Canadian Journal of Chemistry
Revue canadienne de chimie

Using the Centre-of-Mass of Localized Electron Pairs to Quantify Electronegativity

Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2016-0291.R1
Manuscript Type:	Article
Date Submitted by the Author:	18-Jul-2016
Complete List of Authors:	Proud, Adam; University of Prince Edward Island, Chemistry Pearson, Jason; University of Prince Edward Island, Chemistry
Keyword:	electronegativity, electron pair density, extracule, computational chemistry, topology

Using the Centre-of-Mass of Localized Electron Pairs to Quantify Electronegativity

Adam J. Proud and Jason K. Pearson

*Department of Chemistry, University of Prince Edward Island,
550 University Avenue, Charlottetown, PE, C1A 4P3**

Localized electron pair densities are explored with the purpose of developing a relationship between properties of the electron pair centre-of-mass and atomic electronegativities. These electron pair centre-of-mass densities are determined for the localized molecular orbital representing the A–H bond in a compound AH_n (where $n = 1 - 3$) for each of the first and second row atoms with available valence sites. By analyzing the topography of these densities, we observe the migration of the electron pair as the *electronegativity* of atom A changes. We demonstrate strong linear correlations between features of these centre-of-mass densities and various empirically-based electronegativity scales, all of which are defined in significantly different ways. Based on strong agreement with past electronegativity scales, we propose the use of localized electron pair centre-of-mass densities as a simple and intuitive theoretical model for electronegativity. We have thus presented herein our own electronegativity scale, employing Pauling units as is common amongst many existing scales.

Keywords: electronegativity, electron pair density, extracule, computational chemistry, topology.

I. INTRODUCTION

Electronegativity is an important chemical property that is used to explain many periodic trends from polarity and partial charges to atomic size. Understanding electronegativity is paramount in organic chemistry to understand the electrophilic/nucleophilic regions which help guide synthetic procedures. The development of the concept of electronegativity is commonly attributed to Pauling; however, the idea has been discussed since the late 18th century.[1, 2] Regardless, Pauling was the first to quantify the property and his electronegativity scale is still in common use today.[3, 4] Pauling's definition of electronegativity, χ , was based on differences in bond dissociation energies (E_d) of two homonuclear diatomics, A–A and B–B, compared to that of the heteronuclear diatomic, A–B. This was expressed mathematically as

$$\chi_A - \chi_B = \frac{1}{\sqrt{eV}} \sqrt{E_d^{AB} - \frac{1}{2}[E_d^{AA} + E_d^{BB}]} \quad (1)$$

where the dissociation energies are expressed in terms of electron volts (eV). Since this initial quantification of electronegativity, there have been numerous different scales developed in an attempt to accurately quantify this highly useful property.[5–15] These scales are based on various physical properties including bond force constants[7], effective nuclear charge/covalent radii[6, 10], ionization potentials/electron affinities[5], etc. Aside from these empirical approaches, Simons et al. developed the first purely theoretical approach to quantifying electronegativity.[16] This model was based on the positions of floating spherical Gaussian orbitals. However, Boyd and coworkers were the first to develop a theory for quantifying electronegativity based on the topology of the electron density, $\rho(\mathbf{r})$, despite the obvious relationship between the two properties.[17, 18] Their work

revealed a power series relationship between the Pauling electronegativity of atom or group A (when bonded to H, thereby forming the system A–H) and a parameter, the electronegativity factor, F_A , which they define as

$$F_A = \frac{r_H}{N_A \rho(\mathbf{r}_c) r_{AH}} \quad (2)$$

Herein, $\mathbf{r}_c$ is the position of bond critical point of the A–H bond, r_{AH} is the bond length, r_H is the distance between the bond critical point and the hydrogen atom, and N_A is the number of valence electrons associated with atom/group A. While this form of analysis worked quite well for both atomic and group electronegativities, it is a rather complicated relationship. A more simple and intuitive approach would be ideal. Boyd recently stated the need for a more rigorous theoretical basis for electronegativity, noting that the most likely avenue for this basis would be through a topological/topographical approach.[19]

One way to approach this is to examine the distribution of localized electron *pairs* within different chemical systems. The localized pair model (LPM), which was previously developed in our laboratory, accomplishes this goal.[20–22] The LPM was developed specifically to analyze electron pair behaviour within covalent bonds and lone pairs and we are just beginning to demonstrate the wide range of applications of such an approach. These chemically intuitive features are represented mathematically by doubly-occupied localized molecular orbitals (LMOs).[23–28] In the past, we have used the model to demonstrate strong correlations between localized electron pair distributions and both bond dissociation energies[20] and acid dissociation constants,[21] even at the Hartree-Fock level of theory.

