

A Novel Exploration of the Hartree–Fock Homolytic Bond Dissociation Problem in the Hydrogen Molecule by Means of Electron Localization Measures

Eduard Matito, Miquel Duran, and Miquel Solà*

Institut de Química Computacional and Departament de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain; *miquel.sola@udg.es

The workhorse of the wavefunction methods is the Hartree–Fock (H–F) approximation. The H–F procedure is important not only for its own sake but as the starting point for other more crude or more elaborate approximations, such as those represented by the semiempirical methods or those including to some extent electron correlation effects, respectively (1). For this reason, most introductory quantum chemistry textbooks contain a full chapter dedicated to the H–F method (2, 3). At the end of such chapter, it is usually shown that the H–F approach within the restricted formalism provides an inappropriate description of the hydrogen molecule at long bond lengths, which leads to the so-called H–F homolytic bond dissociation problem. This weakness of the restricted H–F method can be reasonably solved by using the unrestricted H–F methodology or more properly by employing configuration interaction (CI) methods. The aim of this work is not to dwell on how to solve the H–F dissociation problem but to provide a new view on this subject by using localization and delocalization indices defined from the second-order density within the atoms-in-molecules (AIM) theory (4, 5). We have observed that many students of introductory courses of quantum chemistry find the concept of localizability of electrons helpful to better grasp this well-known defect of the restricted H–F method. Finally, it is worth mentioning that different authors have treated the hydrogen molecule (although just a few studied the dissociation process) using second-order densities from other interesting perspectives. Thus, Savin and coworkers (6) carried out a discussion in terms of probability, while Ponec (7, 8) and other authors (9–11) present an study in terms of fluctuations, bond orders, or other related quantities.

Density-Based Descriptors

We begin here with a brief review of the concepts used to quantify electron localizability in molecules. Density-based descriptors of electronic structure have gained the first place as functions to characterize the molecular structure and the nature of the bonding in molecules. First attempts to electronic structure characterization were done in the framework of *Lewis bonding theory* (12), that afterwards was completed by the *valence shell electron pair repulsion* (VSEPR) (13–15) method of Gillespie. Later on, molecular orbitals became the preferred tool to discuss molecular electron distribution and to analyze chemical bonding. Although still widely used, in many works this latter method has been replaced or complemented by the use of density-based descriptors of the electronic structure owing to their simplicity. A recent review in this *Journal* studying molecular electron density distributions states this fact (16).

The two methodologies more commonly used in recent years to derive density-based descriptors of molecular bonding are the AIM theory (4, 5, 17, 18), and the electron localization function (ELF) (19–21). In both approaches, subsystems (basins) are defined in terms of the vector field of the gradient of the function involved, namely the electron density or the ELF, respectively. These basins are used to divide the molecular space. Other partitions, such as the Mulliken-like partition in the Hilbert space expanded by the basis functions, are also possible. In the AIM theory, the partition of space is done through *atomic basins* that are defined as the regions in real space bound by zero-flux surfaces in the electron density or by infinity (4, 5, 16–18). Usually, each basin can be assigned to one of the atoms in the molecule.

Localizability To Characterize Electronic Structure

Based on AIM (4, 5, 16–18) partition of space, but easily extended to any other possible subdivision of space, Bader and Stephens (22) introduced a quantity that accounts for electron localizability; the quantity known as exchange-correlation density, γ_{xc} , that can be calculated from density functions, ρ , as follows

$$\gamma_{xc}(\mathbf{r}_1, \mathbf{r}_2) = \gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \quad (1)$$

where \mathbf{r}_1 and \mathbf{r}_2 stand for the coordinates of electrons 1 and 2, respectively, and the second term on the right-hand side contains the well-known electron density first-order density function. The first term is known as the second-order density function or simply electron-pair density and results from integration of the squared wavefunction over the whole space on $n - 2$ of its coordinates:

$$\gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N - 1) \int_{R^3} \dots \int_{R^3} |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_3 \dots d\mathbf{r}_n \quad (2)$$

