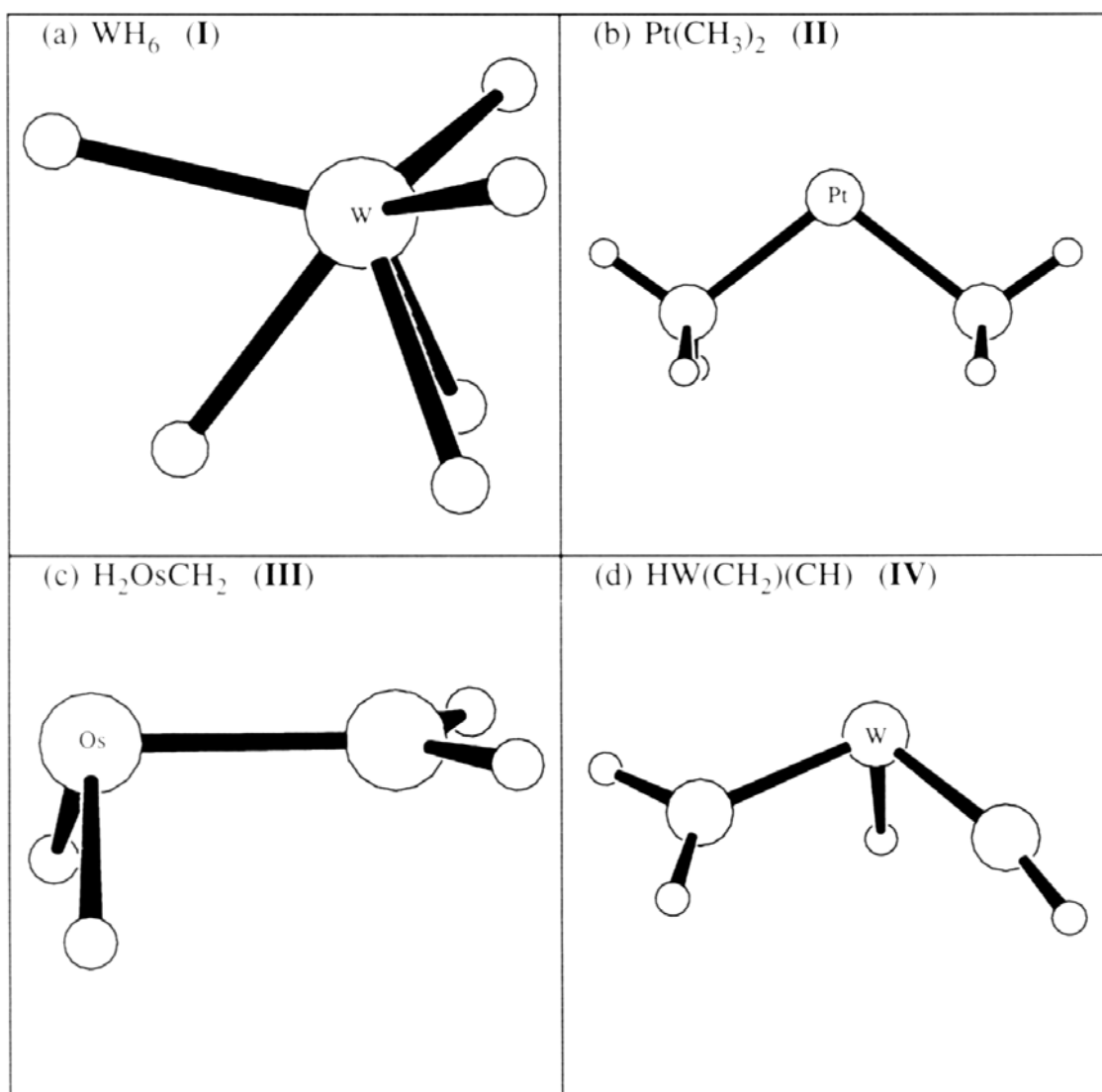
FIGURE 1: *Equilibrium B3LYP/LANL2DZ geometries of* **I-IV**. *Optimized L-M-L' bond angles: (a) 63.7 (3), 67.1 (3), 113.8 (3), 119.7 (6); (b) 102.9 ; (c) 94.1 (2), 105.8 ; (d) 94.2 , 95.2 , 100.5 .*

