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Local properties of quantum chemical systems: The LoProp approach

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A new method is presented, which makes it possible to partition molecular properties like multipole moments and polarizabilities, into atomic and interatomic contributions. The method requires a subdivision of the atomic basis set into occupied and virtual basis functions for each atom in the molecular system. The localization procedure is organized into a series of orthogonalizations of the original basis set, which will have as a final result a localized orthonormal basis set. The new localization procedure is demonstrated to be stable with various basis sets, and to provide physically meaningful localized properties. Transferability of the methyl properties for the alkane series and of the carbon and hydrogen properties for the benzene, naphthalene, and anthracene series is demonstrated. © 2004 American Institute of Physics. [DOI: 10.1063/1.1778131]

I. INTRODUCTION

Quantum chemistry is today a standard tool with which chemists can study fairly large molecules. The information provided by a quantum chemical calculation, an energy and a wave function, can be used in order to allow for comparison between different systems. For small systems it might be enough to calculate molecular properties like the dipole or quadrupole moment. It is also possible to characterize the response properties of a molecule with a polarizability or hyperpolarizability. For larger systems a partitioning of the molecular charge distribution by population analysis and the response property into local contributions is needed. Such partitioning schemes should be computationally cheap, localized properties should have physical meaning, and the localized model should reproduce global properties as molecular multipole moments, polarizabilities, and the electrostatic potential. In addition, this analysis could go further and be used to generate intermolecular forces. Intermolecular forces are commonly expressed by empirical or semiempirical potentials in existing molecular simulation packages. Such potentials are good when they are used to describe systems similar to those for which they have been generated. An alternative way would be to generate the potentials fully *ab initio*. A scheme for localization of multipole moments and polarizabilities is of great value for such purpose.

Available population analysis or partitioning schemes are based on (a) the basis functions, (b) the electrostatic potential, (c) the wave function. To the first set belong the Mulliken¹ and the Löwdin² population analysis. The problem with these approaches is that they vary drastically with the basis set and show no convergence as the size of the basis set is increased. The distributed multipole analysis (DMA) developed by Stone³ also belongs to this group. Here again the

localization is a function of the basis set. To the population analysis methods based on the electrostatic potential belongs the approach of Williams.⁴ The major drawback of these methods are problems of transferability⁵ and that the fitting procedure is statistically underdetermined.⁶ Furthermore, they are computationally expensive. To the third group belongs the well-known atoms in molecules (AIM) method of Bader.^{7,8} This method is computationally expensive, it does not describe correctly the atomic charges for polar bonds and for certain systems it gives a nonchemical partitioning.⁹ To its defense one might mention that the local properties are transferable, a feature which can not be underestimated if the analysis has to give chemical insight. An alternative method for calculating localized charges has been developed by Cioslowski¹⁰ based on the generalized atomic polar tensor, and Lazzeretti and co-workers¹¹ have used a similar approach to partition the total molecular polarizability into local contributions. These procedures are very sensitive to the basis sets used. A third more popular wave function based population analysis is the so-called natural atomic orbital (NAO) analysis developed by Weinhold and co-workers.¹² The method is based on a diagonalization of the individual atomic blocks of the molecular density matrix followed by an occupation-weighted orthonormalization procedure to ensure overall orthogonality. The NAO analysis is computationally cheap and, just as the DMA and AIM approach, exhibits convergence with increasing basis set size. However, the NAO approach is biased in its partitioning of the space around the system by the chemistry (or rather the electron configuration) of the system under study. This might initially seem like an attractive property, but it has its limiting effects in that, for example, the charge analysis of a molecular system in different electronic states does not lead to any conclusion with respect to charge transfer, since the spatial partitioning is different for the different states.

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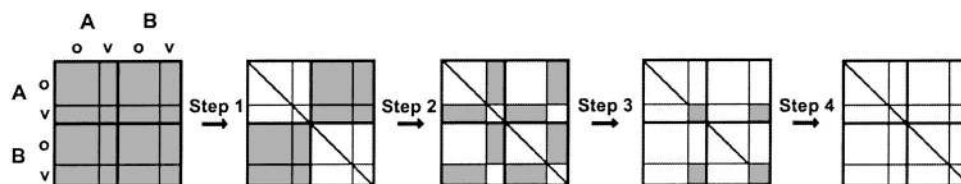


FIG. 1. The overlap matrix as the steps of the orthonormalization procedure progress. *A* and *B* denote two generic atoms and *o* and *v* denote the occupied and virtual orbitals, respectively. The change of the color of the subblocks from gray to white indicates how the portions of the overlap matrix change from nonzero to zero, as the localization scheme proceeds step by step. The bold diagonal line indicates nonzero diagonal elements.

