

# Intrinsic atomic orbitals: An unbiased bridge between quantum theory and chemical concepts

Gerald Knizia<sup>1, a)</sup>

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart

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Modern quantum chemistry can make quantitative predictions on an immense array of chemical systems. However, the interpretation of those predictions is often complicated by the complex wave function expansions used. Here we show that an exceptionally simple algebraic construction allows for defining atomic core and valence orbitals, polarized by the molecular environment, which can exactly represent self-consistent field wave functions. This construction provides an unbiased and direct connection between quantum chemistry and empirical chemical concepts, and can be used, for example, to *calculate* the nature of bonding in molecules, in chemical terms, from first principles. In particular, we find consistency with electronegativities ( $\chi$ ), C 1s core level shifts, resonance substituent parameters ( $\sigma_R$ ), Lewis structures, and oxidation states of transition metal complexes.

## I. INTRODUCTION

Chemical concepts as fundamental as atomic orbitals (AOs) in molecules, covalent bonds, or even partial charges, do not correspond to physical observables and thus cannot be unambiguously defined in pure quantum theory. This leads to the unpleasant situation that quantum chemistry can tell us benzene's heat of formation with  $<2$  kJ/mol accuracy,<sup>1</sup> but, strictly speaking, neither that it has twelve localized  $\sigma$ -bonds and a delocalized  $\pi$ -system, nor what the partial charges on the carbons are. Chemical bonds have even been compared to unicorns—mythical creatures of which everyone knows how they look, despite nobody ever having seen one.<sup>2</sup>

However, qualitative concepts are of essential importance for practical chemistry, and thus a large number of competing techniques were developed for extracting them from quantum chemical calculations. In particular, Bader's atoms in molecules<sup>3</sup> and Weinhold's natural atomic/bond orbital analysis (NAO/NBO)<sup>4,5</sup> are widely used for interpreting molecular electronic structure. Nonetheless, the former is known to produce counter-intuitive results in many cases,<sup>6</sup> and the latter, while undoubtedly having brought countless successes in chemical interpretation, is complicated and pre-imposes various non-trivial assumptions. Concretely, NBO analysis is based on the two notions that atomic orbitals (AOs) in molecules have spherical symmetry and can be obtained by a particular complex series of transformations,<sup>4</sup> and that a Lewis-like bonding pattern for any given molecule *exists* and only needs to be found—by comparing the wave function to all possible Lewis patterns.<sup>7</sup> While normally applicable, violations of both assumptions are conceivable in unusual bonding situations, and might then lead to erratic interpretations. Energy decomposition and related techniques<sup>8–15</sup> are also important and widely used in interpretation, but have different aims.

We here present a new technique to connect quantitative self-consistent field (SCF) wave functions to a qualitative chemical picture. This technique is essentially free of empirical input,

allows for *computing* the nature and shape of chemical bonds, and is not biased towards any preconceived notion of bonding. This is achieved by first defining a new intrinsic minimal basis (IMB),<sup>16</sup> a set of perturbed core- and valence AOs which can exactly describe the occupied molecular orbitals (MOs) of a previously computed SCF wave function. We will show that the intrinsic AOs (IAOs) thus defined can be directly interpreted as the *chemical* AOs, and that partial charges and bond orbitals (IBOs) derived from them perfectly agree with both experimental data and intuitive chemical concepts. In particular, we find a natural *emergence* of the Lewis structure of molecules.

Suggestions to use either unpolarized<sup>17–20</sup> or polarized<sup>21–24</sup> free-atom AOs to interpret molecular wave functions appeared early in the literature, and methods continue being developed. Also IMBs spanning occupied orbitals, as this work is concerned with, have been constructed before;<sup>16,25–31</sup> a particularly advanced one was recently introduced by Laikov,<sup>31</sup> who also discusses the literature in the field. However, despite the conceptual advantages of such IMB, so far none of them have found widespread use comparable to Bader or NAO analysis, and most are technically rather complex and have not been intensively tested with regard to empirical laws and facts. Our contribution is a IMB which is simple and efficient, its use in constructing bond orbitals, and the demonstration that this combination shows excellent promise for interpreting chemical bonding and reactivity. The technique thereby provides a firm quantum mechanical basis for ubiquitous fundamental concepts.

## II. CONSTRUCTION OF INTRINSIC ORBITALS

Assume that we have computed a molecular SCF wave function  $|\Phi\rangle$ .  $|\Phi\rangle$  is defined by its occupied MOs  $|i\rangle = \sum_{\mu} |\mu\rangle C_i^{\mu}$ , where  $\mu \in B_1$  are basis functions from a large basis set  $B_1$ . The key problem in interpreting wave functions is that the basis functions  $|\mu\rangle$  cannot be clearly associated with any atom; each function will contribute most where it is most needed, and due to  $B_1$ 's high variational freedom, this often is not on the atom it is placed on. On the other hand, if one were to expand the MOs over a minimal basis  $B_2$  of free-atom AOs (i.e., a basis consisting of AOs calculated with sufficient radial freedom, but e.g.,

<sup>a)</sup>Electronic mail: knizia@theochem.uni-stuttgart.de

with only AOs 1s,2s,2px-2pz for each C atom), the wave function would be easy to interpret. But it would be inaccurate, and might be even qualitatively incorrect, because free-atom AOs contain no polarization due to the molecular environment. We thus propose to first calculate an accurate wave function  $|\Phi\rangle$ , and then to form a set of polarized AOs  $|\rho\rangle \notin B_2$  which can exactly express  $|\Phi\rangle$ 's occupied MOs  $|i\rangle$ .

For this, we first split the free-atom AOs  $|\tilde{\rho}\rangle \in B_2$  into contributions corresponding to a depolarized occupied space  $\tilde{O} = \sum_i |\tilde{i}\rangle \langle \tilde{i}|$  and its complement  $1 - \tilde{O}$ . Let

$$P_{12} = \sum_{\mu\nu \in B_1} |\mu\rangle S^{\mu\nu} \langle \nu| \quad P_{21} = \sum_{\rho\sigma \in B_2} |\rho\rangle S^{\rho\sigma} \langle \sigma|$$

denote the projectors onto the bases  $B_1$  and  $B_2$ , respectively, where  $S^{\mu\nu}/S^{\rho\sigma}$  are inverse overlap matrices in  $B_1/B_2$ . [Note that concerning projections from the minimal basis  $B_2$  to the large basis  $B_1$ ,  $P_{12}$  is effectively an identity operator]. Then the depolarized MOs

$$\{|\tilde{i}\rangle\} = \text{orth}\{P_{12}P_{21}|i\rangle\} \quad (1)$$

are obtained by projecting the accurate MOs  $|i\rangle$  from the main basis  $B_1$  onto the minimal basis  $B_2$  (which cannot express polarization) and back. As a consequence, the  $|\tilde{i}\rangle$  lie completely within the space spanned by  $\{P_{12}|\tilde{\rho}\rangle, |\tilde{\rho}\rangle \in B_2\}$  and thus the free-atom AOs  $P_{12}|\tilde{\rho}\rangle$  can be exactly split into one subspace corresponding to the occupied orbitals ( $\text{span}\{\tilde{O}P_{12}|\tilde{\rho}\rangle\}$ ) and a second subspace corresponding to the virtual valence orbitals ( $\text{span}\{(1 - \tilde{O})P_{12}|\tilde{\rho}\rangle\}$ ). We can then get the polarized AOs  $|\rho\rangle$  from the free-atom AOs  $|\tilde{\rho}\rangle$  by simply projecting their contributions in  $\tilde{O}$  and  $1 - \tilde{O}$  onto their polarized counterparts  $O = \sum_i |i\rangle \langle i|$  and  $1 - O$ :

$$|\rho\rangle = \left(O\tilde{O} + (1 - O)(1 - \tilde{O})\right)P_{12}|\tilde{\rho}\rangle. \quad (2)$$