Optimized B3LYP/LANL2DZ equilibrium structures for **I-IV** are shown in Figure 1, illustrating the propensity toward strongly bent geometries (e.g., sd^5-like ~65° , ~116° in **I**; sd^2-like ~90° bond angles in **III**, **IV**) that are quite surprising from a VSEPR-like steric or electrostatic perspective. NBO analysis confirms the aptness of the localized Lewis-like description in each case. Table 3 summarizes details of the optimal hybrids, bond polarities, and overall accuracy of the NBO Lewis-like description (in terms of %-ρ_L, the percentage of valence electron density representable by a strictly localized Lewis-like wavefunction), showing the high accuracy (97-99%-ρ_L) of this simple picture. The localized M-C, M-H bond NBOs are all found to be surprisingly apolar (38-53% on M) and to have high "pair" occupancies (1.92-1.98e), comparable to the values found in pure hydrocarbons.

TABLE 3. *NBO descriptors of* **I-IV***, showing overall accuracy of NBO Lewis-like valence electron density* (%-ρ_L) *and metal atom hybridization* (h_M), *bond polarity toward* M (100$|c_M|^2$), *diatomic symmetry type* (σ, π, δ), *and occupancy* (e) *of each M-L bond NBO* $\sigma_{ML} = c_M h_M + c_L h_L$.

species	%-ρ_L	M-L bond NBO			
		type	h_M	$100|c_M|^2$	occ.(e)
I. WH$_6$	97.37	σ_{WH}	$sd^{4.08}$	50.1	1.919
		σ_{WH}	$sd^{6.27}$	43.6	1.976
II. Pt(CH$_3$)$_2$	99.25	σ_{PtC}	$sd^{1.30}$	44.3	1.954
III. H$_2$OsCH$_2$	99.11	σ_{OsH}	$sd^{2.00}$	49.5	1.977
		σ_{OsC}	$sd^{2.53}$	41.6	1.980
		π_{OsC}	d	57.0	1.983
IV. HW(CH$_2$)(CH)	98.54	σ_{WH}	$sd^{1.60}$	43.9	1.961
		σ_{WC}	$sd^{2.38}$	37.7	1.973
		π_{WC}	d	46.9	1.977
		"σ_{WC}"	$sd^{4.11}$	46.2	1.949
		"π_{WC}"	$sd^{7.81}$	44.2	1.971
		π_{WC}	d	52.7	1.960

Figure 2 illustrates the optimized geometry of **H-W☰W-H(V)** and contour diagrams of the *quintuple*-bond NBOs (one of σ_{WW}, two of π_{WW} and two of δ_{WW} type), each displayed in a plane to best display its distinguishing characteristics. The shapes of d_π-d_π metal-metal π-bonds (Fig. 2b,c) differ strikingly from those of main-group compounds (as expected), and both hybridized ($\delta^{(h)}$, Fig. 2d) and unhybridized ($\delta^{(u)}$, Fig. 2e) types of δ-bonds have no counterparts in main-group chemistry. Nevertheless, the localized metal-metal NBOs exhibit a degree of recognizability and transferability that is in many respects similar to that of main-group Lewis structures. This commonality suggests the general efficacy of a unified Lewis-like picture of bonding in *p*- and *d*-block elements. The NBO 5.0 algorithms for automated NRT resonance structure searches have therefore been extended to include such Lewis-like dodectet structures, greatly improving applicability of resonance concepts to transition metal species.

The results presented here for **I-V** are broadly representative of the virtually unlimited possibilities for dodectet-conforming compounds that can be readily envisioned from the mnemonic diagram (12). Particularly interesting are the compounds formed by tetravalent Group 8 elements that represent analogs of common organic species, such as "methane-like" **VI** "allene-like" **VII**, and "butadiene-like" **VIII**,