In addition to the fact that the population analysis should provide physically meaningful charges, the requirement of an accurate representation of the electrostatic potential requires a generalization of the population analysis to higher multipole moments. The Mulliken analysis has been generalized to higher electrostatic moments by Karlström¹³ and, by virtue of construction, the DMA approach can do this too. The computationally inexpensive NAO approach is also easily extendable to multipole moments.

The partitioning of the molecular polarizabilities into local contributions is a more elaborate task (see, for example, the recent review by Rick and Stuart Ref. 14). In addition to the approach suggested by Lazeretti and co-workers,¹¹ two other main routes have been followed. Karlström suggested a scheme based on the polarizability calculated in the uncoupled Hartree-Fock approximation¹⁵ which is simple but crude, whereas Stone and Williams have devised a more elaborate scheme based on numerical integration.^{16,17} Along these lines the work by Day *et al.*¹⁸ should also be mentioned.

A common weakness of the methods that are simple, for example, the Karlström approach,¹⁵ is that the result depends rather strongly on the quality of the basis set used and it gives an unbalanced description of different atoms. The more elaborate methods, like the Stone-Williams approach,^{16,17} are in general less basis set sensitive, but computationally more demanding.

To summarize, there is need for an automatic, computationally inexpensive scheme which gives physically meaningful localized multipole moments and polarizabilities. We shall in this work present a method for localization, LoProp, that is designed to avoid the basis set sensitivity of the simpler methods and the computational complexity of the more elaborate methods. Furthermore, we shall show how to evaluate localized polarizabilities within the LoProp scheme.

In the subsequent section we shall introduce the theoretical basis of the new localization scheme and the technique with which the localized polarizabilities are computed. Finally, results obtained with the new approach are presented.

II. THEORY AND IMPLEMENTATION

The primary subdivision of the space around the atoms in the molecule is deduced from the space of the occupied atomic orbitals of the individual centers. Hence, the only parameter which effects the localization scheme is the classification of the basis functions into “occupied” and “virtual” basis function. It is a requirement for this approach to

have any physical significance that the basis functions which are classified as occupied essentially are the atomic orbitals of each species.

The classification of the orbitals into occupied and virtual can be done in different ways. We have found it convenient to include in the occupied subspace all the doubly occupied and valence orbitals for each atom. The remaining orbitals will belong to the virtual subspace. This means that, for example, in a first row atom the $1s$, $2s$, and $2p$ orbitals are occupied and the remaining orbitals are virtual (more details about the basis sets will be given at the end of Sec. II B).

The localization is organized in four steps, each representing a transformation of the basis from the previous step. The starting point is the original atomic basis set and the procedure goes as follows:

(1) First strict orthonormality in each atomic block is obtained with a Gram-Schmidt orthonormalization or a Löwdin orthonormalization. Using a basis set like an atomic natural orbital (ANO) basis which formally is orthonormal the latter is used to remove any nonorthonormality due to the fact that the contraction coefficients in the basis set are not stored to full numerical representation. For basis sets, where the virtual basis functions are simply uncontracted basis functions an atomic Gram-Schmidt orthonormalization is recommended since it leaves the atomic subspace of the occupied basis functions intact. Since the two orthonormalization procedures have similar effects on an ANO basis set, we suggest that an atomic Gram-Schmidt orthonormalization should always be used.

(2) Two molecular Löwdin orthonormalizations follow, one of the occupied subspaces and one of the virtual subspaces. This step ensures that the basis in the occupied and virtual subspaces, respectively, are orthonormal with a minimal modification compared to the original atomic basis. Note that after this step the occupied and virtual subspaces are not yet orthogonal to each other.

(3) All components of the occupied subspace are projected out of the virtual subspace by a Gram-Schmidt orthonormalization. The occupied subspace is unaffected by this transformation. At this point one has an orthonormal occupied subspace and a virtual subspace, which are orthogonal one to each other.

(4) Finally the virtual subspace is orthonormalized by the Löwdin approach.

The localization procedure is pictorially described in Fig. 1, where the changes in character of the overlap matrix at each step of the transformation are represented.

The final result is a localized orthonormal basis set, the LoProp basis. Each step is a transformation of the basis set and the complete transformation (step 1–4) can be represented by a single transformation matrix (\mathbf{T}) which is the product of the transformation matrices of each individual step ($\mathbf{T}_1, \mathbf{T}_2, \mathbf{T}_3, \mathbf{T}_4$).

$$\mathbf{T} = \mathbf{T}_1 \mathbf{T}_2 \mathbf{T}_3 \mathbf{T}_4. \quad (1)$$

The LoProp diagonalization approach in many extents is similar to the NAO diagonalization procedure.¹² One fundamental difference, though, is that while the NAO diagonalization is applied to the one-particle density matrix, the LoProp procedure involves the diagonalization of the overlap matrix. This might at first inspection be a very subtle difference. However, while the spatial subdivision of the local domains in the NAO approach depends on the electronic configuration, the corresponding spatial subdivision in the LoProp is only, apart from the classification of the atomic orbitals into occupied and virtual, a function of the molecular geometry. This will imply, for example, that a charge analysis of a molecular system in various states can consistently be compared in the LoProp approach whereas the NAO charges do not have the consistency for such a comparison.