The second-order density function can be written in terms of the second-order density matrix (DM2 [DM1]), which is its basis of representation, see for instance ref 23

$$\begin{aligned} \gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{i,j,k,l} \chi_i^*(\mathbf{r}_1) \chi_j^*(\mathbf{r}_2) \Gamma^{(2)}(ij|kl) \chi_k(\mathbf{r}_1) \chi_l(\mathbf{r}_2) \\ \rho(\mathbf{r}_1) &= \sum_{k,l} \chi_k^*(\mathbf{r}_1) \Gamma^{(1)}(k|l) \chi_l(\mathbf{r}_1) \end{aligned} \quad (3)$$

where $\chi(\mathbf{r})$ represents the molecular orbital i and $\Gamma^{(2)}(ij|kl)$ and $\Gamma^{(1)}(k|l)$ are the DM2 and DM1 written in terms of molecular orbitals. The quantity in eq 1 is the difference between a common electron pair distribution, that is, the sec-

ond-order density function and a noninteracting electron pair distribution constructed as two independent electron distributions. Thus, the exchange-correlation density measures the influence of the correlation between pairs of electrons, since we are comparing a pair interacting system with a noninteracting one. The pair regions (r_1, r_2) of the space where its value is greater are due to a higher influence of electron correlation on that sharing zone, where one can expect electron *presence* to be quite important; the function value helps to quantify this importance.

Seven years ago, Fradera, Austen, and Bader (24) gave a name to these quantities when integrated on two certain regions of space, that is, the atomic basins A and B . Exchange-correlation density when integrated over these pair regions turns into the well-known *delocalization index* (DI), $\delta(A, B)$:

$$\begin{aligned} \delta(A, B) &= -\iint_{AB} \gamma_{xc}(r_1, r_2) dr_1 dr_2 - \iint_{BA} \gamma_{xc}(r_1, r_2) dr_1 dr_2 \\ &= -2 \iint_{AB} \gamma_{xc}(r_1, r_2) dr_1 dr_2 \end{aligned} \quad (4)$$

The DI accounts for the electrons delocalized or shared between atomic basins A and B (24, 25). On the other hand, the *localization index* (LI) accounts for the electrons localized in the region A , $\lambda(A)$, and is defined as:

$$\lambda(A) = -\iint_{AA} \gamma_{xc}(r_1, r_2) dr_1 dr_2 = \frac{\delta(A, A)}{2} \quad (5)$$

Its value is always less than or equal to the average number of electrons or the electron population, $N(A)$, in that region, which results from the density integrated over the region:

$$N(A) = \int_A \rho(r_1) dr_1 \quad (6)$$

It is worth noting that the AIM topological analysis provides an exhaustive partition of molecular space, so LIs and DIs obey the following sum rule:

$$\frac{1}{2} \sum_{B \neq A} \delta(A, B) + \lambda(A) = N(A) \quad (7)$$

Substituting eqs 1 and 3 into eqs 4 and 5, we obtain

$$\delta(A, B) = 2N(A)N(B) - 2 \sum_{i,j,k,l} \Gamma^{(2)}(ij|kl) S_{ik}(A) S_{ji}(B) \quad (8)$$

$$\lambda(A) = N(A)^2 - \sum_{i,j,k,l} \Gamma^{(2)}(ij|kl) S_{ik}(A) S_{ji}(A) \quad (9)$$

where overlaps in terms of spinorbitals have appeared in the right-hand side of the above equations, and the notation is as follows:

$$S_{ij}(A) = \int_A \chi_i^*(r_1) \chi_j(r_1) dr_1 \quad (10)$$

Table 1. Atomic Populations (N), Localization (λ), and Delocalization (δ) Indices for a Series of Diatomic Molecules

Molecule	Atom	$N(A)$	$\lambda(A)$	$\delta(A, B)$
H ₂	H	1.000	0.500	1.000
N ₂	N	7.000	5.479	3.042
F ₂	F	9.000	8.358	1.283
LiF	Li	2.060	1.971	0.178
	F	9.940	9.851	–
CO	C	4.647	3.860	1.574
	O	9.354	8.567	–
CN ⁻	C	5.227	4.121	2.210
	N	8.773	7.668	–
NO ⁺	N	5.525	4.323	2.405
	O	8.475	7.273	–

NOTE: Data from ref 24; data computed at the Hartree-Fock level of theory with the 6-311++G(2d,2p) basis set. Values in the last 3 columns correspond to the number of electrons.

