

Pipek–Mezey Orbital Localization Using Various Partial Charge Estimates

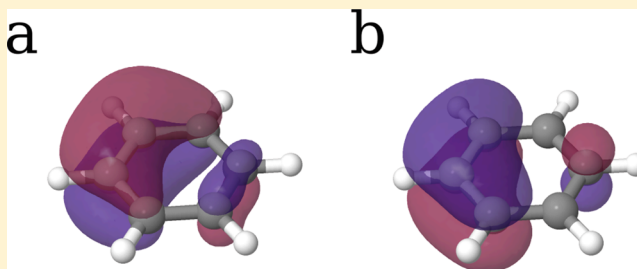
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S Supporting Information

ABSTRACT: The Pipek–Mezey scheme for generating chemically intuitive, localized molecular orbitals is generalized to incorporate various ways of estimating the atomic charges, instead of the ill-defined Mulliken charges used in the original formulation, or Löwdin charges, which have also been used. Calculations based on Bader, Becke, Voronoi, Hirshfeld, and Stockholder partial charges, as well as intrinsic atomic orbital charges, are applied to orbital localization for a variety of molecules. While the charges obtained with these various estimates differ greatly, the resulting localized orbitals are found to be quite similar and properly separate σ and π orbitals, as well as core and valence orbitals. The calculated results are only weakly dependent on the basis set, unlike those based on Mulliken or Löwdin charges. The effect of varying the penalty exponent on the charge in the objective function was studied briefly and was found to lead to some changes in the localized orbitals when degeneracies are present. The various localization methods have been implemented in ERKALE, an open source program for electronic structure calculations.



I. INTRODUCTION

Self-consistent field (SCF) theory, one of the modern computational chemists' most important workhorses, is based on a single-particle picture of electronic systems. Each electron occupies a single, one-particle state—an orbital—which only interacts with the mean field of the other electrons and the Coulombic attraction of the nuclei in the system. The orbitals for a given system can be determined by solving the SCF equations of Hartree–Fock (HF) or Kohn–Sham density functional^{1,2} (KS-DFT) theory. The simplicity of the single-particle picture often has great value for both general understanding of chemistry and the interpretation of experimental results. One example is Fukui et al.'s work on chemical reactions with the frontier orbital concept.^{3–5} Also, the orbital energy eigenvalues obtained in the SCF procedure can be used to estimate changes in the energy when an electron is added or removed from the molecule according to the theorems by Koopmans⁶ (in HF) and Janak⁷ (in KS-DFT).

However, the corresponding eigenstates, i.e., the so-called canonical molecular orbitals (CMOs), are delocal in space, while chemical intuition is typically based on models of localized electrons. But, HF and KS-DFT theories are invariant under unitary transformations of the occupied orbitals. Any such transform gives the same total electron density and the same total energy for the system. Thus, there is no reason *a priori* to favor any single choice of the occupied orbitals, as all of them are equally valid points of view to the physics and chemistry of the studied system⁸ (at the SCF level of theory).

This freedom can be used to construct localized molecular orbitals (LMOs), which can correspond quite well to the models chemists have found useful for rationalizing chemical bonding and geometrical structure of molecules, such as the highly successful valence shell electron pair repulsion (VSEPR) theory.

Several different schemes have been proposed for generating LMOs from CMOs. Some commonly used ones include Foster–Boys⁹ (FB), Edmiston–Ruedenberg¹⁰ (ER), or fourth moment¹¹ (FM) localization, out of which FB is probably the most commonly used. In the present manuscript, we study another commonly used localization method, namely the Pipek–Mezey (PM) scheme.¹² Contrary to the FB, FM, and ER schemes, the PM scheme does not mix σ and π bonds. The scheme is based on maximizing the Mulliken charge¹³ of each orbital:

$$\mathcal{P} = \sum_i \sum_{\text{atoms } A} [\langle i | P_A | i \rangle]^2 \quad (1)$$

where P_A is an operator that projects onto the basis functions centered on atom A , and $\langle i | P_A | i \rangle = Q_A^i$ is the contribution of orbital i to the Mulliken charge of atom A . Alternatively, Löwdin charges can be used instead of Mulliken charges, and they have been shown to yield more localized virtual orbitals.¹⁴

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However, both Mulliken and Löwdin charges are mathematically ill-defined concepts. While basis functions normally are placed on all atoms in the system, a complete basis set for a molecule can in principle also be spanned by a large set of basis functions on a single atom. In the Mulliken or Löwdin schemes, while in the former all atoms are assigned electrons, in the latter all electrons are assigned to the single atom containing the basis functions. This means that *there is no complete basis set limit for the Mulliken or Löwdin charges*, because they depend on the way the limit is approached. Similarly, when atom-centered basis sets on two or more atoms in a molecule are extended toward completion, the basis set can become overcomplete and the expansion of the wave function ill-defined. Although this can be remedied to some extent in the SCF calculation by the procedure of canonical orthonormalization,¹⁵ in which the linearly dependent combinations of basis functions are removed from consideration, the problems still remain for the Mulliken and Löwdin schemes. While a basis function may be centered on an individual atom, thus contributing to the charge of that particular atom in the Mulliken or Löwdin scheme, the basis function itself may be delocalized over a number of atoms, especially in the case of diffuse basis functions. For instance, in the aug-cc-pVDZ basis set,^{16,17} the smallest S-type exponent on carbon is $0.0469/a_0^2$, a_0 being the Bohr radius. This corresponds to a length scale of $a_0/\sqrt{0.0469} \approx 2.44$ Å, which is much larger than, e.g., the typical C–H or C–C bond length (~ 1.1 Å and ~ 1.4 Å, respectively). As a result, the atomic charges obtained are highly dependent not only on the valence basis set but also on the presence of diffuse functions. A scheme to reduce the latter problem for the Löwdin charges has been suggested by Thompson et al.¹⁸