In considering a LPM approach, one way to observe the migration of electrons as a result of electronegativity differences is through the localized extracule density, $E(R)$. This can be obtained from the wavefunction, Ψ , by

$$E(R) = \langle \Psi | \delta(R - \frac{|\mathbf{r}_1 + \mathbf{r}_2|}{2}) | \Psi \rangle \quad (3)$$

*jpearson@upei.ca

where $\delta(x)$ is the one-dimensional Dirac delta function, and r_i is the position vector of electron i . The extracule density describes the probability that the centre-of-mass of an electron pair would be at a specific distance from a given origin.[29–32] Thus, these localized extracules can model the change in position of the electron pair centre-of-mass as a function of the two atoms involved in the bond, thereby providing a measure of the tendency for each atom to attract a *specific* electron pair to itself. For the purposes of this study, hydrogen was bonded to the atom of interest (as it is considered to be neither electron donating, nor electron withdrawing), thereby forming the system A–H, and representing a unique way of quantifying the electronegativity of atom A. The systems of interest in this study are those where A is any first or second row atom that has open valence sites.

While the main goal is not to exactly match existing electronegativity scales, considering that most existing scales agree well with one another, strong correlations to existing models would provide evidence for the validity of this model. Perfect agreement with existing models is not necessary however, as existing models do not even perfectly agree with one another. Considering so many different models have been developed, this points to the absence of a fundamentally strong definition of electronegativity. The model presented herein represents a very simple, yet intuitive model of electronegativity as it explores the distribution of electron *pair* distributions within a single chemical bond. This method has the potential to define electronegativity using a purely theoretical approach.

II. COMPUTATIONAL METHODS

The extracule densities for the systems involved in this study were calculated using a modified version of the recurrence relation developed by Hollett and Gill for position intracules, which model the probability of interelectronic separation distances.[33] Before we can describe the recurrence relation, we must first introduce a few variables. The recurrence relation is developed for a set of Gaussian functions where a Gaussian primitive, $\mathbf{a}$, with exponent α , is given by

$$|\mathbf{a}\rangle = (x - A_x)^{a_x} (y - A_y)^{a_y} (z - A_z)^{a_z} e^{-\alpha|\mathbf{r}-\mathbf{A}|^2} \quad (4)$$

where the angular momentum of $\mathbf{a} = (a_x, a_y, a_z)$ and the function is centred on $\mathbf{A} = (A_x, A_y, A_z)$. Likewise, the Gaussian primitives, $\mathbf{b}$, $\mathbf{c}$, and $\mathbf{d}$ are centred at $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{D}$ with exponents β , γ , and δ , respectively. Using these Gaussian type orbitals, we can define the following

variables:

$$\nu^2 = \frac{(\alpha + \beta)(\gamma + \delta)}{\alpha + \beta + \gamma + \delta} \quad (5)$$

$$\mathbf{U} = \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha + \beta} + \frac{\gamma\mathbf{C} + \delta\mathbf{D}}{\gamma + \delta} \quad (6)$$

$$S_{ab} = \text{Exp} \left[-\frac{\alpha\beta|\mathbf{A} - \mathbf{B}|^2}{\alpha + \beta} - \frac{\gamma\delta|\mathbf{C} - \mathbf{D}|^2}{\gamma + \delta} \right] \quad (7)$$

The fundamental integral for the scalar extracule density is given by,

$$[0000]^{(l)} = \frac{32\pi^{5/2}R^2 e^{-4\nu^2 R^2} S_{ab}}{(\alpha + \beta + \gamma + \delta)^{3/2}} \times \left(\frac{\partial}{\partial \mathbf{U}^2} \right)^l [e^{-\nu^2 U^2} i_0(4\nu^2 UR)] \quad (8)$$

where $i_0(x)$ is the modified spherical Bessel function of the first kind defined as $i_0(x) = \sinh(x)/x$.