Thus, to construct the polarized AOs, it is sufficient to load a tabulated free-atom basis, calculate its overlap with the main basis and within itself, and perform the numerically trivial projection (2). Contrary to the related approach of Ref. 16, no functional optimization or reference to virtual orbitals is required. In this article we will also symmetrically orthogonalize the vectors obtained by (2), to arrive at an orthonormal minimal basis which divides the one-particle space into atomic contributions; the latter will be referred to as intrinsic atomic orbitals (IAOs).

While the construction makes reference to free-atom AOs through basis  $B_2$ , it must be stressed that these are *not* empirical quantities. Free-atom orbitals can be *calculated* with any high-level quantum chemistry program. However, in practice this is not even required because they are already tabulated as part of several standard basis sets; here we take the AO functions of cc-pVTZ, which are spherically averaged ground-state Hartree-Fock orbitals. (Further technical comments on the IAO construction and the choice and nature of the free-atom orbitals are provided in the appendices B and C).

Since IAOs are directly associated with atoms, they can be used to define atomic properties like partial charges. Let us denote the closed-shell SCF density matrix as  $\gamma = 2 \sum_i |i\rangle \langle i|$ ,

Method/Basis	CH <sub>4</sub>		HCN		
	C	H	H	C	N
IAO/def2-SVP <sup>a</sup>	-0.49	+0.12	+0.21	-0.01	-0.20
IAO/def2-TZVPP <sup>a</sup>	-0.52	+0.13	+0.22	-0.01	-0.21
IAO/def2-QZVPP <sup>a</sup>	-0.52	+0.13	+0.22	-0.01	-0.21
IAO/cc-pVTZ <sup>a</sup>	-0.52	+0.13	+0.22	-0.01	-0.21
IAO/aug-cc-pVTZ <sup>a</sup>	-0.52	+0.13	+0.22	-0.01	-0.21
Bader/TZ2P <sup>b</sup>	+0.05	-0.01	+0.19	+0.82	-1.01
Mulliken/DZ <sup>b</sup>	-0.98	+0.25	+0.34	+0.03	-0.38
Mulliken/DZP <sup>b</sup>	+0.05	-0.01	+0.16	+0.28	-0.44
Mulliken/TZ2P <sup>b</sup>	+0.61	-0.15	-0.02	+0.27	-0.25
IAO/cc-pVTZ <sup>c</sup>	-0.49	+0.12	+0.22	-0.03	-0.19
IAO/cc-pVTZ <sup>d</sup>	-0.49	+0.12	+0.21	-0.03	-0.18

TABLE I. (a) Hartree-Fock partial charges via Eq. (3). (b) Kohn-Sham/BP86 partial charges<sup>6</sup> via the Bader and Mulliken methods. (c) As *a*, but with Huzinaga MINI<sup>32</sup> for basis  $B_2$  instead of MINAO (appendix B). (d) As *c*, but with  $B_2$  functions taken from ANO-RCC.<sup>33,34</sup>

where  $i$  are the occupied MOs. We can then define

$$q_A = Z_A - \sum_{\rho \in A} \langle \rho | \gamma | \rho \rangle \quad (3)$$

as the partial charge on atom  $A$ , where  $Z_A$  is the atom's nuclear charge and  $\rho$  its IAOs. Tab. I shows that the partial charges obtained are insensitive to the basis set, follow trends in electronegativities, and some defects seen in other methods (e.g., Bader's description of the CN bond in HCN as ionic) are absent. Partial charges will be further analyzed below.

IAOs provide access to atomic properties, but it is often desirable to get a clearer picture of molecular bonding. We now show that by combining the IAOs with orbital localization in the spirit of Pipek-Mezey (PM),<sup>35</sup> one can explicitly construct bond orbitals (IBOs), without any empirical input, and *entirely within the framework of MO theory*. A Slater determinant  $|\Phi\rangle$  is invariant to unitary rotations  $|i'\rangle = \sum_i |i\rangle U_{ii'}$  amongst its occupied MOs  $|i\rangle$ . We can thus define the IBOs by maximizing

$$L = \sum_A^{\text{atoms}} \sum_{i'}^{\text{occ}} [n_A(i')]^4 \quad (4)$$

with respect to  $U_{ii'}$ . Here  $n_A(i') = 2 \sum_{\rho \in A} \langle i' | \rho \rangle \langle \rho | i' \rangle$  is the number of  $|i'\rangle$ 's electrons located on the IAOs  $\rho$  of atom  $A$ . This construction effectively minimizes the number of atoms an orbital is centered on. Technical notes (e.g., on the choice of exponent 4) and an explicit algorithm to perform the optimization are given in appendix D.

Fig. 1 shows IBOs computed for the acrylic acid molecule. Here 16 of 19 occupied MOs can be expressed to >99% by charge with IAOs on one or two centers, respectively. The three other MOs are part of a  $\pi$ -system: The oxygen  $p$  lone pairs (which have about 7% bonding character), and the C=C  $\pi$ -bond (which has about 3% contributions on the third C atom, and about 1% on the doubly-bonded O). In total, we see a direct correspondence of the obtained IBOs with the classical bonding

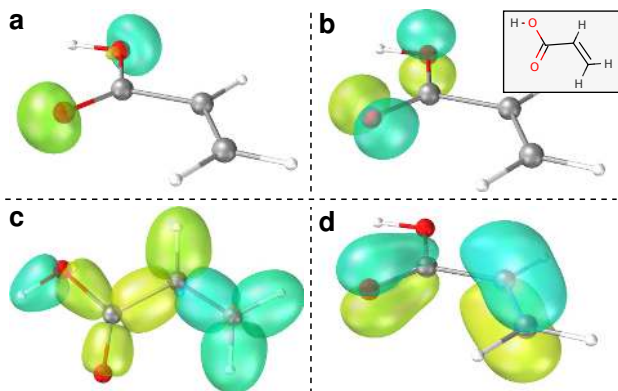


FIG. 1. IBOs of acrylic acid: **a** and **b**: two  $sp$ -hybrid and two  $p$  lone pairs (1-center orbitals). **c** and **d**: eight  $\sigma$ -bonds and two  $\pi$ -bonds (2-center orbitals). Core orbitals are not shown. There are a total of 19 IBOs, expanded over 29 IAOs (5 for each C,O and 1 for each H).

picture:  $\sigma$ -bonds,  $\pi$ -bonds, and lone pairs are exactly where expected, and the  $\pi$ -system is slightly delocalized. We stress again that these 19 IBOs are *exactly equivalent* to the occupied MOs they are generated from: Their anti-symmetrized product is the SCF wave function, and this is a valid representation of its electronic structure. Note that the IBO construction makes no reference to the molecule's Lewis structure whatsoever; the classical bonding picture thus arises as an emergent phenomenon rooted in the molecular electronic structure itself, even if not imposed.