However, as we will show, all of these problems can be overcome by generalizing the PM scheme

$$\mathcal{P} = \sum_i \sum_{\text{nuclei } A} (q_A^i)^2 \quad (2)$$

where the atomic charges q_A^i are derived from methods that are mathematically better defined, such as Becke, Voronoi, Hirshfeld,¹⁹ iterative Stockholder,^{20,21} or Bader approaches,²² all of which are based on the integration of electron density only in the vicinity of each nucleus. An analogous scheme presented in a different form but based on Bader charges has been proposed by Cioslowski²³ (see Appendix B), but this has not become widely used, possibly because the connection to the PM scheme has not been properly appreciated in the literature. One other reason is that efficient algorithms for integration over Bader regions have only recently become available.^{24,25} An approximation to Cioslowski's scheme based on "fuzzy atoms" has been suggested by Alcoba et al.,²⁶ in which the Bader charges are replaced with Becke charges with a special choice of the weight functions. Also this scheme is essentially a modification of the PM scheme. However, we will show that the exact choice of the weight function is not of great importance, as similar LMOs are obtained with a wide variety of choices.

One other alternative has been recently proposed by Knizia in ref 27, in which the partial charges are obtained by projection onto "intrinsic atomic orbitals" (IAOs), which are obtained from orbitals of isolated atoms. The IAO partial charges correspond well with chemical intuition. The corresponding LMOs are then obtained within a PM scheme, and they seem to correspond well with Lewis structures, making the scheme promising for chemical interpretation. However, as we show in

the present work, similar LMOs can also be obtained with a wide variety of other partial charge schemes for PM localization.

We have implemented the Bader, Becke, Voronoi, Hirshfeld, and iterative Stockholder approaches, as well as the Mulliken, Löwdin, and IAO schemes for estimating atomic charges in a generalized PM scheme, which can be used to produce LMOs using a unitary optimization algorithm. Although widely different estimates of the atomic charges are obtained with the various methods, as illustrated below, the LMOs obtained are, nevertheless, quite similar. A proper separation of σ and π bonds is maintained in all the generalized PM methods, as well as a separation of core and valence orbitals.

The organization of the manuscript is as follows. In the next section, we describe the various charge estimates. Then, we describe the computational procedure, followed by a description of the implementation. Results of various localization calculations are then described, and the article concludes with a short discussion and summary.

II. ATOMIC CHARGE ESTIMATES

The Mulliken charge on atom A is given by

$$q_A^i = \sum_{\mu \text{ on } A} (\mathbf{PS})_{\mu\mu} \quad (3)$$

while the Löwdin charge is given by

$$q_A^i = \sum_{\mu \text{ on } A} (\mathbf{S}^{1/2} \mathbf{PS}^{1/2})_{\mu\mu} \quad (4)$$

where \mathbf{S} is the overlap matrix, \mathbf{P} is the density matrix, and the sums run over the basis functions that are centered on atom A . Both schemes rely on the linear combination of atomic orbitals (LCAO) approach and are explicitly dependent on the basis set, as only functions on the atom contribute to its partial charge.

In Knizia's scheme, the partial charges are given by

$$q_A^i = \sum_{\rho \text{ on } A} \langle \rho | \gamma | \rho \rangle \quad (5)$$

where $|\rho\rangle$ are the IAOs of atom A and γ is the one-electron density matrix. The IAOs are constructed by projection from free-atom orbitals, as detailed in ref 27. While eqs 3 and 5 are similar in form in the LCAO formalism, explicit basis set dependence is avoided in Knizia's scheme by projection onto free-atom orbitals. However, a choice for the free-atom orbital basis is necessary. Furthermore, the applicability of the IAO partial charge assignment is inherently limited to the SCF level of theory as the (fully) occupied MOs are used in the construction of the IAO basis.

In contrast, the generalized PM schemes presented here are based on the division of space into atomic regions, eliminating any reference to atomic basis sets or atomic orbitals. This makes them more widely applicable, for example in calculations based on plane waves or real space grids, or calculations at a post-HF level of theory. The Becke charge is given by

$$q_A = \int w_A^B(\mathbf{r}) \rho(\mathbf{r}) d^3r \quad (6)$$

where ρ is the electron density and $w_A^B(\mathbf{r})$ is the Becke weight function of the A th atom. Hirshfeld and Stockholder charges have an analogous definition to eq 6, with the weight function now being defined as

$$w_A^H(\mathbf{r}) = \frac{\tilde{\rho}_A(\mathbf{r})}{\sum_B \tilde{\rho}_B(\mathbf{r})} \quad (7)$$

where $\tilde{\rho}_A$ are the individual, spherically symmetric atomic electron densities. In the Hirshfeld scheme, these are obtained from calculations of isolated atoms,¹⁹ while in the Stockholder scheme an iterative algorithm is used to extract atomic electron densities from the total electron density of the system.²¹

In the Bader scheme, the total electron density is divided into regions separated by surfaces with a vanishing density gradient in the direction normal to the surface. Because a region may contain zero, one, or more nuclei, a regional Bader charge is defined as

$$q_{\mathcal{A}} = \int w_{\mathcal{A}}(\mathbf{r}) \rho(\mathbf{r}) d^3r \quad (8)$$

where the weight function $w_{\mathcal{A}}(\mathbf{r}) = 1$ when the point \mathbf{r} is in the basin of attraction of the charge maximum \mathcal{A} and vanishes otherwise. Correspondingly, the inner sum in eq 2 is taken over Bader regions instead of atomic nuclei.