From this fundamental integral, integrals containing Gaussian primitives of arbitrary angular momentum can be determined from the modified version of the 8-term recurrence relation of Hollett and Gill that is given by:

$$\begin{aligned} [(\mathbf{a} + \mathbf{1}_i)\mathbf{bcd}]^{(l)} &= \frac{\beta(B_i - A_i)}{\alpha + \beta} [\mathbf{abcd}]^{(l)} + \frac{U_i}{\alpha + \beta} [\mathbf{abcd}]^{(l+1)} \\ &+ \frac{a_i}{2(\alpha + \beta)} [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]^{(l)} \\ &+ \frac{a_i}{2(\alpha + \beta)^2} [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]^{(l+1)} \\ &+ \frac{b_i}{2(\alpha + \beta)} [\mathbf{a}(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]^{(l)} \\ &+ \frac{b_i}{2(\alpha + \beta)^2} [\mathbf{a}(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]^{(l+1)} \\ &- \frac{c_i}{2(\alpha + \beta)(\gamma + \delta)} [\mathbf{ab}(\mathbf{c} - \mathbf{1}_i)\mathbf{d}]^{(l+1)} \\ &- \frac{d_i}{2(\alpha + \beta)(\gamma + \delta)} [\mathbf{abc}(\mathbf{d} - \mathbf{1}_i)]^{(l+1)} \end{aligned} \quad (9)$$

which describes how to obtain the integral for augmenting the angular momentum of the i^{th} coordinate ($i = x, y$, or z) by one ($\mathbf{1}_i$).

Two metrics describing the location of the electron pair centre-of-mass, R , were chosen for the purposes of this study. They are the position of the maximum of the extracule density, R^{max} , and the average value of R , $\langle R \rangle$, which is defined as

$$\langle R \rangle = \int_0^\infty R \times E(R) dR \quad (10)$$

As defined, these metrics can be problematic as they are bond length dependent. Thus, for comparative purposes, they were determined as a fraction of the bond length and are denoted $R_{\%}^{\text{max}}$ and $\langle R \rangle_{\%}$. Since both metrics are determined as a ratio with respect to the bond

FIG. 1: Localized extracule densities for the A–H bond in saturated a) first row hydrides, and b) second row hydrides with insets of the A–H bond LMO of F–H and Cl–H for illustrative purposes.

length, all quantities expressed throughout are unitless. All chemical systems were optimized at the Restricted Hartree-Fock level of theory (ROHF for radicals) with a u6-311G(d,p) basis set where the u indicates that the basis set was completely uncontracted. Results using said basis set were adequately converged for the purposes of this study. Molecular orbitals were localized using the Edmiston-Ruedenberg localization scheme[24] that is incorporated within the GAMESS software package.[34] It should be noted that the localized pair model is applicable to any single-determinant method, and thus, one could just as easily use Kohn-Sham orbitals to assess the effects of correlation on electronegativity. Regardless, herein, we will demonstrate that we can obtain strong correlations to existing models of electronegativity even at the HF level.

III. RESULTS AND DISCUSSION

Extracule densities were determined for the A–H bond in each of the saturated first and second row hydrides. Each geometry was optimized and the extracule was determined for the bond LMO describing said bond. The extracules for these hydrides are shown in Figures 1 a) and b). As expected, as we move across the periodic table from left to right, the electron pair centre-of-mass contracts towards the heavy atom (i.e. $R = 0$) due to the increase in electronegativity. This is clearly demonstrated in the two aforementioned metrics (average R and $R_{\max}$) which are tabulated below in Table I.

A second set of calculations were carried out on a set of truncated hydrides (i.e. the full molecular system was A–H). The remaining valence sites were left empty and the multiplicity was adjusted accordingly (i.e. singlet or doublet for systems with an even or odd number of remaining valence electrons, respectively). This set of truncated hydrides was analyzed in order to determine

what effect, if any, the presence of additional hydrogen atoms had on the extracule density of the A–H bond LMO, thereby differentiating between group and atomic electronegativities where the “group” consists solely of H substituents on the heavy atom of interest.

Five separate electronegativity scales were chosen for comparison in this study. They are the Sanderson scale (I)[9], the Pauling Scale (II)[3], the Allred-Rochow scale (III)[10], the Allen Scale (IV)[15], and the Mulliken relation (V)[5]. These particular scales were chosen to cover a wide range of varying definitions for electronegativity. As previously noted, Pauling’s scale was based on the dis-

TABLE I: Metrics of $E(R)$ for the A–H bond LMO in saturated hydrides.