Hereafter we will identify $\delta(A, B)$ with mutual electron sharing between these two regions, and $\lambda(A)$ with electron localization in A ; nothing else is needed to understand subsequent explanations.

Some Examples To Better Understand the Meaning of LI and DI Indices

It is worth mentioning that for molecular bonds with equally shared pairs such as H₂ or N₂, a simple relationship between the DI and the number of Lewis bonded pairs (12) (bond order) is generally found. Table 1 lists several examples of LIs and DIs for a series of diatomic molecules calculated at the H-F/6-311++G(2d,2p) level (24). H₂ is a representative example of a molecule with an equally shared pair of electrons. In this molecule the LI is 1/2 for each atom and the delocalization contribution is 1, which completely agrees with the prediction of the Lewis model (12) for the electronic structure of H₂. Let us now consider the N₂ molecule. According to the Lewis model (12), the LI should have the contribution of 2 from the 1s² core electrons, 2 from the lone pair, and 1.5 from the three shared pairs, giving $\lambda(N) = 5.5$. Moreover, these three equally shared pairs should give a DI of 3, achieving a total contribution of 14, the number of electrons. If we compare these values with the ones in Table 1, we realize that they are quite similar. The fact that $\delta(N, N') > 3$ means that there is a slight delocalization of the non-bonded pair of a N atom onto the basin of the other N atom.

However, with the exception of equally shared pairs, the DI does not reproduce the results of the Lewis model (24). In molecules AB where there is an important charge transfer, the electron pair is not equally shared but partly localized on the more electronegative atom A, and as a consequence, $\lambda(A)$ increases at the expense of $\delta(A, B)$ and $\lambda(B)$. Thus, LiF presents a $\delta(\text{Li}, \text{F})$ of 0.18 and a $\lambda(\text{F})$ equal to 9.85 electrons. It is important to note that the DI of LiF does not imply a Lewis bond formed from 0.18 pairs of electrons, instead it means that in LiF there is a bonded pair that is very unequally shared. This can be further illustrated with the isoelectronic sequence involving N₂, NO⁺, CN⁻, and CO,

all triply bonded molecules whose DI drops in the sequence 3.04, 2.41, 2.21, and 1.57 electrons, respectively. The DIs decrease with the increased electronegativity difference (greater charge transfer) of the atoms involved in the bond.

The H-F Homolytic Dissociation of Molecular Hydrogen

We focus now on the main subject of this contribution, which is the usefulness of DI and LI indices to understand the incorrect behavior of the H-F method in the dissociation of the hydrogen molecule. For the sake of simplicity, we will work with the simplest basis set, that is, a STO-3G minimal basis set, consisting of $1s_A$ and $1s_B$ functions both coming from the contraction of three primitive Gaussian-type functions. The system is studied first at the H-F level of theory and finally in terms of the CI method.

A molecular orbital (MO) scheme of the hydrogen molecule obtained at the H-F level is drawn in Scheme I. In this Scheme, one can see how the two $1s$ atomic orbitals combine to form the σ_g and σ_u^* bonding and antibonding MOs, having the following expressions

$$\begin{aligned}\sigma_g &= \frac{1}{\sqrt{2(S_{AB} + 1)}}(1s_A + 1s_B) \\ \sigma_u^* &= \frac{1}{\sqrt{2(1 - S_{AB})}}(1s_A - 1s_B)\end{aligned}\quad (11)$$

where S_{AB} is the overlap between the atomic orbitals $1s_A$ and $1s_B$. See, for instance, refs 2, 26, and 27.