The Voronoi scheme is similar to the Bader scheme, in that the weight function only has the values $w_A(\mathbf{r}) = 1$ when A is the closest nucleus to the point \mathbf{r} , $w_A(\mathbf{r})$ vanishing otherwise.

The Becke weight function was originally designed to perform a “fuzzy” Voronoi decomposition in order to decompose integrals over the whole system into overlapping atomic contributions that can be calculated efficiently in atom-centric spherical coordinates.²⁸ This is efficient because the r^2 from the Jacobian eliminates the electron density cusp of the nucleus at the origin, and the decay of the weight function away from the origin eliminates the contributions from cusps at the other nuclei.

Since the weight functions only need to satisfy $\sum_A w_A(\mathbf{r}) = 1$, there is a wide range of possible choices for their form, and the atomic charges obtained can differ greatly. However, with a chosen definition of the weight function, the charges are uniquely defined and can be evaluated easily (in any basis set or real space grid).

Atomic size adjustments to DFT quadrature grids were originally proposed by Becke,²⁸ and they have been used in their original²⁹ as well as a slightly modified forms.³⁰ However, they have not, as far as we are aware, been used in state-of-the-art Becke grid implementations for integration in KS-DFT.^{31–34} Since the integration grid is a purely mathematical tool, the atomic size can be considered an irrelevant parameter.³⁴ It has been shown recently that the atomic size adjustments of Becke can be used to obtain partial charges that coincide with chemical intuition,³⁵ but the determination of the necessary size parameters is a nontrivial task because the size of an atom depends on its environment.^{36,37}

Atomic size adjustments were not used in the calculations presented here, but for simplicity we refer to this approach as the Becke scheme. As our results show, the LMOs obtained are remarkably insensitive to the choice of the partial charge scheme; thus there is good reason to believe that the “fuzzy atom” LMOs do not significantly differ from the Becke LMOs either.

III. GENERALIZED PM SCHEME

For clarity, the objective function to be maximized, eq 2, is rewritten in a form that is computationally more convenient:

$$\mathcal{P}(\mathbf{W}) = \sum_{i=1}^n \sum_{A=1}^N [Q_{ii}^A(\mathbf{W})]^p \quad (9)$$

where \mathbf{W} is the unitary matrix connecting the LMO and the CMO bases and p is a penalty exponent, which is necessary because for $p = 1$ the measure is a constant

$$\sum_A Q_{ii}^A(\mathbf{W}) = 1 \quad (10)$$

given by the normalization of the localized orbital. The case $p = 2$ corresponds to the traditional PM scheme. Further penalty (compared to the traditional PM choice) for individual delocal orbitals can be introduced with $p > 2$. Indeed, with IAO charges, $p = 4$ has been found to produce discrete localization in aromatic systems, while $p = 2$ does not.²⁷ The choice $p < 1$ in eq 9 is as well possible in principle, in which case the localization sum would have to be minimized instead. Here, only $p = 1.5$, $p = 2$, and $p = 4$ have been used, and in the following, $p = 2$ if not otherwise stated.

Penalty exponents have been found to be useful for obtaining more localized sets of orbitals in FB and FM localization.^{11,38} However, the role of the penalty exponent is somewhat different in PM compared to FB and FM, as the basic formulation of the PM method already includes a penalty on individual delocal orbitals, as discussed above, while the FB and FM schemes are fundamentally changed by the introduction of a penalty. For this reason, the localized orbitals produced by the PM scheme are not affected as much by the choice of the penalty exponent as the orbitals obtained with the FB and FM schemes.

A. Formulation with Canonical Orbitals. The contribution of LMO j to the partial charge on atom A is

$$Q_{jj}^A(\mathbf{W}) = \sum_{rs} W_{rj}^* Q_{rs}^A W_{sj} \quad (11)$$

where r and s are CMO indices. The CMO charge matrix is

$$Q_{rs}^A = \sum_{\mu \text{ on } A} \frac{1}{2} [c_{\mu r}(\mathbf{S}\mathbf{c})_{\mu s} + c_{\mu s}(\mathbf{S}\mathbf{c})_{\mu r}] \quad (12)$$

for Mulliken charges and

$$Q_{rs}^A = \sum_{\mu \text{ on } A} (\mathbf{S}^{1/2}\mathbf{c})_{\mu r} (\mathbf{S}^{1/2}\mathbf{c})_{\mu s} \quad (13)$$

for Löwdin charges, $c_{\mu r}$ being the coefficient of the μ th basis function in the r th CMO.

In the case of the Bader, Becke, Voronoi, Hirshfeld, and Stockholder schemes, the charge matrix is

$$Q_{rs}^A = \int \phi_r^*(\mathbf{r}) w_A(\mathbf{r}) \phi_s(\mathbf{r}) d^3r \quad (14)$$

where w_A is the weight function used in each case.