A. Localized static properties

A property, O , is evaluated as an expectation value by the expression

$$\langle O \rangle = \text{Tr}(\mathbf{D}\mathbf{O}) = \sum_{\mu\nu} D_{\mu\nu} \langle \mu | \hat{O} | \nu \rangle, \quad (2)$$

where \mathbf{D} is the one-electron density matrix, \mathbf{O} is the matrix with the integrals of the operator \hat{O} , and μ, ν run over the basis functions. Note that the expectation value is invariant to any transformation of the basis. In case of a nonvariational wave function, the one-electron density matrix is replaced with the effective variational one-electron density matrix.¹⁹

The localization of any property, which can be expressed as an expectation value, is now trivially performed by transforming the integrals of the property and one-electron density matrix to the LoProp basis and restricting the trace to the subspace of functions of a single center or the combination of two centers,

$$\langle O_{AB} \rangle = \sum_{\mu \in A, \nu \in B} D_{\mu\nu}^{\text{LoProp}} \langle \mu | \hat{O} | \nu \rangle^{\text{LoProp}}, \quad (3)$$

where A and B index the atoms. $A = B$ and $A \neq B$ correspond to an atom and a bond domain, respectively. Moreover,

$$\mathbf{D}^{\text{LoProp}} = \mathbf{T}^{-1} \mathbf{D} \mathbf{T} \quad (4)$$

and

$$\mathbf{O}^{\text{LoProp}} = \mathbf{T}^{-1} \mathbf{O} \mathbf{T}. \quad (5)$$

For the electronic charges we note that the overlap matrix in the LoProp basis will be diagonal. Hence, the localization scheme will by virtue of construction assign zero charge to the bond domains. We also note that higher order multipole moment operators are origin dependent and that a local origin should be used for these.

With these new localized multipole moments, the molecular potential expanded around a single point, \mathbf{R}_0 , (truncated after dipole moment terms)

$$V(\mathbf{r}) = \frac{q}{|\mathbf{r} - \mathbf{R}_0|} + \frac{\boldsymbol{\mu}_{\mathbf{R}_0} \cdot (\mathbf{r} - \mathbf{R}_0)}{|\mathbf{r} - \mathbf{R}_0|^3}, \quad (6)$$

where $\boldsymbol{\mu}_{\mathbf{R}_0}$ is the expectation value of the operator ($\mathbf{R} - \mathbf{R}_0$), is replaced with a localized multipole center expression

$$V(\mathbf{r}) = \sum_A \frac{q^{(AA)}}{|\mathbf{r} - \mathbf{R}^{(AA)}|} + \sum_{AB} \frac{\boldsymbol{\mu}_{\mathbf{R}^{(AB)}} \cdot (\mathbf{r} - \mathbf{R}^{(AB)})}{|\mathbf{r} - \mathbf{R}^{(AB)}|^3}, \quad (7)$$

where $q^{(AA)}$, $\boldsymbol{\mu}_{\mathbf{R}^{(AB)}}$, and $\mathbf{R}^{(AB)}$ [$\mathbf{R}^{(AA)}$] are the localized charges, dipole moments, and expansion centers, respectively. The localized expansion center is computed as $\mathbf{R}^{(AB)} = [\mathbf{R}^{(A)} + \mathbf{R}^{(B)}]/2$. To simplify the formulation let hereafter $\boldsymbol{\mu}^{(AB)}$ imply $\boldsymbol{\mu}_{\mathbf{R}^{(AB)}}$, $q^{(A)}$ imply $q^{(AA)}$, and $\mathbf{R}^{(A)}$ imply $\mathbf{R}^{(AA)}$.