VI   **VII**   **VIII**
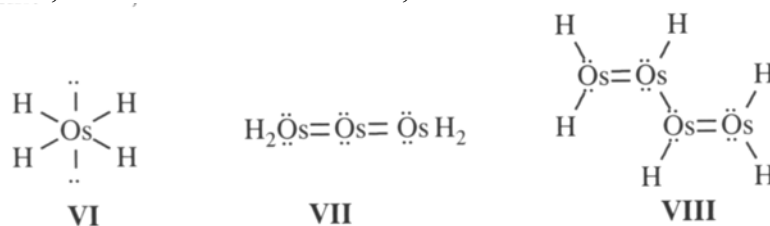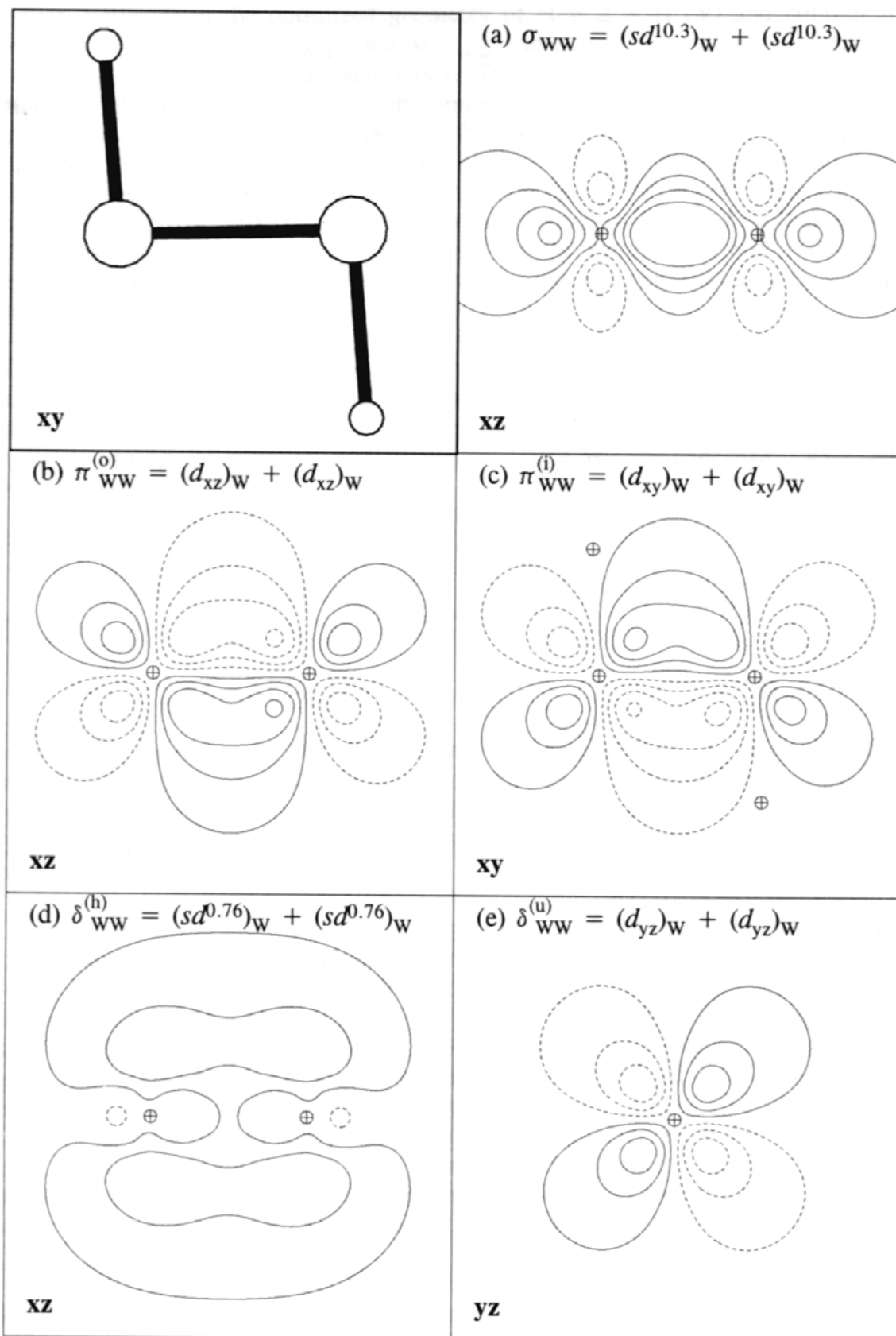
FIGURE 2: *Metal-metal bond NBOs of quintiply-bonded* $\mathbf{H\text{-}W}\equiv\mathbf{W\text{-}H}$ *(%-ρ_L = 99.87%), showing hybrid composition (above) and chosen contour plane (lower left) for each bond.*

It is remarkable, for example, that the localized NBO Lewis-like description **VI** for OsH_4 is more accurate (as judged by %-ρ_L) than the standard localized Lewis structure for methane. Perhaps even more remarkable is the observation that OsH_4 has *three* local minima (T_d, C_{2v}, C_{4v} symmetry), corresponding to the three possible geometries in which all bond angles are either ~109° or ~70°, as allowed by sd^3 hybridization.