In the IAO scheme, the charge matrix is simply

$$Q_{rs}^A = \sum_{\rho \text{ on } A} \langle r|\rho \rangle \langle \rho|s \rangle \quad (15)$$

where $|\rho\rangle$ are IAOs and $|r\rangle$ and $|s\rangle$ are CMOs.

B. σ - π Separation. The PM method preserves the separation of σ and π orbitals of (locally) planar molecules. The coupling of a σ -type and a π -type orbital is given by eq 14 as

Table 1. Calculated Atomic Partial Charges in a Water Molecule Calculated with the Various Methods

	cc-pVTZ		aug-cc-pVTZ		difference	
	O	H	O	H	O	H
Bader	−1.378	0.689	−1.395	0.697	−0.017	0.008
Stockholder	−0.875	0.438	−0.888	0.444	−0.013	0.006
IAO	−0.739	0.370	−0.750	0.375	−0.011	0.005
Mulliken	−0.476	0.238	−0.420	0.210	0.056	−0.028
Hirshfeld	−0.331	0.166	−0.320	0.160	0.011	−0.006
Voronoi	0.743	−0.372	0.753	−0.376	0.010	−0.004
Becke	0.802	−0.401	0.811	−0.405	0.009	−0.004
Löwdin	0.367	−0.183	1.028	−0.514	0.661	−0.331

$$Q_{\pi\sigma}^A = \int \phi_{\pi}^*(\mathbf{r}) w_A(\mathbf{r}) \phi_{\sigma}(\mathbf{r}) d^3r \quad (16)$$

Since any physically meaningful weight function is invariant under reflection about the molecular plane (e.g., $z \rightarrow -z$ for a planar molecule in the (x,y) plane), as are σ orbitals as well, but π orbitals change sign, the coupling vanishes. Thus, the localization criterion (eqs 9 and 11) will not couple σ and π orbitals in planar molecules. Similar results have been obtained for Mulliken (ref 12), Bader (ref 23), and “fuzzy atom” schemes (ref 26).

IV. IMPLEMENTATION

The maximization of eq 9 can be performed using a variety of approaches, e.g., consecutive 2×2 Jacobi rotations,¹⁰ a second-order procedure,³⁹ or a trust-region method.¹⁴ In the present work, the orbitals are localized using unitary optimization.^{40,41} The details of the implementation are discussed elsewhere.⁴² The various charge estimation methods have been integrated in this scheme in the current version of the ERKALE^{43,44} software. Only real orthogonal transformations \mathbf{W} are considered here, as complex unitary transformations turned out not to lead to a higher degree of localization, as determined by the value of the localization sum (eq 9).

When the Becke charge on atom A is calculated, only the integral around the atom in question is necessary, as the integrals over the other atomic regions give zero contribution to the charge on that atom. Accordingly, the atomic integrals in eq 18 are evaluated in spherical coordinates for the Becke charges. However, also the Hirshfeld and Stockholder weights efficiently decompose the system into smooth atomic regions because of their exponential decay away from the nucleus, and thus only a single atomic integral is necessary in these cases as well.

In contrast, in the Bader and Voronoi decompositions, contributions to the partial charge on atom A may come from grids on atoms $A' \neq A$, so a full molecular Becke grid is used. The individual grid points are assigned to Bader regions with a steepest ascent approach.^{24,25}

If the Q_{rs}^A matrices are stored in memory, the memory requirement of the localization calculation would scale as $N_{\text{at}} N^2$, where N is the number of orbitals to localize and N_{at} is the number of atoms in the system. As the size of the system increases, $N \propto N_{\text{at}}$, leading to a memory requirement that increases as N^3 , limiting the applicability of the method to small systems. To overcome this problem, the matrices are recomputed at every iteration in the implementation in ERKALE. Furthermore, eq 14 is written as

$$Q_{rs}^A = \mathbf{c}_r^T \mathbf{S}^A \mathbf{c}_s \quad (17)$$

$$S_{\mu\nu}^A = \int \chi_{\mu}(\mathbf{r}) w_A(\mathbf{r}) \chi_{\nu}(\mathbf{r}) d^3r \quad (18)$$

where the atomic contribution to the overlap matrix \mathbf{S}^A has been identified. Because conventional DFT grids are designed for the integration of the Fock matrix, they are likely suboptimal in computational efficiency and accuracy for the atomic overlap matrix. For this reason, instead of using the exchange-correlation grid generation algorithm³³ normally used in ERKALE, we resort to its predecessor that is optimized for the calculation of the overlap matrix.³⁴

The Hirshfeld densities are obtained in ERKALE by calculating isolated atoms with spherically averaged occupancies, using only the basis functions centered on that atom.

The Stockholder densities are obtained with an iterative procedure following ref 21 by self-consistently decomposing the full molecular electron density into spherically symmetric contributions from the individual atoms. However, in contrast to ref 21, the implementation in ERKALE uses even-spaced atomic grids (spacing of $0.01a_0$), ranging up to $R = 8.5a_0$. Also, a numerically more stable convergence measure for the iterative process

$$\delta = \max_A \int_0^R r^2 |\bar{\rho}_A^n(r) - \bar{\rho}_A^{n-1}(r)| dr \quad (19)$$

is used, $\delta \leq 10^{-5}$ being used in the present work as the threshold for convergence. Here $\bar{\rho}_A^n$ is the spherically averaged charge distribution assigned to atom A at iteration n , with r being the radial distance from the A th nucleus. An adaptive angular grid is used in the iterative determination of the spherically averaged charge distributions. Due to this, the iteration is started from the initial guess $\rho_A^0(r) = \exp(-r)$, which leads to smaller integration grids in the initial iterations than the guess $\rho_A^0(r) = 1$ used in ref 21.