The major improvement of IBOs over PM orbitals is that they are based on IAO charges instead of the erratic Mulliken charges (cf.  $\text{CH}_4$  in Tab. I). As a result, IBOs are always well-defined, while PM orbitals are unsuitable for interpretation because they are unphysically tied to the basis set<sup>19</sup> (they do not even *have* a basis set limit). IBOs lift this weakness while retaining and even improving on PM's computational attractiveness.

### III. CONSISTENCY WITH EMPIRICAL FACTS

Our hypothesis is that IAOs offer a chemically sound definition of atoms in a molecule. But since these are not physically observable, this claim can only be backed by consistency with empirical laws and facts.<sup>36</sup> We thus now investigate whether partial charges derived from IAOs follow expected trends based on electronegativities, C 1s core level shifts, and linear free-energy relationships for resonance substituent effects (Taft's  $\sigma_R$ ). We then go on to see how IBOs reflect bonding in some non-trivial molecules (Section III B), and how coordination complex oxidation states manifest themselves in terms of IAOs (Section III C).

#### A. Partial charges: electronegativities, core level shifts, and substituent effects

We saw in Tab. I that, unlike Mulliken charges, IAO charges are insensitive to the employed basis set, and unlike Bader charges, IAO do not erroneously describe the CN bond in HCN

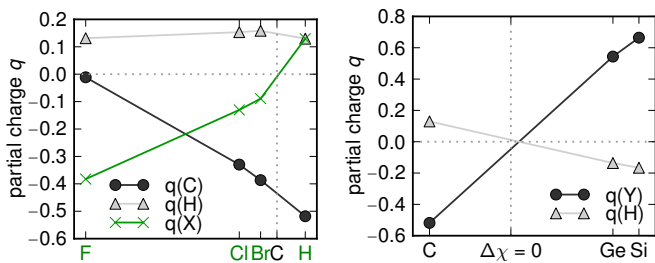


FIG. 2. (a): IAO partial charges in  $\text{CH}_3\text{X}$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{H}$ ) plotted against  $\chi(\text{C}) - \chi(\text{X})$ .  $\Delta\chi = 0$  is marked by a dotted line. (b): Partial charges in  $\text{YH}_4$  ( $\text{Y}=\text{C}, \text{Si}, \text{Ge}$ ), the x-axis is  $\chi(\text{H}) - \chi(\text{Y})$ .

as ionic. We now follow Ref. 6 and investigate IAO charges in relation to electronegativity  $\chi$  differences. We start with the series  $\text{CH}_3\text{X}$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{H}$ ). Due to the (Allen<sup>37</sup>) electronegativities (F: 4.193, Cl: 2.869, Br: 2.685, C: 2.544, H: 2.300), we expect halogens to have a negative charge, getting smaller in the series, and hydrogen to have a positive charge. As shown in Fig. 2a, this is what we find. In Fig. 2b, we show the series  $\text{YH}_4$  ( $\text{Y}=\text{C}, \text{Si}, \text{Ge}$ ). We find charges in close correspondence with  $\chi$  (C: 2.544, Si: 1.916, Ge: 1.994), and the inversion that  $\chi(\text{Si}) < \chi(\text{Ge})$  is properly reflected. If we extrapolate the curves in **a** and **b** to  $\Delta\chi = 0$ , we find in both cases that  $q(\text{X}) \approx 0$  and  $q(\text{Y}) \approx 0$ , respectively. That is, if there is no difference in electronegativity, IAO partial charges predict no bond polarization. This consistency with empirical electronegativities is further reflected in the almost linear shapes of the curves. In the series  $\text{CH}_{4-n}\text{F}_n$  ( $n=0\dots 4$ ), we find C partial charges of -0.52, -0.01, 0.44, 0.85, 1.23. The charge increase by  $\approx 0.5e^-$  per fluorine atom agrees with the understanding of CF bonds in organic chemistry<sup>38</sup> and earlier calculations,<sup>39</sup> contrary to the much smaller charges found in Hirshfeld and Voronoi deformation density (VDD) analysis.<sup>6</sup>

A different test of IAO charges can be performed by comparing to experimental data which are known to be highly correlated with charge states of specific atoms  $A$ . A prime example for this is the C 1s core-level ionization energy shift due to the molecular environment. This shift can be estimated<sup>40</sup> as

$$\Delta\text{IP}_{\text{C } 1s} = k \cdot q_A + \sum_{B \neq A} \frac{q_B}{\|\mathbf{R}_A - \mathbf{R}_B\|} + \Delta E_{\text{relax}}, \quad (5)$$

where the second term is an estimate for the electrostatic potential of the other atoms  $B$ , the last term is a contribution due to core orbital relaxation, and  $k$  is a (hybridization dependent) proportionality constant. This model has been employed to calibrate widely used electronegativity equilibration models,<sup>41</sup> and has been found to be perfectly correlated with both experimental<sup>42</sup> and theoretical<sup>43</sup> mean dipole derivatives (which for the molecules studied here can be interpreted as charges,<sup>43</sup> but not generally<sup>44</sup>). In Fig. 3 we show the results obtained with IAO partial charges based on Hartree-Fock wave functions for all the  $sp^3$  hybridized molecules as studied in Ref. 42. IAO charges were used both for the abscissa and  $V$ , the second term in Eq. (5).  $\Delta E_{\text{relax}}$  was calculated at Hartree-Fock level by a  $\Delta\text{SCF}$  procedure. We here obtain a linear regression coefficient of  $r = 0.997$ , or  $r = 0.9995$  if the two outliers

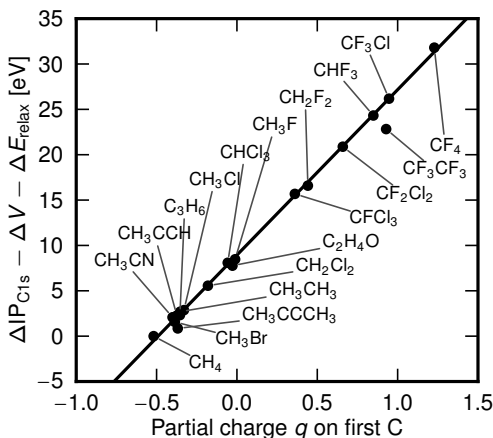


FIG. 3. Partial charge on  $sp^3$  carbon versus experimental C 1s ionization energy shift corrected for core relaxation effects and electrostatic potentials of the other cores (Eq. (5)), relative to methane.