B. Localized polarizabilities

The molecular polarizability $\alpha_{\kappa\lambda}$ is the second order derivative of the energy with respect to the electric field \mathbf{F} or the first order derivative of the dipole moment $\boldsymbol{\mu}$ with respect to the same electric field,

$$\alpha_{\kappa\lambda} = \frac{\partial^2 E}{\partial F_\kappa \partial F_\lambda} = \frac{\partial \boldsymbol{\mu}_\kappa}{\partial F_\lambda} = \frac{\partial \boldsymbol{\mu}_\lambda}{\partial F_\kappa} \quad (8)$$

(here the Greek indices κ, λ indicate the Cartesian axes x, y, z). To proceed we need to express the molecular dipole moment as a function of the localized charges and dipole moments,

$$\boldsymbol{\mu}_{\mathbf{R}_0} = \sum_{AB} \boldsymbol{\mu}^{(AB)} + \sum_A q^{(A)} [\mathbf{R}^{(A)} - \mathbf{R}_0] \quad (9)$$

note that the second summation due to the localization of the charges to only the atomic domains is reduced to a single summation. The molecular polarizability can now be expressed in terms of local responses as

$$\alpha_{\kappa\lambda} = \sum_{AB} \frac{\boldsymbol{\mu}_\kappa^{(AB)}(\mathbf{F} + \delta_\lambda) - \boldsymbol{\mu}_\kappa^{(AB)}(\mathbf{F} - \delta_\lambda)}{2\delta_\lambda} + \sum_A \frac{[q^{(A)}(\mathbf{F} + \delta_\lambda) - q^{(A)}(\mathbf{F} - \delta_\lambda)] [\mathbf{R}^{(A)} - \mathbf{R}_0]_\kappa}{2\delta_\lambda}, \quad (10)$$

where δ_λ is the perturbation in the field. Here we identify a natural decomposition of the polarizability into localized contributions. However, while the first term is clearly origin independent, the same is not true for the second term. Furthermore, since the localized charges in the bond domains are zero we would have no contribution to the localized polarizability in these domains, when the charge redistribution as an electric field is applied. This is a counterintuitive analysis which needs to be addressed. By adding and subtracting the charge at zero field we recast the charge terms to be associated with the change of the charge distribution

$$\sum_A \frac{[q^{(A)}(\mathbf{F} + \delta_\lambda) - q^{(A)}(\mathbf{F} - \delta_\lambda)][\mathbf{R}^{(A)} - \mathbf{R}_0]_\kappa}{2\delta_\lambda} \quad (11)$$

$$= \sum_A \frac{[\Delta q^{(A)}(\mathbf{F} + \delta_\lambda) - \Delta q^{(A)}(\mathbf{F} - \delta_\lambda)][\mathbf{R}^{(A)} - \mathbf{R}_0]_\kappa}{2\delta_\lambda}, \quad (12)$$

where $\Delta q^{(A)}$ is the charge change in atomic domain due to the applied field. To proceed in our analysis and partition of the molecular polarizability we define $\Delta Q^{(AB)}$ as the charge transfer from center A to B induced by the change of the electric field (note the permutational symmetry: $\Delta Q^{(AB)} = -\Delta Q^{(BA)}$). The charge transfer $\Delta Q^{(AB)}$ as a function of the change of the applied electric field is not uniquely defined. The sum of the $\Delta Q^{(AB)}$ s for a fixed A gives

$$\Delta q^{(A)}(\mathbf{F}) = \sum_{B \neq A} \Delta Q^{(AB)}(\mathbf{F}), \quad (13)$$

where

$$\Delta q^{(A)}(\mathbf{F}) = q^{(A)}(\mathbf{F}) - q^{(A)}(\mathbf{0}). \quad (14)$$

A reasonable requirement is that the $\Delta Q^{(AB)}$ s are designed to be as small as possible and that the charge transfer is short range. For this purpose we construct the Lagrangian

$$L = \sum_{AB} [\Delta Q^{(AB)}]^2 f(r_{AB}) + \sum_A \lambda_A \left(\sum_{B \neq A} \Delta Q^{(AB)} - \Delta q^{(A)} \right), \quad (15)$$

where $r_{AB} = |\mathbf{R}^{(A)} - \mathbf{R}^{(B)}|$ and $f(r_{AB})$ is a penalty function which gives the desired localized charge transfer. In our investigations we have worked with two penalty functions

$$f(r_{AB}) = r_{AB}^n, \quad (16)$$

where n is an integer and

$$f(r_{AB}) = \exp\left(\alpha \left[\frac{r_{AB}}{r_A^{\text{BS}} + r_B^{\text{BS}}} \right]^2\right), \quad (17)$$

where α is a constant and r^{BS} is the Bragg-Slater radius of the respective atoms.