V. RESULTS

To compare the performance of the various charge schemes in orbital localization calculations, we study a variety of molecules with geometry optimized at the spin-restricted Hartree–Fock (RHF) level of theory using the cc-pVDZ basis set.¹⁶ We start by examining the basis set dependence of the partial charges in calculations of the water molecule using both the cc-pVTZ and the aug-cc-pVTZ basis sets.^{16,17} The values of the partial charges obtained are given in Table 1. The IAO results have been obtained with a free-atom reference corresponding to the generally contracted⁴⁵ functions from the cc-pVTZ basis set, as in ref 27. Other free-atom references, corresponding to the contracted functions in the cc-pVDZ, cc-pVQZ, and cc-pVSZ basis sets,¹⁶ were found to result in insignificant changes to the IAO partial charges.

As is well-known, Mulliken and Löwdin charges show much larger dependence on the basis set than the other methods, which only depend implicitly on the basis set. This is clearly seen in the difference between the partial charges obtained using the cc-pVTZ and aug-cc-pVTZ basis sets. The change in the Mulliken charges upon augmentation with diffuse functions is roughly a factor 5 larger than for the other methods, while for Löwdin charges, the change is larger by a factor of 50.

The atomic charges obtained with the various methods are widely different. For instance, the Bader and the Becke charges on the O-atom in the H₂O molecule differ by more than two electrons, with the Bader scheme predicting an ionic bond, at variance with chemical intuition. Most methods assign a negative charge to the O atom, while the Löwdin and the Becke estimates give a positive charge—again at variance with chemical intuition. The positive charge assigned by the Löwdin method can be attributed to its mathematical pathology. The positive charge by the Becke method is not surprising, because the method only yields information on the amount of charge in the integration volume of the coordinate space centered on that atom, including no chemical information. As was noted in the Introduction, Becke charges can be made to correspond better to chemical intuition by a meticulous choice of the atomic weight functions resulting in the “fuzzy atom” scheme,^{35–37} but this has not been pursued in the present work.

An important result of the calculations presented here is that the atomic charges do not significantly affect the LMOs obtained. The LMOs procured with all the PM methods are similar, despite the large variation in the total partial charges assigned to the atoms. After all, the total partial charge does not enter the localization calculation. The procedure is based only on the partial charges obtained from the *individual* LMOs. For instance, RHF calculations on an acrylic acid molecule in the aug-cc-pVTZ basis show that all the PM methods give similar results for the LMOs. For example, localization of IAO charges²⁷ results in nearly the same orbitals as those from a Becke or Bader charge calculation, as illustrated in Figures 1, 2, and 3. Here, the σ – π separation is evident in all the PM schemes and enables the inspection of the π -type lone pairs and bonds.

The only clear differences here are seen for the lone pairs. Most methods produce separate s and p lone pairs, while in the IAO and Löwdin methods the former is produced in sp form. We tentatively attribute this to the symmetric orthonormalization procedure used in the IAO and Löwdin methods, which results in nonlocal basis functions.

Because all orbitals are nondegenerate and well localized, the use of another penalty exponent, $p = 1.5$ or $p = 4$, does not result in significant changes to the LMOs, as can be seen from the full set of renderings in the Supporting Information.

We have also carried out calculations of LMOs for cyclopropane, diborane, and sulfur trioxide in a similar fashion and have found that all the PM methods again give similar results. In contrast, other localization methods, such as ER, FB, and FM, do not preserve σ – π separation, in which case the lone pairs and multiple bonds become mixed into equivalent orbitals, and a similar analysis is not possible. The single bonds are localized in a similar fashion by all the methods (ER, FB, FM, and PM).

Calculations of a benzene molecule using the pcemd-4 basis set⁴⁶ show that the CC and CH σ bonds become equally localized by all the PM methods. In contrast, differences arise for the π electrons which are delocalized over the ring, yielding

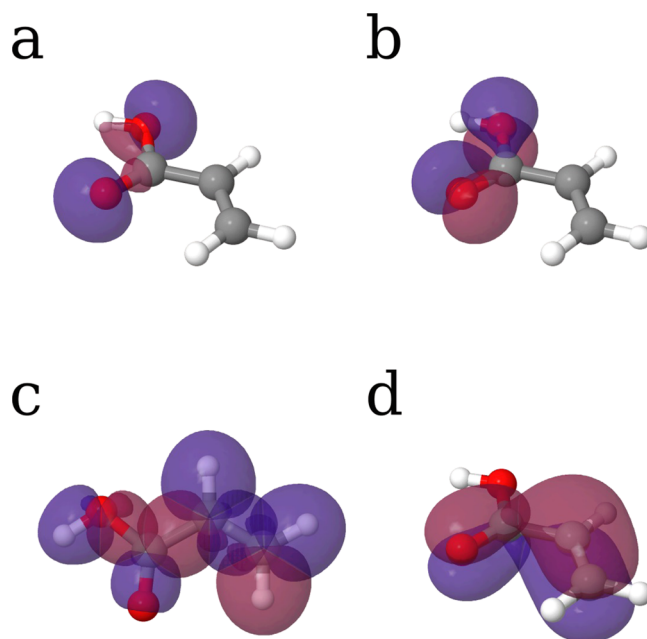


Figure 1. Localized orbitals in acrylic acid, obtained by localization of IAO charges. (a) sp lone pairs. (b) p lone pairs. (c) σ bonds. (d) π bonds. The details of the rendering process are given in Appendix A.