$CF_3CF_3$  and  $CH_3C\equiv CH_3$  are excluded. This is the same level of correlation as obtained with dipole moment derivatives,<sup>42</sup> and much higher than for CHELPS, Bader, or Mulliken charges.<sup>43</sup>

One advantage of Hilbert-space based partial charges over real-space partial charges is that they can be split not only into atomic contributions, but also orbital contributions. Recently Ozimiński and Dobrowolski<sup>45</sup> used this freedom to introduce a set of descriptors for the electronic  $\sigma$ - and  $\pi$ -substituent effects, called sEDA and pEDA, and showed that they are both internally consistent and highly correlated with empirical substituent effect parameters like Taft's  $\sigma_R$ . Concretely, for a substituted benzene  $R-C_6H_5$ , the pEDA parameter is defined as the number of  $p_z$  electrons on the six carbon atoms of the benzene ring, relative to the unsubstituted benzene:

$$pEDA = \sum_{i=1}^6 q_{C_i 2p_z}(C_6H_6) - \sum_{i=1}^6 q_{C_i 2p_z}(R-C_6H_5), \quad (6)$$

where Ozimiński defined this quantity based on NAO population analysis<sup>4</sup> with a specified type of wave function and basis set. In order to demonstrate the potential of IAO charges in the interpretation of chemical reactivity, in Fig. 4 we show that the same kind of correlation with empirical substituent constants is also obtained when calculating pEDA from IAO charges ( $r = 0.966$ ) instead of NAO charges ( $r = 0.943$ <sup>45</sup>). While Fig. 4 still shows considerable scatter, it must be stressed that linear free energy relationships are not strict laws; rather, they are a form of condensing highly complex interactions into an effective, easy to handle, descriptor, in order to facilitate predicting reactivity trends. Consequently, neither the accuracy of the relationships themselves is much better than the correlations obtained here (see, e.g., Fig. 1 in Ref. 46), nor is the internal consistency of different ways of evaluating its substituent constants (e.g.,  $r=0.982$  for  $\sigma_R$  from protonation equilibria versus  $\sigma_R$  from F-NMR shifts of para- and meta-substituted fluorobenzenes, see Sec. 1.D of Ref. 47). This does not diminish their usefulness. Calculating such EDA descriptors as obtained here is computationally trivial, which makes them an attractive

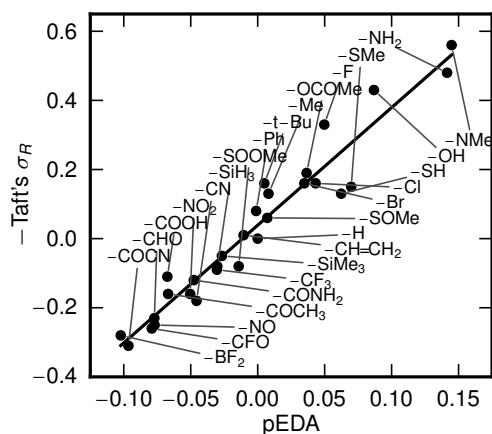


FIG. 4. Correlation of pEDA based on IAO/Hartree-Fock charges versus  $\sigma_R$  substituent constants taken from Tab. IV of Ref.<sup>47</sup>.

quantity in the study of unusual substituents not be contained in common tables, or for testing if the substituents behave differently for different hosts than benzene. Indeed, a similar idea to Ozimiński's has been considered previously,<sup>48</sup> but was much less practical due to being based on carefully crafted real-space integration because Hilbert space approaches were considered unreliable.<sup>48</sup>

## B. Non-trivial bonding in terms of bond orbitals

A deeper insight into the nature of a molecule's bonding can be obtained by calculating its bond orbitals. As previously noted, IBOs are an *exact* representation of SCF wave functions, and we have seen in Fig. 1 that they normally reflect the classical bonding concepts one to one. However, in many molecules the Lewis structure does not tell the entire story. Therefore we now probe how IBOs reflect bonding in some well known, but in different senses non-trivial molecules.

**Benzene:** A straight application of the IBO construction produces the orbitals **a–e** shown in Fig. 5. As expected, both the CC and the CH  $\sigma$ -bonds of the system are completely localized, and can be expressed to >99% with IAOs on only the two bonded centers. As a prototypical delocalized system, this does, however, not hold for the  $\pi$  system. Two aspects are important: (i) The three  $\pi$  orbitals cannot be expressed with IAOs on less than four centers each (in **c–e** having the weights 1.000, 0.444 (ortho), and 0.111 (para)), and (ii) there are two different maximal localizations of the functional Eq. (4), orbitals **c–e** and orbitals **c–e** rotated by  $60^\circ$  in real space. If in Eq. (4) we had chosen to maximize  $\sum n_A(i)^2$  instead of  $\sum n_A(i)^4$ , there would even be a continuum of maximal localizations, also including orbitals **f–h** (which look closer to classical  $\pi$ -bonds), and everything in between. Both kinds of local  $\pi$ -orbitals have been discussed by England and coworkers.<sup>49</sup> In this case the classical resonance structure reflects the nature of the bonding well.

**Cyclopropane:** According to its Lewis structure, cyclopropane is a simple alkane. However, one could expect that the massive ring strain must have some impact on the bond-

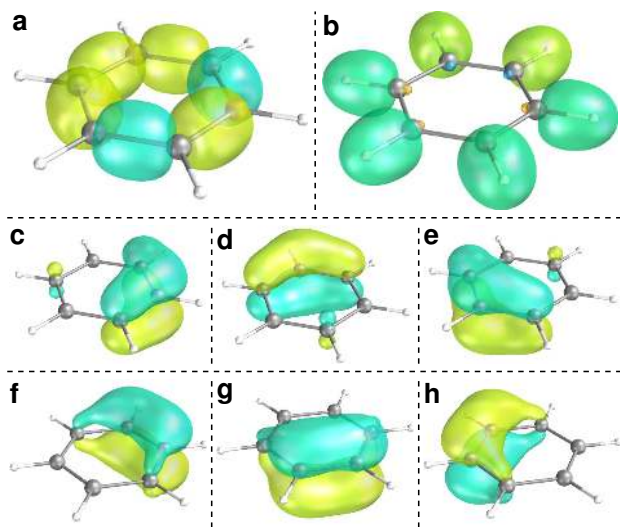


FIG. 5. IBOs of benzene: **a** six CC  $\sigma$ -bonds, and **b** six CH  $\sigma$ -bonds, both localized, and **c-e** one of the two equivalent IBO sets representing the delocalized  $\pi$ -system of three orbitals. **f-h**: See text

ing. Nevertheless, if we calculate the IBOs of this molecule (Fig. 6, **a** and **b**), we find six CH single bonds and three CC single bonds, all perfectly localized (to >99%) on the two bonded centers, with no delocalization whatsoever. However, a closer look reveals that while the carbon part of the CH bond orbitals has about 28%  $s$  character and 72%  $p$  character, (close to the ideal  $sp^3$  hybrid values of  $1/4s + 3/4p$ ), the CC bonds only have 18%  $s$  character and 82%  $p$  character. So although they are localized single bonds, they must be considered an intermediate between a regular  $sp^3$ -hybrid  $\sigma$ -bond and a  $\pi$ -bond. This explains the well-known similarity in reactivity to alkenes.<sup>50</sup> The bent bonds have previously been discussed in Refs. 50–52 and references therein.

Diborane:  $B_2H_6$  has been a serious challenge to the classical bonding picture, with even scientists like Pauling championing an ethane-like structure until proven wrong irrefutably.<sup>53</sup> Its bridged structure was popularized in 1943,<sup>54</sup> and spawned investigations culminating in Lipscomb’s 1976 Nobel price for his “studies on the structure of boranes illuminating problems of chemical bonding”. One could think that this molecule presents a challenge to a IBO bonding analysis. However, IBOs are just the most local exact description of a first-principles wave function, and their construction does not make *any* reference to *any* perceived nature of the bonding. Consequently, for IBO analysis diborane is not different than other molecules, and it uncovers diborane’s two two-electron three-center bonds (Fig. 6d) just as its six standard  $\sigma$ -bonds (**c**), without any problems.