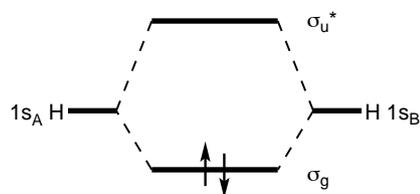
At the restricted H-F level, we enforce the restriction of spinorbitals to be occupied by a couple of electrons. Thus, the restricted H-F ground-state wavefunction with a pair of electrons occupying the lowest energy MO is

$$\begin{aligned}\Psi_o &\equiv |\sigma_g \bar{\sigma}_g\rangle \\ &= \frac{1}{2(S_{AB} + 1)} \left| (1s_A + 1s_B) \overline{(1s_A + 1s_B)} \right\rangle\end{aligned}\quad (12)$$

where the bar above a molecular spinorbital means that this molecular spinorbital contains a β electron. Absence of a bar means α . The excited-state wavefunction corresponding to two electrons occupying the antibonding orbital is

$$\begin{aligned}\Psi_D &\equiv |\sigma_u^* \bar{\sigma}_u^*\rangle \\ &= \frac{1}{2(1 - S_{AB})} \left| (1s_A - 1s_B) \overline{(1s_A - 1s_B)} \right\rangle\end{aligned}\quad (13)$$

The H-F method gives us the molecular orbitals σ_g and σ_u^* to construct the Slater determinant of minimum energy. The CI method constructs all possible Slater determinants using the H-F wavefunction as follows (3). First arranging the n electrons of the H-F determinant in the m spinorbitals chosen as a basis in all possible manners; that generates a set of determinants based in our H-F one. Afterwards a CI wavefunction is generated with the coefficients that expand the set of determinants. In our case, there is no need to use any



Scheme I. Molecular orbitals scheme corresponding to molecular hydrogen.

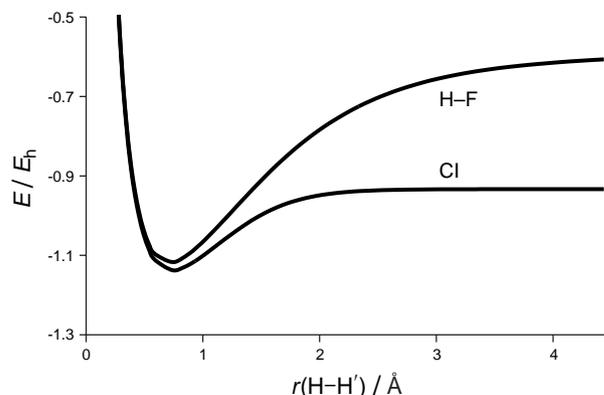


Figure 1. Energy profile for the homolytic bond dissociation of molecular hydrogen at the H-F and CI levels of theory.

other determinants than those corresponding to the biexcitation and the H-F one, because the monoexcitations have different symmetry, hence they do not mix with the other determinants (3). So that we can write the CI wavefunction as follows

$$\Psi_{CI} = c_o \Psi_o + c_D \Psi_D = c_o |\sigma_g \bar{\sigma}_g\rangle + c_D |\sigma_u^* \bar{\sigma}_u^*\rangle \quad (14)$$

where c_o and c_D are the expansion coefficients to be determined in the CI calculation. After application of the variational principle, the above equation gives us the exact result for this minimal basis set within the Born-Oppenheimer approximation when neglecting relativistic effects. At infinite separation of the hydrogen atoms, it is found that (3):

$$\lim_{r \rightarrow \infty} E^{CI} - E^{H-F} = -\frac{1}{2} \langle 1s_A 1s_A | 1s_A 1s_A \rangle \quad (15)$$

The difference between the CI and H-F results at infinite internuclear distance given by eq 15 is exactly the repulsion both electrons feel because of occupying the same spatial part of the spinorbital. Once eq 15 has been deduced (3), the H-F dissociation problem turns out evident: both electrons will always feel each other because they are *restricted* to share the same spatial orbital. If the other contributing configuration given in eq 13 is used (or we work within the unrestricted formalism) the dissociation problem is overcome, since the system is then described as a pondered contribution of different electronic situations, eq 14, leading to a better—actually exact—approach. Figure 1 shows the energy profiles calculated at CI and H-F levels of theory; the error of the H-F approach is especially important for large interatomic distances (3).