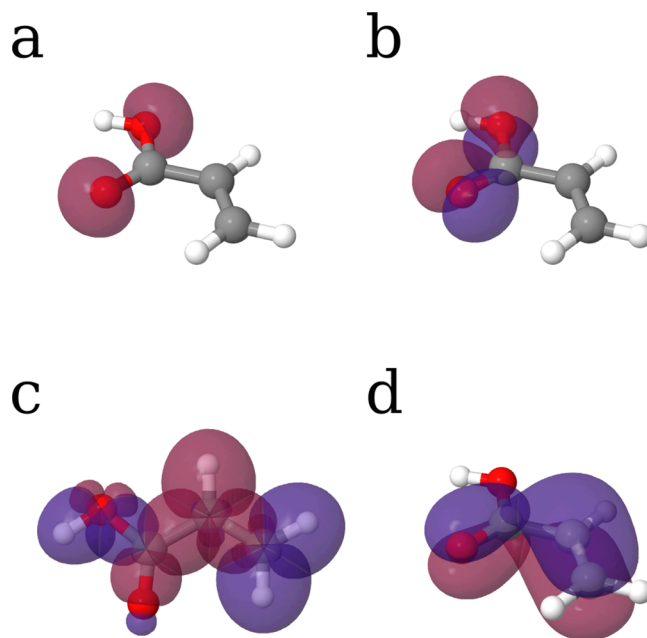


Figure 2. Localized orbitals in acrylic acid, obtained by localization of Becke charges. (a) s lone pairs. (b) p lone pairs. (c) σ bonds. (d) π bonds. The details of the rendering process are given in Appendix A.

three equivalent orbitals differing by a $2\pi/3$ rotation. Here, the amount of delocalization in the individual orbitals is dependent on the method used for the atomic charge estimation and the value used for the penalty exponent p . Two example cases are shown in Figure 4: a node on four carbon atoms with an antinode on the opposite two carbon atoms (less localization), vs a node on three carbon atoms with an antinode on the opposite one carbon atom (more localization). While most of the charge methods produce the former with $p = 2$ and the latter with $p = 4$, the Stockholder and Löwdin charges reproduce the more localized π orbitals already with $p = 2$.

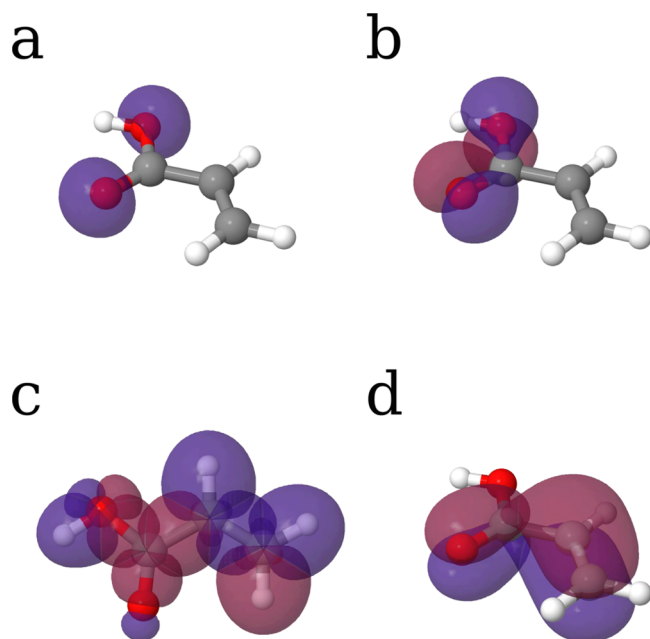


Figure 3. Localized orbitals in acrylic acid, obtained by localization of Bader charges. The legend is the same as in Figure 2. The details of the rendering process are given in Appendix A.

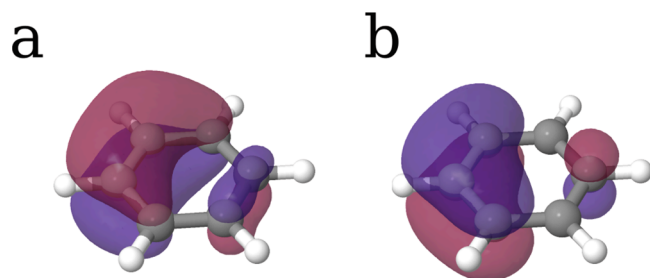


Figure 4. Illustration of the delocalized π orbitals in benzene, with localization based on Becke charges. (a) Less localization with $p = 2$, (b) more localization with $p = 4$. In both cases, there are two more equivalent orbitals rotated by angles of $2\pi/3$ and $4\pi/3$, respectively. The details of the rendering process are given in Appendix A.

Surprisingly, also with $p = 1.5$ all methods produce the more localized case.