Sulfur trioxide:  $SO_3$  is one of the simplest “hypervalent” molecules, apparently violating the octet rule. While a direct  $d$ -orbital bonding has been ruled out,<sup>55–57</sup> hypervalent species remain a debated topic to this day.<sup>58–60</sup> An IBO analysis of  $SO_3$  finds two oxygen lone pairs, one  $\sigma$ - and one  $\pi$ -bond (Fig. 6e) per oxygen. Formally this calls for describing the SO bonds as double bonds. However, the  $\pi$ -bonds have only a small bonding component (83% on oxygen, 15% on sulfur), so it is a matter

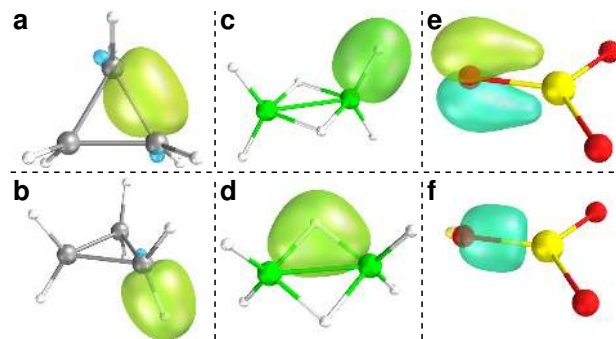
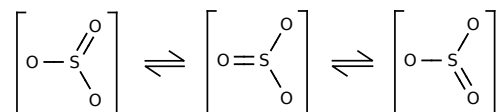


FIG. 6. IBO of some molecules with non-Lewis bonding: **a** CC banana bond and **b** CH  $\sigma$ -bond of cyclopropane, **c** BH  $\sigma$ -bond and **d** BHB 2e3c bond of diborane, **e** SO  $\pi$ -bond and **f** SO  $\sigma$ -bond of sulfur trioxide.

of taste whether they should be called true  $\pi$ -bonds or not. But in any case, they are highly localized (98% on two centers) and clearly not resonating, so the resonance structure



—commonly found in textbooks—is at best misleading.<sup>61</sup> While also the present picture results in a bond order of about 1.3, here the bonds are static and near uncorrelated with each other, unlike in a truly delocalized system like benzene. The simple bonding picture consisting of polar two-center bonds has also been obtained by Cunningham and coworkers in a valence bond analysis.<sup>57</sup>

Bifluoride anion: We see a similar discrepancy to textbook knowledge in the description of  $FHF^-$ . This molecule, still actively researched,<sup>62–65</sup> is alternatively cited as the strongest known hydrogen bond,<sup>66</sup> or as an example for a 4-electron 3-center (4e3c) bond (since an influential paper by Pimentel<sup>67</sup>). However, IBO analysis reveals that it can be perfectly described by six F lone pairs and two HF single bonds, all completely localized. Since the bonds are very polar, there is again no violation of the octet rule: In fact, the H orbital has a population of only 0.6 electrons total (out of the up to two electrons it theoretically could harbor), and the nature of bonding in this molecule is not very different than in HF. That such “4e3c” bonds are often just two polar 2e2c bonds was previously noted by Ponc and coworkers,<sup>68</sup> but this view is not yet generally accepted.<sup>69,70</sup>

### C. Oxidation states of transition metal complexes

The occupancies of individual orbitals, as provided by IAOs, can also be employed to define oxidation states of coordinated transition metals (TMs). This may seem surprising because oxidation states are known to be a vague concept<sup>71</sup> and it is well established that no simple relationship to partial charges exists.<sup>72–74</sup> However, Sit and coworkers recently introduced an interesting perturbative argument which may elucidate the situation, at least for weakly bonded TMs:<sup>75</sup>

For a free, isolated TM ion the oxidation state is unambigu-

ously defined (as its ionic charge), and the ion’s d spin-orbitals are either fully occupied ( $n = 1$ ) or fully unoccupied ( $n = 0$ ). Sit and coworkers<sup>75</sup> then argue that only the fully occupied d spin-orbitals are relevant for the TMs oxidation state, and that this remains to be the case in a coordinated environment: While some overlap of these d orbitals with ligand orbitals may occur, it is normally weak, and thus the bonding and anti-bonding orbitals formed between the TM and the ligand are occupied equally. Consequently, a d-orbital with occupation  $n = 1.0$  in the free ion *remains* at  $n \approx 1.0$  in the complex, while all other d-orbital occupations result from ligand donation<sup>74</sup> to (and bonding with) previously empty d-orbitals. We can thus find the free ion corresponding to a coordinated TM, and therefore its oxidation state, by simply counting the number of d spin orbitals with  $n \approx 1.0$ . This analysis contains two assumptions: (i) the ligands should not be able to withdraw d electrons from the TM instead of bonding to them and (ii) the occupation numbers of the d electrons can be identified.

To address (ii), Sit and coworkers<sup>75</sup> employed a projection onto unpolarized free-ion d AOs, which were additionally not orthogonalized to other orbitals. IAOs might provide a better basis for obtaining such occupations because they take environment polarization into account and they partition all electrons of the molecule into atomic contributions, without double-counting or missing electrons. In the IAO basis one can thus simply diagonalize the TM’s  $5 \times 5$  d-orbital block of the spin-orbital density matrix in order to obtain the sought after occupation numbers (for alpha and beta spin separately), or, alternatively, see how many IBOs fully localize to the TM center. We here applied the diagonalization method to the TM clusters studied in Ref. 76. These are the octahedral  $ML_6$  clusters with  $M=V(II), Mn(II), Mn(III), Fe(II), Fe(III), Ni(II),$  and  $Zn(II)$  combined with ligands  $L=Cl^-, H_2O, CN^-,$  and  $CO$ . For  $Cl^-$  (a weak-field ligand) only high-spin complexes are considered, for  $CN^-$  and  $CO$  (both strong-field ligands) only low-spin complexes, and for  $H_2O$  both high-spin and low-spin calculations are performed. The results are reported in Tab. II. In all complexes we see a clear distinction between the fully and non-fully occupied d orbitals (in most cases occupations *very* near to 1.0 are obtained), and the number of such  $n \approx 1$  orbitals is perfectly consistent with the formal oxidation state as predicted by Sit. The largest deviations are seen for the  $CO$  ligand; this may be related to  $CO$ ’s strong  $\pi$ -acceptor properties, which could cause a violation of condition (i) mentioned above. But in any case, the assignment of oxidation states appears to be straightforward and unambiguous for the complexes considered here. The combination of Sit’s analysis with the here proposed IAO technique may thus offer a useful method for classifying oxidation states also in less transparent complexes.