Localizability as a Tool To Analyze the Homolytic Bond Dissociation Problem

In this section, we will use the definitions of LI and DI to provide an alternative and easy way to understand the homolytic bond dissociation problem in terms of localizability. This approach does not need any MO interpretation and moreover all quantities required can be calculated with handy software, such as the Gaussian 98 (28) and AIMPAC (29) packages.

The following approximations for LI and DI, defined in eqs 4 and 5,

$$\lambda(\text{H}) \approx \frac{1}{2} - c_0 c_D \quad (16)$$

$$\delta(\text{H}, \text{H}') \approx 1 + 2c_0 c_D \quad (17)$$

can be easily derived from the expression of the DM2 (see the Appendix in the Supplemental Material¹¹). As said before, $\lambda(\text{H})$ gives the number of electrons localized in the basin of a H atom, while $\delta(\text{H}, \text{H}')$ is a measure of the electrons delocalized or shared between the two atomic basins.

Equations 16 and 17 enable the calculation of the indices with just the need of the contribution of both configurations at each interatomic distance; no overlap or density matrix is needed. Using this approximation or the exact expression for the DI, the interatomic distance dependence on the DI—absent in monodeterminantal wavefunctions and implicit on the coefficient values—clearly come out, as shown in Figure 2 and in the values of Table 2.

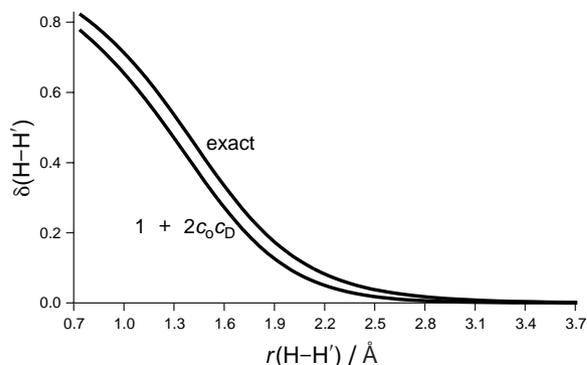


Figure 2. Delocalization indices (electrons) at different interatomic distances. The upper curve is the exact result, while the lower one is calculated using the approximation given by eq 17.

Now, the only task remaining is to compute the CI wavefunction of the hydrogen molecule at different interatomic distances. Some results are collected in Table 2. The indices' tendency is plotted in Figure 3. The graphic shows the expected trend: mutual shared electrons (DI) diminish while atoms separate reaching the down bound zero, indicative of no electron sharing when atoms are infinitely separated. Beside, the electrons localize one on each atom when distance increases; LI comes by the upper bound of one electron per atom when no interaction holds. In contrast, the H–F LI and

Table 2. CI Energy, H–F Energy, CI Coefficients, MOs Overlap, Delocalization and Localization Indices (Exact Values) at Different Interatomic Distances using the STO-3G Basis Set