System	$R_{\%}^{\max}$	$\langle R \rangle_{\%}$	χ of atom A				
			I	II	III	IV	V
LiH	0.977	0.978	0.886	0.980	0.970	0.912	0.970
BeH ₂	0.895	0.873	1.810	1.570	1.470	1.576	1.540
BH ₃	0.835	0.805	2.275	2.040	2.010	2.051	2.040
CH ₄	0.745	0.732	2.746	2.550	2.500	2.544	2.480
NH ₃	0.450	0.664	3.194	3.040	3.070	3.066	3.040
OH ₂	0.378	0.607	3.654	3.440	3.500	3.610	3.680
FH	0.322	0.537	4.000	3.980	4.100	4.193	4.300
NaH	0.984	0.968	0.835	0.930	1.010	0.869	0.910
MgH ₂	0.943	0.909	1.318	1.310	1.230	1.293	1.370
AlH ₃	0.912	0.880	1.714	1.610	1.470	1.613	1.710
SiH ₄	0.882	0.833	2.138	1.900	1.740	1.916	2.280
PH ₃	0.842	0.772	2.515	2.190	2.060	2.253	2.410
SH ₂	0.790	0.712	2.957	2.580	2.440	2.589	2.860
ClH	0.723	0.653	3.475	3.160	2.830	2.869	3.340
$R^2 : R_{\%}^{\max}$	---	---	0.775	0.853	0.914	0.888	0.810
$R^2 : \langle R \rangle_{\%}$	---	---	0.992	0.993	0.973	0.981	0.975

FIG. 2: Correlation between Pauling electronegativities and a) $\langle R \rangle_{\%}$, and b) $R_{\%}^{\text{max}}$ for the first and second row hydrides.

sociation energies of homo and heteronuclear diatomics. Alternatively, Sanderson utilized a measure of compactness of an atom while the Allred-Rochow method related electronegativity to effective nuclear charge and covalent radius. The Allen Scale is based on configuration energies, which were defined as the average one-electron energy of a valence-shell electron in a single atom whereas Mulliken defined it simply as the arithmetic mean of the ionization potential and the electron affinity.

As previously noted, one might expect that the centre-of-mass of the electron pair within a bond LMO would provide an indication of electronegativity. Thus, using the two aforementioned metrics, correlations between each of the given scales and the two metrics were performed. The data for both the saturated and truncated hydrides are presented in Tables I and II, respectively.

For both the saturated and truncated molecular systems, $R_{\%}^{\text{max}}$ did not exhibit strong correlations with established electronegativity values, as is evident based on the coefficients of determination (R^2) being as low as 0.775. Visual evidence for this is provided in Figure 1 a) which depicts the relationship between Pauling electronegativities, χ_{Pauling} and $R_{\%}^{\text{max}}$. This graph clearly demonstrates the presence of three outliers which represent the F–H, O–H, and N–H bonds. These outliers are present for all 5 electronegativity scales and are the major factor for the poor relationships. Upon the removal of these outliers from the dataset, the R^2 value for the relationship with χ_{Pauling} improved from 0.853 to 0.965, along with substantial improvements in the fits for the other four scales.

As the average value of R is more indicative of the full distribution than simply the maximum, one might expect that the relationship between this property and electronegativities would be better. This is strongly supported by the data as when considering $\langle R \rangle_{\%}$, the correlation between the two properties increased significantly

and the F–H, O–H, and N–H bonds were no longer outliers. For this metric, the R^2 values ranged from 0.969–0.993, with the relationship for χ_{Pauling} depicted in Figure 2 b). As evidenced by this plot, there are no points within the dataset that deviate significantly from the linear relationship.

What is more enlightening is to look at the differences between the metrics for the saturated and truncated hydrides. While systems with formulae A–H and A–H₂ are obviously very similar between these two sets, molecules with more valence sites begin to differ significantly in terms of our two metrics. This suggests that this method

TABLE II: Metrics of $E(R)$ for the A–H bond LMO in truncated hydrides.