#### IV. CONCLUSIONS AND OUTLOOK

The proposed IAOs offers a simple and transparent way to relate chemical intuition to quantum chemistry. In particular, the fact that most simple bonds can be expressed to >99% with IAOs on only two atoms strongly indicates that IAOs can be interpreted as *chemical* valence orbitals in molecules. That prop-

erties of individual such orbitals can then be directly calculated, as shown in Fig. 4, may turn out to be a decisive factor in future research on chemical reactivity. Similarly, IAOs may greatly simplify the construction of realistic tight-binding model Hamiltonians and their use in elucidating complex correlated electronic structure phenomena.<sup>77,78</sup>

The proposed IBOs can help to uncover the nature of bonding in molecules—due to their unbiased nature also in unusual cases. However, the IBO construction’s simplicity, ease of implementation, and high runtime efficiency make it an excellent choice also where localized orbitals are used for purely technical reasons (e.g., in local electron correlation methods).

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#### Appendix A: Availability of the IAO and IBO techniques

The techniques have been implemented into the development version of Molpro and will become available with its next public release. Additionally, a complete example implementation of the IAO and IBO constructions will be made available at <http://www.theochem.uni-stuttgart.de/~knizia/> (Python source).

#### Appendix B: Notes on the free-atom atomic orbitals

Effectively, the only empirical input to the entire IAO/IBO construction is the choice of the atomic state from which the free-atom AOs are calculated. For the data presented in the paper (except for the TMs of Tab. II), we used spherically averaged ground-state Hartree-Fock orbitals; these were simply taken from the contracted functions of the cc-pVTZ basis sets<sup>79–81</sup> (the set is called “MINAO” in Molpro). These AOs are sufficiently accurate for the present purpose, but in principle one could re-calculate them with a larger freedom in the radial space of the occupied AOs. For pragmatic reasons we used minimal basis subsets of cc-pVTZ<sup>82</sup> also for the TMs, but in this case cc-pVTZ is derived from averages over important states instead of ground states only.<sup>82</sup> The impact of this choice should be checked at a later point in time.

While one could argue for using AOs from a promoted state<sup>83</sup> or valence state,<sup>84</sup> we here prefer the ground state as reference. This choice is made mainly because it is both observable and unique, and because this way the presented theory obtains the property of generalized observability as defined by Cioslowski and Surján.<sup>85</sup> Initial numerical experiments indicated that in most cases neither choice (ground state, valence state, or promoted state) makes a large difference to results obtained via IAO analysis, and that the presented method is less sensitive to the choice of the free atom state than Hirshfeld or VDD methods.<sup>6</sup> However, some further research on how to best deal with cases in which the atomic character in the molecule differs considerably from the ground state may be warranted.

Complex	$S_Z$	d orbital occupation					Complex	$S_Z$	d orbital occupation				
<i>Fe(II); expected 6 singly occupied d orbitals</i>						<i>Mn(II); expected 5 singly occupied d orbitals</i>							
[FeCl <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	[MnCl <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>
(spin 4)	B	<b>1.00</b>	0.06	0.06	0.01	0.01	(spin 5)	B	0.05	0.05	0.01	0.01	0.01
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.06	0.06	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.05	0.05
(spin 0)	B	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.06	0.06	(spin 1)	B	<b>1.00</b>	<b>1.00</b>	0.05	0.05	0.01
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>
(spin 4)	B	<b>1.00</b>	0.05	0.05	0.01	0.01	(spin 5)	B	0.04	0.04	0.01	0.01	0.00
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	A	<b>0.97</b>	<b>0.97</b>	<b>0.97</b>	0.21	0.21	[Mn(CN) <sub>6</sub> ] <sup>4-</sup>	A	<b>0.98</b>	<b>0.96</b>	<b>0.96</b>	0.20	0.19
(spin 0)	B	<b>0.97</b>	<b>0.97</b>	<b>0.97</b>	0.21	0.21	(spin 1)	B	<b>0.96</b>	<b>0.96</b>	0.20	0.19	0.01
[Fe(CO) <sub>6</sub> ] <sup>2+</sup>	A	<b>0.93</b>	<b>0.93</b>	<b>0.93</b>	0.31	0.31	[Mn(CO) <sub>6</sub> ] <sup>2+</sup>	A	<b>0.94</b>	<b>0.90</b>	<b>0.90</b>	0.32	0.30
(spin 0)	B	<b>0.93</b>	<b>0.93</b>	<b>0.93</b>	0.31	0.31	(spin 1)	B	<b>0.90</b>	<b>0.90</b>	0.32	0.30	0.01
<i>Fe(III); expected 5 singly occupied d orbitals</i>						<i>Mn(III); expected 4 singly occupied d orbitals</i>							
[FeCl <sub>6</sub> ] <sup>3-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	[MnCl <sub>6</sub> ] <sup>3-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.20
(spin 5)	B	0.15	0.15	0.03	0.03	0.03	(spin 4)	B	0.20	0.11	0.02	0.02	0.02
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.13	0.11	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.11	0.09
(spin 1)	B	<b>1.00</b>	<b>1.00</b>	0.13	0.11	0.03	(spin 2)	B	<b>1.00</b>	0.11	0.09	0.02	0.01
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.11
(spin 5)	B	0.09	0.09	0.03	0.02	0.01	(spin 4)	B	0.11	0.08	0.02	0.01	0.00
[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	A	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	0.33	0.28	[Mn(CN) <sub>6</sub> ] <sup>3-</sup>	A	<b>0.99</b>	<b>0.99</b>	<b>0.98</b>	0.29	0.26
(spin 1)	B	<b>0.99</b>	<b>0.99</b>	0.33	0.28	0.01	(spin 2)	B	<b>0.98</b>	0.29	0.26	0.01	0.01
[Fe(CO) <sub>6</sub> ] <sup>3+</sup>	A	<b>0.98</b>	<b>0.96</b>	<b>0.96</b>	0.41	0.37	[Mn(CO) <sub>6</sub> ] <sup>3+</sup>	A	<b>0.97</b>	<b>0.97</b>	<b>0.95</b>	0.38	0.36
(spin 1)	B	<b>0.96</b>	<b>0.96</b>	0.41	0.37	0.02	(spin 2)	B	<b>0.95</b>	0.38	0.36	0.02	0.02
<i>Ni(II); expected 8 singly occupied d orbitals</i>						<i>Zn(II); expected 10 singly occupied d orbitals</i>							
[NiCl <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	[ZnCl <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>
(spin 2)	B	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.05	0.05	(spin 0)	B	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>
[Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	[Zn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>
(spin 2)	B	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.05	0.05	(spin 0)	B	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>
[Ni(CN) <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	[Zn(CN) <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>0.88</b>
(spin 2)	B	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	0.20	0.20	(spin 0)	B	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>0.88</b>
[Ni(CO) <sub>6</sub> ] <sup>2+</sup>	A	<b>0.99</b>	<b>0.99</b>	<b>0.97</b>	<b>0.97</b>	<b>0.97</b>	[Zn(CO) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>
(spin 2)	B	<b>0.97</b>	<b>0.97</b>	<b>0.97</b>	0.28	0.28	(spin 0)	B	<b>1.00</b>	<b>1.00</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>
<i>V(II); expected 3 singly occupied d orbitals</i>													
[VCl <sub>6</sub> ] <sup>4-</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.12	0.12							
(spin 3)	B	0.12	0.12	0.03	0.03	0.03							
[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	A	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	0.07	0.07							
(spin 3)	B	0.07	0.07	0.02	0.01	0.01							
[V(CN) <sub>6</sub> ] <sup>4-</sup>	A	<b>0.94</b>	<b>0.94</b>	<b>0.94</b>	0.19	0.19							
(spin 3)	B	0.19	0.19	0.01	0.01	0.01							
[V(CO) <sub>6</sub> ] <sup>2+</sup>	A	<b>0.90</b>	<b>0.90</b>	<b>0.90</b>	0.25	0.25							
(spin 3)	B	0.25	0.25	0.01	0.01	0.01							

TABLE II. IAO d-orbital occupations of octahedral ML<sub>6</sub> coordination complexes. Shown are the eigenvalues of the 5 × 5 block of the alpha-spin (A) and beta-spin (B) density matrices. Sub-captions note the number of fully occupied d orbitals expected for a TM of the given oxidation state<sup>75</sup>. Orbital occupations we regard as near 1.0 are highlighted.