$r(\text{H}-\text{H}')/\text{Å}$	$E(\text{CI})/E_h$	$E(\text{H}-\text{F})/E_h$	c_0	c_D	$S_{12}(\text{H})$	$\delta(\text{H}, \text{H}')$	$\lambda(\text{H})$
0.7351	-1.1373	-1.1170	0.9943	-0.1064	0.4458	0.8237	0.5881
0.8350	-1.1303	-1.1053	0.9911	-0.1331	0.4493	0.7871	0.6065
1.0350	-1.0936	-1.0561	0.9827	-0.1855	0.4570	0.6955	0.6522
1.2350	-1.0490	-0.9939	0.9679	-0.2515	0.4652	0.5786	0.7107
1.4350	-1.0091	-0.9306	0.9443	-0.3290	0.4728	0.4444	0.7778
1.6350	-0.9790	-0.8719	0.9121	-0.4100	0.4794	0.3125	0.8437
1.8350	-0.9590	-0.8204	0.8746	-0.4848	0.4846	0.2033	0.8984
2.0350	-0.9470	-0.7767	0.8375	-0.5465	0.4888	0.1254	0.9373
2.2350	-0.9403	-0.7406	0.8048	-0.5936	0.4919	0.0753	0.9624
2.3350	-0.9383	-0.7251	0.7907	-0.6122	0.4932	0.0581	0.9709
2.4350	-0.9368	-0.7112	0.7783	-0.6279	0.4943	0.0449	0.9776
2.6350	-0.9350	-0.6876	0.7578	-0.6525	0.4960	0.0268	0.9866
2.8350	-0.9340	-0.6687	0.7425	-0.6698	0.4973	0.0160	0.9920
3.0350	-0.9336	-0.6537	0.7314	-0.6819	0.4982	0.0096	0.9952
3.2350	-0.9334	-0.6418	0.7235	-0.6903	0.4988	0.0058	0.9971
3.4350	-0.9332	-0.6324	0.7180	-0.6961	0.4992	0.0035	0.9983
3.6350	-0.9332	-0.6250	0.7142	-0.6999	0.4995	0.0021	0.9990
3.8350	-0.9332	-0.6190	0.7117	-0.7025	0.4997	0.0012	0.9994
4.0350	-0.9332	-0.6141	0.7100	-0.7042	0.4998	0.0007	0.9996
4.2350	-0.9332	-0.6100	0.7089	-0.7053	0.4999	0.0004	0.9998
4.4350	-0.9332	-0.6066	0.7082	-0.7060	0.4999	0.0002	0.9999
...
∞	$E(\text{H})$	$\frac{E(\text{H}) + (1/4)}{\langle 1s_A 1s_A 1s_A 1s_A \rangle}$	$1/\sqrt{2}$	$-1/\sqrt{2}$	$1/2$	0	1

NOTE: Values in the last 3 columns correspond to the number of electrons.

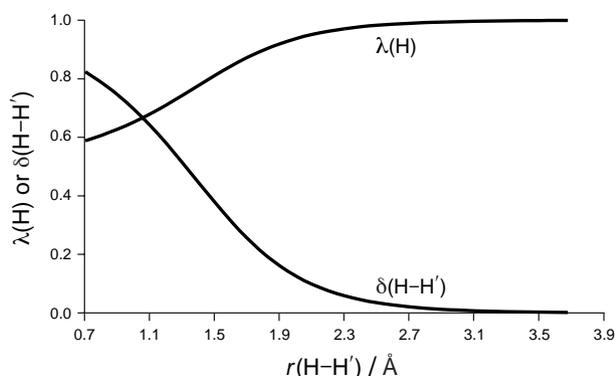


Figure 3. Localizability along the interatomic distance. The ascending curve is the localization index calculated on a hydrogen atom, the descending curve represents the delocalization index between both hydrogens.

DI values remain *constant* at 0.5 and 1 electrons, respectively. From these results, it becomes evident to the students that the failure of the restricted H–F method to correctly dissociate molecular hydrogen in atomic hydrogen is due to its inability to localize the electrons in each hydrogen atom at large interatomic distances. This lack of localization in the H–F method results in the artificial excess of electron repulsion found in eq 15.

Finally, it is worth noting that any attempt to evaluate the electron localization must use two-electron quantities, the pair density being the simplest of such quantities. The analysis of localization versus delocalization during the dissociation process cannot be performed using atomic charges derived from the electron density only. Any method of computing atomic charges, such as the Mulliken population (30), gives an identical charge of 1 electron to each H, irrespectively of the H–H bond length considered or the method of calculation used. Thus, this educational example has the additional value of clearly illustrating to students how the pair density can be used to get a deeper insight into the nature of molecular electronic structure.