System	$R_{\%}^{\text{max}}$	$\langle R \rangle_{\%}$	χ of atom A				
			I	II	III	IV	V
LiH	0.977	0.978	0.886	0.980	0.970	0.912	0.970
BeH	0.896	0.885	1.810	1.570	1.470	1.576	1.540
BH	0.826	0.795	2.275	2.040	2.010	2.051	2.040
CH	0.734	0.717	2.746	2.550	2.500	2.544	2.480
NH	0.434	0.656	3.194	3.040	3.070	3.066	3.040
OH	0.373	0.604	3.654	3.440	3.500	3.610	3.680
FH	0.336	0.552	4.000	3.980	4.100	4.193	4.300
NaH	0.984	0.968	0.835	0.930	1.010	0.869	0.910
MgH	0.935	0.898	1.318	1.310	1.230	1.293	1.370
AlH	0.924	0.890	1.714	1.610	1.470	1.613	1.710
SiH	0.878	0.828	2.138	1.900	1.740	1.916	2.280
PH	0.834	0.766	2.515	2.190	2.060	2.253	2.410
SH	0.786	0.708	2.957	2.580	2.440	2.589	2.860
ClH	0.723	0.653	3.475	3.160	2.830	2.869	3.340
$R^2 : R_{\%}^{\text{max}}$	---	---	0.776	0.851	0.913	0.886	0.809
$R^2 : \langle R \rangle_{\%}$	---	---	0.989	0.987	0.968	0.975	0.969

would be highly useful for defining group electronegativities, and based on the strong correlations with current electronegativity scales, the accuracy of such an approach is expected to be quite high. One might be surprised that better correlations were obtained for the saturated molecular systems as opposed to the truncated hydrides despite the presence of additional hydrogen atoms that could distort the extracule density. However, as hydrogen atoms are considered as the reference for electron-donating versus electron withdrawing, they would be expected to have minimal effects on the extracule density. They simply serve to saturate all valence sites on the heavy atom. Furthermore, the presence of radicals and or paired electrons that would otherwise be involved in bonding interactions is surely to introduce some error into the modelling of the systems. Thus, we propose that saturating all valence sites of atom A with hydrogen atoms is a more accurate way to model the electronegativity for said atom. Conversely, if one were to substitute the hydrogen substituents with other functional groups, one could easily extend this method to determine electronegativities for that full chemical group (e.g. $-\text{CH}_3$ vs $-\text{CH}_2\text{OH}$ or $-\text{CH}_2\text{F}$).

In comparison to the Boyd method, which had a correlation coefficient of 0.991 (for χ_{Pauling}) using the power series relationship between χ_A and F_A , the LPM approach works extremely well ($R^2 = 0.993$). Considering its simplicity, as one only need consider the average distance of the electron pair centre-of-mass from the atom of interest, this model is a simple, intuitive, and accurate approach to quantifying, perhaps even defining, electronegativity from a purely theoretical standpoint.

As the Pauling scale is so popular, many other electronegativity methods are modified to conform to the values of this scale. This is often done by scaling the electronegativity values of the new method to fit within the upper and lower bounds of the Pauling method (F as the upper bound and Cs or Fr as the lower bound). Applying a similar approach here, we use the linear relationship between χ_{Pauling} and $\langle R \rangle\%$ (as shown in Figure 2b) to develop our own electronegativity scale, χ_{LPM} . The electronegativity values obtained from this approach are compiled below in Table III. The largest deviations in the χ_{LPM} values with respect to the Pauling values were for fluorine and sulfur at approximately 0.14 while the smallest deviation was observed for sodium (0.001).

Regardless, the mean absolute deviation for the set of 14 atoms was only 0.054. Furthermore, considering we have strong agreement between our model and the five electronegativity scales (that are significantly different in origin) studied herein, our model demonstrates strong potential for consideration as a novel, purely theoretical, method for describing electronegativity.