### Appendix C: Technical notes on the IAO construction

The explicit matrix form of the projector  $P_{12}$  for contra-variant indices (like basis orbital coefficients) is

$$\mathbf{P}_{12} = \mathbf{S}_1^{-1} \mathbf{S}_{12},$$

where  $[\mathbf{S}_1]_{\mu\nu} = \langle \mu | \nu \rangle$  ( $\mu, \nu \in B_1$ ) is the overlap matrix within basis  $B_1$  and  $[\mathbf{S}_{12}]_{\mu\sigma} = \langle \mu | \sigma \rangle$  ( $\mu \in B_1, \sigma \in B_2$ ) the overlap matrix between  $B_1$  and  $B_2$ . An explicit proof of this form can be found in Eq. (3) of Ref. 86 (note that a projector to a space  $Y$  is defined by mapping any point  $x$  to its closest point  $y \in \text{span}(Y)$ , i.e.  $Px = \text{argmin}_{y \in Y} \|x - y\|_2$ ), but it also can be easily seen by considering the index form  $C_i^\mu = \sum_{\nu\sigma} S^{\mu\nu} S_{\nu\sigma} C_i^\sigma$ , where the inverse overlap matrix  $S^{\mu\nu} \equiv [\mathbf{S}_1^{-1}]_{\mu\nu}$  within  $B_1$  is used to convert one index ( $\nu$ ) back from covariant to contra-variant. (See Ref. 87 for an in-depth discussion of the non-orthogonal tensor formalism in the context of quantum chemistry). The projector  $P_{21}$  is obtained by exchanging all indices 1,2. Note that if the main basis  $B_1$  is sufficiently large (as is normally the case), the vectors from  $B_2$  can be expressed almost exactly in  $B_1$ ; thus,  $P_{12}$  is very close to the identity operator and only included for completeness.

Let  $\mathbf{C}$  denote the orbital coefficient matrix of  $|i\rangle = \sum_\mu |\mu\rangle C_i^\mu$ . Then the matrix form of Eqs. (1),(2) become:

$$\tilde{\mathbf{C}} = \text{orth}(\mathbf{S}_1^{-1} \mathbf{S}_{12} \mathbf{S}_2^{-1} \mathbf{S}_{21} \mathbf{C}),$$

$$\mathbf{A} = \mathbf{C} \mathbf{C}^T \mathbf{S}_1 \tilde{\mathbf{C}} \tilde{\mathbf{C}}^T \mathbf{S}_1 \mathbf{P}_{12} + (1 - \mathbf{C} \mathbf{C}^T \mathbf{S}_1)(1 - \tilde{\mathbf{C}} \tilde{\mathbf{C}}^T \mathbf{S}_1) \mathbf{P}_{12}.$$

The orthonormalization is defined as

$$\text{orth}(\mathbf{C}) = \mathbf{C}[\mathbf{C}^T \mathbf{S}_1 \mathbf{C}]^{-1/2},$$

where  $\mathbf{X}^{-1/2}$  denotes the matrix inverse square root (however, the procedure is invariant to the concrete type of orthogonalization used). The resulting  $[\mathbf{A}]_\rho^\mu$  is the coefficient matrix of the not-yet-orthogonal IAO  $|\rho\rangle = \sum_\mu |\mu\rangle A_\rho^\mu$  ( $\mu \in B_1, \rho \in B_2$ ). Here  $\rho$  should be considered as an index of the free-atom AO the perturbed AO  $|\rho\rangle$  corresponds to. The vectors  $\mathbf{A}$  are subsequently multiplied by  $[\mathbf{A}^T \mathbf{S}_1 \mathbf{A}]^{-1/2}$  from the right to arrive at a symmetrically orthogonalized set of IAO coefficients.

For applications where runtime performance or formula simplicity is of utmost importance (like in analytic gradients), the simpler formula  $\mathbf{A} \approx (\mathbf{S}_1^{-1} + \mathbf{C} \mathbf{C}^T - \tilde{\mathbf{C}} \tilde{\mathbf{C}}^T) \mathbf{S}_{12}$  may also be useful. This formula also leads to a set of AOs which spans the occupied space and gives very similar results in practice. However, it would be obtained if (2) were replaced by  $|\rho\rangle = (1 + O - \tilde{O}) |\tilde{\rho}\rangle = (O\tilde{O} + (1 + O)(1 - \tilde{O})) |\tilde{\rho}\rangle$  and thus can be seen to polarize the virtual space in the wrong direction.

We note that actual inverse overlap matrices should not be used, because this could lead to numerical problems if large and diffuse basis sets were used.<sup>88</sup> Rather,  $\mathbf{X} = \mathbf{S}^{-1} \mathbf{B}$  is a shorthand notation for “solve  $\mathbf{S} \mathbf{X} = \mathbf{B}$ ” using a Cholesky or spectral decomposition of  $\mathbf{S}$ . Alternatively, twice multiplying with  $\mathbf{S}^{-1/2}$  instead of once with  $\mathbf{S}^{-1}$  is also numerically stable.<sup>88</sup>

Let us now discuss why  $|\rho\rangle$  of Eq. (2) spans the occupied space of the MOs. Let  $\tilde{O} = \sum_i |\tilde{i}\rangle \langle \tilde{i}|$  and  $O = \sum_i |i\rangle \langle i|$  as before. Then  $1 = \tilde{O} + (1 - \tilde{O})$  is a resolution of the

identity in the space spanned by  $\{P_{12} |\rho\rangle, \rho \in B_2\}$ , and both  $\text{span}\{\tilde{O} P_{12} |\rho\rangle\}$  and  $\text{span}\{(1 - \tilde{O}) P_{12} |\rho\rangle\}$  are subspaces of certain integer dimension. If we now form  $\text{span}\{O \tilde{O} P_{12} |\rho\rangle\}$  (first term of Eq.(2)), then this space will span the occupied orbitals, provided that the obtained space has the same dimension as the number of occupied orbitals,  $n_{\text{occ}}$ . The reason for this is simply that *any* set of orbitals which retains  $n_{\text{occ}}$  independent directions after projection with  $O = \sum_i |i\rangle \langle i|$  will have this property. In the current case this is a very weak requirement, effectively saying that the molecular wavefunction can be described—to some degree—in terms of free-atom AOs. In practice it will always be given for valence states. Also, in the concrete form of Eq. (2), the occupied space projection  $O\tilde{O}$  is not affected by the second term  $(1 - O)(1 - \tilde{O})$ , which acts in the orthogonal subspace and can thus not interfere with the first term.