Conclusions

The aim of the above discussion has been to show how a detailed quantitative treatment of localizability of electrons in the hydrogen molecule may be presented to the student to get further understanding of the homolytic bond dissociation problem in the restricted H–F method. We have shown that the untenable necessity of molecular spinorbitals to be occupied simultaneously by two electrons is responsible for localization to hold on the same value while dissociation is occurring. When the CI method is used, the localizability of the electrons in the system turns into the intuitive scheme expected for homolytic dissociation: atomic electron localizability increases with interatomic distance until one electron *localizes* in each atom, while *mutual shared electrons* decreases to reach no sharing in the limit of noninteracting fragments. In our opinion, this approach represents an alternative and instructive view that helps the students to better understand the homolytic bond dissociation problem in restricted H–F wavefunctions.

Acknowledgments

Financial help has been furnished by the Spanish MEC Project No. CTQ2005-08797-C02-01/BQU. We are also indebted to the Departament d'Universitats, Recerca i Societat de la Informació (DURSI) of the Generalitat de Catalunya for financial support through the Project No. 2005SGR-00238. EM thanks the Secretaría de Estado de Educación y Universidades of the MECED for the doctoral fellowship no. AP2002-0581. We also thank the Centre de Supercomputació de Catalunya (CESCA) for partial funding of computer time.

Supplemental Material

The derivations for the LI and DI approximations given in eqs 16 and 17 are available in this issue of *JCE Online*.

Literature Cited

1. Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; John Wiley & Sons: New York, 2002.
2. Pilar, F. L. *Elementary Quantum Chemistry*; McGraw-Hill: New York, 1990.
3. Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Macmillan Publishing Co.: New York, 1982.
4. Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9–15.
5. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon: Oxford, 1990.
6. Chamorro, E.; Fuentealba, P.; Savin, A. *J. Comput. Chem.* **2003**, *24*, 496–504.
7. Ponec, R.; Carbó-Dorca, R. *Int. J. Quantum Chem.* **1999**, *72*, 85–91.
8. Ponec, R.; Yuzhakov, G.; Cooper, D. L. *J. Phys. Chem. A* **2003**, *107*, 2100–2105.
9. Ángyán, J. G.; Rosta, E.; Surján, P. R. *Chem. Phys. Lett.* **1999**, *299*, 1–8. (b) Scemama, A. *J. Chem. Theory Comput.* **2005**, *4*, 397–409. (c) Fulton, R. *J. Phys. Chem.* **1993**, *97*, 7516–7529.
10. Modl, M.; Dolg, M.; Fulde, P.; Stoll, H. *J. Chem. Phys.* **1996**, *105*, 2353–2363.
11. Fradera, X.; Solà, M. *J. Comput. Chem.* **2002**, *23*, 1347–1356.
12. Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762–785.
13. Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991.
14. Gillespie, R. J.; Popelier, P. L. A. *Chemical Bonding and Molecular Geometries: From Lewis to Electron Densities*; Oxford University Press: New York, 2001.
15. Gillespie, R. J.; Robinson, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 495–514.
16. Matta, C. F.; Gillespie, R. J. *J. Chem. Educ.* **2002**, *79*, 1141–1152.
17. Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893–928.
18. Bader, R. F. W. *Can. J. Chem.* **1998**, *76*, 973–988.
19. Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397–5403.
20. Savin, A.; Becke, A. D.; Flad, J.; Nesper, R.; Preuss, H.; Vonscherner, H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 409–412.
21. Savin, A.; Nesper, R.; Wengert, S.; Fassler, T. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1809–1832.

22. Bader, R. F. W.; Stephens, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 7391–7399.
23. Lowdin, P. O. *Phys. Rev.* **1955**, *97*, 1474–1489.
24. Fradera, X.; Austen, M. A.; Bader, R. F. W. *J. Phys. Chem. A* **1999**, *103*, 304–314.
25. Fradera, X.; Poater, J.; Simon, S.; Duran, M.; Solà, M. *Theor. Chem. Acc.* **2002**, *108*, 214–224.
26. Willis, C. J. *J. Chem. Educ.* **1988**, *65*, 418–422.
27. Willis, C. J. *J. Chem. Educ.* **1991**, *68*, 743–747.
28. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M.; Peng, C.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, R.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, rev. A11; Pittsburgh, PA, 1998.
29. Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317–328.
30. Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–1840.