The Lagrangian leads to the equation system

$$\mathbf{L}\lambda = \Delta\mathbf{q}, \quad (18)$$

where the matrix elements of \mathbf{L} are computed as

$$L_{AB} = \frac{1}{2f(r_{AB})} + C \quad (19)$$

and

$$L_{AA} = -\sum_{B \neq A} \frac{1}{2f(r_{AB})} + C. \quad (20)$$

C is an arbitrary constant which is added to shift the eigenvector corresponding to

$$\sum_A \Delta q^{(A)} = 0. \quad (21)$$

The equation system is now trivially solved by computing the inverse of the \mathbf{L} matrix and the $\Delta Q^{(AB)}$ are computed as

$$\Delta Q^{(AB)} = -\frac{\lambda_A - \lambda_B}{2f(r_{AB})}. \quad (22)$$

We can now write

$$\begin{aligned} \sum_A \frac{\{\Delta q^{(A)}[\mathbf{F} + \delta_\lambda] - \Delta q^{(A)}[\mathbf{F} - \delta_\lambda]\}[\mathbf{R}^{(A)} - \mathbf{R}_0]_\kappa}{2\delta_\lambda} &= \sum_{A, B \neq A} \frac{\{\Delta Q^{(AB)}[\mathbf{F} + \delta_\lambda] - \Delta Q^{(AB)}[\mathbf{F} - \delta_\lambda]\}[\mathbf{R}^{(A)} - \mathbf{R}_0]_\kappa}{2\delta_\lambda} \\ &= \sum_{A > B} \frac{\{\Delta Q^{(AB)}[\mathbf{F} + \delta_\lambda] - \Delta Q^{(AB)}[\mathbf{F} - \delta_\lambda]\}[\mathbf{R}^{(A)} - \mathbf{R}^{(B)}]_\kappa}{2\delta_\lambda}, \end{aligned} \quad (23)$$

which is explicitly origin independent. Finally the localized polarizability reads as

$$\begin{aligned} \alpha_{\kappa\lambda}^{(AB)} &= \frac{\mu_\kappa^{(AB)}[\mathbf{F} + \delta_\lambda] - \mu_\kappa^{(AB)}[\mathbf{F} - \delta_\lambda]}{2\delta_\lambda} \\ &+ \frac{\{\Delta Q^{(AB)}[\mathbf{F} + \delta_\lambda] - \Delta Q^{(AB)}[\mathbf{F} - \delta_\lambda]\}[\mathbf{R}^{(A)} - \mathbf{R}^{(B)}]_\kappa}{2\delta_\lambda}. \end{aligned} \quad (24)$$

The LoProp scheme has been implemented in the software MOLCAS 6.0.^{20,21}

Test calculations have been performed on the water molecule at the Hartree-Fock SCF (HF-SCF) level in conjunction with various basis sets. The basis sets include the generally contracted basis sets of atomic natural orbital ANO

type of the MOLCAS library;^{22,23} the split valence basis sets of 6-31g type, plus polarization functions,²⁴ and the Dunning correlation consistent polarized valence ζ basis sets, cc-pVnZ.²⁵ The basis sets are generically labeled as B1–B4 to indicate the increasing dimension of each type of basis set. The B1–B4 ANO series includes basis sets contracted to 2s1p, 3s2p1d, 4s3p2d1f, 5s4p3d2f1g for oxygen and 1s, 2s1p, 3s2p1d, 4s3p2d1f for hydrogen, respectively. The B1–B4 6-31g series comprises a 3-21g, 6-31g, 6-31g*, 6-31g** basis set, respectively. The B1–B4 cc-pVnZ series comprises a cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis set, respectively.

The ANO basis sets are built as atomic orbitals and can be directly used in the localization scheme, while the basis sets of 6-31g type and the cc-pVnZ basis sets need to be