### Appendix D: Technical notes on the IBO construction

IBOs retain the attractive computational properties which made PM orbitals so successful, and even improve on them. Just as PM orbitals, IBOs can be obtained by successive  $2 \times 2$  rotations on the occupied MOs.<sup>35</sup> For IBOs this can be done directly in the orthogonal IAO basis; it is thus cheaper and better behaved than PM localization, which is done in the full, non-orthogonal basis and can be problematic for large or diffuse basis sets.<sup>19,89</sup> As for PM orbitals,<sup>90,91</sup> also for IBOs the analytic gradient with respect to geometric perturbations can be determined, enabling their use in geometry optimizations.

Concretely, we used the following algorithm for IBO localization: First, the SCF occupied MOs  $|i\rangle$ , expressed in terms of the original basis  $B_1$ , are transformed into the orthonormal IAO basis via  $\mathbf{C}_{\text{IAO}} = \text{orth}(\mathbf{A})^T \mathbf{S}_1 \mathbf{C}$  (with  $\mathbf{C}$  from Sec. C. Since the IAOs span the occupied space, this transformation is lossless). Then a series of unitary transformations amongst the  $|i\rangle$  is performed, as described next, modifying the set of orbital coefficients  $\mathbf{C}_{\text{IAO}}$ . Finally the new MOs, now localized, but still expressed via  $\mathbf{C}_{\text{IAO}}$  in terms of IAOs, are transformed back to  $B_1$  according to  $\mathbf{C}_{B_1} = \text{orth}(\mathbf{A}) \mathbf{C}_{\text{IAO}}$ . In total we thus obtain a new set of localized MOs, expressed in terms of  $B_1$ , which is related by an unitary transformation to the input SCF MOs. Consequently both MO sets represent identical determinants, and thus any observable property determined from either orbital set is identical.

The iterative optimization is performed as follows: Let  $|i\rangle = \sum |\rho\rangle C_i^\rho$  denote the occupied MOs expressed in terms of orthonormal IAOs  $|\rho\rangle$  (the  $C_i^\rho$  denoting the matrix elements of  $\mathbf{C}_{\text{IAO}}$ ). We then iterate the following process: For each occupied orbital pair  $i, j$  with  $j < i$ :

- Set  $A_{ij} = 0$  and  $B_{ij} = 0$ . Then for each atom  $X$ , increment  $A_{ij}$  and  $B_{ij}$  as either

$$A_{ij} = A_{ij} + 4Q_{ij}^2 - (Q_{ii} - Q_{jj})^2$$

$$B_{ij} = B_{ij} + 4Q_{ij}(Q_{ii} - Q_{jj})$$



(for localization power  $p = 2$ , as in PM<sup>35</sup>) or as

$$\begin{aligned} A_{ij} &= A_{ij} - Q_{ii}^4 - Q_{jj}^4 + 6(Q_{ii}^2 + Q_{jj}^2)Q_{ij}^2 \\ &\quad + Q_{ii}^3 Q_{jj} + Q_{ii} Q_{jj}^3 \\ B_{ij} &= B_{ij} + 4Q_{ij}(Q_{ii}^3 - Q_{jj}^3) \end{aligned}$$

(for localization power  $p = 4$ , as in Eq. (4)), where the charge matrix elements of atom  $X$  are defined as

$$Q_{ij} = \sum_{\rho \in X} C_i^\rho C_j^\rho.$$

- Calculate the rotation angle  $\phi_{ij} = \frac{1}{4} \arctan2(B_{ij}, -A_{ij})$  (where  $\arctan2(y, x) = \arctan(y/x)$ , taking the quadrant into account). Then rotate the orbitals  $|i\rangle, |j\rangle$  by

$$\begin{aligned} |i'\rangle &= \cos(\phi_{ij}) |i\rangle + \sin(\phi_{ij}) |j\rangle, \\ |j'\rangle &= -\sin(\phi_{ij}) |i\rangle + \cos(\phi_{ij}) |j\rangle. \end{aligned} \quad (\text{D1})$$

The orbitals are updated in-place; i.e., in the  $i, j$  iteration, subsequent pairs  $i, j$  already see the rotated orbitals before the entire loop is passed.

The formulas for  $\phi_{ij}$  are obtained by considering the functional  $L(\phi_{ij}) = \langle i' | n_X | i' \rangle^p + \langle j' | n_X | j' \rangle^p$  where  $|i'\rangle$  and  $|j'\rangle$  are defined as in (D1) and  $p = 2$  or  $p = 4$ , and maximizing it with respect to  $\phi_{ij}$ . For  $p = 2$  the given  $\phi_{ij}$  exactly maximizes the functional, for  $p = 4$  some high order terms in  $\phi_{ij}$  are neglected.

We found this approach to work exceedingly well in practice and it typically converges in 5 to 10 iterations over all  $i, j$  pairs. We believe this to be a consequence of the intrinsic molecular electronic structure, which apparently has a *very* deep attractor at the localized orbital solution corresponding to the Lewis structure (where present).

A final comment is required regarding the exponent  $p = 4$  in Eq. (4). In Eq. (4), we prefer  $p = 4$  over the exponent  $p = 2$  of PM because the former leads to discrete localizations in aromatic systems, while the second does not: For example, in benzene the orbital rotation Hessian has a zero eigenmode if  $p = 2$  is used, but not for  $p = 4$ . For other systems both exponents lead to effectively identical results. An exponent of 4 has recently also been found to be effective in diminishing orthogonalization tails in more traditional orbital localization methods.<sup>92,93</sup>

## Appendix E: Methods used in the test calculations

Molecules were built and pre-optimized with Avogadro.<sup>94</sup> Geometry optimizations were done with Molpro,<sup>95</sup> and employed DF-MP2/aug-cc-pVTZ<sup>96,97</sup> for the molecules in the discussion of electronegativities and DF-RKS/PBE/def2-TZVPP<sup>98–100</sup> for everything else. The complexes in Tab. II were not optimized, but average metal-ligand distances were taken from Ref. 101 and combined with  $r_{\text{OH}} = 0.96 \text{ \AA}$ ,  $\alpha_{\text{HOH}} = 104.5^\circ$  (for  $\text{H}_2\text{O}$ ),  $r_{\text{CN}} = 1.15 \text{ \AA}$  (for  $\text{CN}^-$ ) and  $r_{\text{CO}} = 1.15 \text{ \AA}$  (for CO). Geometries and reference values are available upon request.

IAO and IBO calculations were performed either with a development version Molpro or the demonstration script `ibo-ref.py`, which is available on the author's homepage. Calculations employed def2-TZVPP<sup>99</sup> orbital basis sets and univ-JKFIT<sup>100</sup> fitting basis sets unless otherwise noted. For Tab. II, augmented def2-SVP orbital basis sets were used. Orbital visualizations were produced using Mayavi2.<sup>102</sup>

In the calculations of the pEDA values, the substituted benzenes were aligned such that the center of the benzene ring lies at the center of the coordinate system, and the  $x, y, z$  axes point into the directions of the principal axes of inertia of its six C atoms. As this way the pz orbitals were maximally aligned along the  $z$  axis, so that their occupation numbers could be directly read off in the population analysis (some of the rings have slight distortions from planarity, but this has an insignificant effect on the obtained results).

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