TABLE III: χ_{LPM} of the first and second row atoms

System	χ_{LPM} by group						
	1	2	13	14	15	16	17
First row	0.866	1.596	2.069	2.577	3.050	3.447	3.833
Second row	0.929	1.341	1.548	1.876	2.297	2.721	3.130

IV. CONCLUSIONS

We have applied the LPM to the set of first and second row hydrides in an attempt to develop a relationship between the electron pair centre-of-mass and electronegativity. The localized extracule density was an obvious choice for application to electronegativities based on the absolute electronic position information contained within the function. We have demonstrated strong correlations to several pre-existing electronegativity scales and thus, propose that the aforementioned method could be used as a novel method for defining electronegativity. This specific study illustrates another useful application of the localized pair model in addition to those that we have highlighted in past reports.[20–22]

V. ACKNOWLEDGEMENTS

The authors acknowledge the Natural Sciences and Engineering Research Council of Canada, the Canadian Foundation for Innovation (CFI) and the University of Prince Edward Island for the financial support that made this research possible. Computational resources were provided by ACENET, the regional high performance computing consortium for universities in Atlantic Canada. ACENET is funded by the CFI, the Atlantic Canada Opportunities Agency (ACOA), and the provinces of Newfoundland and Labrador, Nova Scotia, and New Brunswick.

- [1] Jensen, W. B. *J. Chem. Educ.* **1996**, *73*, 11–20.
- [2] Jensen, W. B. *J. Chem. Educ.* **2003**, *80*, 279–287.
- [3] Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570–3582.
- [4] Mahaffy, P. G.; Bucat, B.; Tasker, R.; Kotz, J. C.; Treichel, P. M.; Weaver, G. C.; McMurry, J. *Chemistry: Human Activity, Chemical Reactivity*, 1st ed.; Nelson Education, Ltd.: Toronto, 2011.
- [5] Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782–784.
- [6] Gordy, W. *Phys. Rev.* **1946**, *69*, 604–607.
- [7] Walsh, A. D. *Proc. R. Soc., London* **1951**, *A207*, 13–22.
- [8] Huggins, M. L. *J. Am. Chem. Soc.* **1953**, *75*, 4123–4126.
- [9] Sanderson, R. T. *J. Chem. Phys.* **1955**, *23*, 2467.
- [10] Allen, A. L. *J. Inorg. Nuc. Chem.* **1958**, *5*, 264.
- [11] Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540–546.
- [12] Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148–154.
- [13] Phillips, J. C. *Phys. Rev. Lett.* **1968**, *20*, 550–553.

- [14] Michaelson, H. B. *IBM J. Res. Dev.* **1978**, *22*, 72–80.
- [15] Allen, L. C. *J. Am. Chem. Soc.* **1992**, *114*, 1510–1511.
- [16] Simons, G.; Zandler, M. E.; Talaty, E. R. *J. Am. Chem. Soc.* **1976**, *98*, 7869–7870.
- [17] Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182–4186.
- [18] Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652–1655.
- [19] Ayers, P. L. et al. *Comp. Theor. Chem.* **2015**, *1053*, 2–16.
- [20] Zielinski, Z. A. M.; Pearson, J. K. *Comp. Theor. Chem.* **2013**, *1003*, 79–90.
- [21] Hennessey, D. C.; Sheppard, B. J. H.; Mackenzie, D. E. C. K.; Pearson, J. K. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25548.
- [22] Proud, A. J.; Mackenzie, D. E. C. K.; Pearson, J. K. *Phys. Chem. Chem. Phys.* **2015**, *17*, 20194.
- [23] Foster, J.; Boys, S. *Rev. Mod. Phys.* **1960**, *32*, 300–302.
- [24] Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457–464.
- [25] Pipek, J.; Mezey, P. *J. Chem. Phys.* **1989**, *90*, 4916–4926.
- [26] Niessen, W. J. V. *J. Chem. Phys.* **56**, 1972, 4290.
- [27] Lennard-Jones, J. E.; Pople, J. A. *Proc. Roy. Soc. (London)* **1950**, *A202*, 166.
- [28] Lennard-Jones, J. E.; Pople, J. A. *Proc. Roy. Soc. (London)* **1950**, *A210*, 190.
- [29] Coleman, A. J. *Int. J. Quantum Chem.* **1967**, *1*, 457.
- [30] Thakkar, A. J.; Moore, N. J. *Int. J. Quantum Chem.* **1981**, *20*, 393–400.
- [31] Wang, J.; Smith, Jr., V. H. *Int. J. Quantum Chem.* **1994**, *49*, 147–157.
- [32] Thakkar, A. J. In *Density Matrices and Density Functionals*; Erdahl, R. M., Smith, V. H., Jr., Eds.; Reidel: Dordrecht, Holland, 1987; pp 553–581.
- [33] Hollett, J. M.; Gill, P. M. W. *Phys. Chem. Chem. Phys.* **2011**, *13*, 2972–2978.
- [34] Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbery, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.