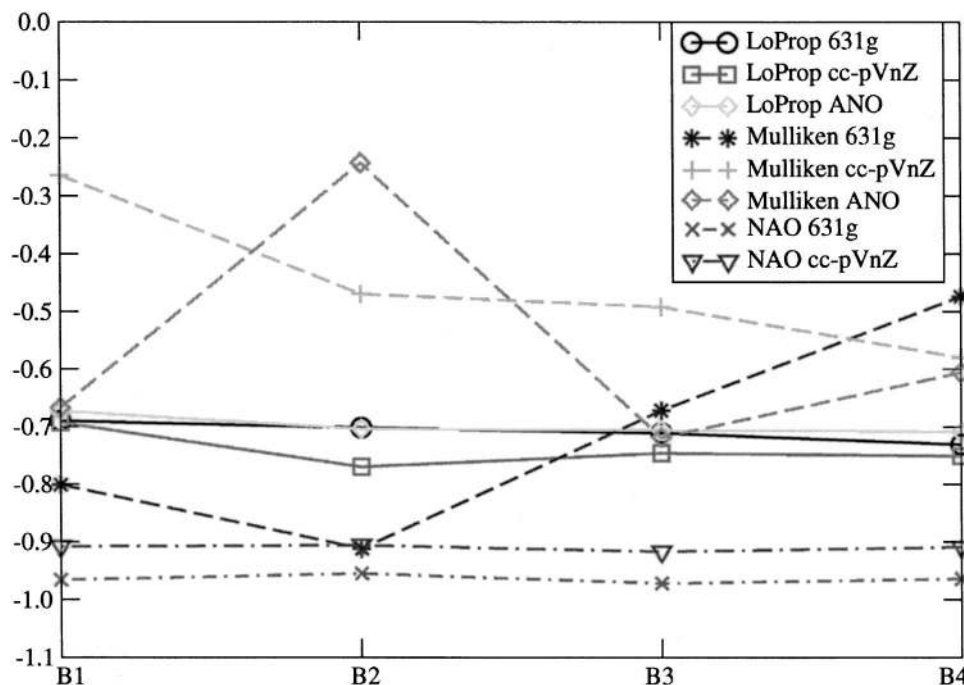


FIG. 2. The oxygen total charge in water computed with different basis set, using the LoProp, Mulliken and NAO partitioning schemes. The indexes $B1$ to $B4$ generically indicate an increasing basis set of a given type. For the specific meaning of $B1$ – $B4$ see the end of Sec. II.

recontracted in order to explicitly express the occupied space. This recontraction has been done by computing the HF-SCF occupied atomic orbitals and adding to the occupied orbitals the virtual orbitals in such a way that the new basis sets span the same space as the original basis sets.

The water calculations also included evaluation of charges according to the Mulliken and NAO analysis.

A series of molecules previously explored by Lazzeretti and co-workers¹¹ has been studied. This comprises the ethane (eclipsed and staggered), propane, and butane molecules. Local charges, dipole moments, and polarizabilities have been computed at the B3LYP/DFT level of theory, using two ANO basis sets contracted as $(C,3s2p1d;H,2s1p)$ and $(C,4s3p2d1f;H,3s2p1d)$, respectively. Localized properties have also been computed for benzene, naphthalene, and anthracene at the HF level of theory using an ANO basis set contracted as $(C,3s2p1d;H,2s1p)$.

III. RESULTS

The results presented here will demonstrate that the LoProp scheme gives localized properties which converge with the basis set size, that the localized and total computed charges and dipole moments are physically meaningful, and that the localized properties and polarizabilities are transferable from a molecular system to another.

The basis set convergence of the LoProp scheme has been tested by computing charges, dipole moments, and polarizabilities of water. In Fig. 2 the oxygen charge in water obtained with the LoProp, Mulliken, and NAO analysis using the three different basis sets are reported. It is evident that the LoProp and NAO localized charges are less dependent on the basis set than the Mulliken charges. Here we would again like to point out that the NAO localization de-

pends on the wave function, and will not allow for comparison of properties of the same molecule in different electronic states. In addition, the NAO partitioning under intermolecular rearrangement will not only be a function of the geometry but also of the character of the wave function at this particular structure. As an example imagine the possibly large change of the NAO analysis as a molecular system passes through an avoided crossing. The LoProp analysis, on the other hand, is only a function of the structure. We believe that this will be of importance when we later on will try to demonstrate transferability of the LoProp parameters.

In Table I, the localized charges, dipole moments, and polarizabilities of water as a function of the size of ANO-type basis sets are reported. As expected, the charges and dipole moments converge more rapidly with the basis set, than the polarizabilities.

To demonstrate the transferability of the localized properties, results of a series of calculations on alkanes are presented. The ethane molecule in the eclipsed and staggered conformation has been investigated. In Table II the localized properties for the two structures computed at the B3LYP level with two different basis set are presented. The LoProp parameters of the terminal methyl groups in propane and butane are reported in Table III. The geometries for ethane, propane, and butane are those reported in Tables IV, V, VI, and VII in the paper by Lazzeretti and co-workers.¹¹ The transferability of the methyl LoProp parameters is demonstrated between propane, butane, and the two different forms of ethane. This result is different with respect to the result obtained by Lazzeretti and co-workers,¹¹ who concluded that their so-called “pair polarizabilities” did not have a fully satisfactory degree of transferability. The transferability of LoProp parameters of functional groups is promising with

TABLE I. Water^a LoProp/HF charges, dipole moments, and polarizabilities for different contractions of the ANO basis set.