Compared to analogous main group compounds, the Lewis-like transition metal compounds are much more susceptible to 3-center, 4-electron hypervalent interactions[29] ("ionic resonance," X-M :Y $\leftrightarrow$ X: M-Y) which increase the formal coordination at the metal center. NBO 5.0 now includes a search for 3-center hyperbonds (keyword: 3CHB) to flag these interesting features of molecular structure. Other systematic differences in d_π-d_π interaction strength and transition metal electronegativity also contribute to the richly distinctive chemistry of the *d*-block.[30] Nevertheless, we believe that considerable insight (including identification of likely synthetic target species) can be gained by recognizing the many similarities between localized Lewis-like bonding in *p*- and *d*-block elements, while also acknowledging their characteristic differences. The many new features of NBO 5.0 should allow standard computational chemistry packages to play an ever more important role in productive extensions of localized bonding concepts.

CORRESPONDENCE: *Frank WEINHOLD, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA; e-mail: WEINHOLD@chem.wisc.edu*

Frank Weinhold and **Clark R. Landis** are both Professors of Chemistry at the *University of Wisconsin*, Madison, where they are currently collaborating on Ref. 30b. F. Weinhold, a member of the *Physical Chemistry Division* and *Theoretical Chemistry Institute*, completed graduate studies at Harvard with *E.B. Wilson, Jr.* and postdoctoral studies at Oxford with *C.A. Coulson*. His current research focuses on the nature of hydrogen bonding and the quantum cluster equilibrium (QCE) model of H-bonded fluids. C.R. Landis, a member of the Inorganic Chemistry Division, completed graduate studies at the University of Chicago, with Jack Halpern. His current research focuses on the nature of bonding at transition metal complexes, the development of empirical force field methods that span the periodic table, mechanistic studies of organotransition metal catalysts, and novel parallel synthetic strategies for making phosphine ligands and accelerating new catalysts for making phosphine ligands and accelerating new catalyst discovery.

NOTES AND REFERENCES

1. P.-O. Löwdin, Phys. Rev. *97*, 1474-1489 (1955). While the present work is formulated in the molecular orbital framework of Hartree-Fock (HF) or density functional theory (DFT), the entire treatment can be readily generalized to *any* wavefunction, including the exact ψ.
2. *Gaussian 98*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
3. F. Weinhold, *J. Chem. Ed. 76*, 1141 (1999).
4. More precisely, the transformation from symmetry-adapted to non-symmetry-adapted form corresponds to a unitary transformation of orbitals that merely multiplies ψ by an overall phase factor, and hence has no effect on the energy, density, or other measurable

properties.

5. J. P. Foster and F. Weinhold, *J. Am. Chem. Soc. 102*, 7211 (1980); A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev. 88*, 899 (1988); F. Weinhold, *Natural bond orbital methods*, in, P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, and P. A. Kollman (eds.), "Encyclopedia of Computational Chemistry" (Wiley, Chichester, UK, 1998) Vol. 3, pp. 1792-1811.

6. For open-shell systems, electrons of different spin generally occupy different spin-orbitals, and the occupancy limit of each spin-orbital is accordingly reduced to one. We consider only closed-shell systems in the present work.

7. G. N. Lewis, *J. Am. Chem. Soc. 38*, 762 (1916); G. N. Lewis, "Valence and the structure of atoms and molecules" (The Chemical Catalog Co., New York, 1923).

8. Mutually orthogonality of a set of orbitals is an elementary prerequisite for associating the orbitals with a physical (Hermitian) operator as eigenfunctions. Overlapping orbitals therefore cannot be considered as eigenfunctions of any "system Hamiltonian" of physical significance.