VI. DISCUSSION AND SUMMARY

We have presented here a generalization of the PM localization scheme where mathematically well-defined estimates of atomic charges are used, unlike the original formulation which is based on Mulliken charges, or a later modification using Löwdin charges. The charge estimates used in the generalized scheme do not rely on the use of atom-centered basis functions and thus can also be applied beyond the scope of LCAO calculations in, for example, plane wave or real space grid based calculations. Although related schemes have been previously proposed,^{23,26} their connection to the PM method had not been made clear. As we have shown, both are equivalent to the PM scheme but differ in the way partial charges are assigned.

The generalized PM scheme presented here consistently produces highly localized orbitals while also maintaining proper σ – π separation and core–valence separation. Furthermore, the partial charges used can be calculated with computational effort

that scales linearly with the size of the system⁴⁷ and could easily be incorporated in any orbital localization algorithm, especially the recently suggested powerful, globally convergent trust region method.¹⁴

By comparing several methods for the assignment of partial charges, we have shown that although the total atomic partial charges vary greatly, the LMOs obtained differ only insignificantly. Furthermore, we have shown that the recent scheme proposed by Knizia²⁷ also gives similar LMOs. Other kinds of charge estimates, in addition to the ones used here, such as electrostatic potential charges,⁴⁸ or the Voronoi deformation density,^{49,50} or iterative Hirshfeld charges,^{51–53} could also be used but would likely lead to similar LMOs.

The choice of the penalty exponent mainly affects the localized orbitals obtained in cases where degeneracies exist and electrons are delocalized, such as in the π orbitals in benzene. Otherwise, the results obtained with the generalized PM method are quite independent of the choice of the penalty exponent because the PM scheme already penalizes individual delocal orbitals.

A clear choice for the value of the penalty exponent did not emerge from the limited studies carried out here, as in most cases similar results were obtained with $p = 1.5$, $p = 2$, and $p = 4$. If the goal is just to obtain chemically intuitive LMOs, the choice of the penalty exponent is not of great importance.

■ APPENDIX A

For the visualization, the orbitals were computed with ERKALE on a grid with a spacing of 0.1 Å and then rendered with Jmol⁵⁴ with an isosurface value c corresponding to an 85% density cutoff:

$$\int_{|\psi(\mathbf{r})| \geq c} |\psi(\mathbf{r})|^2 d^3r = 0.85 \quad (20)$$

similarly to ref 27.⁵⁵ The positive isosurfaces are shown in blue and the negative ones in red.

The density approach treats all orbitals on more of an equal footing than a fixed isosurface value for all orbitals; as for diffuse orbitals, c will be small, producing a diffuse surface, and for well localized orbitals, c will be large, producing a small, confined surface. The values of c were determined for each orbital by evaluating the density on a Becke grid, sorting the densities in decreasing order and computing the smallest value n for which

$$\sum_{i=1}^n w_i \rho_i^2 > 0.85 \quad (21)$$

where the sum over i runs over grid points at \mathbf{r}_i with weight w_i and the density is $\rho_i = |\psi(\mathbf{r}_i)|^2$. The value c is then obtained as

$$c \approx \sqrt{\frac{\rho_n + \rho_{n-1}}{2}} \quad (22)$$

It is important to note that the value of c for core orbitals is sensitive to the used integration grid due to their peaked nature. The bulk of the charge is within a small volume, which typically contains few integration points. For valence orbitals, c is less dependent on the grid. However, because core orbitals are nonetheless well localized, the rendered surfaces will look similar regardless of some variation in c .

■ APPENDIX B

In ref 23, Cioslowski discussed orbital localization by maximization of

$$L = \sum_i \sum_{klmn} C_{ik}^* C_{il} C_{im}^* C_{in} T_{klmn} \quad (23)$$

where **C** is the unitary matrix that connects the CMO and LMO bases and the tensor **T** defines the localization procedure. Cioslowski proposed the use of a tensor given by

$$T_{klmn} = \sum_A \langle kl|_A \rangle \langle mn|_A \rangle \quad (24)$$

where $\langle kl|_A \rangle$ is the overlap of CMOs *k* and *l* in the atomic region *A*. Noting that $\langle kl|_A \rangle$ is given by Mulliken population analysis in the PM scheme, Cioslowski proposed Bader regions to be used in the determination of the atomic overlaps as

$$\langle kl|_A \rangle = \int_{\text{basin}_A} \phi_k^*(\mathbf{r}) \phi_l(\mathbf{r}) d^3r \quad (25)$$

Comparison of eqs 23, 24, and 25 with eq 2 reveals Cioslowski's scheme to be equivalent to PM with the use of a Bader charge:

$$q_A^i = \int_{\text{basin}_A} |\psi_i(\mathbf{r})|^2 d^3r \quad (26)$$

where ψ_i is the *i*th LMO. Similarly, the scheme of Alcoba et al. approximates eq 25 with the “fuzzy atom” scheme,²⁶ thus being equivalent to PM with “fuzzy atom” charges.

■ ASSOCIATED CONTENT

Supporting Information

Localized orbitals for acrylic acid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864.
- (2) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
- (3) Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722.
- (4) Fukui, K.; Yonezawa, T.; Nagata, C. *J. Chem. Phys.* **1953**, *21*, 174.
- (5) Fukui, K.; Yonezawa, T.; Nagata, C. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 423.
- (6) Koopmans, T. *Physica* **1934**, *1*, 104.
- (7) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165.
- (8) Truhlar, D. G. *J. Chem. Educ.* **2012**, *89*, 573.
- (9) Foster, J.; Boys, S. *Rev. Mod. Phys.* **1960**, *32*, 300.
- (10) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457.
- (11) Høyvik, I.-M.; Jansik, B.; Jørgensen, P. *J. Chem. Phys.* **2012**, *137*, 224114.
- (12) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916.