O Basis	2s1p	3s2p1d	4s3p2d1f	5s4p3d2f1g
H Basis	1s	2s1p	3s2p1d	4s3p2d1f
q_O	-0.560	-0.698	-0.709	-0.711
q_H	+0.280	+0.349	+0.354	+0.356
$\mu_x O$	0.000	0.000	0.000	0.000
$\mu_x H$	± 0.164	± 0.060	± 0.088	± 0.086
$\mu_x OH$	± 0.141	± 0.191	± 0.118	± 0.115
$\mu_x Tot.$	0.000	0.000	0.000	0.000
$\mu_y O$	-0.695	-0.445	-0.394	-0.436
$\mu_y H$	0.092	0.046	0.067	0.063
$\mu_y OH$	0.120	0.157	0.123	0.149
$\mu_y Tot.$	-0.804	-0.706	-0.706	-0.707
$\alpha_{xx} O$	-0.222	1.026	1.842	1.799
$\alpha_{xx} H$	0.329	0.378	0.470	0.440
$\alpha_{xx} OH$	2.689	2.541	2.827	2.887
$\alpha_{xx} Tot.$	5.813	6.848	8.417	8.449
$\alpha_{yy} O$	-0.116	1.459	2.996	2.761
$\alpha_{yy} H$	0.077	0.376	0.387	0.360
$\alpha_{yy} OH$	1.005	1.972	2.004	2.143
$\alpha_{yy} Tot.$	2.057	6.159	7.806	7.828
$\alpha_{zz} O$	-0.172	1.727	3.774	3.440
$\alpha_{zz} H$	0.000	0.396	0.363	0.336
$\alpha_{zz} OH$	0.125	1.602	1.568	1.753
$\alpha_{zz} Tot.$	0.077	5.642	7.597	7.651

^aThe coordinates in a.u. are O, (0.0000 0.0000 0.0000); H, (1.4335 -0.9529 0.0000).

respect to the possibility of creating polarizable potentials for molecular mechanics based on LoProp parameters. Tables II and III indicate that the LoProp charges converge faster with increasing basis set than the polarizabilities, as already pointed out for water (Table I). A qualitative comparison between the LoProp and the Lazzeretti and co-workers

TABLE II. Ethane^a (eclipsed and staggered) LoProp/B3LYP atomic charges, magnitude of the dipole moments, and average polarizabilities for two different contractions of the ANO basis set.

C Basis	3s2p1d	3s2p1d	4s3p2d1f	4s3p2d1f	
H Basis	2s1p	2s1p	3s2p1d	3s2p1d	
	Eclipsed	Staggered	Eclipsed	Staggered	Expt.
q_C	-0.388	-0.382	-0.385	-0.379	
q_H	+0.129	+0.127	+0.128	+0.126	
$ \mu _C$	0.049	0.047	0.089	0.083	
$ \mu _{C_1C_2}$	0.000	0.000	0.000	0.000	
$ \mu _H$	0.115	0.115	0.159	0.159	
$ \mu _{C_1H_1}$	0.410	0.408	0.374	0.376	
$\bar{\alpha}_C$	1.138	1.056	1.382	1.352	
$\bar{\alpha}_{C_1C_2}$	3.957	4.167	4.279	4.309	
$\bar{\alpha}_H$	0.720	0.734	0.793	0.793	
$\bar{\alpha}_{C_1H_1}$	2.456	2.476	2.834	2.880	
$\bar{\alpha}_{H_1H_3}$	-0.040	-0.037	-0.013	-0.015	
$\bar{\alpha}_{H_1H_2}$	-0.003	0.060	0.028	0.008	
$\bar{\alpha}_{C_1H_2}$	-0.063	-0.081	-0.006	0.015	
$\bar{\alpha}$			28.873	29.109	30.20 ^b

^aThe coordinates and labeling as in Tables IV and V of Ref. 11.

^bReference 26.

TABLE III. Terminal methyl group in propane^a and butane^b: LoProp/B3LYP atomic charges, magnitude of the dipole moments, and average polarizabilities for two different contractions of the ANO basis set. H₁ and H₂ are bound to C₁ and H₁ is in the plane of symmetry. C₁ is the methyl carbon and C₂ is the methylene carbon.

C Basis	3s2p1d	3s2p1d	4s3p2d1f	4s3p2d1f
H Basis	2s1p	2s1p	3s2p1d	3s2p1d
	Propane	Butane	Propane	Butane
q_{C_1}	-0.392	-0.390	-0.389	-0.387
q_{H_1}	+0.131	+0.131	+0.131	+0.131
q_{H_2}	+0.126	+0.124	+0.122	+0.123
$ \mu _{C_1}$	0.055	0.062	0.106	0.117
$ \mu _{C_1C_2}$	0.029	0.036	0.061	0.076
$ \mu _{C_1H_1}$	0.402	0.403	0.360	0.360
$ \mu _{C_1H_2}$	0.408	0.408	0.379	0.380
$ \mu _{H_1}$	0.114	0.114	0.162	0.162
$ \mu _{H_2}$	0.117	0.117	0.161	0.161
$ \mu _{H_1H_2}$	0.001	0.001	0.010	0.010
$ \mu _{H_2H_2'}$	0.001	0.001	0.009	0.008
$\bar{\alpha}_{C_1}$	1.145	1.163	1.318	1.319
$\bar{\alpha}_{C_1C_2}$	4.111	4.351	4.254	4.484
$\bar{\alpha}_{C_1H_1}$	2.596	2.630	3.034	3.062
$\bar{\alpha}_{C_1H_2}$	2.392	2.382	2.769	2.761
$\bar{\alpha}_{H_1}$	0.753	0.761	0.795	0.799
$\bar{\alpha}_{H_2}$	0.733	0.736	0.761	0.758
$\bar{\alpha}_{H_1H_2}$	-0.033	-0.033	-0.002	-0.002
$\bar{\alpha}_{H_2H_2'}$	-0.036	-0.036	-0.015	-0.014
$\bar{\alpha}$			41.258	53.591
$\bar{\alpha} Expt.^c$			42.26	54.82