9. R. S. Mulliken, *J. Chem. Phys. 46*, 497 (1944); J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc. 84*, 540 (1962); R. Hoffmann, *J. Chem. Phys. 39*, 1397 (1963).

10. R. S. Mulliken, *J. Chem. Phys. 3*, 573 (1935).

11. *Jaguar 3.5*, Schroedinger, Inc., Portland, OR, 1998.

12. High Performance Computational Chemistry Group, *NWCHEM, A computational chemistry program for parallel computers, Version 4.0.1* (2001), Pacific Northwest National Laboratory, Richland Washington 99352.

13. *Q-Chem 1.1*, B. G. Johnson, P. M. W. Gill, M. Head-Gordon, C. A. White, J. Baker, D. R. Maurice, T. R. Adams, J. Kong, M. Challacombe, E. Schwegler, M. Oumi, C. Ochsenfeld, N. Ishikawa, J. Florian, R. D. Adamson, J. P. Dombroski, R. L. Graham, and A. Warshel, Q-Chem, Inc., Export, PA, 1997.

14. Parallel Quantum Solutions, 2013 Green Acres Road Suite A, Fayetteville, Arkansas 72762 (http://www.pqs-chem.com)

15. *GAMESS(-US)*. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, Jr., *J. Comp. Chem.* 14, 1347 (1993). The PC-GAMESS version is available through A. A. Granovsky (http://classic.chem.msu.su/gran/gamess/index.html)

16. *NBO 5.0*, E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin (2001).

17. The procedure to attach or "activate" NBO 5.0 capability varies with the ESS package. For Jaguar, NWChem, Q-Chem, and PQS, NBO 5.0 comes pre-installed. NBO 5.0 also comes pre-installed in PC-GAMESS (to be activated by a password key) but must be manually installed in GAMESS-US (by a procedure described in the manual). An earlier "NBO 3.1" version also comes pre-installed in Gaussian 98, but this can be easily replaced by the current NBO 5.0, using instructions provided in the manual. Current order information for NBO 5.0 program and manual: TCI/NBO Software (lwmorris@facstaff.wisc.edu, 608-262-5153) or the NBO 5.0 website (Ref. 24).

18. S. J. Wilkens, W. M. Westler, J. M. Markley, and F. Weinhold (submitted for publication).

19. J. A. Bohmann, T. C. Farrar, and F. Weinhold, *J. Chem. Phys. 107*, 1173 (1997).

20. E. D. Glendening and F. Weinhold, *J. Comp. Chem. 19*, 593-609, 610-627 (1998); E. D. Glendening, J. K. Badenhoop, and F. Weinhold, *J. Comp. Chem. 19*, 628 (1998).

21. E. D. Glendening and A. Streitwieser, *J. Chem. Phys. 100*, 2900 (1994).

22. J. K. Badenhoop and F. Weinhold, *J. Chem. Phys, 107*, 5406-5421, 5422-5432 (1997); *Int. J. Quantum Chem. 72*, 269 (1999).

23. A. V. Nemukhin and F. Weinhold, *J. Chem. Phys. 97*, 1095 (1992).

24. http://www.chem.wisc.edu/~nbo5

25. Alfa Aesar Research Chemicals, "Metals and Materials Catalog" (1999-2000).

26. L. Pauling, *J. Am. Chem. Soc, 53*, 1367 (1931); J. C. Slater, *Phys. Rev. 37*, 481 (1931).

27.   T. Cleveland and C. R. Landis, *J. Am. Chem. Soc. 118*, 6020 (1996); C. R. Landis, *Adv. Mol. Struct. Res. 2*, 129 (1996).

28.   C. A. Coulson and W. E. Moffitt, *Phil. Mag. 40*, 1 (1935); C. A. Coulson, "Valence," 2nd ed. (Oxford U. Press, London, 1952), Chap. 8.

29.   G. C. Pimentel, *J. Chem. Phys. 19*, 446 (1951); R. E. Rundle, *J. Chem. Phys*. 17, 67 (1941); C. A. Coulson, *J. Chem. Soc. 1964*, 1442 (1964).

30.   (a) C. R. Landis, T. Cleveland and T. K. Firman, *J. Am. Chem. Soc. 117*, 1859 (1995);
      (b) F. Weinhold and C. R. Landis, "Valency and bonding: A natural bond orbital donor-acceptor perspective" (in preparation).