- (13) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
- (14) Høyvik, I.-M.; Jansik, B.; Jørgensen, P. *J. Comput. Chem.* **2013**, *34*, 1456.
- (15) Löwdin, P.-O. *J. Chem. Phys.* **1950**, *18*, 365.
- (16) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
- (17) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.
- (18) Thompson, J. D.; Xidos, J. D.; Sonbuchner, T. M.; Cramer, C. J.; Truhlar, D. G. *PhysChemComm* **2002**, *5*, 117.
- (19) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.
- (20) Lillestolen, T. C.; Wheatley, R. J. *Chem. Commun. (Cambridge, U. K.)* **2008**, 7345, 5909.
- (21) Lillestolen, T. C.; Wheatley, R. J. *J. Chem. Phys.* **2009**, *131*, 144101.
- (22) Bader, R. F. W. *Atoms in Molecules - A Quantum Theory*; Oxford University Press: Oxford, U. K., 1990.
- (23) Cioslowski, J. *J. Math. Chem.* **1991**, *8*, 169.
- (24) Henkelman, G.; Arnaldsson, A.; Jónsson, H. *Comput. Mater. Sci.* **2006**, *36*, 354.
- (25) Rodríguez, J. I.; Köster, A. M.; Ayers, P. W.; Santos-Valle, A.; Vela, A.; Merino, G. *J. Comput. Chem.* **2009**, *30*, 1082.
- (26) Alcoba, D. R.; Lain, L.; Torre, A.; Boicchio, R. C. *J. Comput. Chem.* **2006**, *27*, 596.
- (27) Knizia, G. *J. Chem. Theory Comput.* **2013**, *9*, 4834.
- (28) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 2547.
- (29) Murray, C. W.; Handy, N. C.; Laming, G. J. *Mol. Phys.* **1993**, *78*, 997.
- (30) Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.
- (31) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett.* **1993**, *209*, 506.
- (32) Perez-Jordá, J. M.; Becke, A. D.; San-Fabián, E. *J. Chem. Phys.* **1994**, *100*, 6520.
- (33) Köster, A. M.; Flores-Moreno, R.; Reveles, J. U. *J. Chem. Phys.* **2004**, *121*, 681.
- (34) Krack, M.; Köster, A. M. *J. Chem. Phys.* **1998**, *108*, 3226.
- (35) Mayer, I.; Salvador, P. *Chem. Phys. Lett.* **2004**, *383*, 368.
- (36) Francisco, E.; Pendás, A. M.; Blanco, M. A. *J. Chem. Theory Comput.* **2006**, *2*, 90.
- (37) Matito, E.; Solà, M.; Salvador, P.; Duran, M. *Faraday Discuss.* **2007**, *135*, 325.
- (38) Jansik, B.; Høst, S.; Kristensen, K.; Jørgensen, P. *J. Chem. Phys.* **2011**, *134*, 194104.
- (39) Leonard, J. M.; Luken, W. L. *Theor. Chem. Acc.* **1982**, *62*, 107.
- (40) Abrudan, T. E.; Eriksson, J.; Koivunen, V. *IEEE Trans Signal Process.* **2008**, *56*, 1134.
- (41) Abrudan, T.; Eriksson, J.; Koivunen, V. *Signal Process.* **2009**, *89*–1704.
- (42) Lehtola, S.; Jónsson, H. *J. Chem. Theory Comput.* **2013**, *9*, 5365.
- (43) Lehtola, J.; Hakala, M.; Sakko, A.; Hämäläinen, K. *J. Comput. Chem.* **2012**, *33*, 1572.
- (44) Lehtola, S. ERKALE – HF/DFT from Hel. 2013. <http://erkale.googlecode.com>.
- (45) Raffanetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452.
- (46) Lehtola, S.; Manninen, P.; Hakala, M.; Hämäläinen, K. *J. Chem. Phys.* **2013**, *138*, 044109.
- (47) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *Chem. Phys. Lett.* **1996**, *257*, 213.
- (48) Cox, S. R.; Williams, D. E. *J. Comput. Chem.* **1981**, *2*, 304.
- (49) Bickelhaupt, F. M.; van Eikema Hommes, N. J. R.; Fonseca Guerra, C.; Baerends, E. J. *Organometallics* **1996**, *15*, 2923.
- (50) Guerra, C. F.; Handgraaf, J.-W.; Baerends, E. J.; Bickelhaupt, F. M. *J. Comput. Chem.* **2004**, *25*, 189.
- (51) Bultinck, P.; Van Alsenoy, C.; Ayers, P. W.; Carbó-Dorca, R. *J. Chem. Phys.* **2007**, *126*, 144111.
- (52) Bultinck, P.; Ayers, P. W.; Fias, S.; Tiels, K.; Van Alsenoy, C. *Chem. Phys. Lett.* **2007**, *444*, 205.
- (53) Verstraelen, T.; Ayers, P. W.; Van Speybroeck, V.; Waroquier, M. *J. Chem. Theory Comput.* **2013**, *9*, 2221.

- (54) Jmol: an open-source Java viewer for chemical structures in 3D.
<http://www.jmol.org>.
- (55) Knizia, G. Private communication.