^aThe coordinates and labeling as in Table VI of Ref. 11.

^bThe coordinates and labeling as in Table VII of Ref. 11.

^cReference 26.

scheme¹¹ shows that while LoProp assigns most of the polarizability contribution to the bond rather than to the atoms, the opposite occurs in the Lazzeretti and co-workers scheme. It is also noticed that while the Lazzeretti and co-workers localization assigns pair polarizabilities of similar order of magnitude to bonding and nonbonding pairs of atoms, the LoProp pair values for bonding and nonbonding pairs differ by several orders of magnitude, reflecting the physics of the bonds.

The transferability issue has also been studied in the benzene, naphthalene, and anthracene series of aromatic molecules. Localized charges, dipole moments, and polarizabilities have been determined at the HF level of theory, for structures optimized at the same level of theory. The atom

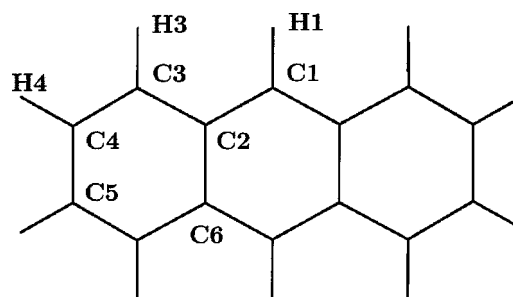


FIG. 3. The structure of anthracene with the atom numbering used in Table IV. The same atom numbering holds for naphthalene and benzene.

TABLE IV. Anthracene, naphthalene, and benzene LoProp/HF atomic charges, magnitude of the dipole moments and average polarizabilities with ANO basis set.

	q			$ \mu $			$\bar{\alpha}$		
	Anthra.	Naphta.	Benz.	Anthra.	Naphta.	Benz.	Anthra.	Naphta.	Benz.
C1	-0.13	-0.12		0.14	0.14		1.31	1.35	
C2	0.00	0.00		0.01	0.01		0.64	0.68	
C3	-0.12	-0.12		0.19	0.14		1.35	1.35	
C4	-0.13	-0.13	-0.14	0.14	0.14	0.13	1.48	1.48	1.39
H1	+0.12	+0.12		0.11	0.11		0.65	0.67	
H3	+0.12	+0.12		0.11	0.11		0.67	0.67	
H4	+0.13	+0.13	+0.14	0.11	0.10	0.10	0.75	0.72	0.68
	$ \mu $			$\bar{\alpha}$					
	Anthra.	Naphta.	Benz.	Anthra.	Naphta.	Benz.			
C1C2	0.03			8.67					
C2C6	0.00	0.00	0.00	4.47	4.47	5.64			
C2C3	0.04	0.01		7.26	6.44				
C3C4	0.01	0.01		8.32	7.17				
C4C5	0.02	0.01		4.85	5.15				
C1H1	0.28			2.43					
C3H3	0.28	0.28		2.52	2.55				
C4H4	0.28	0.28	0.28	3.15	2.94	2.69			

numbering is reported in Fig. 3. Only the atoms which are unique for symmetry or form unique bonds are numbered. Inspection of Table IV shows that all quantities are transferable along the aromatic series for both atomic centers and bonds.

IV. CONCLUSIONS

A new method, LoProp, which makes it possible to partition properties like dipole moments and polarizabilities into atomic and interatomic contributions, has been presented. The method is simple, easy to implement and computationally inexpensive. The extension of the method to compute higher-rank multipoles and polarizabilities is already in progress. The localized properties have the same convergence behavior as the corresponding molecular properties with the basis sets. Transferability of the methyl properties in the alkane series and also of the C, H, CC, CH properties in the benzene, naphthalene, and anthracene series is demonstrated. This is promising since it suggests that it might be possible to generate data base for localized quantities like charges, multipole moments, and polarizabilities and use them to create accurate force fields.

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